Politechnika Lubelska

Water Supply and Wastewater Disposal

Designing, Construction, Operation and Monitoring IV

edited by
Beata Kowalska
Dariusz Kowalski

Lublin 2022

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and Wastewater Disposal

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Contents

A review on commonly used adsorbents using to remove metal ions from wastewater

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Abstract

The metals contained in surface and ground water come mainly from industrial effluents and domestic sewage. Currently, various techniques and processes are used to treat polluted water to remove contaminants from it, including metal ions, for this purpose processes such as extraction, ion exchange, precipitation, or sorption are used. Sorption is one of the most popular and effective methods of wastewater treatment because is a simple, efficient, and economical method. The popularity of this method is due to the availability of various synthetic as well as natural sorption materials. The main advantage of using the separation properties of various sorption materials is the decrease of amounts of metal ions, including heavy metal ions in the natural environment.

This review presents selected adsorbents (natural organic, synthetic organic/polymeric, mineral sorbents) and their modifications used for the recovery of metal ions present in sewage sludge. The basic parameters of the sorption process were also presented, which describe, among others, sorption efficiency.

Keywords: natural organic sorbent, synthetic organic/polymers, mineral sorbents, modified sorbents, removal metal ions, adsorption

1. Introduction

The main source of heavy metal ions present in sewage sludge is industrial effluents and domestic sewage. Sewage sludge is a complex mixture that consists of by-products of wastewater treatment processes of sewage from various domestic and industries sources and rainwater runoff roads through, physical, biological and/or chemical processes. Heavy metals occur in sewage sludge in the form of precipitated, dissolved, co-precipitated with metal oxides, adsorbed, or associated with biological residues. They can take the form of oxides, hydroxides, sulphides, sulphates, phosphates, silicates, organic compounds in the form of humic complexes, and compounds with complex sugars (Gawdzik, 2012; Weiner and Matthews, 2003, Obaid et al., 2018).

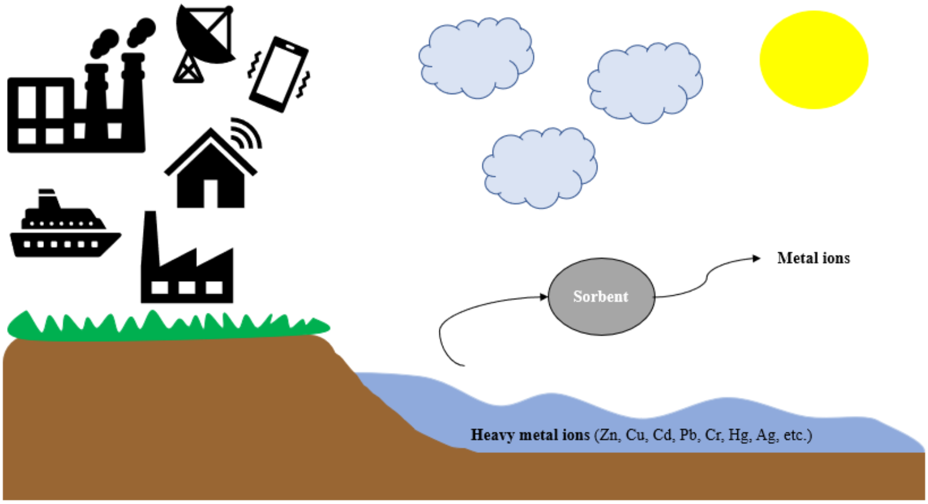

Fig. 1. The scheme of sources metal ions contained in surface and ground water and the way their recovery (own elaboration)

Methods such as chemical precipitation, ion exchange, membrane filtration, flocculation, and adsorption (Cristiani et al., 2021) have long been for the removal of metal ions from solution. One of the commonly used processes for the recovery of metal ions from wastewater is sorption. Sorption consists of the use of adsorbents, i.e. porous solids with a developed specific surface, on which the process of surface bonding of molecules from the liquid or gas phase takes place (Bandura et al., 2017). According to the definition, adsorption is the mass transport of substances from either a gas or liquid state to a solid interface as the result of physical and/or chemical interactions. During the sorption process, the molecules attach to the surface of the chemical through physical and chemical bonding (Ugwu et al., 2020). All adsorbents, both natural and synthetic, contain functional groups that allow metal ions to be adsorbed. Chemically modified adsorbents have a higher adsorption capacity than unmodified adsorbents. As the result, the modified adsorbent enhances the surface-active area of sorbent (Chakraborty et al., 2020). According to researchers, sorption is a very effective, simple and economical process for metal ion removal from wastewaters. The research works conducted so far concern the kinetics and thermodynamics of sorption, possible sorption mechanisms, and factors influencing sorption properties or modification of already existing adsorbents (Zhano et al., 2011; Ishtiag et al., 2020).

The paper presents selected adsorbents (natural, organic, synthetic, organic/polymer, mineral) used for the sorption of metal ions (e.g., Cd^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+}, Fe^{2+}, Cr^{3+}, Cr^{6+}, Ba^{2+}, etc.) from aqueous solutions. It also, describes the basic parameters of the sorption and desorption process.

2. Basic parameters of adsorption and desorption process

2.1. Adsorption process

It was found that the adsorption conditions are influenced by ion concentration, contact time, adsorbent content, and pH solution. The capacity sorption (q_e, mg/g) is a main parameter of the sorption process and describes the ability to bind metal ions by the adsorbent. The metal ions uptake (q_e) on the investigated adsorbent at a given time (t) is given by the following equation (Far et al., 2021):

$$q_e = \frac{V(C_0 - C_e)}{m}, \tag{1}$$

where: V is the volume of the metal ions solution [dm^3], m is the mass of adsorbent [g], and C_0 and C_e are the metal concentrations [mg/dm^3] at $t = 0$ and t, respectively.

Moreover, equation 2 describes the percentage of removal ($\%R_{ads}$) of metal ions (Ishtiag et al., 2020).

$$\%R_{ads} = \frac{C_0 - C_e}{C_0} \cdot 100, \tag{2}$$

where: C_0 and C_e are initial and equilibrium concentrations of metal ions, respectively [mol/dm^3].

Mathematical description of sorption process described below. In the mass exchange mechanism in the process of adsorption from solutions, the following steps are specified:

– diffusion or convection in solution;
– diffusion of particles from the liquid to the interface;

– mass diffusion through the interface;
– diffusion in the liquid phase inside the pores of the adsorbent;
– specific adsorption on the active centers of the adsorbent;
– diffusion in the surface layer of the adsorbent.

A dynamic equilibrium, is a defined separation of the adsorbate between the solution and the adsorbent. The amount of metal ions in the solutions adsorbed (q_e) was describe formula 1. The mechanism of the sorption process that exists between the adsorbent surface and the heavy metal ions can be described with the use of adsorption isotherms for both single and multiple component systems (Ugwu et al., 2020). During the mathematical description of the adsorption equilibrium from dilute aqueous solutions, the equations of the Freundlich (3), Langmuir (4), and Dubinin-Radushkevich (5) isotherms are commonly used (Zhao et al., 2010).

$$q_e = K_F C_e^{\frac{1}{n}}, \tag{3}$$

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e}, \tag{4}$$

$$q_e = q_{max} exp\left(-\left(\frac{RT\ \ln(\frac{C_e}{C_s})}{\beta E_0}\right)^2\right), \tag{5}$$

where: q_e the amount of solute adsorbed at equilibrium, C_e the equilibrium concentrations of sorbate in solution [mol/dm^3] over time [t], C_s the concentrations of sorbate in sorbent [mol/dm^3] over time [t], E_0 solid characteristic energy towards a reference compound, and others parameters or constants: β is constant of Dubinina-Radushkevicha, constant dependent on sorption energy, K_L is constant of Langumir.

2.2. Desorption process

Desorption of metal ions is based on the release of adsorbed ions from the adsorbent surface and their transfer to the receiving phase. It is the reverse of the sorption process. Desorption efficiency ($\%R_{des}$, Eq. 6) is promoted by, among others temperature increase or reduction of the degree of dispersion (Ishatiaq et al., 2020; Ipeaiyeda and Tesi, 2014).

$$\%R_{des} = \frac{C_i}{C_a} \cdot 100, \tag{6}$$

where: C_i is a released matal concentration [mol/dm^3], C_a is an intially sorbed metal concentration [mol/dm^3].

3. Kind of adsorbents

Due to their origin, sorbents are divided into natural organic, synthetic polymeric, and mineral sorbent (Fig. 2). Natural organic sorbents include, i.a peat, sawdust, wood bark, and cellulose that forms during the production of paper. Despite their high absorbency, they are of limited use, e.g., they are not suitable for removing aggressive substances. On the other hand, synthetic polymer sorbents are characterised by high absorbency and low weight. They can be used to remove impurities formed on the water, with the so-called hydrophobic sorbents that do not absorb water. Raw materials such as wood sawdust, bark, and other wood processing wastes can be mineral sorbents. Mineral sorbents are made of natural fibees, while synthetic sorbents are artificial materials made of plastic.

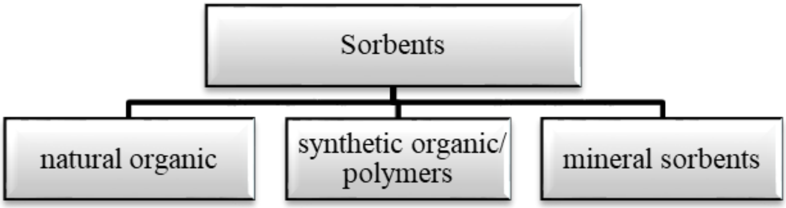

Fig. 2. Kind of adsorbents

Commonly used sorbents are mainly solid materials (granules, mats, pillows, sorption barriers, etc.). They are used to limit the horizontal and vertical migration of substances (Pijarowski and Tic, 2014).

3.1. Natural organic sorbents

Natural organic sorbents are widely used to remove metal ions by sorption process, and including, among others wood sawdust, bark, and peat (Baltinova et al., 2016), which is presented below.

3.1.1. Wood sawdust

Wood sawdust (WSD) is industrial biomass waste used as an adsorbent. WSD was obtained by wood processing units and industries that procedure furniture. This waste is cheap and eco-friendly and is commonly using to remove toxic metal ions from aqueous solutions (Varma et al., 2019).

For example, wood sawdust was used to remove copper, zinc, and cadmium from galvanic wastewater (Tan et al., 2019), e.g., Rahman et al. (2019) used maple sawdust to adsorb copper ions, obtaining maximum adsorption of 9.5 mg/g at pH = 6.0 (Rahman and Islam, 2009). Moreover, like other adsorbents, wood can be modified and used to remove metal ions from an aqueous solution. Rafatullah et al. used meranti sawdust to remove Cu(II), Cr(III), Ni(II), and Pb(II) ions from aqueous solutions with concentrations from 1–200 mg/L. The better adsorption was when the pH of the sample equals 6 for all metal ions (Rafatullah et.al., 2009). In addition Tan et. al. synthesised an innovative adsorbent based on wood flour for Pb(II) removal, assessed the experimental adsorption capacity of this adsorbent as amounting 189.9 mg/g in 180 min. Moreover, the adsorbents high selectivity of the Pb(II), Cu(II), and Zn(II) ions in mixed solution for lead ions (Tan et al., 2019). Other synthesised wood sawdust experimentation was undertaken by Guo et.al. and applied to removal Pb(II) and Cu(II) ions. The capacity sorption for Pb(II) and Cu(II) ions was 241.8 and 95.7 mg/g, respectively (Guo et al., 2020). El-Sheikh et al. (2018) prepared five adsorbents: the Cit-MOW (citric acid-coated magnetic olive wood sawdust) with the adsorption capacities (at pH = 5.6) of: 21.0, 14.4, 17.6 mg/g for Cu(II), Co(II), Zn(II), respectively, while cit-Mag (citric acid-coated magnetite) showed adsorption capacities (at pH = 5.6) of: 5.0, 1.6, 4.4 mg/g for Cu(II), Co(II), Zn(II), respectively (El-Sheikh et al., 2018).

3.1.2. Bark

The bark is a waste from wood processing, which is used as an adsorbent around an amorphous structure, irregular surface. Bark materials were composed mainly of lignin and holocellulose (Georgin et al., 2019). Bark is a cheap natural adsorbent and is commonly used to remove metal ions (Cd(II), Pb(II), Cu(II), Zn(II), Ni(II), Hg(II), Fe(II), Cr(III), Cr(VI)) (Baltinova et al., 2016; Naiya et al., 2009; Hamdaoui, 2016; da Silva Correia et al., 2018; Hashem et al., 2018; Sen et al., 2015).

For example, the bark was used to remove 94.80, 95.50, and 94.23% of Cd(II), Pb(II), and Cu(II) respectively from industrial real wastewater by Kebede et al. (2018). Akar et al. (2019) was used modified and non-modified bark to remove heavy metal ions from wastewater. The highest removal of Cr(VI) obtained 89.6% for non-modified bark and 90.7% for modified bark. The highest removal of Ni(II) was obtained 74.5 and 56.5% for non-modified and modified bark, respectively (Akar et al., 2019). Wajima obtained a modified adsorbent from cedar bark using sulfur-impregnation, and calculated the maximum adsorption capacity, of 0.30–0.74 mmol/g. The order of selectivity of the adsorbent was: Pb(II) > Fe(II) > Cu(II) > Zn(II) > Cd(II) > Ni(II) > Fe(III) (Wajima, 2017). Saeed et al. (2020) investigated the leaves (CL) and bark (CB) of cinnamomum verum to check their effectiveness in reducing the concentration of hexavalent chromium (Cr^{+6} metal ions) in the biosorption process (Saeed et al., 2020). Scientists also studied the application of green synthesis of magnetite nanoparticles from Hevea bark extract to the removal of Cd and Na ions. The highest adsorption capacity for Cd(II) and Na(I) ions was 37.03 and 3.95 mg/g, respectively (Sebastian et al., 2019).

3.1.3. Peat

The peat is a raw material of an extensive capacity, it can be a precursor for the synthesis of an adsorbent, e.g., using to the removal of metal ions from aqueous solutions. Peat is a cheap natural adsorbent, that is friendly to the environment (Men'shchikov et al., 2020).

Thus, Ringqvist et al. (2002) studied sphagnum and carex peat samples for the removal of zinc and copper ions from wastewater. The highest removal of Zn(II) and Cu(II) ions, 97–99%, 85–100%, respectively, were obtained in the effluent from the carex peat sulphide mine, and 37–77% for Zn, and 80–100% for Cu ions in the sphagnum peat sample (Ringqvist et al., 2002). Other scientists described the sorption capacity of peat for nickel(II) and lead(II) ions of 61.27 mg/g and 82.31 mg/g, respectively. The peat was an effective sorbent among natural organic sorbents, and the desorption experiments confirmed the possibility of reusing peat for the removal of harmful metal ions (Bartczak et al., 2018). Ho and Mckay studied the sorption of copper, lead, and nickel ions from an aqueous solution onto sphagnum moss peat (Ho and Mckay, 2000). Balasubramanian et. al. used Indonesian (Sumatra) peat as a metal adsorbent, with the metal ions adsorption of Pb > Cd > Zn for single- and multisolute systems. Desorption tests found that moret than 90% of Pb, Cd, and Zn can be eluted from the peat (Balasubramanian et al., 2009). In addition, peat, except for the above-mentioned metal ions, can be an effective adsorbent for removing chromium and mercury ions (Priyantha and Lim, 2016; Bulgariu et al., 2008). However, modified peat, e.g., coco-peat biomass (CPB) can be used for the removal of Pb(II), Cd(II), Cu(II), and Ni(II) ions from single and quaternary solutions. The biosorption capacity of Pb(II), Cd(II), Cu(II) and Ni(II) ions removal at pH 4 was as 0.440, 0.133, 0.335 and 0.154 mmol/g, respectively (Vijayaraghavan et al., 2016).

3.2. Synthetic organic/polymer sorbents

Porous organic polymers (POP) are of great interest, especially in wastewater treatment, due to their high porosity, flexibility, structure, and good chemical stability. Thanks to that these adsorbents can be used in the adsorption process to remove metal ions from wastewater (Huang et al., 2021).

Synthetic organic/polymeric sorbents were widely used for the recovery of various metal ions from heavy metal ions to noble metal ions. Bratskaya et al. (2016) synthesised a series of polymeric sorbents of pyridylethyl-containing derivatives of polyallylamine, polyethylenimine, and chitosan to the recovery of Au(III), Pt(IV), and Pd(II) ions. The maximum recovery of gold and palladium ions was 95% and 80%, respectively from PEC (when using 0.1 M HCl/1 M thiourea as an eluent) (Bratskaya et al., 2016). Other scientists synthesised new synthetic sorbents during co-precipitation of the PAA and linear and branched PEI and $CaCO_3$ crystallisation from supersaturated solutions for the removal of metal ions (Cu(II), Ni(II), and Co(II)) and their equimolar mixture. The results of the sorption experiments shown the sorption capacity of different ions can be correlated to the polymorph composition of the compounds (Zaharia et al., 2021). Tan et al. synthesised a mesoporous poly-melamine-formaldehyde (mPMF) polymer with a large surface area. This sorbent was characterised by good porosity and a high density of amine and triazine functional groups. Adsorption over mPMF was highly selective for lead ions commonly found in water ions (Na^+, K^+ and Ca^{2+}) (Tan et al., 2013). While Shemshadi et. al. (2012) used seven polymeric sorbents for the removal of Cd(II) from aqueous solution. The investigated adsorbents were obtained by mixing the polymers (PVP, MBAAm-N,N', and PAAm) in various ratios (Shemshadi et al., 2012). Seknal and Bicak (2001) synthesised cross-linked terpolymer beads modified by EDTA. The maximum sorption capacities for Fe^{3+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions, were equal to 1.48, 1.38, 1.72, and 1.8 mmol/g, respectively (Senkal and Bicak, 2001).

3.3. The mineral sorbents

Mineral sorbents are most often used due to the specific structure and absorption properties as well as the high efficiency of such sorbents (Pijarowski and Tic, 2014). Mineral sorbents except for modified mineral adsorbents, include zeolites, clay minerals, and silica adsorbents.

3.3.1. Zeolites

Zeolites are crystalline aluminosilicates that consist of SiO_4 and AlO_4 tetrahedra linked together to form a nanoporous, three-dimensional, cage-like structure (Mandal et al., 2020). It was, various natural zeolites have the ability to exchange different cation ions, e.g., ammonium and heavy metal ions. Moreover, modification of natural zeolites can be carried out by a few methods, for example, acid treatment, ion exchange, or surfactant functionalisation. In this way, modified zeolites were shown to have higher adsorption capacity for organic compounds and anions (Wang and Peng, 2010). Zeolites except for the removal of various metal ions from aqueous solutions are used in membrane processes, e.g., for hydrogen separation in syngas production (Coronas and Santamaria, 2004) or post-combustion CO_2 capture (Raganati et al., 2021; Xu et al., 2019). Modified zeolites are used, to e.g., the adsorption ofbBisphenol-A and propranolol hydrochloride (Rakhym et al., 2021) or for the recovery of heavy metal ions (Cr, As, Pb, Zn, Cu, Ni, Cd, Mn) present in wastewater (Shi et al., 2017).

For example, Hamed et al. studied the removal of heavy metals (such as Fe(III), Ca(II), and Mg(II)) in treated and raw water using modified zeolite. They found that when the pH was 4.5, the removal efficiency of Fe, Ca, and Mg was equal to 98.0%, 97.0%, and 94.9%, respectively (Hamed et al., 2015). Thirumavalavan et. al. synthesised mesoporous materials with commercially available β-zeolite for the adsorption of Pb(II), Cu(II), and Zn(II) ions. The capacity sorption for all synthesised compounds was approx. from 4.3 to 9.8, from 2.0 to 3.8, and from 1.2 to 2.6 mg/g for Pb(II), Cu(II), and Ni(II) ions (Thirumavalavan et al., 2011). Phuoc et. al. (2021) used NaA zeolite for Pb(II) ions adsorption studies in a fixed-bed column configuration. The sorption capacity was 118.5 mg/g with the concentration of Pb(II) ions of 100 mg/L, the adsorbent bed height of 8.1 cm, and the inflow rate of 2.5 mL/min (Phuoc et al., 2021). Borhadd et al. (2015) synthesised the adsorbent from zeolite-A to remove almost 95% of the Pb(II) and Cd(II) ions and approx. 60% of the Ni(II) ions from aqueous solution (Borhade et al., 2015). While Lu et al. (2016) investigated the adsorption of Pb^{2+} and Cu^{2+} on zeolite. The highest adsorption capacities of Pb(II) and Cu(II) ions were 135.5 and 115.5 mg/g, respectively, and for the concentration of a stock solution of metal ions was 10 g/L (Lu et al., 2016).

3.3.2. Clay minerals

Other adsorbents are clay minerals (NCM), which are among the adsorbent minerals. The NCMs are not toxic to the environment, but are inexpensive and can be used as cheap adsorbents (Alshameri et al., 2018). Clay minerals are cheap materials available all over the world and are characterised by chemical and morphological diversity (Chouikhi et al., 2019) The researchers found that the clays and their minerals (natural and modified forms) effectively remove e.g., ammonium (Alshameri et al., 2018), and various heavy metals from aqueous solution (Uddin, 2017).

Schimitt et. al. studied the influence of clay minerals (natural organic matter (NOM)) on the adsorption of various metal ions such as Al, Fe, Zn, and Pb (pH equal 5 and 7). They used kaolinite (KAO) and a smectite/illite mixture (MM) for the removal of metal ions (Schmitt et al., 2002). Gier and Johns (2000) used a series of micas and illite for the adsorption of Ba^{2+}, Pb^{2+}, Cu^{2+}, and Zn^{2+}. It was found that there is selective adsorption of Cu^{2+} ions about to Zn^{2+} and Pb^{2+} ions during the sorption of these silicates (Gier and Johns, 2000). Li et al. (2020) studied the adsorption of a number of cations (Na^{+}, K^{+}, Cs^{+}, Ca^{2+}, Pb^{2+}, Cd^{2+}, Ba^{2+} and Zn^{2+}) on the outer surface and in the montmorillonite interlayer. They investigated the role of interlayer space in determining the efficiency and the mechanism of adsorption. The stability of the adsorbed cations was found to be higher in the intermediate layer than in the outer surface, especially for M^{2+} (Li et al., 2020). Esmaeili et al. (2019) using bentonite as a sorbent for the removal of 99.9% of copper, and nickel ions, and 89.2% of zinc ions.

3.3.3. Silica adsorbents

In recent years, silica adsorbents have been increasingly used as sorbents to remove metal ions from an aqueous solution. The silica sorbents can be effectively used as adsorbents to remove various toxic metal ions (Ouyang et al., 2019; Artiushenko et al., 2020; Klapiszewski et al., 2015).

Najafi et al. (2012) used a modified silica adsorbent NH_2–SNHS (Amino-functionalised silica nano hollow sphere) for the recovery of nickel, cadmium, and lead ions. The highest adsorption capacity of Ni^{2+}, Cd^{2+}, and Pb^{2+} ions onto the investigated adsorbent was 38.982, 49.526, and 143.295 mg/g, respectively (Najafi et al., 2012). Bai et. al. (2012) was synthesised a silica-supported dithiocarbamate adsorbent (Si-DTC) as a new adsorbent for adsorption of Pb(II), Cd(II), Cu(II), and Hg(II) from aqueous solution. After the sorption experiments, the adsorption capacities were decribed, as 0.34, 0.36, 0.32, and 0.40 mmol/g for Pb(II), Cd(II), Cu(II), and Hg(II), respectively (Bai et. al., 2012). Zhao et.al. used chitosan-coated mesoporous microspheres of calcium silicate hydrate for removal of heavy metal ions of Ni^{2+}, Zn^{2+}, Cr^{3+}, Pb^{2+}, Cu^{2+} and Cd^{2+} from aqueous solution. The highest sorption capacity was 796 mg/g for lead ions and the lowest was 400 mg/g for zinc ions (Zhao et al., 2014). The next silica adsorbent is ionic liquid-modified silica gel, which was used to adsorption for Cu^{2+}, Fe^{3+}, Mn^{2+}, and Ni^{2+} ions (Qian et al., 2016). Functionalised cubic mesoporous silica, was used to removel Hg^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} (Chatterjee and Paital, 2018). Also used was modified magnetic mesoporous silica MCM-48 to remove Pb(II), Cu(II), Cr(VI), and Cd(II) ions. The highest sorption capacity of lead, copper, chromium and cadmium ions was 127.24, 125.80, 115.60, and 114.08 mg/g, respectively (Anbia et al., 2015).

4. Summary

Research conducted to date has proved that sorption is an effective and widely used method to remove metal ions from wastewater. This paper presented various kinds of adsorbents (natural organic, synthetic organic/polymers, mineral sorbents) (Table 1) that will enable the high recovery of various metals.

5. Conclusion

Based on the results obtained by various groups of scientists, it can be concluded that natural organic sorbents such as wood sawdust and the modified wood sawdust be used for the recovery of Cr^{3+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, and Ni^{2+} ions, but the peat and modified peats can be effective adsorbent to remove Cr^{6+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+} ions. Bark and modified bark can be used to remove Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Pd^{2+}, Pt^{2+}, and Au^{3+} ions. Except for natural organic sorbents, mineral sorbents are used to remove various metal ions. For example the zeolites and modified zeolites be used for the removal of Cd^{2+}, Fe^{3+}, Ca^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} ions, and the clay minerals for removal of Na+, K^{+}, Cs^{+}, Ca^{2+}, Pb^{2+}, Cd^{2+}, Ba^{2+}, Zn^{2+}, Cu^{2+}, and Ni^{2+} ions. In addition, the silica adsorbent, thanks to its properties, can be an effective adsorbent of Cr^{3+}, Cr^{6+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, and Mn^{2+} ions. The next group of the commonly used sorbents is synthetic organic/polymers sorbents, which allowed the recovery of Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Pd^{2+}, Pt^{2+}, and Au^{3+} ions from aqueous solutions.

A review of various adsorbents for the removal of metal ions shows that the appropriate selection of the sorbent allows for the effective recovery of practically all metal ions from wastewater.

Table 1. Review of selected adsorbents used in sorption processes for metals ions recovery

Kinds of adsorbent	**Adsorbent**	**Metal ions**
Natural organic sorbents	Wood sawdust and modified wood sawdust	Cr^{3+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}
	Peat and modified peat	Cr^{6+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}
	Bark and modified bark	Cr^{3+}, Cr^{6+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, Na^{+}
Synthetic organic/polymers sorbents	Various synthetic sorbents	Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Pd^{2+}, Pt^{2+}, Au^{3+}
Minerals sorbents	Zeolites and modified zeolites	Cd^{2+}, Fe^{3+}, Ca^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}
	Clay minerals	Na+, K^{+}, Cs^{+}, Ca^{2+}, Pb^{2+}, Cd^{2+}, Ba^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}
	Silica adsorbents	Cr^{3+}, Cr^{6+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Mn^{2+}

References

1. Akar, S., Lorstani, B., Sobhanardakani, S., Cheraghi, M., Moradi, O.: Surveying the efficiency of Plantanus orientalis bark as biosorbent for Ni and Cr(VI) removal from plating wastewater as a real sample. *Environmental Monitoring and Assessment*, 191(373), 2019.
2. Alshameri, A., He, H., Zhu, J., Xi, Y., Zhu, R., Ma, L., Tao, Q.: Adsorption of ammonium by different natural clay minerals: Characterization, kinectics and adsorption isotherms. *Applied Clay Science*, 159, 83–93, 2018.

3. Anbia, M., Kargosha, K., Khoshbooei, S.: Heavy metal ions removal from aqueous media by modified magnetic mesoporous silica MCM-48. *Chemical Engineering Research and Desig*n, 93, 779–788, 2015.

4. Artiushenko, O., Avila, E.P., Nazarkovsky, M., Zaitsev, V.: Reusable hydroxamate immobilized silica adsorbent for dispersive solid phase extraction and separation of rare earth metal ions. *Separation and Purification Technology,* 231, 115934, 2020.

5. Bai, L., Hu, H., Fu, W., Wan, J., Cheng, X., Zhuge, L., et al.: Synthesis of a novel silica-supported dithiocarbamate adsorbent and its properties for the removal of heavy metal ions. *Journal of Hazardous Materials*, 195, 261–275, 2011.

6. Balasubramanian, R., Perumal, S.V., Vijayaraghavan, K.: Equilibrium isotherm studies for the multicomponent adsorption of lead, zinc, and cadmium onto indonesian peat. *Industrial & Engineering Chemistry Reseach*, 48, 2093–2099, 2009.

7. Balintova, M., Demcak, S., Pagacova, B.: A study of sorption heavy metals by natural organic sorbents. *International Journal of Energy and Environment*, 10, 189–194, 2016.

8. Bandura, L., Woszuk, A., Kołodyńska, D., Franus, W.: Application of mineral sorbents for removal of petroleum substances: A review. *Minerals*, 7(3), 37, 2017.

9. Bartczak, P., Norman, M., Klapiszewski, Ł., Karwańska, N., Kawalec, M., Baczyńska, M., et al.: Removal of nickel(II) and lead(II) ions from aqueous solution using peat as a low-cost adsorbnet: A kinetic and equilibrium study. *Arabian Journal of Chemistry*, 11(8), 1209–1222, 2018.

10. Borhade, A.V., Kshirsagar, T.A., Dholi, A.G., Agashe, J.A.: Removal of heavy metals Cd^{2+}, Pb^{2+}, and Ni^{2+} from aqueous solution using synthsized azide cancrinite, $Na_8[AlSiO_4]_6(N_3)_{2.4}(H_2O)_{4.6}$. *Journal of Chemical & Engineering Data*, 60(3), 586–593, 2015.

11. Bratskaya, S., Privar, Y., Ustinov, A., Azarova, Y., Pestov, A.: Recovery of Au(III), Pt(II) using pyridyethyl-containing polymers: Chitosan derivatives vs synthetic polymers. *Industrial & Engineering Chemistry Research*, 55(39), 10377–10385, 2016.

12. Bulgariu, L., Ratoi, M., Bulgariu, D., Macoveanu, M.: Equilibrium study of Pb(II) and Hg(II) sorption from aqueous solutions by moss peat. *Environmental Engineering and Management Journal*, 7(5), 511–516, 2008.

13. Chakraborty, R., Asthana, A., Singh, A.K., Jain, B. Susan, A.B.H.: Adsorption of heavy metal ions by various low-cost adsorbents: a review. *International Journal of Environmental Analytical Chemistry*, 1–38, 2020.

14. Chatterjee, S., Paital, A.R.: Functionalized cubic mesoporous silica as a non-chemodosimetric fluorescence probe and adsorbent for selective detection and removal of bisulfite anions along with toxic metal ions. *Advanced Functional Materials*, 28(9), 1704726, 2018.

15. Chouikhi, N., Cecilia, J.A., Vilarrasa-Garcia, E., Besghaier, S., Chlendi, M., Duro, F.I.F., et al.: CO_2 adsorption of materials synthesized from clay minerals: A review. *Minerals*, 9(9), 514, 2019.

16. Coronas, J., Santamaria, J.: State-of-the-art. In zeolite membrane reactors. *Topics in Catalysis*, 29(1–2), 29–44, 2004.

17. Cristiani, C., Iannicelli-Zubiani, M., Bellotto, M., Dotelli, G., Stampino, P.G., Latorrata, S., et al.: Capture mechanism of La and Cu ions in mixed solution by clay and organoclay. *Industrial & Engineering Chemistry Research,* 60(18), 6803–6813, 2021.

18. da Silva Correia, I.K., Santos, P.F., Santana, C.S., Neris, J.B., Luzardo, F.H.M., Velasco, F.G.: Application of coconut shell, banana peel, spent coffee grounds, eucalyptus bark, piassava (Attalea funifera) and water hyacinth (Eichornia crassipes) in the adsorption of Pb^{2+} and Ni^{2+} ions in water. *Journal of Environmental Chemical Engineering*, 6(2), 2319–2334, 2018.

19. El-Sheikh, A., Fasfous, I.I., Al.-Salamin, R.M., Newman, A.P., Immobilization of citric acid and magnetite on sawdust for competive adsporption and extraction of metl ions from environmental waters, *Journal of Environmental Chemical Engineering,* 6, 2018, 5186–5195. DOI:10.1016/j.jece.2018.08.020.

20. Esmaeili, A., Mobini, M., Eslami, H.: Removal of heavy metals from acid mine drainage by native natural clay minerals, batch and continuous studies. *Applied Water Science*, 9(4), 2019, 97.

21. Far, H.S., Hasanzadeh, M., Najafi, M., Nezhad,T.R.M., Rabbani, M.: Efficient removal of Pb(II) and Co(II) ions from aqueous solution with a chromium-based metal-organic framework/activated carbon composites. *Industrial & Engineering Chemistry Research*, 60(11), 4332–4341, 2021.

22. Gawdzik, J.: Mobilność metali ciężkich w osadach ściekowych na przykładzie wybranej oczyszczalni ścieków (The mobility of heavy metals in sewage sludge on the example of a selected sewage treatment plant), *Inżynieria i Ochrona Środowiska*, 15(1), 5–15, 2012 (in Polish).

23. Georgin, J., Franco, D.S., Grassi, P., Tonato, D., Piccilli, D.G.A., Meili, L., Dotto, G.L.: Potential of Cedrella fissilis bark as an adsorbent for the removal of red 97 dye from aqueous effluents. *Environmental Science and Pollution Research*, 26, 19207–19219, 2019.

24. Gier, S., Johns, W.D.: Heavy metal-adsorption on micas and clay minerals studied by X-ray photoelectron spectroscopy, *Applied Clay Science*, 16(5–6), 289–299, 2000.

25. Guo, J., Liu, X., Han, M., Liu, Y., Ji, S.: Poly(N-acrylol-L-histidine)-modified wood sawdust as an efficient adsorbent for low-level heavy metal ions, *Cellulose*, 27, 8155–8167, 2020.

26. Hamdaoui, O.: Adsorption of Cu(II) from aqueous phase by Cedar bark, *Journal of Dispersion Science and Technology*, 38(8), 1087–1091, 2016.

27. Hamed, F. A. E., Yasin, S. I. B., Ali, M. S.: The removal of some metals by natural and modified zeolite from produced water. *Journal of Basic Applied Chemistry*, 5(2), 16–22, 2015.

28. Hashem, Md.A., Momen, Md.A., Hasan, M., Nur-A-Tomal, Md.S., Sheikh, Md.H.R.: Chromium removal tannery wastwater using Syzygium cumini bark adsorbent. *International Journal of Enfironmental Science and Technology*, 16, 1395–1404, 2019.

29. Ho, Y.S., Mckay, G.: The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Research*, 34(3), 735–742, 2000.

30. Huang, L. Liu, R., Yang, J., Shuai, Q., Yuliarto, B., Kaneti, Y., Yamauchi, Y.: Nanoarchitectured porous organic polymers and their environmental applications for removal of toxic metal ions. *Chemical Engineering Journal*, 408, 127991, 2021.

31. Ipeaiyeda, A.R., Tesi, G.O.: Sorption and desorption studies on toxic metals from brewery effluent using eggshell as adsorbent. *Advences in Natural Science*, 7(2), 15–24, 2014.

32. Ishatiaq, F., Bhatti, H.N., Khan, A., Iqbal, M., Kausar, A.: Polypyrole, polyaniline and sodium alginate biocomposites and adsorption-desorption efficiency for imidacloprid insecticide. *International Journal of Biological Macromolecules*, 147, 217–232, 2020.

33. Kebede, T.G., Dube, S., Mengistie, A.A., Nkambule, T.T., Nindi, M.M.: Moringa stenopetala bark: A novel green adsorbnet for the removal of metal ions from industrial effluents. *Physics and Chemistry of the Earth*, Part A/B/C, 107, 45–57, 2018.

34. Klapiszewski, Ł., Bartczak, P., Wysokowski, M., Jankowska, M., Kabat, K., Jesionowski, T.: Silica conjugated with kraft ligin and its use as a novel "green" sorbent for hazardous metal ions removal. *Chemical Engineering Journal*, 260, 684–693, 2015.

35. Li, X., Liu, N., Tang, L., Zhang, J.: Specific elevated adsorption and stability of cations in the interlayer compared with at the external surface of clay minerals. *Applied Clay Science*, 198, 105814, 2020.

36. Lu, X., Wang, F., Li, X-y., Shih K., Zeng E.Y.: Adsorption and thermal stabilization of Pb^{2+} and Cu^{2+} by zeolite. *Industrial & Engineering Chemistry Research*, 55(32), 8767–8776, 2016.

37. Mandal, K., Gu, Y., Westendorff, K.S., Li, S., Pihl, J.A., Grabow, L.C., et al.: Condition-dependent Pd speciation and NO adsorption in Pd/Zeolites. *ACS Catalysis*, 10(21), 12801–12818, 2020.

38. Men'shchikov, I., Shkolin, A., Khozina, E., Fomkin, A.: Termodynamics of adsorber methane storage systems based on peat-derived activated carbons. *Nanomaterials*, 10(7), 1379, 2020.

39. Naiya, T.K., Chowdhury, P., Bhattacharya, A.K., Das, S.K.: Saw dust and neem brark as low-cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions. *Chemical Engineering Journal*, 148(1), 68–79, 2009.

40. Najafi, M., Yousefi, Y., Rafati, A.A.: Synthesis, characterization and adsorption studies of severalheavy metal ions on amino-functionalized silica nano hollow sphere and silica gel. *Separation and Purification Technology*, 85, 193–205, 2012.

41. Obaid, S.S., Gaikwad, D.K., Sayyed, M.I., AL-Rashdi, K., Pawar, P.P.: Heavy metal ions removal from waste water bythe natural zeolites. *Materials Today: Proceedings*, 5,17930–17934, 2018.

42. Ouyang, D., Zhuo, Y., Hu, Y., Zeng, Q., Hu, Y., He, Z.: Research on the adsorption behavior of heavy metal ions by porous material prepared with silicate tailings. *Minerals*, 9(5), 291, 2019.

43. Phuoc, H.N., Le, Q.T., Pham, T.C.T., Le, T.T.: Synthesis of glue-free NaA zeolite granules from natural kaolin for the adsorption of Pb(II) ions in aqueous solution using a fixed-bed column study. *ACS Omega*, 6(32), 21024–21032, 2021.

44. Pijarowski, P.M., Tic, W.J.: Research on using mineral sorbents for a sorption process in the environment contaminated with petroleum substances, *Civil and Environmental Engineering Reports*, 12(1), 83–93, 2014.

45. Priyantha, N., Lim, L.B.L., Wickramasooriya, S.: Adsorption behaviour of Cr(VI) by Muthurajawela peat. *Desalination and Water Treatment*, 57(35), 16592–16600, 2016. DOI:10.1080/19443994.2015.1081835.

46. Qian, G., Song, H., Yao, S.: Immobilized chiral tropine ionic liquid on silica gel as adsorbent for separation of metal ions and racemic amino acids. *Journal of Chromatography A*, 1429, 127–133, 2016.

47. Rafatullah, M., Sulaiman, O., Hashim, R., Ahmad, A.: Adsorption of copper(II), chromium(III), nickel(II), and lead (II) from aqueous solutions by meranti sawdust. *Journal of Hazardous Materials*, 170(2–3), 969–977, 2009.

48. Raganati, F., Miccio, F., Ammendola, P.: Adsorption of Carbon Dioxide for Post-combustion Capture: A Review. *Energy Fuels*, 35(16), 12845–12868, 2021.

49. Rahman, M.S., Islam, M.R.: Effects of pH on isotherms modeling for Cu(II) ions adsorption using maple wood sawdust. *Chemical Engineering Journal*, 149(1–3), 273–280, 2009.

50. Rakhym, A.B., Seilkhanova, G.A., Mastai, Y.: Physicochemical evaluation of the effect of natural zeolite modification with didodecylmethylammonium bromide on the adsorption of bisphenol-A and propanol hydrochloride. *Microporous and Mesoporous Materilas*, 318, 111020, 2021.

51. Ringqvist, L., Holmgren, A., Oborn, I.: Poorly humified peat as an adsorbent for metals in wastewater. *Waste Research*, 36(9), 2394–2404, 2002.

52. Saeed, B., Anwer, H., Naqvi, S., Siddiqui, A., Hashim, S.: Biosorption of hexavalent chromium metal ions from an aqueous solution of leaves and bark of Cinnamomum verum via green rout. *SN Applied Sciences*, 2(526), 2020.

53. Schmitt, D., Taylor, H.E., Aiken, G.R., Roth, D.A., Frimmel, F.H.: Influence of natural organic matter on the adsorption of metal ions onto clay minerals. *Environmental Science & Technology*, 36(13), 2932–2938, 2002.

54. Sebastian, A., Nangia, A., Prasad, M.N.V.: Cadmium and sodium adsorption properties of megnetite nanoparticles synthesized from Hevea brasiliensis Muell. Agr. Bark: Relevance in amelioration of metl stress in rice. *Journal of Hazardous Materials*, 371, 261–272, 2019.

55. Sen. A., Pereira. H., Olivella. M.A., Villaescusa. I.: Heavy metals removal in aqueous environments using bark as a biosorbent. *International Journal of Environmental Science and Technology*, 12, 391–404, 2015.

56. Senkal. B.F., Bicak. N.: Glycidyl methacrylate based polymer resins with diethylene triamine tetra acetic acid functions for efficient removal of Ca(II) and Mg(II). *Reactive and Functional Polymers*, 49(2), 151–157, 2001.

57. Shemshadi. R., Arvand. M., Efendiev. A.A., Zeynalov. N.A.: Application of synthetic polymers as adsorbents for the removal of cadmium from aqueous solutions: Batch experiments. *Caspian Journal of Environmental Sciences*, 10(1), 1–8, 2012.

58. Shi, J., Yang. Z., Dai, H., Lu, X., Peng, L., Tan, X., et al.: Preparation and application of modified zeolites as adsorbents in wastewater treatment. *Water Science & Technology*, 3, 621–635, 2017. DOI:10.2166/wst.2018.249.

59. Tan, M.X., Sum, Y.N., Ying, J.Y., Zhang, Y.: A mesoporous poly-melamine-formaldehyde polymer as a solid sorbent for toxic metal removal. *Energy & Environmental Science*, 11, 2013.

60. Tan, Y., Wang, K., Yan, Q., Zhang, S., Li, J., Ji, Y.: Synthesis of amino-functionalized waste wood flour adsorbent for high-capacity Pb(II) adsorption, *ACS Omega*, 4(6), 10475–10484, 2019.

61. Thirumavalavan, M., Wang, Y.T., Lin, L.C., Lee, J.F.: Monitoring of the structure of mesoporous silica materials tailored using different organic templates and their effect on the adsorption of heavy metal ions. *The Journal of Physical Chemistry C*, 115(16), 8165–8174, 2011.

62. Uddin, M.K.: A review on the adsorption of heavy metals by clay minerals, with special Focus on the past decade. *Chemical Engineering Journal*, 308, 438–462, 2017.

63. Ugwu, A.I., Tursunov, O., Kodirov, D., Shaker, L.M., Al-Amiery, A.A., Yangibaeva, I., Shavkarov, F.: Adsorption mechanism for heavy metal removing using low cost adsorbents: A review. *IOP Conference Series: Earth and Environmental Science*, 614, 012166, 2020.

64. Varma, A.K., Thakur, L.S., Shankar, R., Mondal, P.: Pyrolysis of wood sawdust: Effect of process parameters on products yield and characterization of products. *Waste Management*, 89, 224–235, 2019.

65. Vijayaraghavan, K., Rangabhashiyam, S., Ashokkumar, T., Arockiaraj J.: Mono- and multi-component biosorption of lead(II), cadmium(II), copper(II) and nickel(II) ions onto coco-peat biomass. *Separation Science and Technology*, 51(17), 2725–2733, 2016.

66. Wajima, T.: Preparation of carbonaceous heavy metal adsorbent from cedar bark using sulfur-impregnation. *International Journal of Chemical Engineering and Application,* 8(4), 272–276, 2017.

67. Wang, S., Peng, Y.: Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal,* 156(1), 11–24, 2010.

68. Weiner, R.F., Matthews, R.A.: Environmental Engineering, Elsevier Science, Burlington 2003.

69. Xu, M., Chen, S., Seo, D.K., Deng, S.: Evaluation and optimalization of VPSA processes with nanostructured zeolite NaX for post-combustion CO_2 capture, *Chemical Engineering Journal*, 371, 693–705, 2019.

70. Zaharia, M.M., Bucatariu, F., Doroftei, F., Loghin, D.F., Vasiliu, A.L., Mihai, M.: Multifunctional $CaCO_3$/polyelectrolyte sorbents for heavy metal ions decontamination of synthetic waters. *Colloids and Surfaces A: Physicochemical and Engineering Aspect*s, 613, 126084, 2021.

71. Zhao, G., Wu, X., Tan, X., Wang, X.: Sorption of heavy metal ions from aqueous solution: A review. *The Open Colloid Science Journal,* 4, 19–31, 2010.

72. Zhao, J., Zhu, Y.J., Wu, J., Zheng, J.Q., Zha, X.Y., Lu, B.Q., Chen, F.: Chitosan-coated mesoporous microspheres of synthesis and application as a highly efficient adsorbent for heavy metal ions. *Journal of Colloid and Interface Science,* 418, 208–215, 2014.

Statistical investigations of methods for calculation of hydraulic friction factor in water distribution pipelines

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Abstract

The most widespread solutions of Colebrook-White equation are studied in the article. The hydraulic equations for determination of the friction coefficient were proceeded statistically. Mean, maximum, minimum, standard deviation and mean deviation from friction coefficient of *Colebrook-White* were calculated for the friction coefficient derived from each equation. The results of the comparative analysis of the evaluation criteria are adduced for the whole range of independent parameters *Re* and *k*/*d*. Mathematical equations are proposed for the most accurate calculation of the hydraulic friction coefficient.

Keywords: *Colebrook-White* equation, hydraulic friction factor *Darcy H*, water distribution pipelines, *Lambert* function, absolute pipe roughness, *Reynolds* number, hydrodynamic processes

1. Introduction

The cost of water supply networks in the total cost of water supply systems occupies a significant share, which often exceeds 50%, so even minor errors in their design significantly affect the economic performance of the system as a whole (Halperin, 2010; Merkl, 2008). Under such conditions, the requirements for the quality of hydraulic calculations of pipeline systems increase significantly.

In the world practice of hydraulic calculations of pipe networks of water supply and sewerage facilities, a method based on the use of the *Colebrook-White* equation proposed in 1938 has become widespread (Colebrook and White, 1937; Moody, 1944; Hager, 2010).

$$\frac{1}{\sqrt{\lambda}} = -2log\left(\frac{k}{3{,}71d} + \frac{2{,}51}{Re\sqrt{\lambda}}\right), \tag{1}$$

where λ is the coefficient of hydraulic resistance along the length of the pipe (*Darcy* coefficient – *Darcy H.*); *d* is the diameter of the pipe, m; *Re* – Reynolds number (*Reynolds O*); *k* is the absolute roughness of the inner surface of the pipe (average height of the protrusions on the inner surface of the pipe, which determine its roughness), m; *k/d* is the relative roughness of the inner surface of the pipe.

Equation (1) describes the dependence of $\lambda = f(k/d;\ Re)$ in the region of turbulent flow, i.e. in the whole range of changes of the studied parameters $3.6 \cdot 10^3 \leq Re \leq 10^8$ and $2 \cdot 10^{-2} \geq k/d \geq 5 \cdot 10^{-4}$. At the same time, it is obvious from the equation (1) that with a significant increase in the value of the parameter $Re \rightarrow \infty$ its second component tends to zero ($2.51/Re\sqrt{\lambda} \rightarrow 0$), and the equation itself takes the form of the equation of Nikuradse (Genić et al., 2011; Haaland, 1983):

$$\frac{1}{\sqrt{\lambda}} = -2log\left(\frac{k}{3.71d}\right). \tag{2}$$

Equation (2) describes the dependence of the parameter λ in the turbulent zone, which depends entirely on the relative roughness of the inner surface of pipe and does not depend on the parameter *Re*. At the same time, for $k \rightarrow 0$, the first component of the equation (1) is equal to zero, which occurs for a perfectly smooth inner surface of pipe.

$$\frac{1}{\sqrt{\lambda}} = -2log\left(\frac{2.51}{Re\sqrt{\lambda}}\right). \tag{3}$$

The equation (3) describes the pattern of the change of the parameter λ exclusively depending on the change of the parameter *Re* for the zone of absolutely smooth pipes ($k = 0$).

The boundary between the transition and turbulent zones is described by the equation (Arbeitsblatt, 2020; Ettema, 2006; Bollrich, 2013):

$$\sqrt{\lambda} = \frac{200}{Re_t}\frac{d}{k}. \tag{4}$$

Whereby, taking into account the equation (2), the equation (4) takes form:

$$Re_t = -400\frac{d}{k}log\left(\frac{k}{3.71d}\right). \tag{5}$$

Figure 1 shows graphs of the dependence of the coefficient of hydraulic resistance along the length of the pipe $\lambda_{Col\text{-}W}$, calculated by the equation *Colebrook-White* (1) in a wide range of changes in the independent parameters – $3{,}6{\cdot}10^3 \leq Re \leq \infty$ and $2{\cdot}10^{-2} \geq k/d \geq 0$.

The equation (1) refers to transcendental functions that do not satisfy the elementary mathematical equations, and is recognized as the one that most fully takes into account the main factors that affect the value of the parameter λ. However, the difficulties that arise during the calculations of λ by the equation (1) cause the search for such mathematical equations that would allow to obtain results that most accurately correspond to the calculations using the equation (1). Numerous scientific papers have proposed a large number of solutions to this problem (Altshul and Kiselev, 1975; Genić et al., 2011; Zanke, 1993). However, the presence of numerous proposals designed to solve this problem indicates both a significant scientific interest in it and the incompleteness of the available solutions. In a number of scientific works devoted to the analysis of existing methods for calculating the parameter λ, recommendations and substantiation of the best methods are given (Genić et al., 2011; Lipovka and Lipovka, 2014; Semkło et al., 2015).

Our research is based on the methods of calculating the parameter λ, which are widely used in the engineering practice, but have not been the subject of analytical research in other scientific papers, and methods recommended as the most advanced in research papers and in technical regulations.

The line $k/d = 0$ outlines the range of water movement in hydraulically smooth pipes; line a – a ($Re \to \infty$) delineates the boundary between the hydraulic resistance in the transition and turbulent zones of rough pipes.

The equation of Altschul (1950) proposed by the author in 1950, became widespread for calculating the value of the parameter λ.

$$\lambda = 0.11\left(\frac{68}{Re} + \frac{k}{d}\right)^{0.25}. \tag{6}$$

The results of calculations by this equation, although are not identical to the results of calculations by the equation (1), but approach them (Smyslov, 1979).

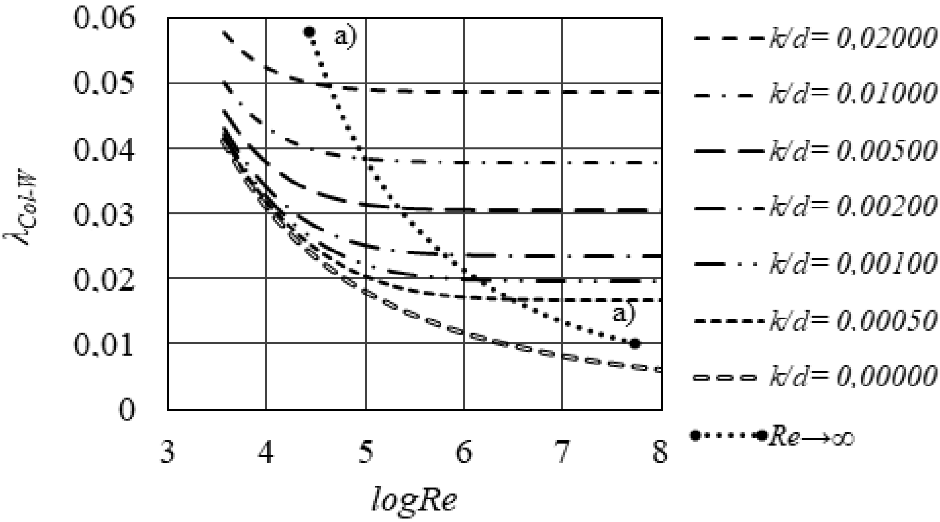


Fig. 1. Graphs of the dependence of λ_i on Re for $3.6 \cdot 10^3 \leq Re \leq \infty$ and $0 \leq k/d \leq 2 \cdot 10^{-2}$, constructed from the results of calculations by the equation (1)

For hydraulic calculations of pipelines made of different materials, in the engineering practice of Ukraine, Russia and other Eastern European countries, the use of several mathematical equations is widespread (DSTU-NBV.2.5-40, 2009; SNiP II-G.3-62, 1963; Shevelev, 1973). Thus, for not new steel pipes, the roughness of the inner surface of which is equivalent to the artificial roughness, which can be depicted by applying sand with a grain size of 1 mm (k = 0.001 m) on their inner surface, Shevelev (1973) proposed to calculate the value of the parameter λ for the transition zone by the equation (SNiP II -G.3-62, 1963):

$$\lambda = \frac{1}{d^{0{,}3}}\left(1.5 \cdot 10^{-6} + \frac{\nu}{v}\right)^{0.3}, \tag{7}$$

and for the turbulent zone:

$$\lambda = \frac{0.021}{d^{0.3}}, \tag{8}$$

or after applying the parameter $k = 0.001$ in the equations (7 and 8) and carrying out certain transformations, they will take the form:

$$\lambda = 0.211\left(\frac{k}{3.71d} + \frac{179.7}{Re}\right)^{0,3}, \tag{9}$$

$$\lambda = 0.247\left(\frac{k}{3.71d}\right)^{0,3}, \tag{10}$$

In order to simplify the use of mathematical equations (7–10), their author proposed appropriate spreadsheets for determining λ (Shevelev, 1973).

To determine the parameter λ of plastic pipes Dobromyslov (2004) proposed a complex mathematical equation designed to obtain the most accurate results λ (DSTU-NBV.2.5-40, 2009):

$$\sqrt{\lambda} = \frac{0.5\left[\frac{b}{2} + \frac{1.312(2-b)\log(3.7d/k\,)}{logRe - 1}\right]}{log(3.7d/k)},$$

$$b = 1 + \frac{logRe}{log\left(\frac{500d}{k}\right)}. \tag{11}$$

The proposed equation is recommended to be used for hydraulic calculations of pipes with the roughness coefficient of their inner surface not less than 0.01 mm ($k \geq 0.00001$ m) (DSTU-NBV.2.5-40, 2009).

In the world practice of hydraulic calculations of pipe networks for the approximate solution of the *Colebrook-White* equation, the mathematical equation has become widespread (Goudar and Sonnad, 2006; Brunaet al., 2018; Semkło et al., 2015; Sonnad and Goudar, 2006):

$$\frac{1}{\sqrt{\lambda}} = 0.8686ln\left(\frac{0.4587Re}{(S-0.31)^{\frac{S}{S+1}}}\right),$$

$$S = 0.124Re\frac{k}{d} + \ln(0.4587Re). \tag{12}$$

The parameters included in the equations (11, 12) are identical to those in the equation (1), but the structure of these equations differs significantly, and is characterized by a certain inconvenience of their practical application. Under boundary conditions, Re → ∞, or k → 0, the equations (6–12) differ significantly from the equation (1) under the same conditions, which indicates the possibility to obtain somewhat different results of calculations using these equations.

There are a large number of mathematical equations designed to obtain the results of calculations of λ_i as close as possible to the results of calculations on the equation (1) in the whole range of its application (Re → ∞, or k → 0). Among these equations are the mathematical equation of Haaland S.E., and the equations Zigrang and Sylvester (1982), Zanke (1993), Offor and Alabi (2016), which have gained recognition in the practice of engineering calculations:

– equation of Haaland (1983) (Genić et al., 2011):

$$\frac{1}{\sqrt{\lambda}} = -1.8log\left[\frac{6.9}{Re} + \left(\frac{k}{3.7d}\right)^{1,11}\right]; \tag{13}$$

– equation of Zigrang and Sylvester (1982) (Genić et al., 2011):

$$\frac{1}{\sqrt{\lambda}} = -2log\left(\frac{k}{3.7d} - \frac{5.02}{Re}log\left(\frac{k}{3.7d} - \frac{5.02}{Re}log\left(\frac{k}{3.7d} + \frac{13}{Re}\right)\right)\right); \tag{14}$$

– equation of Zanke (1993) (ATV-DVWK-A 110, 2003; Rüdiger, 2009):

$$\lambda = \left[-2log\left(2.72\frac{(log(Re))^{1,2}}{Re} + \frac{k}{3.71d}\right)\right]^{-2}; \tag{15}$$

– equation of Offor and Alabi (2016) (Bruna et al., 2018; Popov et al., 2010):

$$\frac{1}{\lambda} = -2log\left(\frac{k}{3.71d} - \frac{1.975}{Re}\left(ln\left(\left(\frac{k}{3.91d}\right)^{1,092} + \frac{7.627}{Re + 395.9}\right)\right)\right). \tag{16}$$

From the analysis of the equations (13-16) follows that for Re → ∞ these equations are transformed into the equation of Prandtl and Nikuradse (Kiseleva 1972), and for *k/d* → 0 they acquire more complex form, although they have quite similar values of the parameter λ.

In modern studies of hydrodynamic processes, much attention is paid to the use of the function of Lambert (1758) (Yanyshev, 2015; Brkić, 2012). To calculate the value of the coefficient λ in (Brkić, 2012), Brkić (2012) recommended the equation:

$$\frac{1}{\sqrt{\lambda}} = -2 \cdot log\left(\frac{5.02 \cdot W\left[\frac{Re \cdot ln(10)}{5.02}\right]}{Re \cdot ln(10)} + \frac{k}{3.71d}\right), \tag{17}$$

where *W* is the function of Lambert.

The presence of the W – function in the equation (17) allows to provide an approximate calculation of the value of the coefficient λ (Brkić, 2012). But in order to use this mathematical equation, an appropriate software product is necessary.

As a result of scientific research, we have proposed a mathematical equation that has a high convergence of the results of calculations with the results of calculations on equation (1) and is suitable for calculation of the parameter λ in the whole range of application of the *Colebrook-White* equation:

$$\frac{1}{\sqrt{\lambda}} = -2log\left(-\frac{5.02}{Re}log\left(-\frac{5.02}{Re}log\left(-\frac{5.02}{Re}log\left(-\frac{5.02}{Re}log\left(\frac{12.84}{Re} + \frac{k}{3.71d}\right) + \frac{k}{3.71d}\right) + \frac{k}{3.71d}\right) + \frac{k}{3.71d}\right) + \frac{k}{3.71d}\right). \tag{18}$$

It follows from the above that in the mentioned methods the most controversial issue is the conceptual approach to calculating the parameter λ by the equation (1). It should be noted, that the inaccuracies in determining this parameter, cause errors in the selection of pumps that supply water to pressure networks. Underestimation of the values of λ causes the system to malfunction, and its overestimation leads to the use of pumps of excessive power, which, in turn, has a negative impact on the economic performance of the system as a whole.

The aim of the research is to evaluate the conformity of the calculation results of the parameter λ according to the known methods (equations 6–18) to the calculation results according to the equation (1) and on this basis to substantiate a better method of determining the coefficient of hydraulic friction in water supply pipelines.

Numerical studies of the equations (1–18) to determine λ were performed for pressure pipes of circular cross section in the range of change of independent parameters included in the equation (1) $3.5 \cdot 10^3 \leq Re \leq 10^8$, $0.0001 \leq k/d \leq 0.02$.

The task of the research was to determine the mathematical equation that can most accurately describe the studied parameter.

Statistical evaluation of the calculated value of the coefficient λ by the studied equations and the *Colebrook-White* equation was performed according to the following procedure (Asker et al., 2014; Genić et al., 2011):

– for all studied equations (1–18) the pattern of change of independent parameters *Re* and *k/d* in the whole range of study was identical;

– the correspondence of the coefficient λ_i, calculated by the equations (6–18) to the value of the same parameter $\lambda_{Col\text{-}W}$, calculated under the same conditions, by the equation (1), was chosen as an estimation parameter;

– all calculations were performed using *Microsoft Excel*;
– on the basis of the analysis of calculations results of the coefficient λ using various methods, the substantiation of the mathematical equation which allows to receive the most exact results was carried out;
– following criteria were chosen to evaluate the studied equations (Asker et al., 2014):

– mean relative deviation;

$$Rel = \frac{1}{n}\sum_{i=1}^{n}\frac{\lambda_{Col-W} - \lambda_i}{\lambda_{Col-W}}, \tag{19}$$

– maximum relative deviation;

$$Rel_{max} = \frac{\lambda_{Col-W} - \lambda_i}{\lambda_{Col-W}}, \tag{20}$$

– minimum relative deviation;

$$Rel_{min} = \frac{\lambda_{Col-W} - \lambda_i}{\lambda_{Col-W}}, \tag{21}$$

– standard deviation;

$$SD = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\lambda_{Col-W} - \lambda_i}{\lambda_{Col-W}}\right)^2}, \tag{22}$$

– mean deviation;

$$MD = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\lambda_{Col-W} - \lambda_i}{\lambda_{Col-W}}\right|, \tag{23}$$

where λ_{Col-W} is the value of the parameter λ, calculated by the equation of *Colebrook-White* (1); λ_i is the value of the parameter λ, calculated by the equations (6–18); *n* is the number of calculated values.

It should be noted that the criteria for the average values of *Rel*, *SD*, *MD* are a qualitative assessment of the average values of the studied parameters in a wide range of changes *Re* and *k/d*, while the evaluation criteria Rel_{min} and Rel_{max} allow us to have an idea of the range of deviations of the value λ_i from the value λ_{Col-W}, for certain values of *Re* and *k/d*. This feature of the evaluation criteria Rel_{min} and Rel_{max} allows, depending on the requirements of engineering practice, to determine the areas of rational application of a given mathematical equation.

According to the mathematical equations (1–18) a series of numerical experiments was performed and the graphs presented in Figure 2 were constructed. A common feature of the graphs of all figures (Fig. 2) is the presence of deviations ($R = [\lambda_{Col-W} - \lambda_i] / \lambda_{Col-W}$) of the calculated value of λ_i by the expressions (6–18) from the value of $\lambda_{Col\text{-}W}$. The value of such deviation varies depending on the values of the parameter *Re* and *k/d*. All graphs have no sudden peaks and are described by smooth lines. Moreover, such deviations are observed mainly in the region of small values of the parameter *log(Re)*, with increasing of which the value of the parameter *R* decreases. In certain figures, the graphs are characterized by both negative and positive values of the ordinates (Fig. 2 – b, c, f–j). The graphs of individual figures (Fig. 2 – b–f, h–j) have extreme values of deviations (R), which may cause significant errors in hydraulic calculations. This should be taken into account when making engineering decisions. In a part of the figures (Fig. 2 – a, d, e), all graphs within the conducted researches are located in the zone of negative values of ordinates.

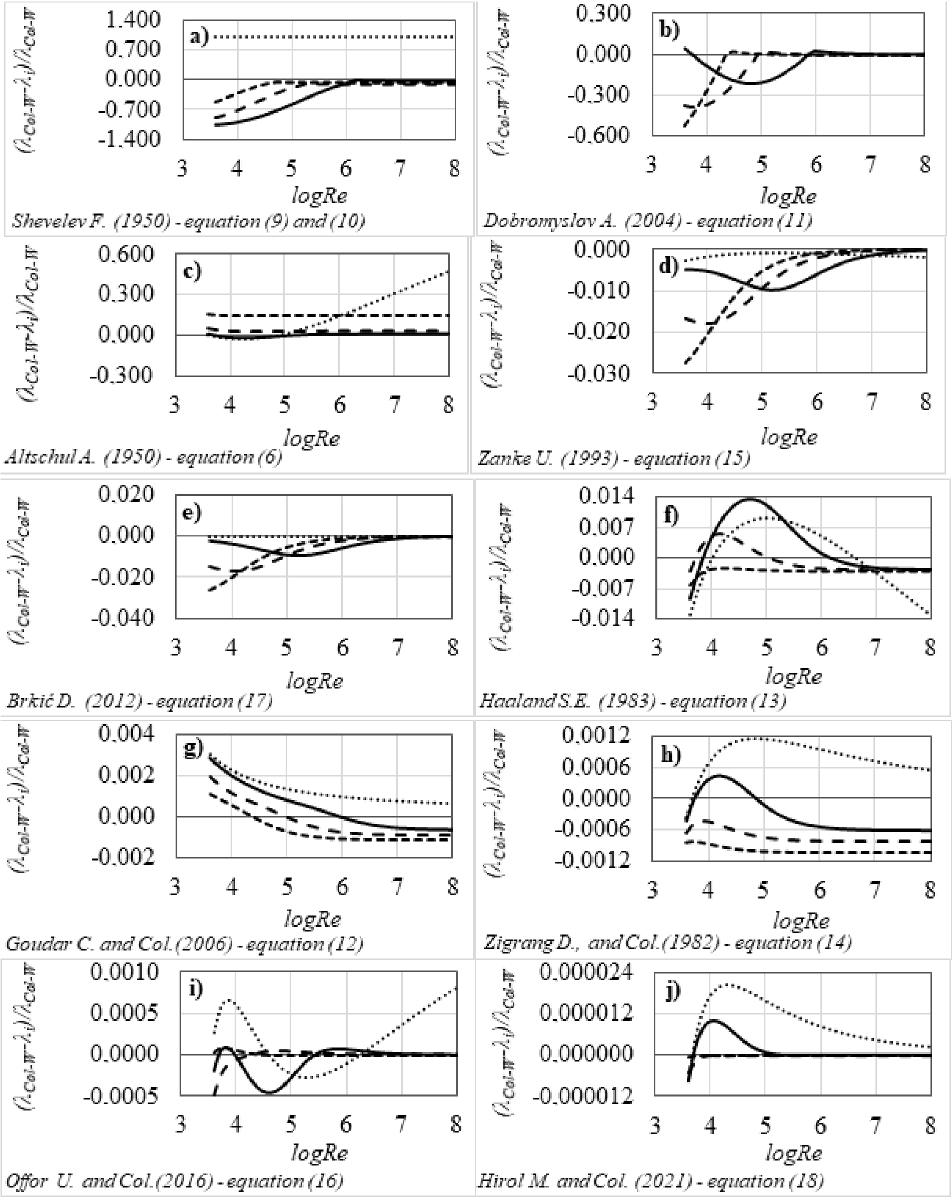
In a part of the graphs, the value of the parameter *R* becomes significant and occurs in the range of $-1.12 \leq R \leq 0.15$ (Fig. 2 –a, b, c). The graphs $R = f\,(logRe)$ for (Fig. 2 – c) are located mainly above the abscissa and are almost parallel to it. The value of the parameter *R* for these graphs, especially for the large values of *k/d* (*k/d* = 0.02) is quite noticeable and reaches 0.15, and the range of its change is $-0.02 \leq R \leq 0.15$.

For the rest of the graphs (Fig.2 – d, e, f) the value of the parameter of relative deviation *R* is significantly smaller ($-0.03 \leq R \leq 0.015$) than the similar parameter for the graphs (Fig.2 – a-d) ($-1.12 \leq R \leq 0.15$). This indicates that the calculation of the parameter λ by the corresponding mathematical equations (13, 15, 17) provides results with a deviation from the results of calculations by the equation of *Colebrook – White* less than 5%.

The best results of calculations of the parameter λ were achieved by the equations (12, 14, 16, 18), as evidenced by the graphs of Figures 2 – g–j. The value of the parameter *R* obtained according to these equations usually did not exceed $R \leq 0.003$. Ignoring the difference in the shape of the graphs shown in Figure 2 – g, h the value of the range of limits of change of the parameter *R*, within the studies, in both cases (Figure 2–g and 2–h) was proportional $-0.001 \leq R \leq 0.003$. The results of calculations of the parameter λ by the equation (16) were slightly better, and the limits of the range of change of the parameter *R* had a slightly smaller value: $-0.0005 \leq R \leq 0.0001$.

The most complete correspondence between the results of calculations on the studied equations (6–18) and equation (1) in the course of research was obtained for the equation (18). The value of the parameter *R* for this equation did not exceed 0.00001, and the range of its change was $-0.000007 \leq R \leq 0.00001$.

The results of studies of the correspondence of the parameter $\lambda_{Col\text{-}W}$, calculated by the equation (1), and the calculated value of λ_i obtained by the equations (6–18) served as a basis for a deeper analysis according to the previously described method.



Shevelev F. (1950) - equation (9) and (10)
Dobromyslov A. (2004) - equation (11)
Altschul A. (1950) - equation (6)
Zanke U. (1993) - equation (15)
Brkić D. (2012) - equation (17)
Haaland S.E. (1983) - equation (13)
Goudar C. and Col. (2006) - equation (12)
Zigrang D., and Col. (1982) - equation (14)
Offor U. and Col. (2016) - equation (16)
Hirol M. and Col. (2021) - equation (18)

Fig.2. Graphs of the function $Rel_i = (\lambda_{Col-W} - \lambda_i)/\lambda_{Col-W} = f(Re; k/d)$ for the mathematical equations (1-18) under the condition ------- – *k/d* = $2{\cdot}10^{-2}$; — — — – *k/d* = $5{\cdot}10^{-3}$; ——— – *k/d* = $5.6{\cdot}10^{-4}$; ·········· – *k/d* = 0

The magnitude of the mean and minimum relative deviation *Rel* and Rel_{min} between the results of calculations by the equations (1) and (6) (A. Altshul), respectively, are *Rel* = $-3.9{\cdot}10^{-2}$ and $Rel_{min} = -2.0{\cdot}10^{-2}$. At the same time, the maximum value of Rel_{max} reaches $1.5{\cdot}10^{-1}$, which when calculating the pressure loss in the pipelines leads to the use of a larger value of the total required pressure in the system, and thus, it leads to an increase in electricity consumption. Since the maximum value of the standard and mean deviations of λ_i from $\lambda_{Col\text{-}W}$ (Rel_{max} = $1.5 \cdot 10^{-1}$; SD = $6.6 \cdot 10^{-2}$; MD = $4.3 \cdot 10^{-2}$) calculated by the equation (6) are large, this led to a relatively small spread of equation (6) in engineering calculations. Certain limitations of this equation are noted in the works of other authors (Asker et al., 2014; Genić et al., 2011; Popov et al., 2010). It should be noted that in almost the entire range of changes of the independent parameters $Re \to \infty$, $k/d \to 0$ the values of λ by the equation (6) are less than $\lambda_{Col\text{-}W}$, as evidenced by the absence of a "minus" sign before the numerical values of the evaluation criteria Rel, Rel_{max}, Rel_{min}, shown in the Table 1.

The value of the evaluation criterion Rel for the equations (7–10) (Shevelev, 1950) is $Rel = -3.4 \cdot 10^{-1}$. The value of $Rel_{max} = -1.1 \cdot 10^{-2}$ and $Rel_{min} = -1.1 \cdot 10^{\pm 0}$ (Table 1). It follows from the above that under certain conditions the obtained results of calculations by the equations (7–10) are close to the results of calculations by the equation (1), but the significant value of the values of the evaluation criteria $SD = 4.7 \cdot 10^{-1}$, $MD = 3.4 \cdot 10^{-1}$ and $Rel_{max} = -1.1 \cdot 10^{\pm 0}$ for the equations (7–10) reduce the value of its practical application.

The values of the evaluation criteria for the equation (11) (Dobromyslov, 2004) are quite close to the values of the evaluation criteria of the equation (6), and therefore the restrictions noted for the equation (6) also apply for the equation (11) (Table 1). The difference between the evaluation criteria for this equation is that the evaluation criterion Rel_{min} has a negative and close to zero value, which indicates the presence of a zone of independent variable parameters ($Re \to \infty$ and $k/d \to 0$), in which the value of $\lambda_{Col\text{-}W} \leq \lambda_i$. In addition, in the zone of smooth pipes ($k/d \to 0$) the value of Rel increases significantly, and for $k/d = 0$ the equation (11) has no rationally significant solutions. Such features of the equation (11) cause certain restrictions on its wide practical application.

Calculations of λ_i by the equation (10) (Goudar and Sonnad, 2006) and their subsequent statistical processing show that the values of almost all evaluation criteria (Rel, Rel_{max}, Rel_{min}, SD, MD) are significantly better than those that characterize the previous equations (Table 1). The minus sign in front of Rel indicates that the values obtained by the equation (10) are preferably greater than the values of $\lambda_{Col\text{-}W}$ obtained by the equation (1). As in the previous case, with a negative value of the evaluation criteria Rel and Rel_{min}, the Rel_{max} criterion has a positive value, which indicates the presence of a zone of values of independent variable parameters ($Re \to \infty$ and $k/d \to 0$), in which the values of $\lambda_{Col\text{-}W} \geq \lambda i$. It should be noted that the evaluation criteria for the equation (12) increase as the parameter *Re* increases ($Re \rightarrow \infty$), which has a somewhat negative effect on the accuracy of the results of calculations of the parameter λ.

Table 1. The results of statistical calculations of λ using equations (6–18) for $3.6\cdot10^3 \leq Re \leq \infty$ and $0 \leq k/d \leq 2\cdot10^{-2}$

Nr	**Publication**	**Values of evaluation criteria**				
		Rel	***Rel*** $_{max}$	***Rel*** $_{min}$	***MD***	***SD***
1	Equation (6) (Altschul, 1950)	$-3.9\cdot10^{-2}$	$1.5\cdot10^{-1}$	$-2.0\cdot10^{-2}$	$4.3\cdot10^{-2}$	$6.6\cdot10^{-2}$
2	Equations (9) and (10) (Shevelev, 1950), (for not new pipes)	$-3.4\cdot10^{-1}$	$-1.1\cdot10^{-2}$	$-1.1\cdot10^{\pm0}$	$3.4\cdot10^{-1}$	$4.7\cdot10^{-1}$
3	Equation (11) Dobromyslov, 2004) (DSTU-NBV.2.5-40:2009)	$-9.2\cdot10^{-2}$	$4.4\cdot10^{-2}$	$-5.2\cdot10^{-1}$	$9.9\cdot10^{-2}$	$1.6\cdot10^{-1}$
4	Equation (12) (Goudar and Sonnad, 2006)	$1.6\cdot10^{-4}$	$2.9\cdot10^{-3}$	$-1.1\cdot10^{-3}$	$8.6\cdot10^{-4}$	$1.0\cdot10^{-3}$
5	Equation (13) (Haaland, 1983)	$7.6\cdot10^{-4}$	$1.3\cdot10^{-2}$	$-9.3\cdot10^{-3}$	$3.9\cdot10^{-3}$	$5.0\cdot10^{-3}$
6	Equation (14) (Zigrang and Sylvester, 1982)	$-5.8\cdot10^{-4}$	$4.4\cdot10^{-4}$	$-1.0\cdot10^{-3}$	$6.2\cdot10^{-4}$	$6.8\cdot10^{-4}$
7	Equation (15) (Zanke, 1993)	$-6.9\cdot10^{-3}$	$-1.5\cdot10^{-5}$	$-2.7\cdot10^{-2}$	$6.9\cdot10^{-3}$	$9.3\cdot10^{-3}$
8	Equation (16) (Offor and Alabi, 2016)	$-4.6\cdot10^{-5}$	$9.0\cdot10^{-5}$	$-5.5\cdot10^{-4}$	$7.5\cdot10^{-5}$	$1.4\cdot10^{-4}$
9	Equation (17) (Brkić, 2012)	$-6.5\cdot10^{-3}$	$-1.5\cdot10^{-5}$	$-2.6\cdot10^{-2}$	$6.5\cdot10^{-3}$	$8.9\cdot10^{-3}$
10	Equation (18) (Hirol et al., 2021)	$4.7\cdot10^{-7}$	$9.9\cdot10^{-6}$	$-7.7\cdot10^{-6}$	$9.2\cdot10^{-7}$	$2.3\cdot10^{-6}$

Note: the "minus" sign before the numerical value of the evaluation criterion indicates a smaller calculated value of λ_i, calculated by the equations (6–18), in comparison with the value of $\lambda_{Col\text{-}W}$, calculated by the equation (1)

The value of the average relative deviation of the results of calculations by the equation (13) (Haaland, 1983) has a positive value and is equal $Rel = 7.6\cdot10^{-4}$, which is commensurate with the similar value of the evaluation criterion for the equation (12), but the value of other evaluation criteria (Rel_{max}, Rel_{min}, *SD, MD*) are characterized by significantly larger values, which indicates a certain decrease in the accuracy of calculations (Table 1). In addition, as the values of the Reynolds number (*Re*) increase and tend to infinity ($Re \rightarrow \infty$), the value of the evaluation criteria increases, which is obviously due to the presence of the exponent in the equation (13) for the parameter *k/d*.

The *Rel* criterion calculated for the equation (14) (Zigrang and Sylvester, 1982) has smaller values ($Rel = -5.8\cdot10^{-4}$) compared to the values of the similar criterion for the equations (4–9), although slightly higher than the value of similar criterion for the equations (12) and (13), and the maximum value of the evaluation criterion Rel_{max} is $-4.4\cdot10^{-4}$. In addition, the values of the evaluation criteria Rel_{min}, SD and MD in this equation are somewhat inferior to the correspondent values by the equation (12) (Table 1). Along with a certain increase in the evaluation criteria of the equation (14) in comparison with similar criteria for the equation (12), the advantage of the equation (14) is the relative constancy of these criteria in the boundary zones ($3.6\cdot10^3 \le Re \le 10^6$ and $0.0001 \le k/d \le 0.02$) of independent variable parameters.

The absolute values of the evaluation criteria for the equation (15) (Zanke, 1993) approach the values of the similar criteria obtained for the equation (12). Moreover the values of the SD and MD criteria are almost identical. At the same time, the value of the parameter λ in almost the entire range of change of the studied parameters ($3.6\cdot10^3 \le Re \le 10^6$ and $0.0001 \le k/d \le 0.02$) exceed the value of the correspondent parameter obtained by the equation (1). The values of the evaluation criteria Rel and Rel_{max} for the equation (15) are also almost an order of magnitude higher than the values of similar parameters for the equation (12). The smaller values of the estimation parameters for the equation (15) somewhat limit its application.

The values of almost all evaluation criteria that characterize the equation (16) (Offor and Alabi, 2016) are significantly smaller than similar criteria previously considered in the equations (6–15). The most noticeable difference is characteristic for the criterion of mean relative deviation Rel_{min}. Its value is almost two orders of magnitude smaller than the smallest similar indicator of the previous equations. The values of such evaluation criteria as SD, MD, although with a smaller difference, but are also smaller than similar criteria for the previous equations (Table 1).

According to the results of calculations of the values of the evaluation criteria (Rel, Rel_{max}, Rel_{min}), carried out by the equation (17) (Brkić, 2012) in the whole range of changes of independent parameters ($3.6\cdot10^3 \le Re \le 10^6$ and $0.0001 \le k/d \le 0.02$) it can be ascertained that $\lambda_{Col\text{-}W} < \lambda_i$, and hence Rel, Rel_{max}, Rel_{min} have a negative value. The value of the mean relative deviation for the equation (17) is $Rel = -6.5\cdot10^{-3}$, which is significantly smaller than the values of the same indicator for the equations (6–11) but is greater than for the equations (12–15). The maximum value of the relative deviation λ_i from $\lambda_{Col\text{-}W}$ ($Rel_{max} = -1.5\cdot10^{-5}$) is reached at $k/d \to 0.033$ and $Re \to 3600$, but with increasing k/d in the whole studied range of change of Re the value of the relative deviation Rel_i is stabilized and is significantly smaller than Rel_{max}. A feature of the results of calculations by the equation (17) is the relative constancy of the deviations of Rel_i in the whole range of changes of the independent parameters. However, the presence of a zone of independent parameters Re and k/d, for which there is a significant deviation of the evaluation criteria, imposes certain restrictions on its wide practical application.

An analysis of the evaluation criteria Rel, Rel_{max}, Rel_{min}, SD, MD determined by the values of the parameter λ_i, calculated by the equation (18) proposed by the authors of this article, showed that they all have significantly smaller deviations compared to the deviations calculated by all equations (6–17). It should be noted that the equation (18), like the equations (14–16) for $Re \to \infty$, takes the form of the equation of Prandtl and Nikuradse (Kiseleva, 1972). However, the structure of all mentioned equations for the condition $k/d = 0$ differs significantly from each other and is not identical under this condition for the equation (1), which has an impact on the final result of calculations. The SD value for the equations (14–16) is $6.8 \cdot 10^{-4}$, respectively, $9.3 \cdot 10^{-3}$ and $1.4 \cdot 10^{-4}$, while for the equation (18) $SD = 2.3 \cdot 10^{-6}$. The values of all other evaluation criteria for the equation (18) are significantly better than the values of similar criteria for other equations (Table 1). This value of the average of the relative deviations of the values of λ_i and $\lambda_{Col\text{-}W}$, calculated by the equations (1) and (18) indicates high similarity between them and allows to conduct engineering calculations by the equation with high accuracy (18). The maximum value of the relative deviation in the range of changes of independent parameters is $Rel_{max} = 9.9 \cdot 10^{-6}$, which cannot significantly affect the final results of calculations in solving practical engineering problems. The value of $Rel_{min} = 0.00$ neither has an effect on the final results of engineering calculations. The value of the criteria SD and MD, which characterize the correspondence between λ_i and $\lambda_{Col\text{-}W}$, in the studied case, respectively, yield $SD = 2.3 \cdot 10^{-6}$, $MD = 9.2 \cdot 10^{-7}$. This indicates a fairly good correlation of the results of calculations using the equations (1) and (18).

It should be noted that the standard deviation is a characteristic of the degree of scattering of the calculated values (λ_i) obtained by the equations (6–18) in comparison with the results of the calculations ($\lambda_{Col\text{-}W}$) by the equation (1). In this case, the standard deviation slightly enhances the effect of larger deviations on the result of estimating the accuracy of the calculated equations. The indicator of the mean deviation, or the arithmetic mean of the absolute values of the deviations, gives a generalized characteristic of the range (amplitude) of the deviations of the studied parameter.

Figure 3 shows the rating of the studied mathematical equations (6–18) for calculating the values of the parameter λ, compiled by the standard and mean deviations of λ_i from $\lambda_{Col\text{-}W}$. It should be noted that for some mathematical equations the values of the evaluation criteria SD and MD on the scale of the graph are to the right side of 1, i.e., their value exceeds 1%, and the others – to the left side, what means that deviations of the results using these equations are significantly less than 1%.

The largest value of the standard deviation (*SD*) is observed for the equations (7–10). Its value reaches almost 25%. The generalized characteristic of the range (amplitude) of deviations $MD \approx 17\%$ is also the largest for this equation (Figure 3). This indicates that the values of λ_i, calculated by the equations (7–10), in the whole range of changes of independent parameters ($3.6\cdot10^3 \le Re \le 10^6$ and $0,0001 \le k/d \le 0.02$) are significantly overestimated. A similar situation can be observed for the accuracy of calculations by the equations (6) and (11), although the values of the evaluation criteria are slightly smaller than the values of the same criteria for the equations (7–10) (Table 1, Figure 3). Such significant values of the evaluation criteria *SD* and *MD* for the equations (6–11) indicate the need to improve the common method of hydraulic calculation of pipelines.

The values of the *SD* and *MD* criteria for the equations (12–18) are significantly smaller than the values of same criteria for the equations (6–11). However, even in this case, when justifying the choice of mathematical equation for engineering calculations, not only the criteria *SD* and *MD* should be taken into account, but also the evaluation criteria *Rel*, Rel_{max}, Rel_{min}, because their values may be unacceptable in terms of accuracy requirements to the hydraulic calculations of pipes. For example, for small values of the evaluation criteria *SD* i *MD*, the value of Rel_{max}, Rel_{min} for the equations (13, 15), respectively, is $Rel_{max} = 1.3\%$ and $Rel_{min} = -2.7\%$ (Table 1).

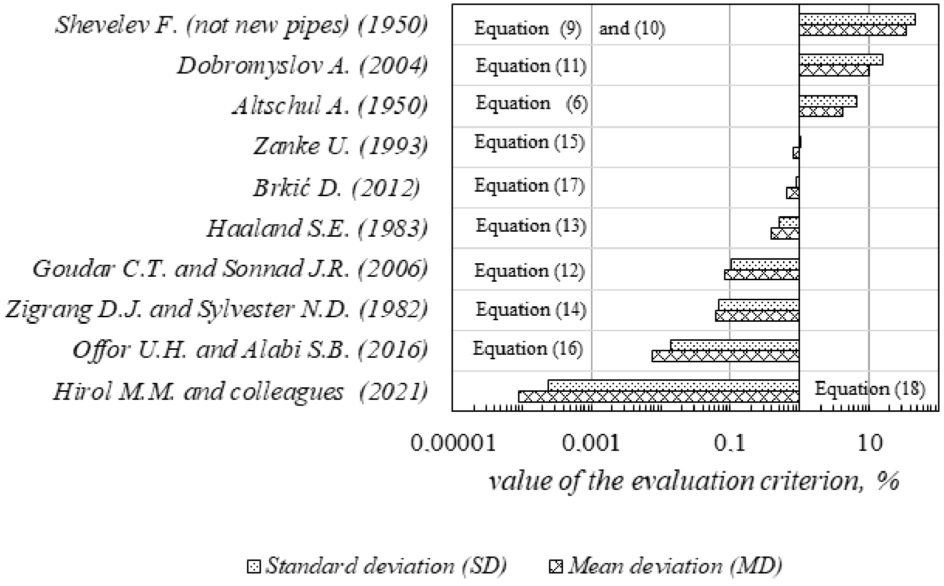


Fig. 3. Rating evaluation of the studied equations (6–18) according to the value of criteria of *SD* and *MD* in the whole range of study $3.5\cdot10^3 \le Re \le 1\cdot10^8$, $0.0001 \le k/d \le 0.02$

It should be taken into account that for $Re \rightarrow \infty$ the mathematical equations (13–18) are transformed into the equation (2), i.e., the results of calculations on these equations in the turbulent zone, in contrast to the results of calculations on the equations (6–12), will be equal to each other. But for the zone of smooth pipes ($k/d \rightarrow 0$) the equations (6–18) differ from the equation (3) and differ significantly from each other, which affects the results of calculations for these equations also in the transition zone.

In the zone of smooth pipes, the highest absolute value of the evaluation criteria $|Rel_{max}|$, $|Rel_{min}|$ is observed for the equations (7–11) and exceeds 100%, while the maximum absolute values of the criteria $|Rel_{max}|$, $|Rel_{min}|$ for the equations (6), (15) and (17) are within $1\% \leq (|Rel_{max}|; |Rel_{min}|) \leq 50\%$. The lowest values of the mentioned criteria are observed for the equations (12), (14), (16) and (18). These values vary within $0.001\% \leq (|Rel_{max}|; |Rel_{min}|) \leq 1.0\%$. At the same time, under the condition $k/d \rightarrow 0$ for the equation (11) there are no solutions (Figure 4).

If it is necessary to obtain a more accurate definition of λ_i, obviously, it is necessary to analyze the possibility of using the equations (14), (16), (18).

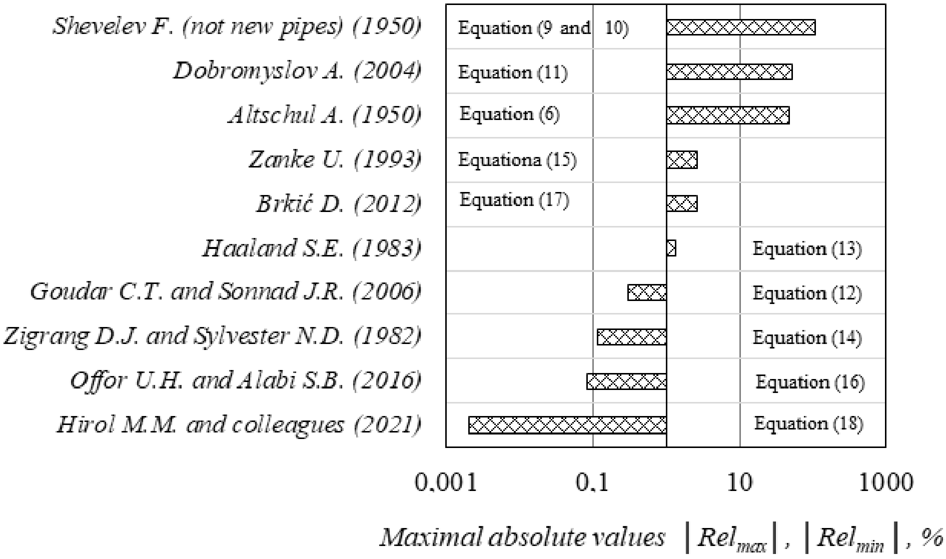


Fig. 4. Rating evaluation of the studied equations (6-18) by the largest absolute values of $|Rel_{max}|$, $|Rel_{min}|$ in the study range $3.5 \cdot 10^3 \leq Re \leq \infty$, $0.00 \leq k/d \leq 0.02$

Of all the considered mathematical equations (6–18), the most accurate results of calculations of λ_i can be obtained by the equation (18). It is characterized by the lowest values of all evaluation criteria (Rel, Rel_{max}, Rel_{min}, SD, MD) in the whole range of changes of independent parameters ($3.5 \cdot 10^3 \leq Re \leq 10^8$, $0.0001 \leq k/d \leq 0.02$), i.e. the highest accuracy of calculations of λ, can be achieved by applying the equation, proposed by the authors of this article.

2. Conclusions

In the world practice of hydraulic calculations of pipeline systems, the non-algebraic equation of Colebrook-White has become the most widespread. Much attention has been paid to finding an approximate solution to this equation in many scientific papers.

The results of the statistical analysis in this work show that the most effective mathematical equations that have acceptable values of evaluation criteria are the equations (12–18). The best values of the evaluation criteria are characteristic of the mathematical equation (18), proposed by the authors of this work.

Mathematical equations (6–11) have large values of evaluation criteria, which indicates significant deviations of the parameter λ_i calculated using these equations from $\lambda_{Col\text{-}W}$. In hydraulic calculations of pipeline systems, such equations require additional justification of their feasibility.

References

1. Altshul, A.D., Kiselev, P.G.: Hydraulics and aerodynamics (Fundamentals of fluid mechanics). Ed. 2nd, reworked. and ext. Stroyizdat, M., 323, 1975.
2. Asker, M, Turgut, O.E., Coban, M.T.: A review of non-iterative friction factor correlations for the calculation of pressure drop in pipes. *Bitlis. Eren. Univ. J. Sci. & Technol.*, 4(1), 8, 2014.
3. ATV-DVWK-A 110. Hydraulische Bemessung von Freigefälledruckleitungen zum Abwassertransport. LfUG-Merkblatt: Freigefälledruckleitungen. Dr.-Ing. habil. Detlef Aigner Technische Universität Dresden, 2003.
4. Bollrich, G.: Technische Hydromechanik 1: Grundlagen. Beuth Wissen. Band 1 von Technische Hydromechanik. Wissen: Bauwesen. Beuth Verlag, 450, 2013.
5. Brkić, D.: Determining friction factors in turbulent pipe flow. *Chemical Engineering*, 119(3), 34–39, 2012.
6. Bruna, D., Pimenta, A.D., Robaina, M.X., Peiter, W. M., Jardel H.K and Luis H.B.B.: Performance of explicit approximations of the coefficient of head loss for pressurized conduits. *Revista Brasileira de Engenharia Agrícola e Ambiental*, 22(5), 301–307, 2018.

7. Ciechanowski, Z., Matakiewicz, M., Pomianowski, K.: Zasady budowy wodociągów. Podręcznik do uzytku inzynierów i sluchaczy inzynierii lądowej i wodnej politechniki Lwowskiej. Lwów, 1914 r. Reprint wydania. Seidel-Przywecki, Warszawa, 321, 2008.
8. Colebrook, C.F. and White C.M.: Experiments with fluid friction in roughened pipes. *Proceedings of the Royal Society A – Mathematical, Physical & Engineering Sciences,* 367–381, 1937.
9. Dobromyslov, A.Y.: Tables for hydraulic calculations of pressure pipes made of polymeric materials. M.: tTOO Izdatelstvo VNIIMP, 209, 2004.
10. DSTU-NBV.2.5-40: 2009. Engineering equipment of buildings and structures. External networks and structures. Design and installation of water supply and sewerage networks made of plastic pipes. Ministry of Regional Development of Ukraine. Kyiv, 2010.
11. DWA-A 113:2020:2020. Arbeitsblatt, Hydraulische Dimensionierung und Leistungsnachweis von Abwasserdrucksystemen. Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall (Verlag).
12. Kiseleva, P.G. ed.: Handbook of hydraulic calculations. Ed. 4, reworked and ext. M.: Energiya, 1972.
13. Ettema, R.: Hunter Rouse – His Work in Retrospect. *Journal of Hydraulic Engineering*, 132(12), 1248–1258, 2006.
14. Genić, S., Arandjelović, I., Kolendić, P., Jarić, M., Budimir, N., and Genić, M.: A Review of explicit approximations of Colebrook's equation. *FME Transactions,* 39, 67–71, 2011.
15. Haaland, S.E.: Simple and Explicit equations for friction factor in turbulent pipe flow. *J Fluid Eng ASME,* 105, 89–90, 1983.
16. Hager, W.H.: Wastewater Hydraulics. Theory and Practice. Second Edition. Springer, Verlag, Berlin,2010.
17. Halperin, E.M.: Improving the calculation model of the ring water supply network (discussion). *Water Supply and Sanitation*, 2, 51–54, 2010.
18. Lipovka, A.Y., Lipovka, Y.L.: Determining Hydraulic Friction Factor for Pipeline Systems. Journal of Siberian Federal University. *Engineering & Technologies,* 1(7), 62–82, 2014.
19. Merkl, G.: Technik der Wasserversorgung: Praxisgrundlagen für Führungskräfte. Oldenbourg Industrieverlag GmbH. München. 2008.
20. Moody, L.F.: Friction factors for pipe flow. *Trans. Am. Soc. Mech. Eng.,* 66, 671–684, 1944.

21. Offor, U.H., Alabi, S.B.: An Accurate and Computationally Efficient Explicit Friction Factor Model. *Advances in Chemical Engineering and Science*, 6, 237–245, 2016.

22. Popov, G., Nikolov, G., Bojadgiev, M., Klimentov, K.: Analysis of accuracy when calculating of the friction factor in pipes. Annual of the university of mining and geology "St. Ivan Rilski". *Geology and Geophysics*, 53(1), 159–162, 2010.

23. Rüdiger, J.: Gasnetzsimulation durch Potentialanalyse. Dissertation vorgelegt von Dipl. Ing. Jens Rüdiger aus Dresden-Hamburg, 2009.

24. Semkło, Ł., Urbaniak, R., Nygard, A.: Analiza porównawcza wzorów na współczynnik strat liniowych w transporcie rurociągowym. Instytut Naukowo-Wydawniczy "TTS". *TTS Technika Transportu Szynowego*, 22(12), 1366–1369, 2015.

25. Shevelev, F.A.: Hydraulic resistance of metal pipes of large diameters. *Hydraulic Engineering*, 1, 1950.

26. Shevelev, F.A.: Tables for hydraulic calculation of steel, cast iron, asbestos-cement, plastic and glass water pipes. Ed. 5th, ext. M., Stroyizdat, 1973.

27. Smyslov, V.V.: Hydraulics and aerodynamics: A textbook for universities. – translated from Ukrainian, Kiev: High School. Main Publishing House, 1979.

28. SNiP II -G.3-62: 1963. Building codes and regulations. Part II, section D. Chapter 3. Water supply of design norm, Moscow, 1963.

29. Sonnad, J.R., Goudar, C.T.: Turbulent Flow Friction Factor Calculation Using a Mathematically Exact Alternative to the Colebrook-White Equation. *Journal of Hydraulic Engineering*, 132, 863–867, 2006.

30. Yanyshev, D.S.: Application of the Lambert function in the theory of turbulent friction. *Trudy MAI* (electronic journal), 50, 2015. http://trudymai.ru/upload/iblock/98a/primenenie-funktsii-lamberta-v-teorii-turbulentnogo-treniya.pdf?lang=ru&issue=50 (In Russ.).

31. Zanke, U.: Zur Berechnung von Strömungs-Widerstandswerten. *Wasser und Boden*, 1, 14–16, 1993.

32. Zigrang, D.J., Sylvester, N.D.: Explicit approximations to the Colebrook's friction factor. *AICHE J*, 28, 514–515, 1982.

Problems of advanced nitrogen removal from municipal wastewaters in Kharkov (Ukraine)

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Abstract

Among the methods of nitrogen removal biological method is the most effective, economical and environmentally friendly. Deep removal of nitrogen compounds is carried out using microbiological nitrification, denitrification, the anammox process. The purpose of the work is to study composition of nitrogen pollution in wastewater, delivered into the Kharkiv WWTP, to determine the nitrifying capacity of activated sludge in aeration tanks and to demonstrate prospects of the treatment efficiency increase through an advanced nitrogen removal. Hydrochemical analysis of aqueous media was conducted via standard methods according to Ukraine standards demands The nitrifying capacity of activated sludge of treatment facilities was determined using the biochemical and the microbiological methods. It was found that in the municipal wastewater, entering the WWTP, organic nitrogen makes approximately 50 percent of the total nitrogen value. The total load of ammonium nitrogen and organic nitrogen on the treatment plants was extremely higher than the permitted level. It was determined that the concentration of nitrifying bacteria in the activated sludge and its enzymatic nitrifying activity were high enough for municipal wastewater treatment plants. The deep treatment process in the aeration tank with activated sludge includes deep nitrification, while anammox process and the denitrification process do not occur at all. $N\text{-}NH_4$ concentration after the treatment essentially decreases (up to 92.5%). The most perspective way to increase efficiency of the nitrogen compounds removal is to increase time of the aerobic treatment to allow advanced oxidation of organic compounds and to improve the nitrification process (decrease of residual ammonium nitrogen concentration) and organization of a denitrification process for deep removal of nitrites and nitrates.

Keywords: biological wastewater treatment, municipal wastewater, deep removal of nitrogen compounds, nitrification, nitrifying capacity of activated sludge, denitrification

1. Introduction

In countries where supply of potable water relies on surface waters (Central Europe, Northern America and Southern Africa) pollution by nitrogen and phosphorus compounds (eutrophication) is one of the most actual problems for maintaining ecological safety (EPA, 2009). To prevent eutrophication of water bodies and restore aquatic environment quality it is necessary to minimize emission of nutrients into receivers. The sources of these elements are the discharge of insufficiently treated municipal and industrial wastewater from treatment plants (WWTP) and flushes from agricultural and urban areas (storm wastewater (Gmur, 2003; Henze et al., 2004; Malovanyy et al., 2014; Iurchenko et al., 2020).

The decrease of nutrients content is possible through preliminary treatment of wastewater directly at the source (mainly in case of industrial effluents), and/or application of modern technologies increasing efficiency of treatment processes at municipal WWTP. Since, the first alternative can be problematic due to the technical and economical reasons, the second way – the increase of efficiency of nitrogen compounds removal – is considered as a viable option. Given that eutrophication of natural sources of drinking water becomes a global problem the implementation of highly efficient removal techniques for nutrients (nitrogen and phosphorus) is necessary.

Generally, nitrogen compounds are partially removed from the municipal wastewater during a conventional biological treatment processes performed in the activated sludge tanks (Gmur, 2003; Henze et al., 2004; Semenova et al., 2012; Gnida et al., 2016). Generally, the conventional biological treatment process is efficient enough. However sometimes a restrictive requirements regarding the composition of discharged wastewater may be exceeded.. Such efficiency also does not satisfy modern requirements for protection of natural reservoirs against the eutrophication. In Ukraine, majority of wastewater treatment plants were built on the basis of normative documents developed approximately 40 years ago (SNiP 2.04.03-85 "Canalization. External networks and constructions"). These documents are based on the kinetics and efficiency of organic carbon removal (COD, BOD). Nevertheless, during modernization and designing of new treatment plants advanced nitrogen compounds removal processes are being eventually introduced in Ukraine (Gmur, 2003; Henze et al., 2004; Nezdoyminov, 2013).

Currently, various methods of nitrogen compounds removal are known, among them physicochemical (release of ammonia, ionic exchange, chlorination by activated chlorine, reverse osmosis, electrochemical methods) and biological methods. The biological methods are based on microbiological processes with use of the activated sludge, and are considered as the most effective, and safe for the environment (Henze et al., 1999; Choubert et al., 2005; Yagov, 2008; Gujer, 2010; Holmes et al., 2019). Transformation of nitrogen compounds during the traditional biological treatment process includes following stages: microbiological assimilation, ammonification, and partial nitrification (Semenova et al., 2012; Holmes et al., 2019). During the advanced nitrogen removal, additionally advanced nitrification and denitrification are introduced (Henze et al., 2004; Semenova et al., 2012; Nezdoyminov, 2013). Microbiological nitrification is a chemoautotrophic process occurring in two phases. The ammonium oxidizing bacteria (AOB) carry out the first phase of nitrification in aerobic conditions, oxidizing ammonium up to the nitrite. In the second phase of nitrification – nitrite bacteria (NOB) oxidize nitrites to nitrates in aerobic conditions (Ward et al., 2011). To remove nitrites/nitrates from wastewater a denitrification process is applied (more precisely – of dissimilation denitrification) (Semenova et al., 2012). The dissimilation denitrification is a catabolic process of the heterotrophic microbiological reduction of nitrites/nitrates by protons of organic substrata under anaerobic conditions.

During biological wastewater treatment a change of aerobic and anaerobic conditions is carried out due to a consecutive passage of the sludge through anaerobic and aerobic zones of the activated sludge tanks (division of oxygen modes in space) or due to change of anaerobic and aerobic periods of processing in the same reactor of full mixture (division of oxygen modes in time). Reactors in which aerobic conditions (created by pneumatic aeration) and anaerobic conditions (created by stirring) are performed within a single reactor are called the sequencing batch reactors (SBR) (Choubert et al., 2005). Technological schemes of nitrification-denitrification processes (Henze et al., 1999; Gmur 2003; Henze et al., 2004) can be divided according to following parameters:

– number of sludge systems in the process (single sludge system or two-sludge system);

– number of aeration and stirring zones (one-stage, two-stage or circulating mode);

– type of organic substrate, used for denitrification (external organic substrate, for example methanol – "post-denitrification", or without external substrate – "pre-denitrification");

– operating mode (flow-through scheme or seqencing work scheme – aerobic and anaerobic conditions alternate in the same zone).

To implement such technologies, foreign and domestic experts have currently developed more than ten types of technological schemes, which are based on both physico-chemical and biological processes of wastewater treatment.

Now leading experts in the field of environmental protection associate the possibility of a radical improvement in the quality of water treatment from nitrogen compounds with the anammox process – anoxide oxidation of ammonium during the reduction of NO^{2-} to gaseous nitrogen by anammox-planktomycetam (Ding et al., 2013; Malovanyy et al., 2014; Wu et al., 2019;

Jiantao et al., 2020; Iurchenko and Tsytlishvili 2020). But this environmental and economic advantages method can be carried out in certain conditions of wastewater treatment (high concentration of NH_4^+, absence of organic compounds, low concentration of dissolved O_2).

According to modern concepts, nitrifying microorganisms include: ammonium oxide bacteria and archaea (AOB and AOA), which carry out 6-electron oxidation of NH_3 to NO_2^- (phase I nitrification), and nitrite oxide bacteria (NOB, phase II nitrification), which perform 2-electron oxidation NO_2^- to NO_3^-, as well as "complete NH_3 oxidizers" (comammox) bacteria, which carry out the 8-electron oxidation of NH_3 to NO_3^- (Ding et al., 2013; Lancaster et al., 2018; Wu et al., 2019).

The ecological risk of nitrogen presence is related with its form. Nitrites are considered as the most toxic, nitrates as the safest, while ammonium occupies the average position in such classification (Henze et al., 2004; EPA, 2009). Required treatment efficiency is based on standards for treated effluents discharged into water bodies. Different values of admissible nitrogen concentrations are presented in Table 1. In the EU countries only the total concentration of nitrogen (or Kjeldahl nitrogen – the sum of $N\text{-}NH_4$ and N-organic) in wastewater is standardized, and in the eutrophication sensitive areas should not exceed 10 mg/L for wastewater from settlements up to 100 thousand person equivalents (PE), and 15 mg/L for wastewater from settlements above 100 thousand PE. In Ukraine only soluble mineral nitrogen forms are under scrutiny. The admissible concentration of mineral soluble nitrogen is 9.55 mg/L for fish farming reservoirs and 13.16 mg/L for reservoirs, used for drinking supply. Concentrations of organic nitrogen are not supervised, and the absence of this control parameter extremely complicates the rational organization of wastewater treatment process, and also diminishes efficiency of the eutrophication protection measures.

Concentrations of nitrogen compounds in wastewater are variable and changeable at various stages of treatment process. Transformation of nitrogen compounds begins already during transport of wastewater to the treatment facilities. In particular, carbamide disintegrates with formation of ammonium (ammonification process) as a result of microbial destruction, and ammonium concentration in the wastewater entering treatment plants can range from 20 up to 50 mg/L. Concentrations of nitrates and nitrites in transported wastewater decrease due to the spontaneous denitrification - microbiological restoration of these compounds to gaseous compounds of nitrogen (mainly – N_2). Concentrations of nitrate-ions at the entrance to the treatment plant is insignificant, and also content of nitrite-ions is low (usually less than 1 mg/L) (Henze et al.; Gmur, 2003; Yagov, 2008).

Content of organic nitrogen compounds (high-molecular-proteins, proteids, low-molecular-amino acids, amines, amides, carbamide) in wastewater discharged into the sewer system can achieve 50−70 percent of the total quantity of nitrogen compounds. But as a result of ammonification processes during wastewater transport a share of the organic nitrogen decreases down to 15−35% at the entrance to the treatment plant (Henze et al., 2004; Yagov, 2008).

The most radical transformation of all nitrogen forms occurs during the biological treatment process. At the beginning, ammonium and organic nitrogen are removed with organic compounds (BOD, COD) during assimilation processes of the activated sludge. The next major stage of the biological treatment is nitrification, i.e. the microbiological oxidation of ammonium nitrogen into nitrite- and nitrate-ions. At the advance treatment in anaerobic (anoxic) conditions nitrite- and nitrate-ions are reduced to gaseous nitrogen by microbiological way (denitrification) (Henze et al., 2004; Yagov, 2008; EPA, 2009).

The purpose of this work is to present composition of nitrogen pollution in wastewater delivered into the Kharkov biological treatment plant, to determine the nitrifying capacity of activated sludge in aeration tanks and to demonstrate prospects of the treatment efficiency increase through an advanced nitrogen removal.

2. Materials and Methods

The Kharkov city is a big industrial center of Ukraine. There are two wastewater treatment plants in the Kharkiv city with the total capacity of 1.1 million m^3 per day. The sequence of treatment processes at these facilities includes mechanical and biological processes, disinfection and sludge processing. The following study presents results for one of the treatment plants (Kharkiv biological WWTP, with capacity of 300 000 m^3) where municipal and industrial wastewaters are delivered.

Investigations of the process of wastewater nitrification in biological treatment plants were focused on: i) determination of nitrogen compounds concentrations (ammonium nitrogen, nitrites and nitrates) in the dynamics of processing in the aeration tank; ii) determination nitrifying capacity of the activated sludge of these treatment facilities.

Hydrochemical analysis of aqueous media ($N\text{-}NH_4$ – colorimetric with Nessler’s reagent, $N\text{-}NO_2$ – colorimetric with α-naphthylamine, $N\text{-}NO_3$ – colorimetric with sodium salicylate, organic N ($N_{org.}$) – after wet mineralization titrometrically, pH – electrometrically, COD – arbitration method adding potassium dichromate) was conducted via standard methods according to Ukraine standards demands (List, 2013). The oxygen concentration in aqueous media was established using a portable oxygen meter (model YSI 55, Dissolved Oxygen Meter (USA)).

The nitrifying capacity of activated sludge of treatment facilities was determined using the biochemical method (Iurchenko, 2007) on the basis of the activity of the enzyme, catalyzing the reaction of hemolitoautotrophic oxidation of ammonium – hydroxylamine oxidoreductase (Lancaster et al., 2018).

In laboratory inhibitory experiments with activated sludge, to suppress nitrification and identify the process for incubation, we used wastewater models (similar in salt composition to urban wastewater, but without organic compounds) and pyrazole, an inhibitor of the first phase of nitrification, at a concentration of 10 mg/L.

The concentration of nitrifying bacteria of the first nitrification phase (AOB) in activated sludge was determined using the microbiological method of limiting dilutions (Vinogradova et al., 2012). Statistical processing of data was conducted via computer program Microsoft Excel.

3. Results and discussion

3.1. Nitrogen compounds in the Kharkiv wastewater

To study an influence of industrial wastewater with different contents of nitrogen compounds we focused on effluents from machine-building (heavy agricultural machinery) and milk processing plants. These factories discharge the biggest volume of industrial wastewater to the studied treatment plant. Results show (Table 1) that organic and ammonium nitrogen forms from the machine-building plant are present at small concentrations and not exceed effluent discharge standards for wastewater facilities in the Kharkiv area (the max possible admissible concentration for submission in a sewer network in Kharkiv is 18 mg/L). Concentrations of ammonium nitrogen from the milk processing plant were higher than values for wastewater from the machine-building plant approximately 5 times, and for organic nitrogen 10 times. Since, during the biological treatment process most of organic nitrogen mineralizes up to ammonium nitrogen, resulting load of the latter one at the treatment facility exceeds admissible level. Total nitrogen concentrations (organic nitrogen + ammonium nitrogen) are at the level of 11.3 up to 21.8, that exceeds the admissible level (18 mg/L). Concentrations of nitrogen oxidized forms – nitrites and nitrates – in both types of industrial wastewater are low. These data correspond with the characteristics of the content of nitrogen compounds in industrial wastewater obtained by other researchers. (Gmur, 2003; Malovanyy et al., 2014; Gnida et al., 2016).

In the municipal wastewater entering the biological treatment plant (Table 2), organic nitrogen makes approximately 50 percent of the total nitrogen value, which confirms the data of others authors (Gmur, 2003; Henze 2004; Yagov 2008; Jiantao et al., 2020). In the treated effluent its share decreases down to 36%.

Table 1. Concentration of various forms of nitrogen in the industrial wastewater

Industrial wastewater	**Concentration N (mg/L)**				
	organic	**NH_4^+**	**NO_2^-**	**NO_3^-**	**total**
Machine-building plants	9.0–12.0	2.3–9.8	0–0.14	0–0.5	13.0–22.3
Milk plants	56.0–121.0	10.6–22.0	0–0.28	0–0.4	66.4–141.1
Standards for wastewater entering WWTPs	No standard	18.0			No standard

Table 2. Concentration of nitrogen forms in the raw and treated wastewater at the Kharkiv WWTP (monthly average values)

Wastewater	**Concentration N (mg/L)**				
	organic	**NH_4^+**	**NO_2^-**	**NO_3^-**	**total**
Raw wastewater	16.8	16.2	0.3	0.4	33.7
Treated wastewater	7.0	1.8	1.0	9.5	19.3
Standards for treated wastewater	No standard	1.8	0.76	7.9	No standard

3.2. Indicators of municipal wastewater treatment from nitrogen compounds in aerotanks

Wastewater treatment at Kharkiv municipal WWTP No. 2 is carried out according to the traditional scheme: grates, sand traps, primary sedimentation tank, aeration tank, secondary sedimentation tank, disinfaction.

Averaged annual data of regular control of $N\text{-}NH_4$, $N\text{-}NO_2$ and $N\text{-}NO_3$ concentrations in incoming and discharging wastewaters from the wastewater treatment plant №2 into the river Udy are presented in Fig. 1.

As it is shown, $N\text{-}NH_4$ concentration after the treatment essentially decreases (up to 92.5%). In that time nitrite and nitrate concentrations increasing which are an obvious characteristic, firstly, of the deep wastewaters treatment and, secondly, of passing the full nitrification process (first and second phases).

Biological wastewater treatment takes place in four corridor aeration tanks with concentrated supply of activated sludge and dispersed supply of wastewater to the first half of the 2nd corridor (Fig. 2).

As presented in Fig. 3, concentrations of nitrates start to increase at the 2nd corridor of the aeration tank, and reach maximum values at the exit from the aeration tank (the end of 4th corridor). The concentration of nitrate nitrogen at the outlet of the aeration tank exceeds the permissible level (Table 2). That proves high activity of the nitrification process where not only $N\text{-}NH_4$, present in wastewater, is oxidized actively, but also this form of nitrogen is formed as a result of the mineralization of N_{org}. The residual concentration of N_{org} remains high at the exit from the aeration tank in comparison with specifications of EU for wastewater discharged in natural reservoirs. This fact can be explained by a partial resistance of nitrogen incorporated into organic compounds to the biological oxidation (Henze et al., 1999), and a partial mineralization of activated sludge.

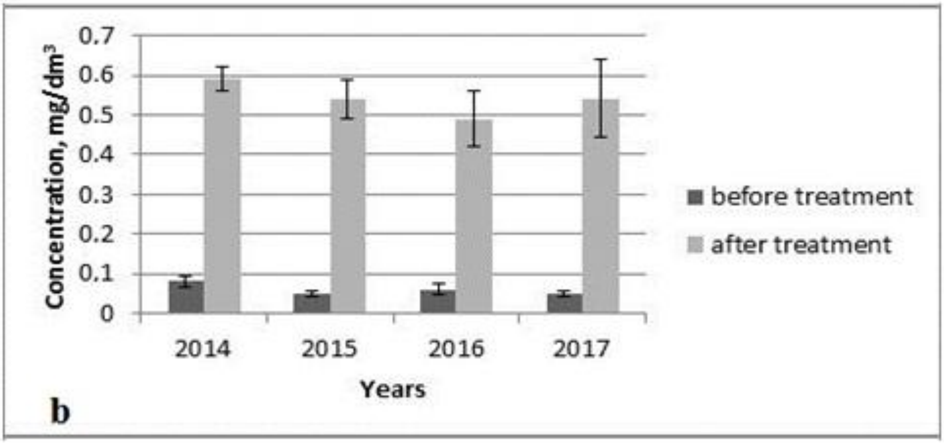

Fig. 1a. Average annual concentration dynamics of ammonium nitrogen (a) in wastewater before and after treatment (Iurchenko et al., 2020)

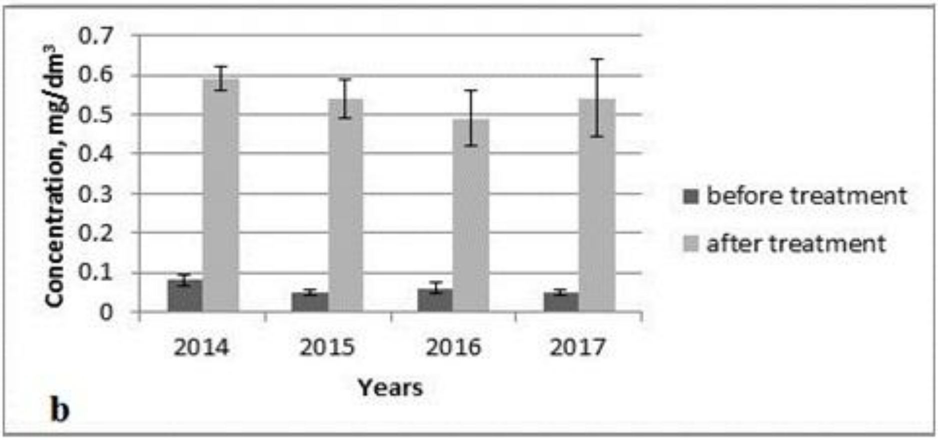

Fig. 1b. Average annual concentration dynamics of nitrite nitrogen (b) in wastewater before and after treatment (Iurchenko et al., 2020)

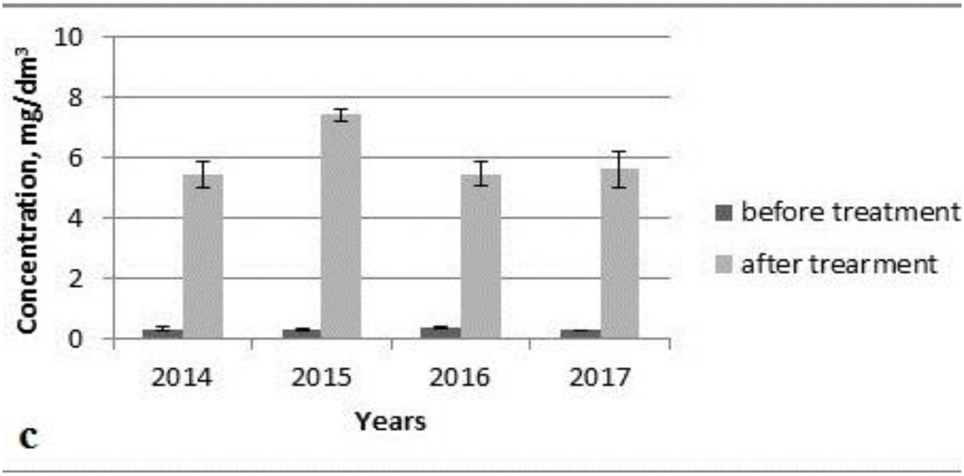

Fig. 1c. Average annual concentration dynamics of nitrate nitrogen (c) in wastewater before and after treatment (Iurchenko et al., 2020)

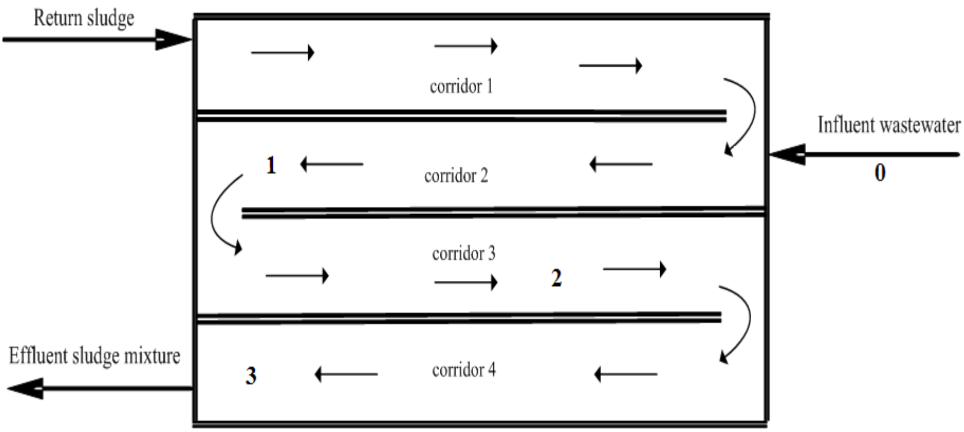

Fig. 2. Scheme of the flows in aeration tank at the Kharkiv WWTP and sampling points during research (sampling points 0 – etntering sewage, 1 – 2-nd corridor, 2 – 3-rd corridor, 3 – the end of 4th corridor)

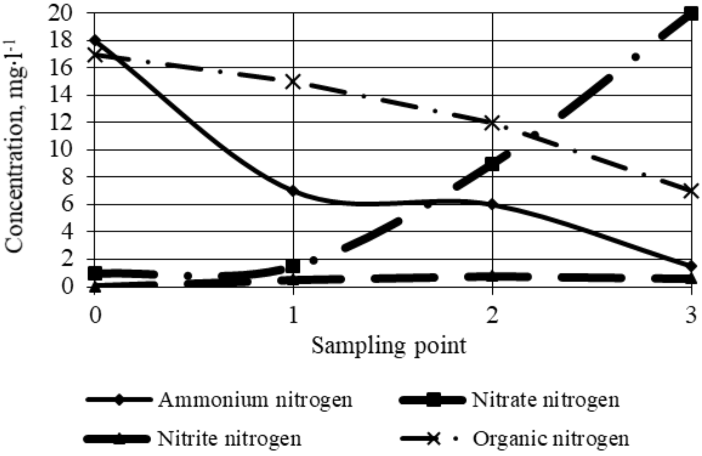

Fig. 3. Scheme of the flows in aeration tank at the Kharkiv WWTP and sampling points during research (sampling points 0 – etntering sewage, 1 – 2-nd corridor, 2 – 3-rd corridor, 3 – the end of 4th corridor)

Data of microbiological nitrification bacteria concentration determination in activated sludge of biological wastewater treatment plant and its nitrifying activity are presented in Table 3.

Table 3. Microbiological characteristics of the nitrifying ability of activated sludge from the municipal wastewater treatment plant No. 2

Sludge samples	**COD, mg/l**	**O_2, mg/l**	**Concentration of AOB, cells/$g_{org.\ sludge}$**	**Activity of hydroxylamine oxidoreductase, µg formazan/ ($g_{dry\ sladge}$·min)**
Beginning of aeration tank (point 1)	110–160	1.2–1.6	10^6–10^7	99.3–194.0
Ending of aeration tank point 3)	30–52	2.2–2.4	10^6–10^8	105.5–321.0

As the presented data show, AOB concentration in activated sludge from wastewater treatment plant in the ending of aeration tank-displacer increases as a result of passing nitrification in this zone and reaches 10^6–10^8 cells/$g_{org.\ sludge}$. Similar concentrations of AOB were found in activated sludge of municipal WWTP and other specialists (Fitzgerald et al., 2015). An increase in the nitrifying capacity of sludge was also evidenced by an increase in its hydroxylamine oxidoreductase activity. The concentration of nitrifying bacteria in the activated sludge and its enzymatic nitrifying activity were high enough for municipal wastewater treatment plants (Iurchenko, 2007).

Oxidation of ammonium nitrogen in the anammox process (the presence of anammox bacteria in activated sludge) can be established in laboratory experiments when suppressing nitrification using an inhibitor (pyrazole) as the difference between the mass of oxidized $N\text{-}NH_4$ in the variant "sludge with an inhibitor of autotrophic nitrification" and "sludge killed by heat denaturation". In the conducted sludge studies, this difference was practically zero. Consequently, the anammox process in the surveyed structures did not develop, which was facilitated by the absolute concentrations of $N\text{-}NH_4$ (low to optimize this process), rather high concentrations of COD and dissolved oxygen. Similar results were obtained (Shanyun et al., 2015), which showed that the contribution of anammox bacteria to removed nitrogen during traditional biological treatment of municipal wastewater is 2.1–6.9%.

Calculation of balance for oxidized and reduced forms of nitrogen in the entrance and exit from the biological reactor testifies, that in the investigated biological reactor the denitrification process of nitrates and nitrites practically does not occur. Concentration of nitrates in the treated wastewater exceeds limit values (7.9 mg/l). This threatens with excessive removal of sludge from secondary sedimentation tanks during spontaneous denitrification. It is necessary to organize denitrification in biological treatment facilities before the settling stage (Gmur, 2003). For denitrification of superfluous nitrates nitrogen the organic substrate the ratio $BOD:N\text{-}NO_3 \sim 4$ is necessary (Gmur, 2003; Henze, 2004). Since, at the entrance to the biological reactor concentration of BOD_5 in wastewater exceeds 110 mg/l denitrification more than 28 mg/l $N\text{-}NO_3$ is possible through partial recycling of treated wastewater at the entrance to the biological reactor.

Optimization of the denitrification process at the Kharkiv WWTP is considered as the most perspective way to achieve the European specifications on total nitrogen concentrations in the treated wastewater. Modernization process of the investigated biological treatment plant is focused on the increase of the nitrogen and phosphorus removal efficiency. This requires taking into account detailed information on organic nitrogen concentrations entering the treatment facility and its transformations during processing.

4. Summary and Conclusions

The current study based on the Kharkiv WWTP allowed us to draw following conclusions:

– N_{org} concentration in wastewater entering the investigated treatment plant makes about 49.9 percent of the total N; the highest concentration of Norg occurs in the milk processing plant effluents;

– the total load of ammonium nitrogen and organic nitrogen (which in the process of biological wastewater treatment turns into ammonium nitrogen during the mineralization of organic compounds) on the treatment plants was extremely higher than the permitted level. Treatment processes in the aeration tank with activated sludge include deep nitrification, while anammox process and the denitrification process do not occur at all;

– the concentration of nitrifying bacteria in the activated sludge and its enzymatic nitrifying activity were high enough for municipal wastewater treatment plants;

– the most perspective way to increase efficiency of the nitrogen compounds removal is to increase time of the aerobic treatment to allow advanced oxidation of organic compounds and to improve the nitrification process (decrease of residual ammonium nitrogen concentration) and organizing a denitrification process for deep removal of nitrites and nitrates;

– modernization of the investigated facility shall also point out the necessity of improving of standardization for nitrogen compound concentrations in the Ukraine wastewaters.

References

1. Choubert, J.M., Racault, Y., Grasmick, A., Beck, C., Heduit, A.: Maximum nitrification rate in activated sludge process at low temperature: key parameters, optimal value. *E-Water official Publication of the European Water Association (EWA)*, 1–13, 2005.
2. Ding, S., Zheng, P., Lu, H., Chen, J., Mahmood, Q., Abbas, G.: Ecological characteristics of anaerobic ammonia oxidizing bacteria. *Appl. Microbiol. Biotechnol*, 97, 1841–1849, 2013. DOI:10.1007/s00253-013-4697-0.
3. EPA 2009 Nutrient Control Design Manual. State of Technology Review Report. *Environmental Protection Agency*. (EPA/600/R-09/012), Cincinnati, OH 45268.
4. Fitzgerald, C. M., Camejo, P., Oshlag, J. Z., Noguera, D. R.: Ammonia-oxidizing microbial communities in reactors with efficient nitrification at low-dissolved oxygen. *Water Research*, 70, 38–51, 2015.
5. Gmur, N.S.: *Tehnologicheskie i biohimicheskie procesy ochistki stochnyh vod na soorugeniyah s aerotenkami. (Technological and biochemical processes of wastewater treatment on constructions with aerotanks)*. AKVAROS, Moskva 2003 (in Russian).
6. Gnida, A., Wiszniowski, J., Felis, E., Sikora, J., Surmacz-GórskaJ., Miksch, K.: The effect of temperature on the efficiency of industrial wastewater nitrification and its (geno) toxicity. *Archives of Environmental Protection*, 42(1), 27–34, 2016. DOI:10.1515/aep-2016-0003.

7. Gujer, W.: Nitrification and me – A subjective review. *Water Resources*, 44(1), 1–19, 2010.

8. Henze, M., Gujer, W., Mino, T., Matsuo, T., Wentzel, M.C., Marais, G.R., Loosdrecht, M.C.M.: Activated Sludge Model No.2d. ASM2d. *Wat. Sci. Tech*., 39(1), 165–182, 1999.

9. Henze, M., Armoes, P., Lya-Kur-Yansen, Y., Arvan, E. *Ochistka stochnyh vod* (*Wastewater treatment*). Mir, Moskva 2004 (in Russian).

10. Holmes, D. E., Yan, D., Smith, J. A.: Nitrogen cycling during wastewater treatment. *Adv Appl Microbiol*, 106, 113–192, 2019. DOI:10.1016/bs.aambs.2018.10.003. Epub 2018 Dec 10.

11. Iurchenko, V.O. *The development of scientific and technological foundations for the operation of sewage systems in the conditions of biochemical oxidation of inorganic compounds*. diss ... Doctors of tech. Sciences. Kharkiv 2007 (in Russian).

12. Iurchenko, V., Radionov, M., Ivanin, P., Melnikova, O.: Influence of Deep Treated Wastewater Discharge on Nitrification Activity in a Natural Reservoirs. *Ecological engineering: Scientific Journal,* 21(8), 146–155, 2020. DOI:10.12911/22998993/126984.

13. Iurchenko, V.O., Tsytlishvili, K.O.: Sclad i migvydovi vidnosyny v immobilizovanyh azottransformujuchyh microbiotzenozah ochysnyh sporud (Composition and interspecific relations in immobilized nitrogen-transforming microbiocenoses of treatment facilities). *Zbirnyk naukovyh pratz Umanskogo natzionalnogo universiteta sadivnytzva,* 96(1), 355–368, 2020. DOI:10.31395/2415-8240-2020-96-1-355-368 (in Ukraine).

14. Ji, J., Peng, Y., Li, X., Zhang, Q., Liu, X.: A novel partial nitrification-synchronous anammox and endogenous partial denitrification (PN-SAEPD) process for advanced nitrogen removal from municipal wastewater at ambient temperatures. *Water Research,* 175, 115–690, 2020. DOI:10.1016/j.watres.2020.115690.

15. Lancaster, K.M., Caranto, J.D., Majer, S.H., Smith Joule, M A.: Alternative Bioenergy: Updates to and Challenges in Nitrification Metalloenzymology. *Joule*, 2(3), 421–441, 2018.

16. Wu, L., Shen, M., Li, J., Huang, S., Li, Z., Yan, Z. Peng, Y.: Cooperation between partial-nitrification, complete ammonia oxidation (comammox), and anaerobic ammonia oxidation (anammox) in sludge digestion liquid for nitrogen removal. *Environmental Pollution,* 254, Part A, 2019, 112965. DOI:10.1016/j.envpol.2019.112965.

17. List of methods for performing measurements (determinations) of the composition and properties of samples of environmental objects, emissions, wastes and discharges provisionally allowed for use by the State Inspectorate of Ukraine, approved by the Head of the State Environmental Inspectorate of Ukraine – Chief State Inspector of Ukraine for Environmental Protection on 01.03.2013 (in Ukraine).
18. Malovanyy, A., Plaza, E., Trela, J., Malovanyy, M.: Combination of ion exchange and partial nitritation/Anammox process for ammonium removal from mainstream municipal wastewater. *Water Science & Technology,* 70(1), 144–151, 2014. DOI:10.2166/wst.2014.208.
19. Nezdoyminov, V.I.: Kinetic models of single-core biological systems with carbon oxidation, nitrification and denitrification. *Engineering Systems and Technogenic Safety,* 5(103), 150–153, 2013 (in Russian).
20. Wang, S., Peng, Y., Ma, B., Wang, S., Zhu, G.: Anaerobic ammonium oxidation in traditional municipal wastewater treatment plants with low-strength ammonium loading: Widespread but overlooked. *Water Research,* 84, 1–378, 2015.
21. Semenova, E., Shaginurova, G., Kirilina, T., Sirotkin, A.: Biotransformation of nitrogen compounds in wastewater treatment technologies. *Water Chemistry and Ecology,* 1, 26–32, 2012.
22. Ward, B.B., Arp, D.J., Klotz, M.G. *Nitrification. American Society for Microbiology.* DC, USA, Washington 2011.
23. Yagov, G.V.: Kontrol soderganiya coedineniy azota pri ochistke stochnyh vod (Control of the content of nitrogen compounds in wastewater treatment). *Vodosnabgenie i sanitarnaya tehnika,* 7, 1–6, 2008 (in Russian).

Selected methods of arsenic and mercury removal from wastewater - their advantages and limitations

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Abstract

Arsenic and mercury, which are by-products in many industries, pose a serious threat to the environmental ecology and human health, due to their toxicity, persistent nature, bioaccumulation and rapid distribution in the food chain. For many years, intensive research has been carried out in order to develop methods allowing for the effective removal of these hazardous pollutants from various types of wastewater. These technologies include traditional systematically modified methods, such as adsorption, chemical precipitation or ion exchange, as well as novel techniques based on utilization of membrane processes. There is also an emerging trend of employing various types of microorganisms (for example, bacteria, fungi or algae) in the treatment of wastewater from metal ions. This review presents the latest developments in using selected traditional and modern methods to remove arsenic and mercury from wastewater and discusses their advantages and limitations.

Keywords: arsenic, mercury, wastewater treatment, adsorption, ion exchange, chemical precipitation, membrane separation, biological methods

1. Introduction

The systematic reduction of the available drinking water resources is caused by many factors, such as, inter alia, climate change causing long-term droughts, increasing number of people on earth and the related development of various industries and, consequently, an increase in water consumption for domestic as well as industrial purposes and water pollution (Azimi et al., 2016). Providing long-term reliability of water supply of adequate quality is not easy, drinking water infrastructure is often based on the use of water from various sources, i.e., groundwater, surface water from rivers and lakes (Kloosterman et al., 2021) or rainwater (Bui et al., 2021; Khayan et al., 2019). However, it was reported that intensive extraction of water from the environment (e.g. groundwater) has a negative impact on its quality (Arasteh and Shoaei, 2020; Farid et al., 2019), which in the future may contribute to further reduction in the supply of water suitable for drinking. One of the solutions to the growing problem of water shortage is the treatment and reuse of wastewater. As different types of sewage may contain various hazardous pollutants, complex treatment methods dedicated to the removal of specific chemical compounds (micro- and macro-contaminants) are being developed (Ratola et al., 2012, Zhang et al., 2016, Nair et al., 2021). Although, as a result of the evolution of modern technologies and industrial processes, new chemical compounds known as "emerging pollutants" (Gopinath et al., 2020) occur in the wastewater, it is often conventional pollutants, such as heavy metals, that are the greatest problem.

Heavy metals characterized by high density (usually greater than 5 g/cm^3) posing a major threat to the living organisms, are present in greater amounts in industrial wastewater (e.g. originating from mines, metallurgy, electrolysis, electroplating, pesticides, medicine, paints, etc.), but can also be found in municipal wastewater (Du et al., 2020). They are toxic, non-biodegradable, and easily absorbed by plants and other organisms. When introduced into the human body, they can contribute to many health problems, including cancer. For example, arsenic can cause skin damage or cardiovascular problems, and mercury can damage the kidneys, circulatory and nervous systems (Chen et al., 2020).

The effect of heavy metals on the human body depends on the type of metal, its form, exposure period and concentration, therefore acceptable limits have been defined for the concentration of particular heavy metals, for example in drinking water (EPA, 2021; CMH, 2006; WHO, 2011). Proper treatment of industrial wastewater must also lead to a reduction in the concentration of heavy metals in line with applicable standards (WHO, 2006) and plays a key role in reducing arsenic and mercury emissions to the environment. For this reason, in recent years, new, more efficient and more environmentally friendly methods of removing heavy metal ions from water and wastewater have been developed, and already known methods have been modified. Many of them are based on solutions allowing for reduction of toxicity in order to meet technology-based treatment standards (Gunatilake, 2015).

Arsenic and mercury contaminations of the environment have been recognized as one of the most significant pollutants closely related to human activity (As – development of the wood, agricultural, food and chemical industries; Hg – mining and fossil fuel combustion), and their toxicity and remediation have become a subject of widespread interest, which has led to the development of various methods for their removal from wastewater (Alka et al., 2021, Albatrni et al., 2021). The most established technologies include, among others, adsorption, ion exchange, chemical precipitation and membrane processes (Rathi and Kumar, 2021; Azimi et al., 2016). Recently, biological methods (e.g. based on the use of microalgae, bacteria, fungi), which are usually less expensive and more environmentally friendly, are also increasingly utilized (Wang and Chen, 2009). This article discusses selected, currently used techniques of removing arsenic and mercury ions from wastewater, as well as their advantages and disadvantages (e.g. processes efficiency, their impact on the environment, and costs associated with their implementation). Particular attention was devoted to biological processes (e.g. biosorption) that may be alternative or complementary to conventional methods.

2. Selected arsenic and mercury removal methods

2.1. Adsorption

The adsorption process based on mass transfer between the liquid phase and the solid phase of an adsorbent consists of three basic stages: a) the penetration of metal ions (pollutants) from the solution to the adsorbent surface; b) adsorption of the pollutant on the adsorbent surface; and finally c) penetration in the adsorbent structure (Azimi et al., 2017). The proper selection of the adsorbent material has a key influence on adsorption efficiency. An adsorbent with a sufficiently large surface should allow not only to carry out the adsorption process with appropriate efficiency but should also be inexpensive and easily available.

In general, as far as the mechanism of the adsorption process is concerned, a distinction can be made between physical and chemical adsorbents/adsorption processes. The process of chemical adsorption is based on the formation of bonds between functional groups present on the surface of the adsorbent and metal ions, whereas in physical adsorption weak van der Waals interactions between the adsorbent and metal ions are generated (Albatrni et al., 2021). It has been reported, that adsorption efficiency is strongly influenced not only by the properties of functional groups of the adsorbent, but also by other properties, such as surface area, pore size, and pore size distribution, initial concentration of pollutants and adsorbent, as well as pH (Hadi et al., 2015). The simplest representative of physical adsorbents is activated carbon, commonly used for this purpose, while chemical adsorbents include, among others, humic acid substances (Chen et al., 2020). Traditional carbon materials have been successfully applied for many years to remove both arsenic (Mohan and Pittman, 2007, and references therein) and mercury (Hadi et al., 2015 and references therein) from wastewater. However, while traditional adsorption is often a very effective method, one of its limitations is that different types of adsorptive material particles are fine powders that are difficult to separate from aqueous solution/wastewater. Such powders also cannot be used in column applications due to their low hydraulic conductivity. Therefore, modified media such as activated carbon, sand, natural rock, ceramics, zeolite, or organic polymers coated with metal oxides have been increasingly used (Siddiqui and Chaudhry, 2017). Other modified carbon adsorbents were also successfully applied to remove arsenic and mercury ions from wastewater. For example, Asasian and Kaghazchi (2015) utilized sulfurized activated carbons (SACs) for the removal of mercury from the aqueous phase and reported that accelerated adsorption, especially in the initial stages of batch mode contact, was the important advantage of this solution compared to the use of unmodified activated carbons. Moreover, they found a negligible inflow of sulfur compounds to the treated wastewater, which is an important issue for environmental protection. Lin and Chen (2014) developed mesoporous Fe/carbon aerogel (CA) structures, which are efficient adsorbents for arsenic ions and due to their ferromagnetic behavior can be easily separated from the solution using an external magnetic field. Increased interest in iron-based materials, not only iron doped carbon adsorbents but also iron-containing combined metal oxides, iron-based layered double hydroxides, iron-doped polymer/biomass materials, iron-doped inorganic minerals, etc., is related to the fact that they have great potential to remove arsenic from wastewater (high efficiency, low cost, availability, easy operations) (Hao et al., 2018). For economic and environmental reasons, methods based on the use of various types of waste as adsorbents are also being developed. For example, Sarkar et al. (2017) utilized iron ore slime, which is mining waste, as an adsorbent for the removal of lead and mercury from wastewater. They reported that the major component of slime was hematite and that high surface area was the influencing parameter for efficient adsorption of heavy metals. Lee et al. (2018) used iron impregnated biochar – a carbon-rich, fine-grained, porous substance, obtained from sludge – a product of biological treatment of wastewater, to remove arsenic and phosphate, oxyanionic pollutants, from the aqueous phase and reported that the applied adsorption system enables efficient removal of pollutants, and the process itself is short, not laborious and inexpensive. Buddhika et al. (2020) utilized laterite grains made from crushing laterite brick as an adsorbent for removing chromium and arsenic from wastewater and reported a relatively high As adsorption compared to the use of commercially available zeolite and autoclaved aerated concrete adsorbents. However, their results of desorption experiments indicated that the tested laterite exhibited strong irreversibility for the adsorbed As (arsenic immobilization), which is the disadvantage of the material used.

Despite the many advantages of the emerging innovative functional substances (such as carbon nanotubes, various composite materials, waste, for example, sludge), one of the major limitations of arsenic and mercury adsorption from wastewater is the necessity of desorbing these pollutants. Due to the toxicity and impact of arsenic and mercury on the environment, the used adsorbents cannot be disposed of in landfills after the adsorption process. Regeneration of adsorbents is usually expensive, time-consuming, and their regeneration time and regenerant volume limit the utilization of adsorption in practical engineering applications (Hu et al., 2017).

2.2. Ion exchange

Ion exchange is one of the more recent and more frequently used methods to remove heavy metal ions from wastewater. Its mechanism is based on the interchange of different ions between the solid and liquid phases. In this process, first the ion-exchange reaction takes place, then the heavy metal ion is physically absorbed, and next a complex counterion-functional group is formed. The last step is hydration, which can take place on the pores of the adsorbent or on the surface of the solution (Azimi et al., 2016, and references therein). To carry out the ion exchange process, various media (e.g. inorganic materials – zeolites, clay minerals, organic materials-cellulose, carbonic materials) and ion exchange resins are used (Cobzaru and Inglezakis, 2015). Ion exchange resins are insoluble, porous polymers containing different functional groups (with either positive or negative charge, being exchange sites) that can participate in the exchange of mobile ions in reversible reactions. Adsorption selectivity of a resin depends on the characteristics of the functional groups and pH of the solution.The efficiency of the entire ion-exchange process is also influenced by other factors, such as its duration, temperature, concentration of metal ions in the solution, properties of the used resins (Silva et al., 2018).

Hua et al. (2020) in a comprehensive review on the use of ion exchange methods to remove mercury ions from aqueous solutions (e.g. wastewater), drew attention to the essential advantages of this solution, such as: high process efficiency, almost no secondary pollution (small amount of sludge), low time consumption, and ease of automation (which is of great importance when the process is carried out on a larger scale over a longer time). It is also important that the process can be carried out using various types of ion exchangers for example, basic anion exchangers, acidic cation exchangers, selective ion exchangers, which means that the method can be used to treat various types of wastewater (Chiarle et al., 2000; Hua et al. 2020). Research is systematically carried out to design and use new substances in ion exchange processes, both commercially available chemicals and substances resulting from the modification of known materials. The introduced solutions are primarily aimed at increasing the efficiency of the process and its selectivity, simplifying the procedure, but also reducing costs. For example Alguacil and Escudero (2020) eliminated mercury (II) from acidic aqueous solutions, by the cationic ion exchange resin Lewatit SP112 and reported that the utilized resin have good Hg(II) – loading ability, and mercury loaded onto the resin can be easily eluted by various solvents. Moreover, easy to separate zero valent mercury was successfully obtained. Ugrina et al. (2021) applied sulfur-impregnated natural zeolite clinoptilolite for Hg(II) removal from aqueous solutions and found that sulfur-impregnation increased the sorption of Hg(II) by 3.6 times compared to natural zeolite. Sinyakova et al. (2014) and Eparina and Sinyakova (2018) performed experiments based on the utilization of polysurmin as an ion exchanger dedicated to the removal of mercury from multi-component solutions (containing several, different heavy metal ions) and reported that the used material exhibits specific selectivity for Hg^{2+} ions demonstrating high capacity.

The ion exchange method is a well-established solution as far as removing mercury ions from aqueous solutions is concerned. However, in the case of removing arsenic ions, there are additional limitations. It has been shown that this method can usually be used to remove As (V) but is not useful for uncharged As(III) species present in aqueous solutions (Hao et al., 2018; and references therein). However, the ion exchange method can be utilized to separate As(V) and As(III). For example Guo and Liu (2012) separated arsenic (III) and arsenic (V) by the application of strong anion-exchange resin (AG 1-X8), due to its adsorption of As(V) in acetate form and no adsorption of neither As(V) or As(III) in chloride form. In addition, some of the ion exchangers currently used allow the removal of arsenic from low – As (V) wastewater, and many types of industrial wastewater are characterized by a high concentration of this pollutant. Therefore, research is being conducted to find an ion exchanger allowing the removal of arsenic from high-As(V) solutions. For example, Lu et al. (2021) used Cobalt(Co) – loaded resin for the removal of As(V) from wastewater and reported that this material provides a simple and effective (removal efficiency exceeded 99%) way to remove arsenic from wastewater with high As(V) content. However, in the case of a wide variety of wastewater containing large amounts/different forms of arsenic, the development of an ion-exchange resins and their use in modern purification systems can be quite expensive (Hao et al., 2018; Chen et al., 2020).

2.3. Chemical precipitation

The process of chemical precipitation, one of the oldest methods of removing heavy metal ions from wastewater, is based on a reaction in which the precipitant reacts with heavy metal ions present in an aqueous solution, leading to the formation of insoluble solids (Azimi et al., 2017; Hargreaves et al., 2016). They are separated in the next step using a variety of techniques, such as for example, sedimentation or filtration. Despite the fact that chemical precipitation is a simple and well-known method, it is not very popular at present due to numerous limitations, which include not very high efficiency of the process, the need to use a large amount of chemicals and determine exactly the correct pH, and also the necessity to proper manage the resulting products of the process. The generated sludge usually has no commercial value and must be stored in specialized landfills, which is associated with additional costs (Mauchauffee and Meux, 2007). This traditional method of removing metal ions from wastewater also has high energy requirements (Shrestha et al., 2021). Despite many limitations, due to their simplicity, chemical precipitation methods are still applied, with the use of new compounds that allow for more efficient removal of arsenic and mercury ions. For example, Blue et al. (2010) reported that aqueous mercury and arsenic precipitation can be performed by utilizing the synthetic dithiolate, BDTH2 (1,3-benzenediamidoethanethiol) and closely related derivatives. Results of their experiments have shown that BDTH2 does not become inactive through oxidation to disulfide and can be applied to mercury-containing water as acidic, basic, and ethanolic solutions. Generated precipitates were stable and leached (at low-ppm levels) only under extremely acidic and basic conditions. Another solution is to introduce modifications to known precipitation methods to obtain more stable products. For example, Hu et al. (2019) used a well-known method of removing arsenic from wastewater by precipitating it as arsenic sulfide, but they introduced a modification of hydrothermal mineralization. Hydrothermal mineralization was an effective method for better stabilization of As_2S_3 (transformation of amorphous arsenic sulfide into crystallized As_2S_3, which leached to a lesser extent). However, it should be emphasized that the efficiency of the precipitation process depends to a large extent on the composition of the treated wastewater, which is best evidenced by the latest research results obtained by Ostermeyer et al. (2021), who performed experiments in which arsenic precipitation as arsenic sulfide was tested under industrially relevant conditions. In general, precipitation of arsenic as As_2S_3 produces relatively little waste sludge, has the potential for lower chemical consumption and for selective metal removal. However, their results showed, that components in the industrial wastewater affected the removal of As. Selective precipitation of arsenic was observed, but depended on speciation, S:As ratio and presence of other metals in the examined solution.

2.4. Chemical precipitation

Membrane separation, now widely used for both the separation of specific components and the concentration of solvents and solutes is based on the difference in permeability of substances. This method also plays an increasingly important role in water treatment processes (e.g. desalination) and is used in wastewater treatment (Albatrni et al., 2021, and references therein). Due to some differences (e.g. membrane permeability, porosity, pore size, applied pressure) related to membrane processes, techniques such as: reverse osmosis, ultrafiltration, microfiltration, nanofiltration and electrodialysis were distinguished (Azimi et al., 2016). Membrane techniques play an important role in removing mercury from wastewater when it is in a colloidal form. In such cases, the application of chemical precipitation, ion exchange or adsorption methods is not sufficient. However, membrane processes depend on many parameters. Urgun-Demirtas et al. (2012) used various membrane techniques (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) to remove mercury ions from refinery wastewater and reported that the processes depend on various factors (form and concentration of mercury, particle size distribution, operating pressures) and that the parameters of the processes carried out must be separately established for each technique. The effectiveness of membrane processes was also reported to depend on the established parameters in the case of arsenic removal from wastewater (Jadhav et al., 2018). Membrane processes can be successfully utilized in arsenic removal from contaminated water to meet the maximum contaminant level set by WHO and they additionally allow to reduce the amount of generated hazardous sludge which is one of the limitations of the use of traditional solutions (e.g. chemical precipitation) (Kullab et al., 2017). Recently, new materials that can be used in membrane processes to remove mercury and arsenic ions from wastewater more efficiently are systematically searched for. It is also important to reduce the cost of membrane processes. For example, Zhang et al. (2018) applied a novel thiol-covered polyamide (nylon 66) microfiltration membrane for the removal of Hg from wastewater and reported that the generated membrane exhibited high oil/water separation efficiency, outstanding mercury adsorption ability, and good stability. Hubadillah et al. (2019) prepared a low-cost hydrophobic kaolin hollow fiber membrane and applied it for arsenic removal from wastewater. The applied membranes were not expensive and allowed to meet the required standard of maximum contaminant level.

In general, membrane techniques have many advantages, they are effective, their use is not associated with the utilization of large amounts of chemicals, the processes are not long or labor-intensive and can be carried out in mild conditions. However, they also have limitations. As Verma et al (2021) noted "fouling of the membrane is perhaps the only barrier to the emergence of membrane technology and its full acceptance". The solution to this problem may be the use of graphene oxide-based nanofiltration, which has become very popular in recent years. Graphene oxide and derivatives are materials that can be used as a thin and flexible membrane sheet with high chemical stability and high mechanical strength (Zunita, 2021). An important advantage of membrane techniques is that they can be used in combination with other methods, to overcome the limitations (Verma et al., 2021).

2.5. Biological methods

In recent decades, methods of removing metals, including arsenic and mercury from wastewater based on the use of various organisms, e.g. bacteria, yeasts, molds and different types of algae have been of particular interest. In biological wastewater treatment processes, various, complex reactions occur between the removed ions and biomass components (e.g. ion exchange, coordination) (Hua et al., 2020). The main advantages of biological methods are: access to a wide range of inexpensive materials (biomass), low cost of the whole procedure, no secondary pollution, and the utilization of processes that naturally occur in the environment (with the improvement of certain parameters) (Hua et al., 2020; Chen et al., 2020).

One of the phenomena used in the biological removal of heavy metals from wastewater is bioaccumulation, in which microorganisms use proteins to capture and sequester metal ions in the intracellular space for utilization in cellular processes (Diep et al., 2018). Research on the applicability of microorganisms to purify wastewater from heavy metals is of a very diverse nature. For example, Sher et al. (2020) isolated heavy metal-resistant bacterium, Micrococcus luteus strain AS_2 from industrial wastewater and reported that bacterial strain showed resistance against arsenic and mercury, and also against other heavy metal ions. The bioremediation efficiency (E) of bacterial biomass, which can serve as an indicator for the isolated bacterium to employ as a potential candidate for the removal of arsenic was 99% after 10 h of process. There are many bacterial strains with proven high resistance to heavy metals, including arsenic (e.g. due to the efficient oxidation potential of arsenite), for example Pseudomonas monteilii and Bacillus infantis (isolated from arsenic contaminated wastewater) (Sher et al., 2021) or Bacillus cereus and Acinetobacter junii (isolated from industrial wastewater) (Naureen and Rehman, 2016). Similarly, it has been shown that Vibrio fluvialis (isolated from the effluent discharge sites of industrial area) (Saranya et al., 2017) and Pseudomonas aeruginosa (isolated from a non-active sanitary landfill) (Imron et al., 2019) could be successfully used as a strain for the ecofriendly removal of mercury. In general, bacterial strains with high resistance to arsenic and mercury can potentially be used in the future to remove heavy metals ions from wastewater for green chemistry (Sher et al., 2021).

Many studies are based on utilization of genetically modified orgasms, including bacteria. Such GM microorganisms allow for increased uptake and sequestration of heavy metal ions, and thus increase the efficiency of the process (Diep et al., 2018). Techniques for removing metals via genetically modified microorganisms are considered an environmentally safe and a economically viable strategy (Sharma et al., 2021). Recently, also a combination of different methods, including these based on the application of bacteria, have been increasingly used. For example, Kamde et al. (2019) studied removal of arsenic from real wastewater employing modified bio-oxidation followed by adsorptive filtration method in a novel continuous flow through the reactor. Their results showed that used combination of methods improved the removal efficiency of arsenic and other heavy metal ions from wastewater samples.

Aquatic plant species can also be used to remove arsenic and mercury from wastewater. Jasrotia et al. (2017) investigated the effectiveness of aquatic macrophyte and microphyte (water hyacinth Eichhornia crassipes and algae Chlorodesmis sp. and Cladophora sp.) for phytoremediation of water samples contaminated with high arsenic concentration. They found that only algae Cladophora sp. was effective enough (reduction of arsenic concentration from 6 to < 0.1 mg/L in 10 days of retention) to be used on a larger scale. In the case of Eichhornia crassipes and Chlorodesmis sp., the efficiency of the arsenic removal process did not exceed 50%. The application of Cladophora sp. can be a simple and cost effective method of arsenic removal, e.g. in rural areas and the treated water can be used for irrigation. Cladophora sp. algae immobilized in alginate beads and silica gel has been also successfully applied for the biosorption of mercury from aqueous solutions (Mokone et al., 2018). It has been reported that biosorption occurred on a homogeneous layer and ion exchange was the dominant mechanism. Jaafari and Yaghmaeian (2019) utilized freshwater algae Chlorella coloniales for the biosorption of Cr, Cd, Co, Fe and As from aqueous solutions using the Box-Behnken design. They noticed that at low arsenic concentrations, Chlorella coloniales showed high bioaccumulation efficiency (96%), but at high concentrations the bioaccumulation efficiency decreased. Huang et al. (2019) utilized Scenedesmus obtusus XJ-15 microalgae in novel strategy based on incubating algae cells in high phosphate cultures to modify the surface, then obtaining P-rich biomass as adsorbents to enhance Hg (II) removal, then charring the Hg-laden biomass to prevent phosphate leaching and immobilize Hg (II). Algae biomass has shown such great potential in removing water pollutants, that it is used to synthesize engineered algae adsorbents suitable for the adsorptive management of various pollutants, including metals such as arsenic and mercury (Lee et al., 2022).

The methods of removing arsenic and mercury based on the use of yeast/fungi are also becoming more and more popular because they are efficient, inexpensive and safe for the environment (Chang et al., 2020). Oyetibo et al. (2016) studied intracellular accumulation and extracellular micro-precipitation of Hg during growth stage of the Yarrowia spp. Idd1 and Idd2 strains, and reported that results of performed experiments revealed excellent Hg removal (> 97%) by the yeast strains. Moreover, it has been shown that the tested yeast strains can also be effectively used in the technology of biological treatment of Hg contaminated water due to their high self-aggregation and separation activity from the aquatic environment. Mohebbrad et al. (2019) used Saccharomyces cerevisiae yeast to remove arsenic from solutions and found that the As removal efficiency increased at low pH under acidic conditions and that S. cerevisiae can be utilized as a cheap and effective adsorbent. Often, in order to increase efficiency of metals ions removal process, methods are developed that use various microorganisms, for example, bacteria and fungi (i.e. ureolytic fungal strain Metschnikowia pulcherrima and bacterial strain Raoultella planticola) (Eltarahony et al., 2021). Such approach ensures detoxification and sequestration of heavy metals in stable and durable matrices.

It is currently assumed that the methods of biological arsenic and mercury removal from wastewater may dominate conventional methods in the future, due to the wide applicability (they can be used for various types of wastewater containing different pollutants), high efficiency and relatively low cost. Recently, research is also carried out to reduce these costs, one solution is for example the integration of biomass production from algae and wastewater treatment by these microorganisms (Priyadharshini et al., 2021).

3. Summary and Conclusions

The development of methods dedicated to removal of hazardous metals ions, including arsenic and mercury is very important, both for the protection of the environment and for human health. Most of the research efforts have focused on modifications of known conventional methods (for example adsorption, ion exchange or chemical participation), which allow to increase the efficiency of the processes, reduce the amount of hazardous by-products, lower the costs and simplify operations. The removal of arsenic and mercury using novel membrane separation technologies or various microorganisms is also very promising. This study presents the latest achievements in the above-mentioned methods used to remove arsenic and mercury from wastewater and their most important limitations. Table 1 provides a brief summary of the most important advantages and disadvantages of the selected methods. For example, adsorption is a well-known and relatively simple process, and the number of available adsorbents continues to increase, but a serious limitation is the need to desorb hazardous pollutants, which is often expensive and difficult. Even in the case of methods commonly considered as eco-friendly, based on the use of microorganisms, challenges arise, such as for example, obtaining appropriate biomass or eliminating the impact of other wastewater contamination on the efficiency of the treatment process. Due to the systematic development of various industries, the increase in care of the environment and the dwindling resources of drinking water, it can be assumed that in the near future, further intensive development of methods intended for purification of water and wastewater treatment from hazardous pollutants, such as arsenic and mercury will be observed.

Table 1. Main advantages and disadvantages of selected methods of arsenic and mercury removal from wastewater

Method	The main advantages	The main limitations	References
Adsorption	Well established and a very effective method, typically characterized by low costs and easy operations. The possibility of using various adsorbents.	The necessity to regenerate the adsorbents – usually costly, time consuming, often requires complex processes.	Azimi et al., 2017, Hu et al., 2017,
Ion exchange	High process efficiency, almost no secondary pollution (small amount of sludge), low time consumption, and ease of automation. The possibility of using various types of ion exchangers.	This method can usually be used to remove As (V) but is not useful for uncharged As (III) species present in aqueous solutions.	Chiarle et al., 2000, Hua et al. 2020. Hao et al., 2018.
Chemical precipitation	Traditional method of removing metal ions from wastewater, characterized by great simplicity.	Not very high efficiency, the need to use a large amount of chemicals. The necessity to proper manage the resulting sludge, which usually has no commercial value and must be stored in specialized landfills. Method characterized by high energy requirements.	Mauchauffe and Meux, 2007, Shrestha et al., 2021.

Method	The main advantages	The main limitations	References
Membrane separation	Membrane techniques are effective, their use is not associated with the utilization of large amounts of chemicals, the processes are not long or labor-intensive and can be carried out in mild conditions.	Membrane fouling is a major barrier to the large-scale use of this technique.	Verma et al., 2021.
Biological methods	Access to a wide range of inexpensive materials (biomass), low cost of the whole procedure, no secondary pollution, and the utilization of processes that naturally occur in the environment.	Limited use for wastewater containing large amounts of various pollutants. The need to create appropriate conditions for the proper development of the organisms used.	Hua et al., 2020; Chen et al., 2020.

References

1. Albatrni, H., Qiblawey, H., El-Naas, M.H.: Comparative study between adsorption and membrane technologies for the removal of mercury. *Separation and Purification Technology*, 257, 117833, 2021.

2. Alguacil, F. J., Escudero, E.: The removal of toxic metals from liquid effluents by ion exchange resins. Part XII: Mercury(II)/H+/Lewatit SP112. *Revista de Metalurgia*, 56(1), 160, 2020.

3. Alka, S., Shahir, S., Ibrahim, N., Jibrin, M. Ndejiko, M. J., Vo, D.N., Manan, F. A.: Arsenic removal technologies and future trends: A mini review. *Journal of Cleaner Production*, 278 (1), 123805, 2021.

4. Arasteh, S.M., Shoaei, S.M.: An assessment of the effects of excessive groundwater abstraction on the quality of groundwater resources of the Zanjan Plain, Iran. *Environmental Earth Sciences*, 79(23), 523, 2020.

5. Asasian, N., Kaghazchi, T.: Sulfurized activated carbons and their mercury adsorption/desorption behavior in aqueous phase. *International Journal of Environmental Science and Technology*, 12(8), 2511–2522, 2015.

6. Azimi, A, Azari, A., Rezakazemi, M., Ansarpour, M.: Removal of Heavy Metals from Industrial Wastewaters: A Review. *ChemBioEng Reviews*, 4(1), 37–59, 2017.

7. Buddhika, A., Bandara, P., Mudalige, G., Kumara, P., Matsuno, A., Saito, T., et al.: Examination of crusher laterite brick for removal of chromium and arsenic from wastewater. *International Journal of GEOMATE,* 19(74), 22–30, 2020.

8. Bui, T.T., Nguyen, D.C., Han, M., Kim, M., Park, H.: Rainwater as a source of drinking water: A resource recovery case study from *Vietnam. Journal of Water Process Engineering*, 39, 101740, 2021.

9. Chang, J.J., Shi, Y., Si, G.Z., Yang, Q.C., Dong, J., Chen, J.Q.: The bioremediation potentials and mercury(II)-resistant mechanisms of a novel fungus Penicillium spp. DC-F11 isolated from contaminated soil. *Journal of Hazardous Materials*, 396, 122638, 2020.

10. Chen, B., Chen, Y., Xu, L., Zhang, Y., Li, H.: Research and development on industrial heavy metal wastewater treatment technology. *IOP Conf. Series: Earth and Environmental Science*, 585, 012051, 2020.

11. Chiarle, S., Ratto, M., Rovatti, M.: Mercury removal from water by ion exchange resins adsorption. *Water Research,* 34(11), 2971–2978, 2000.

12. Chinese Ministry of Health (CMH). Standards for Drinking water quality. National Standard of the Peoples Republic of China, GB 5749, 2006.

13. Cobzaru, C., Inglezakis, V.: Progress in Filtration and Separation, Chapter Ten – Ion Exchange, 425–498, Elsevier Ltd., 2015.

14. Diep, P., Mahadevan, R., Yakunin, A.F.: Heavy Metal Removal by Bioaccumulation Using Genetically Engineered Microorganisms. *Frontiers in Bioengineering and Biotechnology*, 6(157), 157, 2018.

15. Du, P., Zhang, L.R., Ma, Y.T., Li, X.Y., Wang, Z.L., Mao, K., et al.: Occurrence and Fate of Heavy Metals in Municipal Wastewater in Heilongjiang Province, China: A Monthly Reconnaissance from 2015 to 2017. *Water*, 12 (3), 728, 2020.

16. Eltarahony, M., Kamal, A., Zaki, S., Abd-El-Haleem, D.: Heavy metals bioremediation and water softening using ureolytic strains Metschnikowia pulcherrima and Raoultella planticola. *Journal of Chemical Technology and Biotechnology,* 96, 3152–3165, 2021.

17. Eparina, E.A., Sinyakova, M.A.: Sorption of Mercury(II) Ions on Inorganic Ion Exchangers under Dinamic Conditions. *Russian Journal of General Chemistry*, 88(13), 2837–2842, 2019.

18. Farid, H.U., Ahmad, I., Anjum, M.N., Khan, Z.M., Iqbal, M.M., Shakoor, A., Mubeen, M.: Assessing seasonal and long-term changes in groundwater quality due to over-abstraction using geostatistical techniques. *Environmental Earth Sciences,* 78(13), 386, 2019.
19. Gopinath, K.P., Madhav, N.V., Krishnan, A., Malolan, R., Rangarajan, G.: Present applications of titanium dioxide for the photocatalytic removal of pollutants from water: A review. J*ournal of Environmental Management,* 270, 110906, 2020.
20. Gunatilake, S.K.: Methods of Removing Heavy Metals from Industrial Wastewater. *Journal of Multidisciplinary Engineering Science Studies*, 1(1), 12–18, 2015.
21. Guo, H.M., Liu, C.H.: Separation of Inorganic Arsenic Species from Aqueous Solution by Anion Exchange Column and Its Application in Study of Arsenic Removal. *Chinese Journal of Analytical Chemistry*, 40 (7), 1092–1097, 2012.
22. Hadi, P., To, M.H., Hui, C.W., Lin, C.S.K., McKay, G.: Aqueous mercury adsorption by activated carbons. *Water Research*, 73, 37–55, 2015.
23. Hao, L., Liu, M., Wang, N., Li, G.: A critical review on arsenic removal from water using iron-based adsorbents. *RSC Advances*, 8, 39545–39560, 2018.
24. Hargreaves, A.J., Vale, P., Whelan, J., Constantino, C., Dotro, G., Cartmell, E: Mercury and antimony in wastewater: fate and treatment. *Water Air and Soil Pollution,* 227(3), 89, 2016.
25. www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations. January 2021.
26. Hu, B., Yang, T., Liu, W., Zhang, D., Chen, L.: Removal of arsenic from acid wastewater via sulfide precipitation and its hydrothermal mineralization stabilization. *Transactions of Nonferrous Metals Society of China*, 29(11), 2411–2421, 2019.
27. Hu, J.L., Yang, X.S., Liu, T., Shao, L.N., Zhang, W.: Dynamic desorption of arsenic from polymer-supported hydrated iron(III) oxide in a wastewater treatment plant. *Water Science & Technology,* 76(9–10), 2380–2388, 2017.
28. Hua, K., Xu, X., Luo, Z., Fang, D., Bao, R., Yi, J.: Effective Removal of Mercury Ions in Aqueous Solutions: A Review. *Current Nanoscience,* 16(3), 353–375, 2020.
29. Huang, R., Huo, G.C., Song, S.X., Li, Y.T., Xia, L., Gaillard, J.F.: Immobilization of mercury using high-phosphate culture-modified microalgae. *Environmental Pollution*, 254, 112966, 2019.

30. Hubadillah, S.K., Othman, M.H.D., Ismail, A.F., Rahman, M.A., Jaafar, J.: A low cost hydrophobic kaolin hollow fiber membrane (h-KHFM) for arsenic removal from aqueous solution via direct contact membrane distillation. *Separation and Purification Technology*, 214, 31–39, 2019.

31. Imron, M.F., Kurniawan, S.B., Soegianto, A.: Characterization of mercury-reducing potential bacteria isolated from Keputih non-active sanitary landfill leachate, Surabaya, Indonesia under different saline conditions. *Journal of Environmental management*, 241, 113–122, 2019.

32. Jaafari, J., Yaghmaeian, K.: Optimization of heavy metal biosorption onto freshwater algae (Chlorella coloniales) using response surface methodology (RSM). *Chemosphere*, 217, 447–455, 2019.

33. Jadhav, S.V., Hayrynen, P., Marathe, K.V., Rathod, V.K., Keiski, R.L., Yadav, G.D.: Experimental and Modeling Assessment of Sulfate and Arsenic Removal from Mining Wastewater by Nanofiltration. *International Journal of Chemical Reactor Engineering*, 16(1), 20160103, 2018.

34. Jasrotia, S., Kansal, A., Mehra, A.: Performance of aquatic plant species for phytoremediation of arsenic-contaminated water. *Applied Water Science*, 7(2), 889–896, 2017.

35. Kamde, K., Dahake, R., Pandey, R.A., Bansiwal, A.: Integrated bio-oxidation and adsorptive filtration reactor for removal of arsenic from wastewater. *Environmental Technology*, 40(10),1337–1348, 2019.

36. Khayan, K., Husodo, A. H., Astuti, I.,Sudarmadji, S., Djohan, T.S.: Rainwater as a Source of Drinking Water: Health Impacts and Rainwater Treatment. *Journal of Environmental and Public Health*, 2019, 1760950, 2019.

37. Kloosterman, R.A., van der Hoek, J.P., Herder, P.: Resilient Drinking Water Resources. *Water Resources Management*, 35(1), 337–351, 2021.

38. Kullab, A., Martin, A.R., Saask, A.: Removal of Toxic Compounds from Water by Membrane Distillation (Case Study on Arsenic). Sustainable Membrane Technology for Water and Wastewater Treatment. *Green Chemistry and Sustainable Technology*, 243–263, 2017.

39. Lee, M.E., Jeon, P., Kim, J.G., Baek, K.: Adsorption characteristics of arsenic and phosphate onto iron impregnated biochar derived from anaerobic granular sludge. *Korean Journal of Chemical Engineering*, 35(7), 1409–1413, 2018.

40. Lee, X.J., Ong, H.C., Ooi, J., Yu, K L., Tham, T.C., Chen, W.H., Ok, Y.S.: Engineered macroalgal and microalgal adsorbents: Synthesis routes and adsorptive performance on hazardous water contaminants. *Journal of Hazardous Materials*, 423, 126921, 2022.
41. Lin ,Y.F., Chen, J.L., Magnetic mesoporous Fe/carbon aerogel structures with enhanced arsenic removal efficiency. *Journal of Colloid and Interface Science*, 420, 74–79, 2014.
42. Lu, Z., Li, X., Qi, X.: Cobalt-loaded resin can effectively remove arsenic in wastewater. *Environmental Technology and Innovation*, 21, 101354, 2021.
43. Mauchauffee, S., Meux, E.: Use of sodium decanoate for selective precipitation of metals contained in industrial wastewater. *Chemosphere*, 69(5), 763–768, 2007.
44. Mohan, D., Pittman, C.U.: Arsenic removal from water/wastewater using adsorbents – A critical review. *Journal of Hazardous Materials*, 142(1–2), 1–53, 2007.
45. Mohebbrad, B., Bonyadi, Z., Dehghan, A.A., Rahmat, M.H.: Arsenic removal from aqueous solutions using Saccharomyces cerevisiae: Kinetic and equilibrium study. *Environmental Progress and Sustainable Energy*, 38, S398–S402, 2019.
46. Mokone, J.G., Tutu, H., Chimuka, L., Cukrowska, E.M.: Optimization and Characterization of Cladophora sp Alga Immobilized in Alginate Beads and Silica Gel for the Biosorption of Mercury from Aqueous Solutions. *Water Air and Soil Pollution*, 229(7), 215, 2018.
47. Nair, K.S., Manu, B., Azhoni, A.: Sustainable treatment of paint industry wastewater: Current techniques and challenges. *Journal of Environmental Management*, 296, 11310, 2021.
48. Naureen, A., Rehman, A.: Arsenite oxidizing multiple metal resistant bacteria isolated from industrial effluent: their potential use in wastewater treatment. *World Journal of Microbiology and Biotechnology*, 32(8), 133–139, 2016.
49. Ostermeyer, P., Bonin, L., Folens, K., Verbruggen, F., García-Timermans, K., Verbeken, K., et al.: Effect of speciation and composition on the kinetics and precipitation of arsenic sulfide from industrial metallurgical wastewater. *Journal of Hazardous Materials*, 409(5), 124418, 2021.
50. Oyetibo, G.O., Miyauchi, K., Suzuki, H., Endo, G.: Mercury removal during growth of mercury tolerant and self-aggregating Yarrowia spp. *AMB Express*, 6, 99, 2016.

51. Priyadharshini, S.D., Babu, P.S., Manikandan, S., Subbaiya, R., Govarthanan, M., Karmegam, N.: Phycoremediation of wastewater for pollutant removal: A green approach to environmental protection and long-term remediation. *Environmental Pollution*, 290, 117989, 2021.
52. Rathi, B.S., Kumar, P.S.: A review on sources, identification and treatment strategies for the removal of toxic Arsenic from water system. *Journal of Hazardous Materials*, 418, 126299, 2021.
53. Ratola, N., Cincinelli, A., Alves, A., Katsoyiannis, A.: Occurrence of organic microcontaminants in the wastewater treatment process. A mini review. *Journal of Hazardous Materials*, 239, 1–18, 10, 2012.
54. Saranya, K., Sundaramanickam, A., Shekhar, S., Swaminathan, S., Balasubramanian, T.: Bioremediation of Mercury by Vibrio fluvialis Screened from Industrial Effluents. *Biomed Research International*, 6509648, 2017.
55. Sarkar, S., Sarkar, S., Biswas, P.: Effective utilization of iron ore slime, a mining waste as adsorbent for removal of Pb(II) and Hg(II). *Journal of Environmental Chemical Engineering*, 5(1), 38–44, 2017.
56. Sharma, P., Sirohi, R., Tong, Y., W., Kim, S.H., Pandey, A.: Metal and metal(loids) removal efficiency using genetically engineered microbes: Applications and challenges. *Journal of Hazardous Materials*, 416, 125855, 2021.
57. Sher, S., Ghani, A., Sultan, S., Rehman, A.: Bacterial Strains Isolated from Heavy Metals Contaminated Soil and Wastewater with Potential to Oxidize Arsenite. *Environmental Processes An International Journal*, 8(1), 333–347, 2021.
58. Sher, S., Hussain, S.Z., Rehman, A.: Phenotypic and genomic analysis of multiple heavy metal-resistant Micrococcus luteus strain AS_2 isolated from industrial waste water and its potential use in arsenic bioremediation. *Applied Microbiology and Biotechnology*, 104(5), 2243–2254, 2020.
59. Shrestha, R., Ban, S., Devkota, S., Sharma, S., Joshi, R., Tiwari, A.P., Kim, H.Y., Joshi, M.K.: Technological trends in heavy metals removal from industrial wastewater: A review. *Journal of Environmental Chemical Engineering*, 9(4), 105688, 2021.

60. Siddiqui, S.I., Chaudhry, S.A.: Removal of arsenic from water through adsorption onto metal oxide-coated material. Applications of Adsorption and Ion Exchange Chromatography in Waste Water Treatment, *Materials Research Foundations,* 15, 227–276, 2017.
61. Silva, R.A., Hawboldt, K., Zhang, Y.H.: Application of resins with functional groups in the separation of metal ions/species – a review. *Mineral Processing and Extractive Metallurgy Review,* 39 (6), 395–413, 2018.
62. Sinyakova, M.A., Semenova, E.A., Gamuletskaya, O.A.: Ion exchange of copper(II), lanthanum(III), thallium(I), and mercury(II) on the "polysurmin" substance. *Russian Journal of general Chemistry,* 84(13), 2516–2520, 2014.
63. Ugrina, M., Gabersek, M., Dakovic, A., Nuic, I.: Preparation and Characterization of the Sulfur-Impregnated Natural Zeolite Clinoptilolite for Hg(II) Removal from Aqueous Solutions. *Processes*, 9(2), 217, 2021.
64. Urgun-Demirtas, M., Benda, P.L., Gillenwater, P.S., Negri, M.C., Xiong, H., Snyder, S.S.: Achieving very low mercury levels in refinery wastewater by membrane filtration, *Journal of Hazardous Materials*, 215–216, 98–107, 2012.
65. Verma. B., Balomajumder. C., Sabapathy. M., Gumfekar. S.P.: Pressure-Driven Membrane Process: A Review of Advanced Technique for Heavy *Metals Remediation. Processes*, 9(5), 752, 2021.
66. Wang, J., Chen, C.: Biosorbents for heavy metals removal and their future. *Biotechnology Advances,* 27 (2),195–226, 2009.
67. WHO. A compendium of standards for wastewater reuse in the Eastern Mediterranean Region. Document WHO-EM/CEH/142/E, 2006.
68. WHO. Guidelines for Drinking Water Quality (4th ed). WHO Press, Geneva, Switzerland, 2011.
69. Zhang, M., Zhao, B.L., Hu, L., Li, T.T., Qiang, X.L.: Recent advances in oily wastewater treatment. *Oxidation Communications*, 39(4), 3415–3423, 2016.
70. Zhang, Q.D., Liu, N., Cao, Y.Z., Zhang, W.F., Wei, Y., Feng, L., Jiang, L.A.: A facile method to prepare dual-functional membrane for efficient oil removal and in situ reversible mercury ions adsorption from wastewater. *Applied Surface Science*, 434, 57–62, 2018.
71. Zunita, M.: Graphene Oxide-Based Nanofiltration for Hg Removal from Wastewater: A Mini Review. *Membranes,* 11 (4), 269, 2021.

Study of the process of removing organic substances by systems of varios ion exchangers with simultaneous production of deeply demineralized water

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Abstract

In order to study the possibility of removing organic substances with the simultaneous production of deeply demineralized water, various sorption systems containing ion-exchange and mixed-action filters have been tested. The studies were carried out on strongly acidic cation exchangers KU-2-8, KU-23 and strongly basic anion exchangers AV-17-8, AV-17-10P, which, within the same acidity and basicity, differed in gel and macroporous structure, respectively. Sorption of organic substances was studied on technical (untreated) ion exchangers, converted to the corresponding form (H^+ or OH^-) and repeatedly subjected to the process of sorption - regeneration, by passing distilled water and 0.05 and 0.01 N Na2SO4 solutions. It was found that organic substances are almost completely removed both from water and from solutions by a system containing the cation exchanger KU-2-8, anion exchanger AB-17-8 and a mixed filter (KU-2-8 + AV-17-8). It was found that in all other systems, at low concentrations of organic substances in the initial solution, the sorption of organic substances by resins occurs only at the beginning of the process when a certain amount of solution passes, and then the reverse process takes place – the washing out of organic substances from the resin. in other systems, at low concentrations of organic substances in the initial solution, their sorption by ion exchangers does not occur, after passing a certain amount of solution, the reverse process takes place - they are washed out of the resin. It has been established that the studied macroporous ion exchangers are not suitable for removing organic substances in systems with the simultaneous production of deeply desalinated water.

Keywords: mixed – action filter, ion exchangers, sorption

1. Introduction

Deeply demineralized water is an industrial necessity and the range of its technological use is quite wide. Thus, large volumes of deeply demineralized water are consumed in the heat and power industry, which significantly extends the service life of steam and hot water equipment. In addition, this fully demineralized aqueous solution has found application in metallurgical and petrochemical industries, in which a number of enterprises can operate only on deeply demineralized water. In pharmacy, this is injection water and in the food industry, some food products and alcoholic beverages (Slavinskaya, 2013; Petrov et al., 2021; Bejanidze et al., 2020).

It should be noted that the distillation of the source water does not solve the problems with deep desalination, the distillation unit does not purify the water to the required purity, it is necessary to treat the water with ion exchange resins – ion exchangers at the subsequent stage of water treatment after distillation (Bejanidze et al., 2020).

Many of the enterprises (energy, electronic, chemical), consuming large amounts of water, have certain requirements for the quality of the water used, have special water treatment systems, consisting of several stages (Mitryasova and Pohrebennyk, 2020). If deep desalination of water is required, one of the stages is the stage of water softening, which is carried out using ion exchange resins (ion exchangers) (Bejanidze et al., 2019).

During operation, ion exchangers are subjected to a gradual negative impact of organic substances that are present in water in the form of natural and man-made compounds. The organic composition of natural waters is formed with the participation of soil and peat humus, plankton, higher aquatic vegetation, animal organisms, as well as organic substances introduced into water bodies in connection with the anthropogenic development of urban settlements, industry and agriculture. When higher vegetation decomposes, carbohydrates, organic acids, tannins, lingin, hemicellulose and resins enter the water (Matilainen et al., 2010).

Humic compounds, phenols, hydrocarbons, surfactants, less often – dyes, alcohols, ethers, aldehydes and ketones are found in natural waters more often than other organic substances. Significant amounts of organic matter enter the water as a result of decay of vegetation and the death of plankton, especially lower algae and radiant fungi (Sillanpää et al., 2018).

Their excessive amount in the source water leads to "aging" (poisoning) of ion exchangers, which reduces the productivity and reliability of operation of desalination plants. In this regard, the content of organic substances in the process water of many industries is strictly limited. With a significant content of organic substances, it is necessary to carry out preliminary purification of the source water (coagulation or treatment with activated carbon) (Poborov et al., 2010).

Organic contaminants can be removed from water in two ways: destruction (oxidation) by strong oxidants such as chlorine, oxygen, ozone, as well as harsh ultraviolet radiation to CO_2 and H_2O and extraction by sorption, coagulation and membrane methods (GOST 20298-74). Molecules of organic water pollutants come in different sizes and molecular weights. Thus, humic and fulvic acids, the content of which prevails in natural waters, make it difficult to obtain especially pure water, for example, for nuclear and heat power engineering.

Coagulation treatment allows you to remove only a part of high molecular weight substances (GOST 20301-74). Consequently, organic matter is usually not completely removed in water treatment systems.

The purpose of this work is to study the possibility of using mixed-action filters (FDM) for additional purification of water from organic substances and the selection of an effective pair of cation and anion exchangers with simultaneous production of deeply demineralized water.

2. Materials and Methods

In this work, samples of ion exchangers for industrial use have been investigated. The matrix of the ion exchanger is a water-insoluble polymer, however, the ions in the ion exchanger (counterions) are in a dissociated state, as a result of which an exchange reaction between the solution and the ion exchanger is possible. The charge of counterions is compensated by oppositely charged groups of ions chemically bonded to the polymer matrix of the ion exchanger. According to the degree of dissociation, ion exchangers are divided into strongly acidic and strongly basic ones, almost completely dissociated in solution, and into partially dissociated ones – weakly acidic and weakly basic.

The work investigated strongly acidic and strongly basic ion exchangers, which, within the same acidity or basicity, differed in different structures:

– KU-2-8 is a strongly acidic cation exchanger with a gel structure, contains fixed functional sulfo groups – SO_3H^- on aromatic rings, the cation exchanger matrix is obtained by sulfonation of styrene copolymer grains and 8% divinylbenzene. The cation exchanger was prepared for work in accordance with the requirements of the State Standard (GOST 10896-78) and translated into H^+ form;

– KU-2-8 – strongly acidic cation exchanger of gel structure, repeatedly (5-10 times) subjected to the process of sorption – regeneration;

– KU-23 – strongly acidic cation exchanger of macroporous structure, copolymer of styrene and divinylbenzene, active – sulfo group;

– AV-17-8 – strongly basic anionite of gel structure, obtained by copolymerization of styrene and divinylbenzene, followed by amination of the polymer. The active group is quaternary trimethylammonium groups.

The anionite was prepared in accordance with the requirements of the State Standard and converted to OH^- form (GOST R 55684-2013; ISO 8467:1993);

– AV-17-8 – strongly basic anionite of gel structure, repeatedly (5–10 times) subjected to the process of sorption – regeneration;

– AV-17-10P – strongly basic anion exchanger of macroporous structure, copolymer of styrene and divinylbenzene, repeatedly (5–10 times) subjected to the process of sorption – regeneration.

– The preparation of ion exchangers was carried out in accordance with the requirements of the state standard.

The studies were carried out on a laboratory setup (Fig.1) according to the following method:

– A glass column (3) was loaded with 20 ml of the KU-2-8 cation exchanger, from which the ion exchanger fraction with a grain size of 0.25 mm was preliminarily separated and 1 liter was passed from the vessel (1) distilled water, at a rate of 2 L/h. Then, sodium sulfate solution was passed from vessel (2) at the same rate until pH = 5 in the filtrate was reached. For analysis, 200 ml of filtrate was take;

– Glass columns (3,4) were loaded, respectively, with 20 ml of the KU-2-8 cation exchanger and 30 ml of the AB-17-8 anion exchanger, from which the ion exchanger fraction with a grain size of 0.25 mm was preliminarily separated. The columns were connected in series. The container (1) was connected to the column (3) and distilled water was passed into the columns (3) and (4) at a rate of 2 l/h, in an amount of 1000 ml. Then the container (1) was closed, and the container (2) with sodium sulfate solution was connected to the column (3). Sodium sulfate solution was passed into columns (3) and (4) at the same rate until pH = 5 was reached in the filtrate. For analysis, 200 ml of filtrate was taken.

– Glass columns (3,4) were loaded, respectively, with 20 ml of the KU-2-8 cation exchanger and 30 ml of the AB-17-8 anion exchanger, from which the ion exchanger fraction with a grain size of 0.25 mm was preliminarily separated. Column (5) was a mixed-bed filter, which was loaded with 10 ml of KU-2-8 cation exchanger and 15 ml of AB-17-8 anion exchanger. Distilled water was initially passed through all three columns at a rate of 2 L/h and in an amount of 1000 ml, and then at the same rate a sodium sulfate solution was passed until the filtrate reached pH = 5. For analysis, 200 ml of filtrate was taken.

In the process of deep desalination, the content of the filtrate was monitored by changes in pH, oxidizability, and electrical conductivity of the solutions, and the data obtained were compared with the initial parameters of distilled water and sodium sulfate solution (0.01N and 0.05N Na_2SO_4). The pH of solutions was measured on a universal ionomer, electrical conductivity – with a conductometer, oxidizability – by the permanganate method (Mitryasova and Pohrebennyk, 2020).

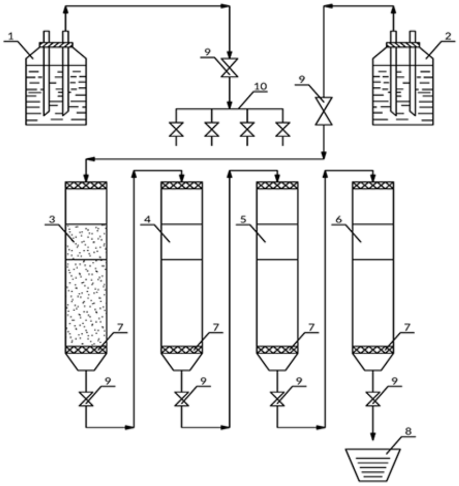

Fig. 1. Laboratory setup: 1, 2 – containers with distilled water and solutions of 0.05N or 0.01N Na_2SO_4, respectively; 3 – glass column for the cation exchanger; 4 – glass column for anionite; 5 – glass column for FSD; 6 – glass column for regeneration; 7 – porous glass filter; 8 – measuring container; 9 – overlapping valve; 10 – solution distributor

3. Results and discussion

The results obtained in the study of the possibility of sorption of organic substances by ion exchangers processed by different methods, with the simultaneous production of deeply demineralized water, are presented in table 1 and on Fig. 2, 3.

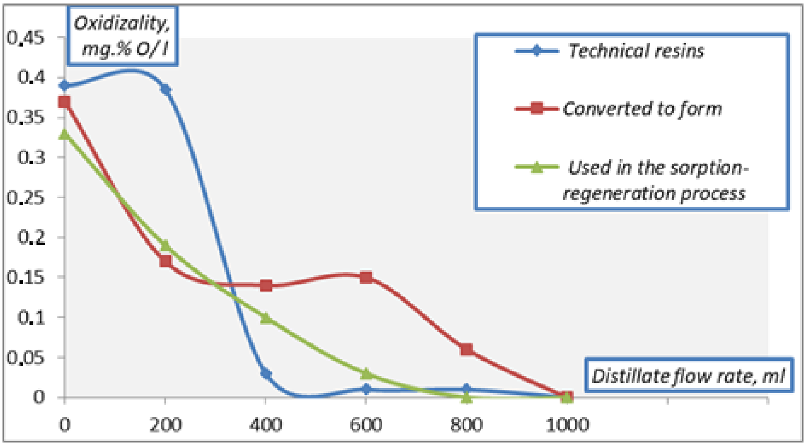

Fig.2. Sorption of organic substances from distilled water by ion exchange resin systems (KU-2-8 + AV-17-8)

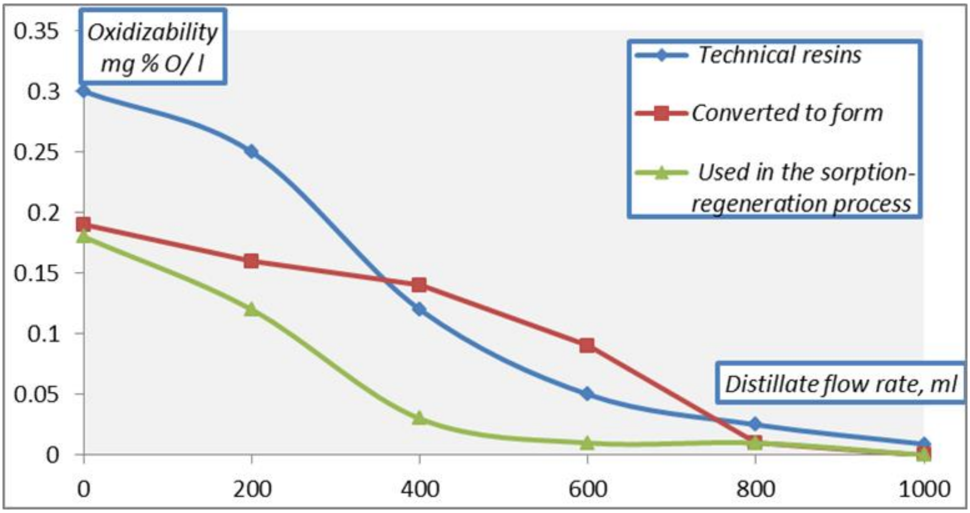

Fig.3. Sorption of organic substances from distilled water by ion exchange resin system (KU-2-8 + AV-17-8 + FSD (KU-2-8 + AV-17-8)

Analysis of the filtrates showed that after passing distilled water in an amount of 1 liter, in all systems consisting of filters containing ion exchangers of a gel structure (KU-2-8 and AV-17-8), the amount of organic matter in the filtrate is zero, that is, organic substances are removed completely, pH = 6.0 is reached, and the electrical conductivity of the filtrate is – $1 \cdot 10^{-5}$ S/m. This indicates that in all cases when using the KU-2-8 cation exchanger and the AV-17-8 anion exchanger, regardless of their form, we get deeply demineralized water.

When passing 0.05 N Na_2SO_4, in systems consisting of the same ion exchange filters (KU-2-8 and AV-17-8), it was found that the electrical conductivity of the filtrate in all studied systems decreases 10 times compared to the value of the initial electrical conductivity solution and is equal to $7 \cdot 10^{-2}$ S/m., and to achieve pH = 5.0 in the filtrate, a different amount of solution is required (200–3000 ml.).

When testing systems consisting of filters with technical ion-exchange resins KU-2-8 and AV-17-8, it was found that in both systems pH = 5.0 and filtrate purification from organic substances are not achieved. For other systems, complete removal of organic substances from the filtrate was achieved with a different amount (within 200–1200 ml) of 0.05N Na_2SO_4 solution (Fig.4, 5).

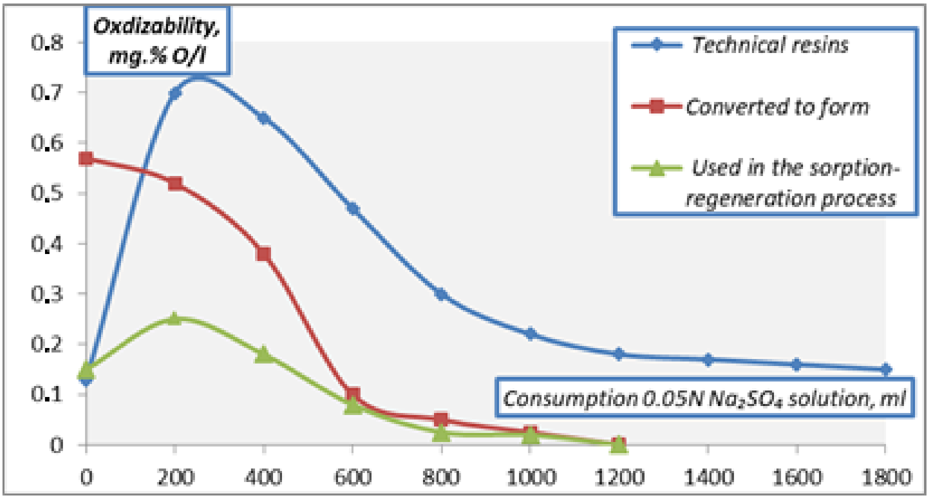

Fig.4. Sorption of organic substances from Na_2SO_4 solutions by systems of foreign exchange resins (KU-2-8 + AV-17-8)

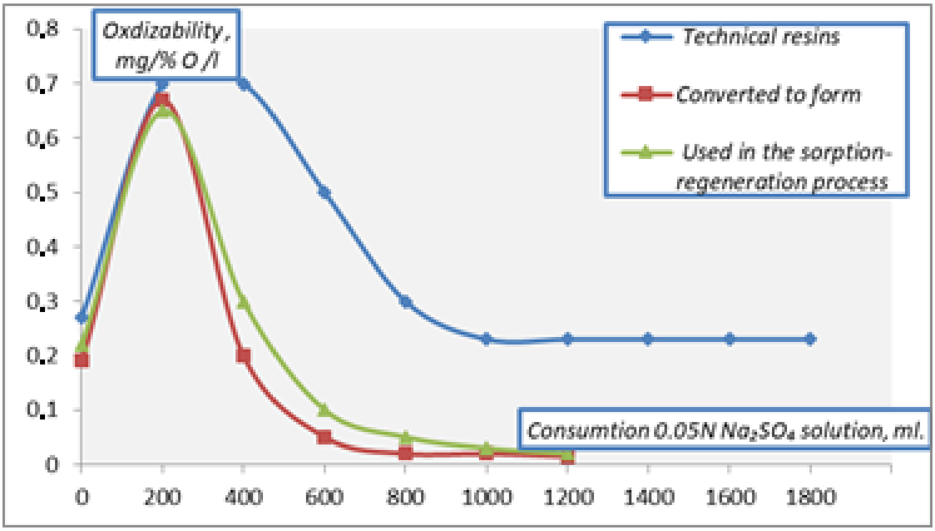

Fig.5. Sorption of organic substances from Na2SO4 solutions by systems of foreign exchange resins (KU-2-8 + AB-17-8 + FSD (KU-2-8 + AB-17-8)

It has been established: when using systems consisting of porous ion exchangers – strongly acidic cation exchanger KU-23 and strongly basic anion exchanger AV-17-10P, organic substances are not sorbed both from distilled water and from 0.05 N Na_2SO_4 solution.When this system is supplemented with a mixed-action filter, they are completely removed from distilled water, and to remove them from the sodium sulfate solution, it is required to pass 3 liters through the system solution, which is unprofitable for deep water demineralization systems, that is, the use of porous ion exchangers for this purpose is not advisable.

Table 1. Sorption of organic substances by ion-exchange and mixed filters during deep desalination of water from distilled water

System	**Initial oxidizability mgO/l**	**Oxidation after passing 1l water, mgO/l**	**pH, after passing 1l water**	**Electrical conductivity æ, S/m·10^{-5}**
KU-2-8 + AV-17-8 technical resins	0.38	0	6.5–7.5	1
KU-2-8 + AV-17-8 converted to form	0.37	0	6.0–6.9	1
KU-2-8 + AB-17-8 used in the sorption-regeneration process	0.33	0	6.0–6.5	1
KU-2-8 + AV-17-8 + FSD (KU-2-8 + AV-17-8) technical resins	0.30	0.09	6.0	1
KU-2-8 + AV-17-8 + FSD (KU-2-8 + AV-17-8) converted to form	0.19	0	5.9	1
KU-2-8 + AV-17-8+ FSD (KU-2-8 + AV-17-8) used in the sorption-regeneration process	0.18	0	6.0	1
KU-2-8 + AV-17-8v(used in the sorption-regeneration process) + FSD (KU-2-8 + AV-17-8) technical resins	0.24	0	6.0	1
KU-23 + AV-17-10П	0.16	Sorption is not going	6.2	1

It should be noted that in all studied systems, when passing both distilled water and sodium sulfate solution with a low initial concentration of organic substances, their sorption on ion exchangers was not observed.According to this technique, studies were carried out to remove organic substances from dilute solutions – 0.01N Na_2SO_4 with simultaneous production of deeply desalinated water. The studies were carried out on two systems, which consisted of ion-exchange filters and FSD – mixed-bed filters: one system consisted of ion exchangers repeatedly subjected to the sorption-regeneration process KU-2-8, AV-17-8 and their mixtures, and the second contained in H^+ and OH^- form the same ion exchangers – cation exchanger, anion exchanger and their mixture. It was found that in both systems, from dilute solutions, the sorption of organic substances by resins at the beginning of the process occurs completely, the oxidizability of the first portion of the filtrate (800 ml) was zero, and in subsequent portions it changed. This indicates that solutions of low concentration, after passing a certain amount of them into the resin, themselves wash out organic substances from it.

Table 2. Sorption of organic substances by ion-exchange and mixed filters during deep desalination of water from 0.05N Na_2SO_4 solutions (initial pH = 1.9, æ = 1.5·10–1S/m)

System	**Initial oxidizability, mgO/L**	**The volume of solution missed before the sorption of organic substances, ml**	**The volume of solution, ml, Skipped to achieve pH = 5**	**Electrical conductivity æ, S/m ·10^{-2}**
KU-2-8 + AV-17-8 technical resins	0.13	Sorption is not going	2800	70
KU-2-8 + AV-17-8 converted to form	0.57	1000	1200	69
KU-2-8 + AB-17-8 used in the sorption-regeneration process	0.15	1200	2000	70
KU-2-8 + AV-17-8 + FSD (KU-2-8 + AV-17-8) technical resins	0.27	Sorption is not going	Not achieved	70
KU-2-8 + AV-17-8 + FSD (KU-2-8 + AV-17-8) converted to form	0.19	100	1000	69
KU-2-8 + AV-17-8+ FSD (KU-2-8 + AV-17-8) used in the sorption-regeneration process	0.22	200	200	69
KU-2-8 + AV-17-8v (used in the sorption-regeneration process) + FSD (KU-2-8 + AV-17-8) technical resins	0.17	1200	2000	69
KU-23 + AV-17-10П	0.22	Sorption is not going	2400	70
KU-23 + AV-17-10П + FSD (KU-2-8 + AV-17-10П)	0.48	3000	4400	70

4. Conclusions

In order to remove organic substances, with the simultaneous production of deeply demineralized water, various systems have been studied, consisting of ion-exchange and mixed-action filters, containing strongly acidic and strongly basic ion exchangers of gel and macroporous structure treated by different methods. It was found that organic substances, both from water and from solutions, are almost completely removed by a system containing ion exchangers subjected to a repeated process of sorption - regeneration, namely by a system containing filters made of KU-2-8 cation exchanger, AV-17-8 anion exchanger and a mixed-bed filter (KU-2-8 + AV-17-8). It was found that in all other systems, at low concentrations of organic substances in the initial solution, the sorption of organic substances by resins occurs only at the beginning of the process when a certain amount of solution passes, and then the reverse process takes place – the washing out of organic substances from the resin. It was found that the studied macroporous ion exchangers are not suitable for achieving the above goal.

References

1. Slavinskaya, G.V., Kuznetsova, N.S., Kurenkova, O.V.: Sorption post-treatment of river water from organic matter after reagent coagulation. Scientific bulletin of the Voronezh State University of Architecture and Civil Engineering. *Building and Architecture*, 4(32), 116–124, 2013.

2. Petrov, O., Iwaszczuk, N., Kharebava, T., Bejanidze, I., Pohrebennyk, V., Nakashidze, N., Petrov, A.: Neutralization of Industrial Water by Electrodialysis. *Membranes*, 11(2), 101. 2021. DOI:10.3390/membranes11020101.

3. Bejanidze, I., Petrov, O., Pohrebennyk, V., Kharebava, T., Nakashidze, N., Didmanidze, N., Davitadze, N., Petrov, A.: Sorption of organic electrolytes and surfactants from natural waters by heterogeneous membranes. *Applied Sciences (Switzerland),* 10(20), 7383, 2020.

4. Bejanidze, I., Petrov, O., Kharebava, T., Pohrebennyk, V., Davitadze, N., Didmanidze, N.: Study of the healing properties of natural sources of Georgia and modeling of their purification processes. *Applied Sciences (Switzerland)*, 10(18), 6529, 2020.

5. Bejanidze, T., Kharebava, V., Pohrebennyk, N., Didmanidze, N.: The study of composition and physical and chemical properties of some natural waters of Georgia. In: Sobczuk, H., Kowalska, B. (eds.): *Water Supply and Wastewater Disposal. Designing, Construction, Operation and Monitoring*, 8–23, Politechnika Lubelska, Lublin, 2020.

6. Mitryasova, O., Pohrebennyk, V.: Hydrochemical indicators of water system analysis as factors of the environmental quality state. Studies in Systems, Decision and Control. *Sustainable Production: Novel Trends in Energy, Environment and Material Systems*, 198, 91–104, 2020.

7. Bejanidze, I., Pohrebennyk, V., Kharebava, T., Koncelidze, L., Jun, S.: Correction of the chemical composition of the washing waters received as a result of H Cation exchange of ion- exchange Resin. *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM*, 19(5.1), 133–140, 2019.

8. Bejanidze, I., Kharebava, T., Davitadze, N., Koncelidze, Z, Koncelidze, L.: In: *Purification of natural and wastewater by electromembrane methods*, 178, Batumi (in Georgian), 2019.

9. Matilainen, A., Vepsäläinen, M., Sillanpää, M.: Natural organic matter removal by coagulation during water treatment. A review. *Advances in Colloid and Interface Science,* 159, 189–197, 2010.

10. Sillanpää, M., Ncibi, M.Ch., Matilainen, A., Vepsäläinen, M.: Removal of natural organic matter in drinking water treatment by coagulation: A comprehensive review. *Chemosphere,* 190, 54–71, 2018.

11. Poborov, A., Kornlova, N., Platonov, N.: Method of deep desalination of water, 12–09, WO2010140916A1, 2010.

12. GOST 20298-74 Ion exchange resins. Cation exchangers. Technical conditions.

13. GOST 20301-74 Ion-exchange resins. Anionites. Technical conditions.

14. GOST 10896-78 Preparation of ion exchanger for analysis.

15. GOST R 55684-2013 (ISO 8467: 1993). Drinking water. Method for determination of permanganate oxidizability.

Environmental management and marketing tools for minimization of high carbon motor fuels pressure on water bodies caused by mining enterprises transport activity

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Abstract

The existence of the potential environmental danger of the mining enterprises transport activity on the air environment, for aquatic and terrestrial ecosystems, human health, etc. was proved on the basis of the analysis of the harmful effects caused by vehicles functioning on the high-carbon motor fuel. The study shows that monitoring of air pollution, surface and groundwaters contamination on the areas located near potentially ecologically dangerous highways, especially the ones under the influence of mining enterprises, is an important task for environmental safety ensuring. The regularities of changes in the concentration of particulate matter and gaseous vehicle emissions in the surface atmospheric air layer were clarified and generalized for the purposes of ecological management and marketing, as well as for the development of scientifically substantiated decisions and recommendations. The influence of emission components on water bodies located nearby the investigated highways was described. With the help of a mathematical modeling approach based on the method proposed by Berland and supplemented by Kholodnov with colleagues the features of dispersion of the main toxicants – components of exhaust gases and dust emissions from the cargo, transported without coverage, were determined in the MathCAD programming environment. Spatial mathematical models (dispersion fields) representing the air pollution by aerosol and gas emissions caused by mining enterprises transport activity (on the example of a granite quarry located near the river Ros basin) were developed; a computational experiment was conducted and on its basis the most potentially dangerous directions and speeds of the average wind were determined. The experiment showed that the pressure of the mining enterprise transport activity on the surface and groundwaters, atmospheric air, soil cover, etc. is very significant; it considerably changes the ecological conditions of aquatic and terrestrial ecosystems, increases the risk to the health of people working at the enterprise. Created models and software tools can be used for the development of recommendations and management decisions in the field of environmental safety, replacement of high-carbon motor fuel with more environmentally friendly types, in particular, mixtures and fuels of biological origin.

Keywords: surface and groundwaters contamination, environmental management and marketing tools, high-carbon motor fuels, ecological and health risk, particulate matter, exhaust gases, air pollutant dispersion, mining enterprises transport activity

1. Introduction

Exhaust emissions from road transport increase every year because of the constantly amplified traffic activity and the use of heavy diesel vehicles. Recently it was scientifically substantiated that engines operating on diesel fuel emit significantly higher levels of particulate matter PM and nitrogen oxides NO_x than any other engine type. According to the experts (Petrea, 2007), each liter of traditional fuel produces during combustion approximately 100 g of CO, 30 g of NO_x, 20 g of volatile organic compounds (VOC) or hydrocarbons C_xH_y (methane or non-methane), 2.5 kg of CO_2 (that is not considered as a pollutant but significantly contributes to the greenhouse effect (GHE)) and other emissions such as sulphur (SO_2, H_2S) and heavy metals (HM) compounds (lead Pb, cadmium Cd, copper Cu, zinc Zn, nickel Ni, chromium Cr, selenium Se), fine particles (or particulate matter), ammonia NH_3, etc.

These compounds and substances contaminate the environment and thus cause many local problems in terms of air, water and soil pollution, as well as some global problems such as GHE, risks to public health, etc. Some of the pollutants even have a mutagenic effect on human health (HH), for example, benzene C_6H_6, 1,3-butadiene C_4H_6 and polycyclic aromatic C_xH_y.

According to the experts, surface freshwater bodies occupy about 4.0% of Ukrainian territory, which is about 24.1 thous. km^2. These are, in particular, rivers (large and small), lakes (natural and artificial), special reservoirs, ponds, canals, etc. Ukrainian rivers are mainly located in the Black and Azov Seas basins, as well as in the Baltic Sea basin (~ 4.4%).

The largest number of rivers belongs to the Dnieper (27.7%), Danube (26.3%), Dniester (23.7%) and Southern Bug (9.3%) basins (www.menr.gov.ua). Thus, in Ukraine in natural conditions water resources are formed by the basin principle; therefore, rivers are dynamic systems that obey zonal laws. Water resources management, according to art. 13 of the Water Code of Ukraine, is also carried out on a basin principle basis.

Surface water quality is negatively affected not only by discharges from industrial and agricultural enterprises, utilities, etc. but also by mine and quarry water discharges, which often get into the water bodies without proper deep treatment. Of the total amount of wastewater discharged into Ukrainian water bodies, polluted water is ~ 13%, normatively treated – ~ 25%, normatively pure without treatment – ~ 58% and mine or quarry water, which is not categorized – up to ~ 4% (Tomiltseva et al., 2017).

According to rough estimates of the researcher A. I. Tomiltseva (Tomiltseva et al., 2017), together with wastewater 275.2 tons of oil products, 22.7 thous. tons of suspended solids, 5.6 thous. tons of ammonium nitrogen, 45.4 thous. tons of nitrates, 1.55 thous. tons of nitrites, 238.2 tons of synthetic surfactants, 4541.0 tons of phosphates, 431.1 tons of iron and many other pollutants penetrate into the water basin.

Pollution of interstratal groundwater, as a rule, is local in nature and significantly depends on technogenic pressure on the geological environment, as well as on the protection level of groundwater itself. In particular, groundwater in the areas affected by mining activities is usually contaminated with chlorides Cl^-, sulfates SO_4^{2-}, nitrates NO_3^-, ammonia NH_3, rhodanides NCS^-, phenols, petroleum products, compounds of manganese Mn, lead Pb, strontium Sr and other HM; moreover, the concentrations of these substances may exceed the maximum permissible concentrations (MPC) by several times.

Roads, which are actively used by mining enterprises for cargo transporting, put an additional and very significant pressure on all environment components – atmospheric air, soil and water bodies. Recently, due to the significant increase in the intensity of traffic (including private vehicles) and large-scale transport activity of enterprises (usually by heavy diesel transport), this problem was exacerbated, and therefore requires additional attention and urgent solution.

According to scientists, today a high danger to the environment is caused by the contamination of soils, groundwater and surface waters with HM compounds, petroleum products and solid fine particles PM, firstly, due to the airborne emissions of motor vehicle exhausts; secondly, due to the washing away of sewage from the road surface; and thirdly, due to the ingress of toxicants from roadside soils into groundwater and surface water, transfer with wind currents, their transformation due to secondary pollution processes.

In particular, the rate of penetrating into the environment of petroleum products from only one vehicle (even light one) varies from milligram fractions to several milligrams per second. And the most significant danger, according to (Polkowska et al., 2007), is caused by road washes, which usually contain aromatic (polyaromatic) petroleum products C_xH_y, aerosol particles, HM compounds, dust contamination with rock material, brake pad, tires and road pavement wear products. These compounds directly or due to the secondary transfer of toxicants get into human, animal and plant organisms, in particular, into the organisms of aquatic creatures, disrupting their normal functioning.

Thus, the aim of the work is to identify sources of environmental pressure and risks to HH from the high-carbon motor fuels use by mining enterprises transport activity; investigate the dispersion features of aerosol pollutants and gaseous components of exhaust gases in the environment by the method of mathematical modeling; assess the level of ecological danger for aquatic ecosystems from motor transport activity of mining enterprises located near water bodies; analysis of the harmful effects on the health of people living in the areas of influence of mining enterprises, highly loaded roads, etc.

1.1. Particulates as a Health Risk and Risk for Surface and Groundwaters Contamination Factor

Atmospheric aerosol deposition today is one of the most important environmental issues because it can not only change the ecological state of the particular territory or region but also affect the Earth surface albedo in general. Aerosols affect both environment state and HH. In particular, inhalation of small aerosol particles can cause such illnesses as lungs cancer, asthma, respiratory and cardiovascular diseases, as well as various birth defects and even premature death.

Thus, PM air pollution is a serious problem, especially in big cities and industrially developed regions. And it should be noted, that in such regions PM pollution levels will not stay constant, they will increase over time. Particulates suspended in the atmosphere have different origins and compositions and they are often formed and interact with each other during a long period of time in random ways.

The upper limit for PM corresponds to dimensions of about 100 μm, while the smallest particles are about 0.002 μm. But taking into account the fact that smaller particles have a greater effect on HH than the larger ones, usually only PM having a specific diameter or less are reported. For the purposes of air quality monitoring the PM index is used as the most common measure of suspended particles concentration. The PM index is determined as the amount of PM that is present in the given volume. The most usual units to measure PM concentration are $\mu g\ m^{-3}$ – micrograms of particulate matter per cubic meter of the air (Baird and Cann, 2012).

Government agencies in our country and many other countries monitor PM_{10}, which corresponds to the total concentration of all suspended particles with a diameter less than 10 μm. They are inhalable particles because they can be breathed by humans and animals into the lungs. According to the World Health Organization (WHO) data, the typical concentration for PM_{10} in the urban area is (20...30) $\mu g \cdot m^{-3}$.

In developed countries, the $PM_{2.5}$ index is also used. It includes all and only fine particles, which are also called respirable particles. The respirable range includes only PM particles that can deeply penetrate the lungs, where there are no specific biological mechanisms to catch these particles and then move them out. In the urban areas, $PM_{2.5}$ values are usually in the (10...20) $\mu g \cdot m^{-3}$ range, although background concentrations are only (1...5) $\mu g \cdot m^{-3}$ (Baird and Cann, 2012).

Several researchers started to use the term $PM_{10-2.5}$, which, although are called "coarse", in fact corresponds only to the smallest particles covered by the traditional coarse particles definition. Also a new term ‘ultrafine’ is currently applied to the particles with extremely small diameters, which are usually less than 0.1 μm. At the same time, ‘nanoparticles’ are even smaller – they are usually less than 0.02 μm. Most ultrafine particles are of a technogenic origin. In the past, instead of the PM index, the total suspended particulates (TSP) values (the concentration of all particulates suspended in the air) were often reported.

One of the most important reasons explaining why inhaled particles cause such significant damage to HH is their ability to carry into the lungs various organic molecules and metal ions on their surface. Substances that can dissolve into the body of the particle are said to be absorbed by it, while substances that simply stick loosely to the particle surface are considered as adsorbed. For example, large organic molecules can be adsorbed onto the surface of carbon particles (‘soot’). Also a lot of insoluble airborne particles are covered by the water film that can dissolve other substances.

Today $PM_{2.5}$ particles are recognized to be even more relevant than PM_{10}. So large particles are of a less concern to HH than the small (or ‘fine’) ones for the following reasons (Baird and Cann, 2012):

– coarse particles settle down more quickly, so their inhalation by humans is reduced and people are less sensitive to them;

– when coarse particles are inhaled they can be quite efficiently filtered by the nose and throat physiological systems and most of them will not move to the lungs. But when fine particles are inhaled they usually travel deep into the lungs (so this is why they are called respirable particles), where they can be adsorbed on cell surfaces and therefore can affect HH;

– the ratio of a surface area to mass for bigger particles is smaller than that for smaller ones, so their ability to transport adsorbed gas molecules to various parts of the human respiratory system is relatively smaller;

– such devices as spray towers, electrostatic precipitators and even cyclone collectors are efficient only for removement of coarse particulates from the air. More efficient for fine particles removement are baghouse filters, which are represented by finely woven fiberglass fabric bags through which air is forced to flow.

In Ukraine, the following standards have been adopted at the legislative level for PM: average daily maximum permissible concentration $MPC_{a.\,d.} = 0.15\ mg \cdot m^{-3}$, while maximum permissible single concentration $MPC_{m.\,s.} = 5\ mg \cdot m^{-3}$. However, it should be noted that PM emission, as a rule, causes damage at short distances from the pollution source, although due to the secondary pollution processes, the area of harmful effects of aerosols can be significantly expanded.

1.2. Conditions for dispersion of aerosols and gaseous emissions in the air environment

One of the main tasks of engineering and environmental monitoring is the development of precise, scientifically substantiated forecasts for the changes of environmental situations in the areas adjacent to loaded roads, assessment of the level of their environmental safety. And particularly, the methods of mathematical modeling are among the ones that allow not only to predict potential changes due to mining enterprises motor transport activity but also to determine the most dangerous meteorological conditions and assess the safety of road exploitation by the studied enterprises.

Studies show that vehicle emissions mainly contaminate soils and water bodies near roads, although it is known that even at a distance of (60...100) m from the road, this impact is still significant. In particular, the concentration of petroleum products in soils near the highway may be about 4–5 times higher than the same concentration in soils located at a distance of more than 100 m from the road (Yurchenko et al., 2011).

Vehicle emissions, including aerosol particles, are dispersed and transformed in the air according to certain laws. For example, PM larger than 0.1 mm tends to settle and contaminate roadside soil due to gravitational forces. Solid dispersed particles smaller than 0.1 mm, as well as gaseous emissions (CO, NO_x, SO_2, H_2S, C_xH_y and others) propagate in the air mainly under the action of diffusion processes. In this case, they can be transported by wind currents (mechanical transfer) over long distances and transformed due to physico-chemical and/or biochemical interactions both with each other and with environmental components, other toxicants, etc.

The movement of a large number of small particles (vortices) is accompanied by turbulent diffusion (TD), which leads to turbulent mixing of various components of atmospheric air – gases, water vapor and droplets, impurities in various aggregation states. The motion of dust particles, soot and other impurities is studied, taking into account such factors as gravity, particle air resistance force, horizontal wind drift, vertical wind inhomogeneity and the presence of horizontal and vertical fluctuations of the atmospheric velocity field.

In addition, the level of pollution of the air, roadside soils and water basin by vehicle emissions, including contamination caused by the functioning of enterprises heavy vehicles, depends significantly on the concentration, chemical (and fractional) composition of emissions; dispersion of aerosols; physico-chemical properties, structure and aggregation state, activity, etc.

of pollutants, as well as from meteorological and climatic conditions, the height of the emission source above the earth surface, the ability to transport particles or gases over long distances, etc.

As a rule, atmospheric impurities are polydisperse, therefore, for mathematical modeling of their dynamics, it is necessary to take into account such processes as:

– transfer of impurity and TD of its particles;

– change in the dispersed composition and aerosol concentration due to kinetic processes, in particular, the processes of condensation, coagulation, sedimentation, etc.

Since all these processes take place in a turbulent atmosphere, and the earth surface is orographically and thermally inhomogeneous, the study of the dynamics of aerosol particles (and gaseous emissions) dispersion is carried out, as a rule, using hydrothermodynamic models. During modeling it is necessary to take into account that secondary processes also occur in the atmosphere – chemical reactions, physico-chemical and phase transformations, as a result of which the formation (and dispersion) of various intermediate substances occurs.

According to research (Kabaeva, 2007), the time of sedimentation of particles of a finely dispersed fraction is mainly determined by the vertical inhomogeneity of the wind speed and turbulence parameters. However, the author found that the wind speed insignificantly (no more than by 10%) affects the settling time of particles, while the presence of a turbulent component of the atmospheric velocity for a particular small-diameter particle can significantly affect the settling time. At the same time, for heavier particles dispersed in the air, the gravity force prevails over Stoke's force, and therefore such particles settle faster.

The equation of motion of a fine dust particle in vector form can be represented in the following way (Eq. (1)):

$$m\frac{d\vec{u}}{dt} = m\vec{g} + 6\pi\rho_a \nu R(\vec{W} - \vec{u}), \tag{1}$$

where: m – particle mass, $\vec{u}(\vec{r},t)$ – vector of particle speed, ρ_a – atmospheric density, ν – kinematic viscosity, R – effective radius of the aerosol particle, $\vec{W}(\vec{r},t)$ – vector of atmosphere speed.

Thus, as can be seen, the process of sedimentation of solid aerosol particles under the action of gravity in a turbulent air flow can be considered as consisting of two main processes – continuous sedimentation of certain particles and disorderly in direction, frequency and amplitude movement of particles with descents and rises. In this case, as was noted, the sedimentation rate of solid fine particles strongly depends on their size, chemical composition and, accordingly, on the physico-chemical properties.

For the vertical motion of a Stoke's particle in a horizontal flow, taking into account the gravity force, the mathematical equation can be written in the form of Eq. (2):

$$\frac{dv_p}{dt} + \beta v_p = \beta V' \sin \omega t - g, v_p(0) = 0, \tag{2}$$

where: v_p – particle sedimentation rate, t – the moment of time under consideration; β – particle inertia factor, i.e. the so-called ‘time constant’; ω – Lagrangian pulsation frequency; V – the amplitude of the transverse component of the turbulent flow pulsation speed.

In practice, during the formation of mathematical equations for the models of dispersion of harmful impurities in the atmosphere, approximate ideas about the structure of air flows are usually used. This, firstly, makes it easier to formulate the boundary conditions of the model, and, secondly, it allows to build an algorithm for conducting an experiment to determine the parameters of the equations of motion of air flows.

The temperature gradient characterizing the vertical change in the air temperature is determined by the degree of heating of the earth surface and the surface layer of the air; and the more the earth surface is heated, the more intense is the vertical movement of air flows (Gulyaev and Dranishnikov, 2005). If the heated air expands adiabatically (without exchanging heat with the surrounding air masses), then its temperature rises by approximately 1°C for every 100 m, and this flow has the same properties as the surrounding air masses, and, therefore, it will not have additional acceleration. This state of the atmosphere is called neutral.

If the temperature of the ambient air decreases with height so that its vertical gradient is bigger than the adiabatic one (such conditions can be observed when the earth surface is highly heated by the sun), then the air stream moving from below has some acceleration. The heated jets go up, while the cold ones go down. Such meteorological conditions of the atmosphere are called unstable convective.

In turn, if the vertical gradient of the air temperature is close to zero or becomes negative (that is, the temperature rises with height), then the vertically rising air flow turns out to be colder than the surrounding air masses, and its movement stops. These are the so-called stable inversion conditions of the atmosphere.

In order to quantify the state of the atmosphere stability, the ratio of the vertical temperature gradient and wind speed is used – either in the form of a dimensionless Richardson stability criterion or in the form of its empirical analogs. In our study the stratification criterion A was used.

The state of the atmosphere is also characterized by such indicators as:

– instability (very strong, moderate or weak);
– an indifferent state;
– stability (weak, moderate or strong).

As for the influence of the underlying surface properties, the turbulent regime of the air flows, and, consequently, the nature of the dispersion of toxicants, as well as the concentration field of the impurity near the earth surface, change under the influence of unevenness and properties of the relief. In the complex landforms, local air circulation occurs, ascending and descending currents are formed, and the direction of the wind changes.

In order to take into account the influence of the relief and the presence of the water bodies on the values of harmful impurities surface concentrations, the coefficient η is used, which is assumed to be 1 if, within a radius of 50 pipe heights from the source, the difference in terrain marks does not exceed 50 m per 1 km. In other cases, a relief correction is determined on the basis of cartographic material highlighting the relief within a radius of 50 pipe heights from the source, but not less than 2 km.

An approximate relief correction can be done based on the following considerations:

– for slopes up to (0.1...0.15)° and drops up to 100 m, the correction η is 1.3...1.5;

– when the emission source is located near a mountain range with terrain slopes up to (0.15...0.25)°, the correction is equal to 2;

– if the source is located in a hollow or gorge with a depth of (100...200) m with a slope of ~(0.20...0.30)° and more, the relief correction is taken equal to 3 (Gulyaev and Dranishnikov, 2005).

In the paper of Olenkov (2017) it is noted that due to the topographic features of the area (i.e. orography of the area) changes in the distribution of temperature and humidity in the surface layer of the atmospheric air are also possible. These factors have a very significant impact on the atmospheric diffusion of impurities, causing their mixing, transformation and local concentration in certain areas and layers.

Thus, the features of the dispersion of pollutants near loaded highways are determined by the height of the emission source above ground level; atmospheric stratification; average wind speed and direction; traffic conditions, structure and characteristics of traffic flows (TF); orography of the underlying surface; peculiarities and density of buildings (if they are present), etc. Highways are represented in this case as a set of point emission sources, taking into account the principle of superposition of the concentration fields of a particular impurity.

According to the Environmental Protection Agency (USA) and the European Environment Agency data, there are more than 140 air pollution models (Dorokhov et al., 2014). All models for predicting the air pollution levels by certain features are classified as shown in Fig. 1.

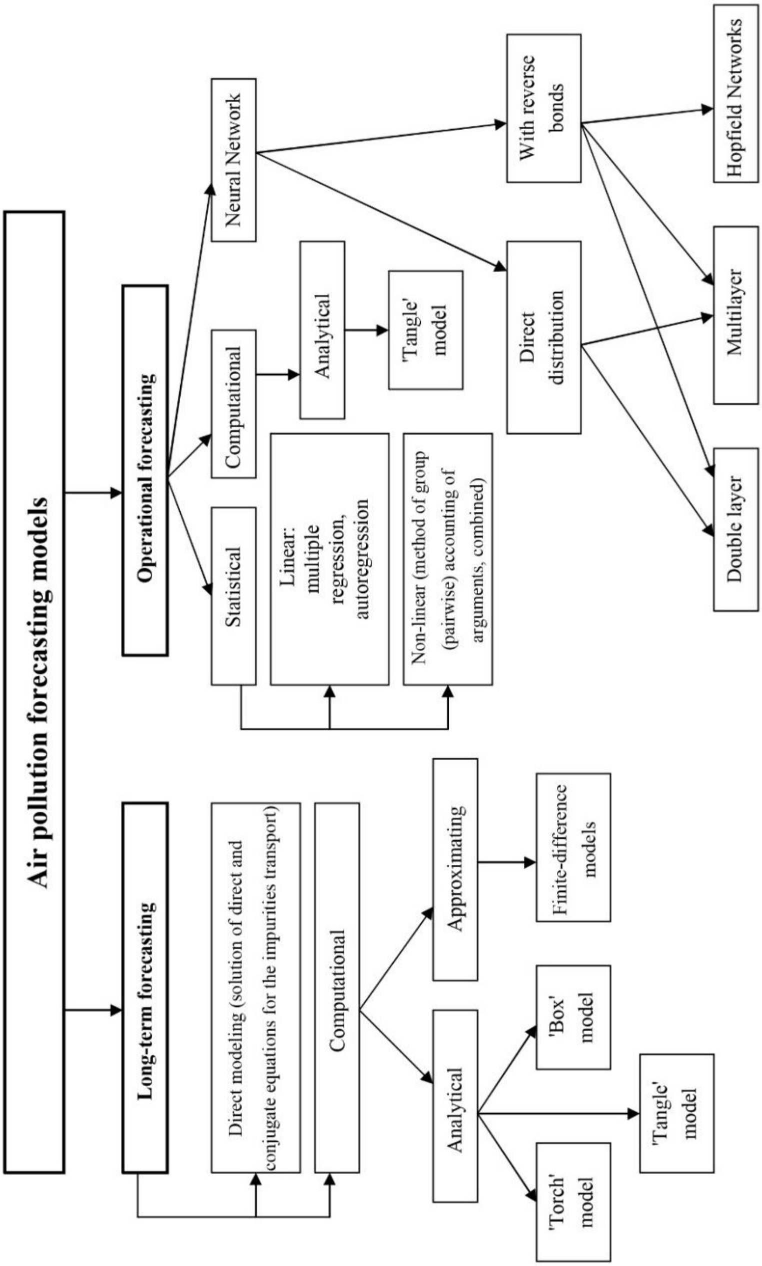


Fig. 1. Classification of the most widespread models of harmful impurities dispersion in the atmospheric air (Gulyaev and Dranishnikov, 2005)

With the simultaneous presence in the atmosphere of several harmful substances (as a rule, close either in chemical structure or in the nature of the biological effect on the human body), which have a total effect, for each such group of substances the total indicator q is calculated using Eq. (3), which should not exceed the value of 1, namely:

$$q = \sum_{i=1}^{n} \frac{C_i}{MPC_i} \leq 1, \tag{3}$$

where: $C_1, C_2, \ldots, C_n$ – concentrations of harmful impurities in the air at the same terrain point, mg·m^{-3}; MPC_1, MPC_2, ..., MPC_n – the corresponding maximum permissible single concentrations of these substances in the air environment, mg·m^{-3}.

In addition to the orography of the terrain and temperature stratification of the atmosphere, such factors as geographical location, meteorological and climatic conditions (including the microclimate of the particular areas) also significantly affect the air circulation pattern.

In particular, in the lower layer of the air environment, the wind speed is usually much lower than in the higher layers, and therefore the unfavorable conditions for the accumulation of harmful impurities in the surface layer of airspace are created.

In addition, in the warm season, due to the strong heating of asphalt and concrete over highways, powerful upward flows are formed, which hinder the horizontal movement of air masses. Various meteorological factors also affect the formation and development of air pollution in different ways, which requires further study, including with the help of mathematical modeling methods.

2. Materials and Methods

A variety of methods can be used to calculate and estimate emission levels from road transport which depend on such parameters, as pollutants nature, the transport mode and type of a vehicle, climatic, meteorological and road conditions, intensity and density of traffic, etc. In the study in order to assess the level of pollution of the atmospheric air surface layer and determine the technogenic impact on the water basin of the river Ros (on the example of the area located near the granite quarry in the village Teptiyivka, Boguslav district of Kyiv region, Ukraine) a calculation method based on the transport activity, as well as the method of modeling of aerosol and motor vehicles gaseous emissions dispersion fields, have been used.

To develop mathematical models of pollutants dispersion and concentration in the roadside territories ground layer for the local pollution assessment and prediction of the ecological situation of the studied territories and water bodies, a special M. E. Berland method (Berlyand, 1975) was used in the interpretation of scientist V. O. Kholodnov with colleagues (Kholodnov et al., 2007). The idea of the method of torch approximation is detailed in the scientific works (Kofanov et al., 2020; Pohrebennyk et al., 2020; Kofanov and Kholkovskyi, 2017).

A specialized computer program was created in the MathCAD environment in order to develop mathematical models of the dispersion of solid finely dispersed particles (aerosols) and other toxicants that differ in nature, fractional composition, physico-chemical properties and, consequently, diffusion capacity. This program allowed to visualize toxicants dispersion fields and estimate on the basis of the developed models the pollution level of the atmospheric air surface layer, and eventually to draw a conclusion about the multiplicity of the impurities MPC under the most unfavorable meteorological conditions, when the average wind speed reaches dangerous values and there is an intense vertical turbulent exchange.

3. Results and Discussion

3.1. Management tools for the assessment of environmental risk and risk to human health caused by environmental pollution

There are many differences in the defining terms "risk", "environmental risk", "health risk", etc. In our study the most common definition – ‘risk is a quantitative measure of danger which consequences are taken into account’ (Vaganov and Man-Sung, 2001) is used. So:

$$R = P \cdot Q, \tag{4}$$

where: R – is the value of the risk, which is equal to the multiplication of the probability of the considered event (process) P by the measure of the expected consequences (damage) Q. In this case, the full measure of the consequences of this event should include various types of damage – social, environmental, economic, moral, etc.

It should be noted that the probability P in Eq. (4) is a fairly conditional indicator since it refers to a specific event or a specific risk scenario.

According to Kolluru (1996), it is possible to allocate 5 types of risks, namely:
– risks which threaten safety;
– risks which threaten health;
– risks which threaten the environment (environmental risks);
– public welfare risks and finally;
– financial risks.

The study focuses on the management of HH and environmental risks caused by pollution from the mining enterprises motor transport activity and high-carbon motor fuel usage.

Kolluru (1996) determines environmental risks as a set of impacts, effects, interactions between populations, communities, ecosystems at both micro- and macrolevels. However, he notes that the degree of uncertainty of these effects, interactions and causal relationships remains quite significant (Kolluru, 1996).

HH risks, on the other hand, have a quite high probability; quite often they do not have serious consequences, and, most importantly, most of them do not appear immediately, i.e. they have prolonged effect. In practice, such risks are difficult to identify and evaluate. Quite often, environmental risks can also pose risks to the health of residents, workers and other population segments. Although, for example, the USA Environmental Protection Agency considers environmental risks separately from HH risks (Vaganov and Man-Sung, 2001).

In 1994, international organizations such as the United Nations Environment Program (UNEP), the United Nations Industrial Development Organization (UNIDO), the International Atomic Energy Agency (IAEA) and the World Health Organization (WHO) have developed guidelines and methodologies for evaluating and management of environmental and HH risks associated with the industrial complexes functioning and, in particular, energy companies (Tab. 1).

According to these recommendations, the result of a certain danger is damage that is applied both to people and the environment. That is, both types of risk (both environmental and public health risk) usually have to be considered and assessed in a complex, taking into account the simultaneous and, most importantly, the multidirectional action of many different factors.

A group of research centers in the Netherlands has developed special tools for calculating environmental risks "Ecoindicator 95" and "Ecoindicator 99", which are based on the study and assessment of the life cycle impact of certain products, production processes, etc. (Goedkoop, 1995; Goedkoop and Spriensma, 2000). The idea of the methods is to take into account the resources used by the enterprise, as well as pollutants that penetrate the environment throughout the life cycle of a product or production process. For example, energy production, cargo transportation, etc.

According to the method (Goedkoop, 1995; Goedkoop and Spriensma, 2000) 9 of the main processes that can harm HH and/or damage ecosystems should be considered during the assessment of the impact of the product life cycle. And each of these processes is matched by certain determined by management experts weighting coefficient (Tab. 2).

Further calculations according to the tools (Goedkoop, 1995; Goedkoop and Spriensma, 2000) are performed according to the algorithm presented in Fig. 2 (Vaganov and Man-Sung, 2001). According to this algorithm, the complex ecoindicators given in the scheme take into account 3 components of damage:

- HH;
- ecosystems;
- natural resources.

Table 1. Main signs of environmental risks associated with the threat to HH and the state of the habitat

Categories	**For HH**	**For environment**
The nature of the risk source action	– continuous; – one-time (emergency).	
Contingent (groups) at risk	– population of the particular area; – enterprise personnel.	
Action duration	– short-term; – medium-term; – long-term.	
Consequences	By degree of severity: – fatal (risk of death); – non-fatal (in particular, risk of injury, illness, etc.). By the time of appearance: – immediate; – distant.	By distribution: – local; – regional; – global. By duration: – short-term; – medium-term; – long-term.

Each of these components, in turn, is characterized by its own total indicator, the value of which is used as a rationing coefficient for further calculations. In addition, the so-called weighting coefficients are also used, which characterize the relative contribution of each of these components of the loss (Tab. 3).

The damage to health is expressed by DALYs – disability-adjusted life years, which means that both YLL – years of life lost and YLD – years lived disabled are summed up. Next, the resulting amount is divided by the number of residents, in our example – residents of Europe (Goedkoop, 1995; Goedkoop and Spriensma, 2000).

Damage to ecosystems, according to the tools (Goedkoop and Spriensma, 2000), is expressed with the help of two indicators – a fraction of the ecosystem species, which have been affected by the particular technogenic impact, as well as a fraction of the ecosystem species, which have disappeared as a result of this technogenic impact. Then these values are multiplied by the ecosystem area and the exposure time of the particular factor.

Table 2. Processes causing harm to HH and their habitat: weighting coefficients and detection criteria (for European countries, in accordance with (Goedkoop, 1995; Goedkoop and Spriensma, 2000)

Processes	**Weighting coefficients**	**Detection criteria**
Ozone layer depletion	100	Probability of one death per year per $1 \cdot 10^6$ inhabitants
Pesticides influence	25	5% ecosystem degradation
Carcinogenic substances influence	10	Probability of one death per year per $1 \cdot 10^6$ inhabitants
Increasing the acidity of water bodies	10	5% ecosystem degradation
Eutrophication	5	5% ecosystem degradation
HM influence	5	The concentration of cadmium Cd as one of the main ecotoxicants among HM, is taken into account
Winter smog influence	5	Recording of complaints during the period of smog, especially from asthmatics and the elderly people
Summer smog influence	2.5	
Greenhouse effect	2.5	Temperature rise by 0.1^0C every 10 years; 5% ecosystem degradation

Table 3. Coefficients of rationing and weighting used to calculate damage indicators (Goedkoop, 1995; Goedkoop and Spriensma, 2000)

Indicator type	**Coefficients**	
	Rationing	**Weighting**
Damage indicators for HH	0.0155	0.3
Indicators of damage to ecosystems	5130	0.5
Indicators of damage to natural mineral resources	5940	0.2

Tab. 4 shows the indicators for HH damage caused by the main impacts calculated per one inhabitant of Europe.

In the paper, the impact of such dangerous factors as natural waters acidification and eutrophication was considered. For this factor the damage indicator is 375 SSD$\cdot$m$^2\cdot$year (SSD is the share of species that have disappeared as a result of this technogenic impact); the indicator is related to one year of each technogenic impact duration.

Table 4. Indicators of damage for HH caused by the main types of impact, expressed in units of DALYs/year – the given number of lost years, referred to one year (Goedkoop and Spriensma, 2000)

Impact type	**Damage indicator per inhabitant*** **DALYs/year**
Respiratory system diseases (impact of inorganic substances)	0.0108
Climate change	0.00239
Carcinogenic effects	0.00200
Ozone layer depletion	0.000219
Respiratory system diseases (impact of organic substances)	0.0000684
Ionizing radiation	0.0000268
Total damage for HH	0.0155

Note * Damage indicator was calculated for one European resident

Damage to natural mineral resources is calculated separately for minerals (natural resources of inorganic origin) and fossil (high-carbon) fuels. Thus, according to the calculations for the full life cycle for the studied technological operations, namely – trucking (load capacity of 28 tons), the complex ecoindicator value is 0.34 per 1 ton·km (Goedkoop, 1995), which is almost in 1.5–2 times less than the complex ecoindicator of electricity production, respectively, high and low voltage per 1 kWh.

Ecoindicators (Goedkoop and Spriensma, 2000) also include indicators of HH damage caused by various dangerous pollutants. Three values were calculated:

– the damage factor (DF);
– the normalized damage factor (NDF);
– the weighted damage factor (WDF).

NDF is obtained by dividing the DF by the rationing coefficient (total damage to HH which is equal to 0.0155 DALYs/year), while WDF is equal to NDF multiplied by the weighting coefficient (0.3). The values of all 3 damage factors are expressed in DALYs units and refer to 1 kg of the substance that penetrated one of the 3 components of the environment (atmosphere, hydrosphere, pedosphere).

As an example, the indicators of damage to HH caused by exposure to certain harmful substances are shown in Tab. 5. And indicators of damage to HH caused by exposure to certain inorganic substances on the respiratory tract are shown in Tab. 6. Thus, among the studied compounds of mineral origin, the greatest hazard to HH is represented by the fine fraction of dust dispersed in the air. And among the oxides, the greatest harm to the respiratory tract of humans is caused by the nitrogen oxides NO and NO_2.

Table 5. Indicators of damage to HH caused by exposure to certain harmful substances (Goedkoop and Spriensma, 2000)

Substances	**Atmospheric air**			**Water body**			**Soil**		
	DF	**NDF**	**WDF**	**DF**	**NDF**	**WDF**	**DF**	**NDF**	**WDF**
Benzo(a)pyrene	0.004	0.257	0.077	2.99	193	57.9	0.002	0.133	0.04
Dioxins	179	11500	3460	2020	1.3·105	3.9·104	7.06	455	137
Arsenic	0.025	1.59	0.476	0.066	4.24	1.27	0.013	0.851	0.255
Cadmium	0.135	8.71	2.61	0.071	4.59	1.38	0.004	0.257	0.077
Chromium(VI)	1.75	113	33.9	0.343	22.1	6.64	0.271	17.5	52.5
Nickel	0.024	1.52	0.455	0.031	2.01	0.602	0.004	0.254	0.076

Table 6. Indicators of damage to HH caused by the impact of inorganic (mineral) substances on the human respiratory tract (Goedkoop and Spriensma, 2000)

Substances	**DF**	**NDF**	**WDF**
Dust, 2.5 μm fraction	$7.0\cdot10^{-4}$	0.045	0.0135
Dust, 10 μm fraction	$3.8\cdot10^{-4}$	0.024	0.0073
NO	$1.4\cdot10^{-4}$	0.0088	0.0026
NO_2	$8.9\cdot10^{-5}$	0.0058	0.0017
SO_2	$5.5\cdot10^{-5}$	0.0035	0.0011
SO_3	$4.4\cdot10^{-5}$	0.0028	0.00085
NH_3	$8.5\cdot10^{-5}$	0.0055	0.00165
CO	$7.3\cdot10^{-7}$	$4.7\cdot10^{-5}$	$1.4\cdot10^{-5}$

Therefore, Tab. 7 shows the indicators of damage to air, water and soil caused by exposure to various toxicants. At the same time, three types of factors of harmful impact on certain components of the environment were also calculated, namely: DF, NDF and WDF.

The values of the factors are given in the SSD units (in $m^2\cdot$year) and were calculated for 1 kg of the toxicant that has penetrated the particular environmental component.

Therefore, in terms of the indicator of environmental risk caused by the air pollution, the studied toxicants can be arranged in the following sequence (for HM it is about the toxicity of their compounds):

dioxins > Cd > Ni > Cr > Zn > Pb > Cu > Hg > As > benzo(a)pyrene.

When the water basin is contaminated with toxicants, a similar series due to the different solubility of chemical compounds in water has a slightly different appearance, namely:

dioxins > Cd > Hg > Cu > Ni > Cr > benzo(a)pyrene > Zn > As > Pb.

When soil is contaminated, a series of environmental risk changes slightly and looks like this:

dioxins > Cd > Ni > benzo(a)pyrene > Cr > Zn > Hg > Cu > As > Pb.

Thus, for the most ecotoxicants the WDF values are reduced in the sequence: soil > air > aquatic environment (except for lead, for which the order of decreasing of WDF value is different: air > soil > aquatic environment).

In addition, Tab. 7 shows that among HM the first place on the toxicity of compounds is occupied by Cadmium.

Table 7. Indicators of damage caused by exposure to certain toxicants to environmental components (Goedkoop and Spriensma, 2000)

Substances	**Atmospheric air**			**Water body**			**Soil**		
	DF	**NDF**	**WDF**	**DF**	**NDF**	**WDF**	**DF**	**NDF**	**WDF**
Benzo(a)pyrene	142	0.028	0.014	36.8	0.007	0.0036	7250	1.41	0.707
Dioxins	$1.3\cdot10^5$	25.7	12.9	$1.9\cdot10^5$	36.5	18.2	$2.9\cdot10^5$	40.7	20.4
Arsenic	592	0.115	0.058	11.4	0.0022	0.0011	610	0.119	0.059
Nickel	7100	1.38	0.692	143	0.028	0.014	7320	1.43	0.713
Chromium*	4130	0.805	0.403	68.7	0.013	0.0067	4240	0.827	0.413
Zinc	2890	0.563	0.282	16.3	0.0032	0.0016	2980	0.581	0.290
Copper	1460	0.285	0.142	147	0.285	0.0142	1500	0.285	0.146
Cadmium	9650	1.88	0.941	480	0.29	0.047	9940	1.94	0.969
Lead	2540	0.495	0.248	7.39	0.0014	$7.2\cdot10^{-4}$	12.9	0.0025	0.0013
Mercury	829	0.162	0.081	197	0.038	0.019	1680	0.32	0.164

Note: *Chromium indicator of environmental damage was calculated without taking into account its valence.

So the most widespread ways of pollution of water bodies and their ecosystems with solid fine particles PM and HM compounds will be considered. Dust accumulating in the roadside territories contains not only solid particles – products of tire wear, paving material, anti-corrosion coatings, fuels, lubricants and additive components but also dust particles that appear in the environment due to the transportation of cargo without coverage.

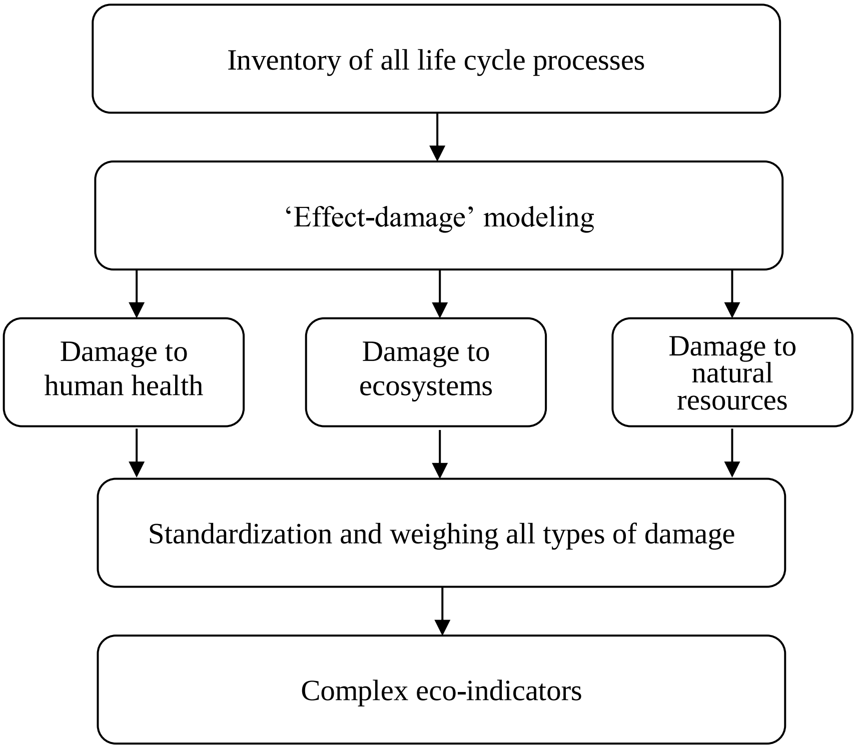


Fig. 2. Scheme for calculating complex ecoindicators according to the tools (Goedkoop, 1995; Goedkoop and Spriensma, 2000)

These solid particles, as was noted, can be transported by the air and transport flows over long distances, settle in the roadside areas: they can be also absorbed by surface waters, penetrate into organs and tissues of living organisms, accumulate in food chains.

Due to the active adsorption of harmful substances (including polyaromatic compounds, compounds of heavy and other metals – lead, nickel, cobalt, chromium, zinc, copper, iron, manganese and especially dangerous cadmium, which is quite mobile in soils and groundwater), these solid particles with a highly developed surface significantly increase the danger to humans and higher animals.

In this context, the main tasks of analyzing and managing environmental risk and risk to HH from the impact of mining enterprises motor transport activity are to study the impacts and interactions between technogenic factors and environmental components, forecast potential consequences of such impacts and quantify the risks. Thus, the study provided a theoretical substantiation for the impact on aquatic ecosystems from mining enterprises traffic flows by modeling fields of PM and gaseous pollutants dispersion both from vehicle exhausts and fine dust leakages from the cargo rock materials.

3.2. Analysis of the technogenic impact of mining enterprise motor transport activity (on the quarry example) on ingredient and dust pollution of the Ros river water basin

The risk management strategy is based on choosing the risk level within acceptable limits, i.e. from minimum to acceptable level.

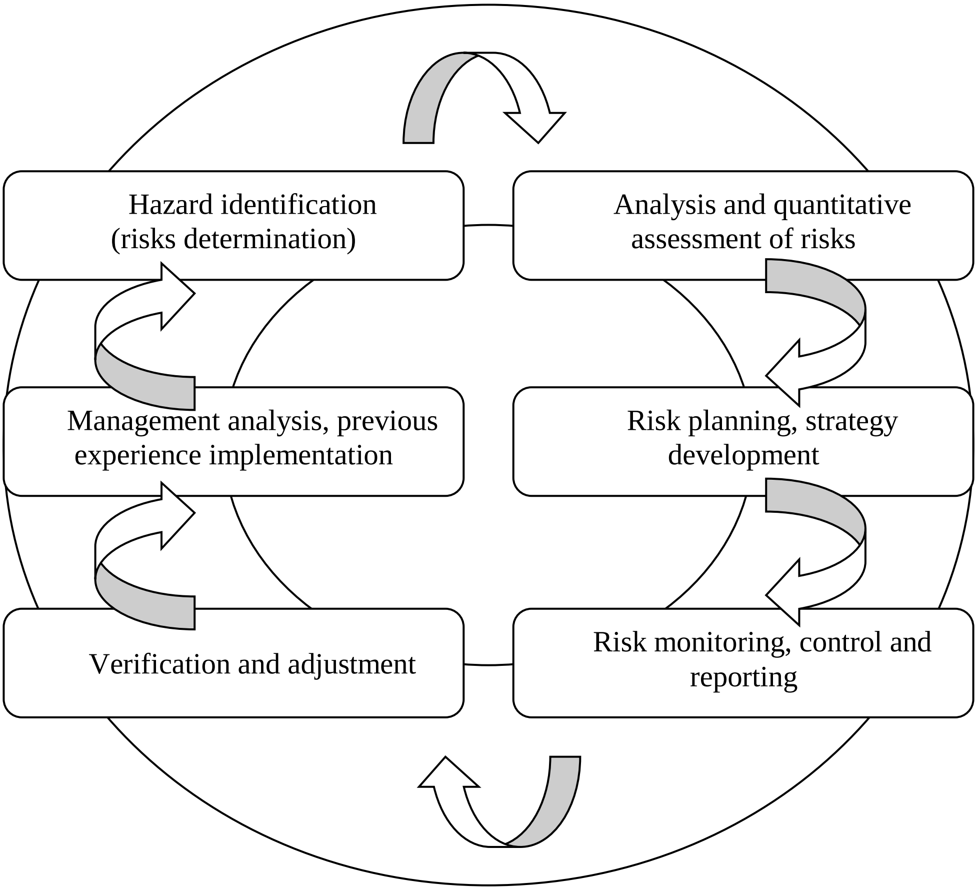


Fig. 3. Generalized scheme of environmental safety management by risk approach (Nihorodova, 2021)

It is well known that there is no human economic activity that is completely safe for humans and/or the environment. At the same time, the theory of risk assumes that the risk of the activity should be reduced to the extent that, firstly, is practically achievable, and, secondly, that corresponds to the "costs–benefit" principle (Nihorodova, 2021). The general scheme of environmental safety management of a certain industrial facility or territory, based on a risk approach, is shown in Fig. 3.

In the risk theory, an acceptable level of environmental risk is a risk that is less than or equal to the maximum permissible risk. Minimum risk is the level of environmental risk, below which further risk reduction is economically impractical and/or life-threatening. But it should be noted that these values are not sustainable, they also depend on the level of economic development of the country and its environmental policy (Nihorodova, 2021).

In particular, in (Bondar et al., 2019) the following types and values of risks were chosen as the basis for environmental safety assessments:

– insignificant risk – no more than 10^{-6};
– acceptable risk – more than 10^{-6}, but less than $5 \cdot 10^{-5}$;
– high (tolerable) risk – more than $5 \cdot 10^{-5}$, but less than $5 \cdot 10^{-4}$;
– unacceptable risk – more than $5 \cdot 10^{-4}$.

However, according to (Nihorodova, 2021), for Ukraine as a European country, the following threshold values should be a guide for determining the levels of acceptable risk:

– minimum risk – $< 10^{-8}$;
– maximum allowable risk $< 10^{-5}$.

Thus, the assessment of environmental risk and risk to HH is a prerequisite for estimating the level of environmental hazard, especially given the lack and some uncertainty of information to make substantiated decisions or implement management measures.

According to the hierarchical classification of methods for estimating the state of environmental danger of the territory or object, the methods of risk assessment, as well as methods of index (expert) assessment are considered as one of the most promising ones. The paper (Saaty, 2008) describes T. Saaty hierarchy analysis method, which is used to make management and marketing decisions in various fields. In particular, this method can be used to find optimal solutions to the problem of ensuring the quality of air and water environments, soils, etc.

During hierarchy analysis method implementation experts or expert groups assign to each of the influence factors the appropriate degree of advantage. In particular, in this study, the degree of preference was determined according to the classical fundamental scale of absolute values.

In accordance with this scale, if the degree of preference is equal to 1, then the two considered alternatives are equally advantageous in terms of the management purpose. If the degree of preference is equal to 9, then there is an absolute predominance of alternative or criterion "A" over "B" (Saaty, 2008).

So, the degrees of advantage determined by experts are imported to a special software component developed by our team on the basis of the ‘ahp’ package. Then further calculations and visualization are performed with the use of RStudio software.

The results of calculations according to the T. Saaty hierarchy analysis method are represented as a percentage for each of the alternatives and for each criterion and sub-criterion. The obtained results are automatically structured from a greater value o a smaller one depending on the weight value. The hierarchy analysis method is very effective and acknowledged tool used for solution of traditional marketing managerial problems and thus it can be effectively used also for solving environmental marketing issues.

Thus, the area of influence of transport activity of several mining enterprises on the river Ros basin was chosen as the object of the study. In particular, LLC "VO Boguslavsky Granite" is located on the left bank of the river Ros in the village Teptiyivka, Boguslav district, Kyiv region (Fig. 4). The main production of the enterprise includes the extraction and sale of granite crushed stone of different fractions.

Development of the deposit began in 1969, and today the production volumes reach up to 400 thous. m^3 of gravel per year (www.bgkcomspec.com.ua). Thus, for its 50 years of existence, the company has sent to customers huge volumes of products and materials. The geography of transportation is quite wide and cargo is carried out mainly by motor transport and usually with high-carbon motor fuel usage. In particular, the company offers specialized trucks such as Scania, Volvo, MAN or even self-removal for transportation of products.

In addition to LLC ‘VO Boguslavsky Granite’, near the river Ros basin there are also such mining enterprises as:

– public corporation Belotserkovsky granite quarry ‘Koshyk’ (Bila Tserkva, Koshyk tract, Kyiv region);

– LLC Rokytnianskyi granary (village Ostrov, Rokytne district, Kyiv region);

– RGC LLC Rokytnianskyi granite quarry (Rokytne town, Rokytne district, Kyiv region);

– LLC "KSL" Olshanytsky quarry (village Bushevo, Rokytne district, Kyiv region) and

– LLC RESOURCE Rudoselsky granite quarry (village Rude Selo, Volodarsky district, Kyiv region).

As it was noted, the levels of air pollution of adjacent areas and the water basin by dust emissions, as well as by harmful substances from the exhausts of internal combustion engines depend on the road network conditions, traffic flows characteristics, other factors and thus have a geometric reference to roads and intersections.

Fig. 4. A fragment of the map-scheme of the location area of LLC "VO Boguslavsky Granite" and its motor transport activity in the Ros river basin (built on the basis of Google Maps data)

There are several methods of determining the amount of harmful substances emissions from vehicle exhaust gases, which in Ukraine are regulated by relevant legislation. EU countries generally use IAEA-recommended methods based on the Pasquill-Gifford empirical model. At the same time, the equation based on the TD theory was implemented and became the basis for the industry standard of Ukraine GSTU 218-02071168-096-2003 and KD 52.9.4.01-09.

The study is based on the method (www.uazakon.com), as well as on the improved and tested by national researchers methods (Mateichyk et al., 2013; Mateichyk and Nykonovych, 2011), based on the data of mileage emissions of vehicle exhausts harmful substances on a certain section of the highway. Description of the methodology and reference data are provided in (www.uazakon.com; Kofanov et al., 2020; Kofanov and Kholkovskyi, 2017).

Thus, according to the results of the analysis of the road situation of the studied highway (Fig. 4), sections of the road with potentially increased ecotoxicological impact on the river Ros basin, as well as on groundwater and cover of the studied areas near functioning mining enterprises were identified.

For modeling of dispersion and concentration fields of pollutants in the two-meter height roadside airspace, besides the main TF characteristics, the following ones were determined:

- geographical position of the beginning and end of the section of the highway (determined using Google Maps and GPS software package);
- length of sections;
- the presence of a protective "green" strip and its vegetation;
- distance to the nearest buildings, nature and density of building;
- the number of traffic lanes in each direction;
- the average speed of TF movement (separately for cars, trucks, buses, etc.);
- weather and meteorological conditions;
- the roughness of the underlying surface, etc.

The TF structure was characterized by the ratio of the vehicles of a certain type; separately the share of diesel trucks as the main source of PM emissions (soot particles) from the vehicle exhaust gases was determined. At the same time, the volumes of harmful substances emissions by vehicle engines were determined by the intensity of TF movement, the share of trucks, the mode of their movement, fuel consumption volume, etc.

According to estimates of (Sheludchenko, 2020), pollutant emissions for the highways of categories I-a and I-b can reach: for carbon monoxide CO – up to 17.6 kg/h·km; for carbon dioxide CO_2 – ~278.5 kg/h·km; for NO_x – ~1.9 kg/h·km; for C_xH_y – ~2.9 kg/h·km. If the share of diesel vehicles in the TF is more than 25%, PM emissions can reach approximately 1.9 kg/h·km (for roads of categories I-a and I-b), 1.2 kg/h·km (for category II roads) and 0.4 kg/h·km (for category III roads).

3.3. Pollutants dispersion in the atmosphere in the area of the granite quarry transport activity influence as an effective tool for environmental management and marketing

So, in this part of the paper spatial mathematical models of dust impurities PM_{10} and gas emission concentration fields (for example, nitrogen oxides) will be presented and analyzed. These spatial models were created on the basis of the authors' algorithm and a computer program developed in the MathCAD program environment (Kofanov, 2018; Kofanov et al., 2020). The torch approximation model that was used in the study is a solution of the TD semi-empirical equation (Berlyand, 1975) and for a linear pollution source as for a set of point emission sources it looks like this:

$$Q = \frac{M}{(1+n)\cdot k_1 \cdot \varphi_0 \cdot x^2 \cdot \sqrt{2\cdot\pi}} \cdot e^{-\frac{u_1 \cdot H^{1+n}}{k_1 \cdot (1+n)^2 \cdot x} - \frac{y^2}{2\cdot\varphi_0^2 \cdot x^2}}, \tag{5}$$

where: M – emission source output (mass of the substance emitted by pollution source per unit of time); n – a dimensionless parameter characterizing the atmosphere stability; u_1 – the coefficient in the formula for the wind speed profile; k_1 – the coefficient in the formula for the TD profile of the impurity in the atmosphere; φ_0 – the standard deviation for wind direction pulsations; H – the height of the emission source above the ground.

Eq. (5) is used to model the light impurities dispersion when the exchange coefficient increases linearly with height, and the wind speed changes according to the degree law (Berlyand, 1975). During the development of the pollutant dispersion spatial model the coordinate system is oriented so that the OX axis coincides with the direction of the mean wind; the OY axis is turned in the TF direction, and the OZ axis is perpendicular to the TF movement.

The concentration from a linear emission source is equal to the superposition from the point sources according to Eq. (6):

$$Qp = \int_{L1}^{L2} Q \cdot (a - L \cdot \sin(\beta), b - L \cdot \cos(\beta))dL, \tag{6}$$

where: a and b − new coordinates in the redirected in direction of the average wind coordinate system, which is related to the original coordinates by Eq. (7); L – the length of the investigated highway section, m.

$$a = x \cdot cos\beta + y \cdot sin\beta, \tag{7}$$

$$b = -x \cdot sin\beta + y \cdot cos\beta,$$

where: β – the angle between the direction of the average wind and the direction of the TF movement on the highway.

Dimensionless concentrations matrix with reflection on the graph isolines of the dependence of the multiplicity of exceeding the impurities maximum permissible single concentration $MPC_{m.\,s.}$ from the distance from the road were built according to Eq. (8):

$$Q' = \frac{Q_p}{MPC_{m.s.}} . \tag{8}$$

The method used for estimating TF emissions was tested by researchers (Mateichyk et al., 2013; Mateichyk et al., 2015) and showed good results.

Thus, in Fig. 5a–7a the visualization of the solid fine particles dispersion fields is shown and in Fig. 5b–7b – of the nitrogen oxides emissions (in terms of nitrogen dioxide NO_2) on the studied area of the high ecotoxicological pressure from the mining enterprise (granite quarry) motor transport activity.

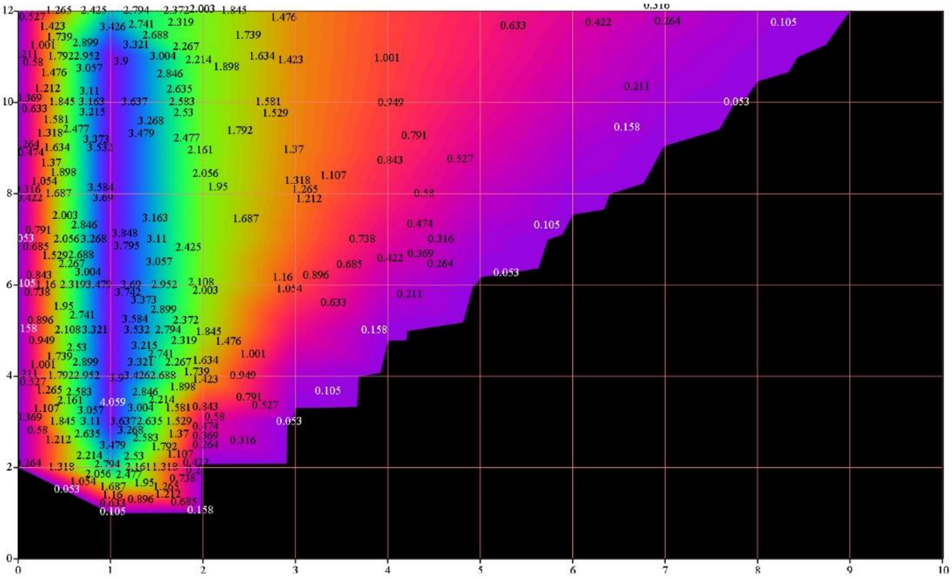
With the help of a computational experiment, the most dangerous for the river Ros basin direction and speeds of the average wind were determined; the development of the ecological situation under certain meteorological conditions was predicted. During the study of dispersion and concentration of the fine soot particles, it was assumed that the dispersion of PM with a size of ≤ 10 µm obeys the laws typical to the dispersion of gaseous substances, while for the larger particles, these laws change.

As you can see, aerosol pollution mostly stays near the highway. However, due to stronger wind flows, as well as due to the mechanical and physico-chemical transfer of pollutants, the river Ros basin is in a potential zone of harmful effects of vehicle pollution, especially considering that the shortest distance from the road to the water surface is about 220 m and the minimum distance to residential buildings is ~720 m.

In turn, light nitrogen oxides spread in the direction of the average wind over long distances and in almost all studied directions, which causes not only secondary but also primary pollution of the river Ros basin, threatens its ecosystem.

For the spatial models of dispersion of the studied toxicants in the surface air layer shown in Fig. 5–7 we have proposed the following gradation of the pollution levels:

- environmentally hazardous, if the multiplicity of exceeding the MPC of the impurity is from 8.0·MPC and above;
- high, if this ratio is (4.4…8.0)·MPC;
- average – the multiplicity of exceeding the MPC of the impurity is (1…4.4)·MPC;
- environmentally safe level, if there is no MPC exceeding.



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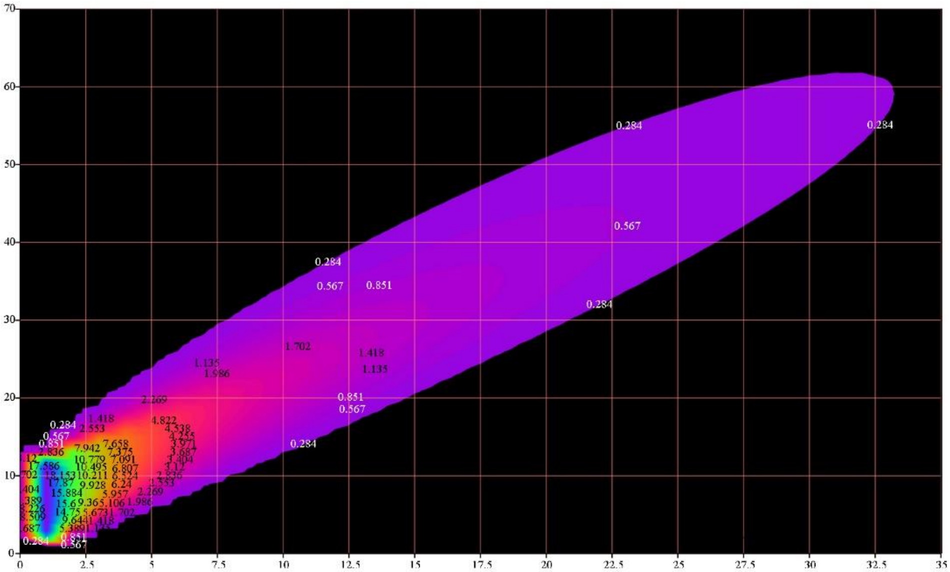

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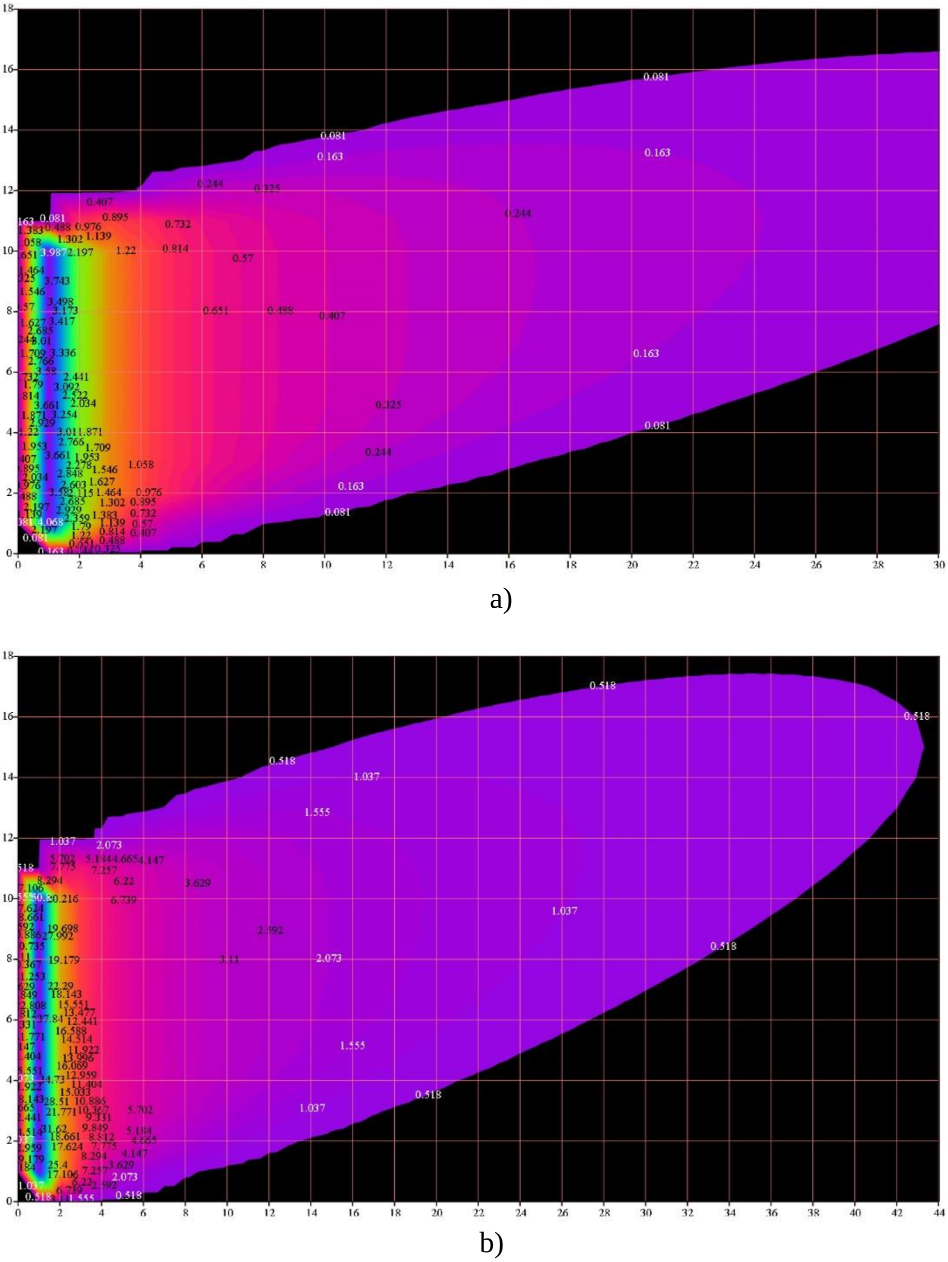
Fig. 5. Dispersion fields of a) PM_{10} aerosols; b) nitrogen oxides in terms of nitrogen dioxide NO_2 on the studied road section in the area of the mining enterprise influence at the north average wind with a speed of 5 m/s



a)

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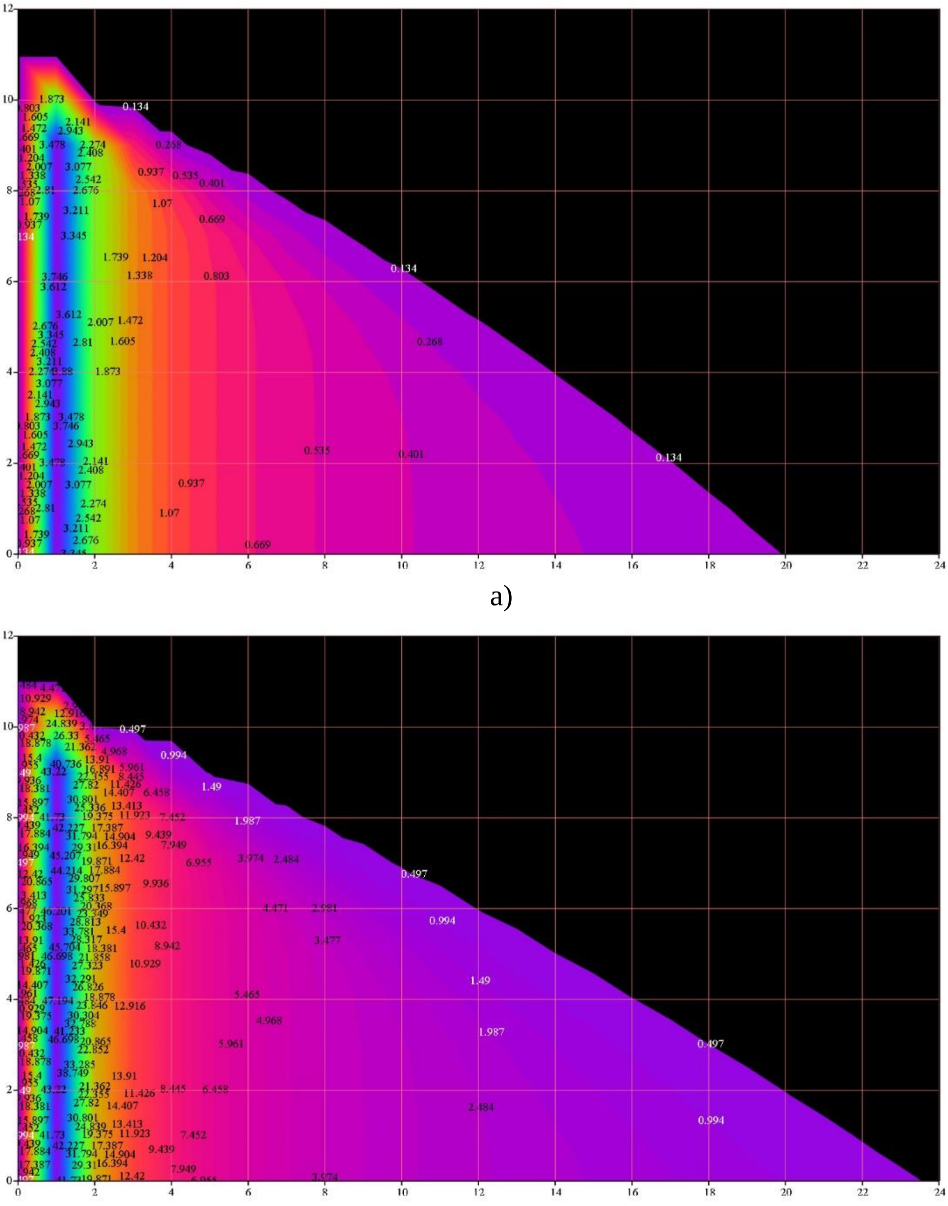
Fig. 6. Dispersion fields of a) PM_{10} aerosols; b) nitrogen oxides in terms of nitrogen dioxide NO_2 on the studied road section in the area of the mining enterprise influence at the northeast average wind with a speed of 5 m/s



a)

b)

Fig. 7. Dispersion fields of a) PM_{10} aerosols; b) nitrogen oxides in terms of nitrogen dioxide NO_2 on the studied road section in the area of the mining enterprise influence at the northwest average wind with a speed of 5 m/s

During the study of impurities dispersion fields the synergistic effects of air pollution, in particular, by several impurities of unidirectional action, as well as some geometric features of the road were not taken into account. The synergistic effect is manifested by: acetone and phenol; acetone, acrolein and phthalic anhydride; ozone, nitrogen dioxide and formaldehyde; carbon monoxide, nitrogen dioxide, formaldehyde and hexane; sulfur dioxide and sulfuric acid aerosol; sulfur dioxide and hydrogen sulfide; sulfur dioxide and nitrogen dioxide and other components of vehicle engine emissions (Gulyaev and Dranishnikov, 2005). At the same time, the problem of taking into account the geometric features of the road can be solved by refining pollutants dispersion fields using a discrete interpolation method developed and tested by national scientist Y. R. Kholkovsky (Kofanov and Kholkovskyi, 2017).

It is known that green plantings can help to clean the atmospheric air and reduce the toxic effects of exhaust on HH and the environment. Therefore, taking into account the fact that the studied objects have a potentially increased ecotoxicological impact on the river Ros basin, it is the ‘green screens’ (mostly in summer) that can significantly reduce the volume of harmful substances penetrating the aquatic environment. However, in our opinion, it is not enough to just plant trees, we must take into account the fact that pollution from vehicle harmful exhaust gases occurs in the surface air layer, and therefore trees will weaken but not hold up most of these pollutants.

According to the conducted investigation, planting shrubs with a height of ~ (2…3) m, as well as sowing high enough grasslands (non-allergenic ones) can become a good decision, because due to increasing the surface roughness and creating a so-called multi-stage continuous ‘green screen’ they will effectively reduce ecotoxicological load on the airspace and, as a consequence, on the water basin of the river. And this is especially important for the reduction of the technogenic load on the aquatic environment and airspace caused by aerosol pollution.

In addition, today for the protection of roadside territories from vehicle emissions, special screens are used. For the construction of such screens, for example, wastes of roads construction or reconstruction can be used. A good example of integrated application of technical and biological protection methods is the construction of a concrete-soil embankment with its subsequent greening, which will not only protect the surrounding areas from pollution but also have a decorative purpose (Sheludchenko, 2020).

4. Summary and Conclusions

1. Management of environmental risk caused by ingredient pollution of the water basin due to the use of high-carbon motor fuel during cargo transportation by mining enterprises is an important component of the national environmental safety system and is a part of the whole national security system. Taking into account the complexity of environmental safety achievement, it is necessary to consider a significant number of different factors, both internal and external.

The most important issues in this context include not only ensuring reliable environmental monitoring of changes in surface and groundwaters in the area affected by the mining activities, but also the solution of the issues for improving the ecological friendliness of heavy vehicles and, consequently, reducing emissions of pollutants penetrating atmospheric air and water bodies, both from the vehicle exhaust gases and the cargo dust from the mining enterprises production, as well as due to the inflow of toxicants from the surface runoff from the roads.

The ecological friendliness of vehicles, especially with the diesel truck engines, can be increased not only by improving the engines and catalytic converters design but also by replacing high-carbon motor fuel with more ecological fuels, including vegetable fuels; fuels obtained from production and consumption waste; by modifying fuels with various additives, using mixed biofuels in order to power engines, etc.

For the environmental risk assessment, it is also necessary to take into account the climatic and meteorological conditions, the orography of the area of the mining activity, including the nature and density of greening, the intensity of erosion processes, etc.

2. The algorithm for the development of the spatial mathematical models was proposed and theoretically substantiated in terms of the realization of environmental management and marketing tasks. These models can be used for predicting the dispersion of such components of vehicle emissions, as PM and nitrogen oxides, which are mostly emitted by heavy diesels and cause significant danger for the environment and HH. In order to build mathematical models of PM and nitrogen oxides dispersion in the surface layer of the air, the method of Beryland (2) and Kholodnov (9) was used on the basis of the application of the semiempirical equation of TD.

3. A computational experiment was carried out with the help of the developed spatial models and on its basis potentially dangerous for the river Ros basin directions and speeds of average wind were determined. It helped to provide recommendations for implementation of effective management and marketing decisions in the areas of mining enterprises influence.

The developed mathematical models also make it possible to accurately estimate the technogenic pressure from the functioning of heavy diesel engines on the environment and, in particular, on water bodies, as well as to assess the risks to HH. Based on the analysis of literature data and our own long-term scientific work, it was concluded that it is necessary not only to improve the design of vehicles and engines but also to change the physical and chemical properties of motor fuels in order to obtain environmentally friendly fuels, including alternatives.

4. The proposed methodology and management mechanism can be used in automated monitoring of the air and surface water quality, as well as to assess and predict the formation of dangerous to HH and the environment concentrations of harmful substances in areas affected by mining enterprises transport activity, because it allows to take into account not only meteorological and climatic conditions of PM and gas emissions but also traffic intensity, TF density and structure, geometric features of the road, the presence and type of vegetation, buildings, etc.

In addition, calculations and computational experiment show that the usage of high-carbon motor fuels for truck engines is harmful to the environment and HH, as it noticeably increases environmental risks and causes more pressure on the climate because of the significant emissions of greenhouse gases and aerosols.

References

1. Baird, C., Cann, M.: Environmental Chemistry. W.H. Freeman and Company, New York 2012.

2. Berlyand, M. E.: Sovremennye problemy atmosfernoy diffuzii i zagryazneniya atmosfery (Current problems of atmospheric diffusion and air pollution). Gidrometeoizdat, Leningrad 1975 (in Russian).

3. Bondar, A.I., Mashkov, O.A., Zhukaskas, S.V., Nygorodova, S.A.: Ecological threats, risks and environmental terrorism: system definition. *Ekolohichni nauky: naukovo-praktychnyi zhurnal*, 2(25), 113–122, 2019.

4. Dorokhov, O., Kharitonenko, G., Dorokhova, L.: Methods and models of atmospheric air condition’s assessment. *Montenegrin J. of Ecology*, 1(1), 47–52, 2014.

5. Goedkoop, M., Spriensma, R.: The Eco-indicator 99. A damage oriented method for Life Cycle Impact Assessment. Methodology Report. Amersfoort, The Netherlands 2000. URL: http://www.pre.nl/download/EI99_methodology_v2.pdf.

6. Goedkoop, M.: The Eco-indicator 95. Final Report. Utrecht, The Netherlands 1995. URL: http://www.pre.nl/eco-indicator95/ei-95-reports.htm.
7. Gulyaev, V.M., Dranishnikov, L.V.: Monitoring okruzhayushchey sredy: uchebnik dlya stud. spets. 7.070801 ‘Ekologiya i okhrana okruzhayushchey sredy’ (Environmental monitoring: textbook for stud. sp. 7.070801 ‘Ecology and environmental protection’). DGTU, Dneprodzerzhinsk 2005 (in Russian).
8. Kabaeva, I.V.: Sovershenstvovanie metodov rascheta rasseivaniya pylevykh vybrosov predpriyatiy stroiindustrii. Avtoreferat dissertatsii na soiskanie uchenoy stepeni kandidata tekhnicheskikh nauk: spets. 03.00.16 Ekologiya (Improvement of methods for calculating the dispersion of dust emissions from construction industry enterprises. Summury of dissertation for the degree of candidate of technical sciences: 03.00.16 Ecology). Volgograd, 2007 (in Russian).
9. Kholodnov, V.A., Reshetilovskiy, V.P., Lebedeva, M.Yu., Borovinskaya, E.S.: Sistemnyy analiz i prinyatie resheniy. Komp’yuternoe modelirovanie i optimizatsiya ob”ektov khimicheskoy tekhnologii v Mathcad i Excel (System analysis and decision making. Computer modeling and optimization of chemical technology objects in Mathcad and Excel). SPbGTI (TU), Saint Petersburg 2007 (in Russian).
10. Kofanov, O., Kofanova, O., Vasylkevych, O., Zozul’ov, O., Kholkovsky, Yu, Khrutba, V., Borysov, O., Bobryshov, O.: Mitigation of the environmental risks resulting from diesel vehicle operation at the mining industry enterprises. *Mining of Mineral Deposits*, 14(2), 110–118, 2020. DOI: 10.33271/mining14.02.110.
11. Kofanov, O., Yu, K.: Geoekologicheskie Aspekty Modelirovaniya Lokal'nogo Zagryazneniya Prizemnogo Atmosfernogo Vozdukha Otrabotavshimi Gazami Avtotransportnykh Sredstv (Geoecological Aspects Of Modeling Of Local Pollution Of Surface Atmospheric Air By Exhaust Gases Of Motor Vehicles). *Gornaya Mekhanika I Mashinostroenie*, 4, 20‒33, 2017 (in Russian).
12. Kofanov, O.: Modeling of dispersion and local concentration of pollutants in the roadside airspace. *Bulletin of NTU "KhPI". Series: New solutions in modern technologies,* 9 (1285), 190–197, 2018. DOI:10.20998/2413-4295.2018.09.28.
13. Kolluru, R.V.: Health Risk Assessment: Principles and Practices. Risk Assessment and Management Handbook for Environmental, Health, and Safety Professionals, New York 1996.

14. Mateichyk, V.P., Hryshchuk, O.K., Vaihanh, H.O., Blazhchuk, O.V.: Doslidzhennia vplyvu rezhymiv rukhu transportnoho potoku na riven zabrudnennia prydorozhnoho seredovyshcha (Investigation of the influence of traffic flow modes on the level of roadside pollution). *Visnyk Nats. transportnoho universytetu. Ser. Tekhnichni nauky,* 2(32), 174−181, 2015 (in Ukrainian).

15. Mateichyk, V.P., Nykonovych, S.O., Sapozhnyk, Yu. V.: Otsinka rivnia zabrudnennia atmosfernoho povitria transportnymy potokamy (Estimation of the level of air pollution by transport flows). *Visnyk Nats. transportnoho universytetu,* 27, 78−83, 2013 (in Ukrainian).

16. Mateichyk, V.P., Nykonovych, S.O.: Rozrobka metodyky vyznachennia vytrat palyva ta masovykh vykydiv zabrudniuiuchykh rechovyn transportnym potokom (Development of methods for determining fuel consumption and mass emissions of pollutants by transport flow). *Visnyk Nats. transportnoho universytetu,* 24(2), 93−99, 2011 (in Ukrainian).

17. Methods for calculating emissions of pollutants and greenhouse gases into the air from vehicles. Order of the State Statistics Committee of Ukraine № 452 of 13.11.2008. URL: http://uazakon.com/documents/date_3a/pg_gmcywc/index.htm.

18. Nihorodova, S.A.: Metodyka otsiniuvannia ekolohichnykh zahroz ta ryzykiv rehionu z vykorystanniam aerokosmichnykh tekhnolohii ta ekspertnykh otsinok. Dysertatsiia na zdobuttia naukovoho stupenia kandydata tekhnichnykh nauk 21.06.01 – Ekolohichna bezpeka (Methods of assessing environmental threats and risks in the region using aerospace technologies and expert assessments. The dissertation on the scientific degree of the candidate of technical sciences 21.06.01 Environmental safety). Kyiv 2021 (in Ukrainian).

19. Olenkov, V.D.: Uchet vetrovogo rezhima gorodskoy zastroyki pri gradostroitel'nom planirovanii s ispol'zovaniem tekhnologiy komp'yuternogo modelirovaniya (Accounting for the wind regime of urban development and planning using computer modeling technologies). *Vestnik YuUrGU. Ser. ‘Stroitel'stvo i arkhitektura’*, t. 17, 4, 21–27, 2017. DOI: 10.14529/build170403 (in Russian).

20. Petrea, D.M.V.: Emissions of Non-Methane Volatile Organic Compounds (NMVOC) from Vehicular Traffic in Europe. Thesis submitted to Bergische Universität Wuppertal for the degree of Doctor of Natural Sciences, Wuppertal 2007.

21. Pohrebennyk, V., Kofanov, O., Kofanova, O.: Application of modeling tools for monitoring the state of roadside territories and nearby surface waters. In: Sobczuk, H., Kowalska, B. (eds.): *Water Supply and Wastewater Disposal. Designing, Construction, Operation and Monitoring*, 239–254, Politechnika Lubelska, Lublin 2020.
22. Polkowska, Ż., Skarżyńska, K., Dubiella-Jackowska, A., Staszek, W., Namieśnik, J.: Evaluation of pollutant loading in the runoff waters from a major urban highway (Gdansk Beltway, Poland). *Global NEST Journal*, 9(3), 269–275, 2007.
23. Saaty, T.L.: Prinyatie resheniy pri zavisimostyakh i obratnykh svyazyakh. Analiticheskie seti (Decision making with dependencies and feedbacks. Analytical networks). LKI, Moscow 2008.
24. Sheludchenko, L.S.: Teoretychni osnovy ta metody zabezpechennia ekolohichnoi bezpeky avtotransportnykh merezh. Dysertatsiia na zdobuttia naukovoho stupenia doktora tekhnichnykh nauk 21.06.01 – ekolohichna bezpeka (Theoretical bases and methods of environmental safety of motor transport networks. The dissertation on a scientific degree of the doctor of technical sciences 21.06.01 environmental safety). Kyiv 2020 (in Ukrainian).
25. Tomiltseva, A.I., Yatsyk, A.V., Mokin, V.B. et al.: Ekolohichni osnovy upravlinnia vodnymy resursamy: navch. posib. (Ecological bases of water resources management: the textbook). Instytut ekolohichnoho upravlinnia ta zbalansovanoho pryrodokorystuvannia, Kyiv 2017 (in Ukrainian).
26. Vaganov, P.A., Man-Sung, I.: *Ekologicheskie riski (Environmental risks).* Saint Petersburg 2001 (in Russian).
27. www.bgkcomspec.com.ua (October 2021).
28. www.menr.gov.ua/news/31768.html (October 2021).
29. Yurchenko, V.O., Bryhada, O.V., Mykhailova, L.S., Vyrozhemskyi, V.K., Korotchenko, M.V.: Ekolohichna nebezpeka emisii naftoproduktiv pry ekspluatatsii avtomobilnykh dorih (Environmental danger of oil emissions during road operation). *Zbirnyk naukovykh prats ‘Dorohy i mosty’,* 13, 139–142, 2011.

Food Processing Wastewater Biological Treatment

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Abstract

The food industry is characterized by the use of large amounts of water per unit of production and by the formation of highly concentrated wastewater. However, the wastewater of some enterprises has pH values that are outside the range of 6.5–8.5, significant concentrations of fats and require adjustment of the nutrients content. Given the ability to biologically oxidize organic wastewater contaminants and technological, economic and environmental benefits, aerobic biological treatment methods play a crucial role in preventing water pollution by wastewater from the food industry. Intensification of biological wastewater treatment of food industry enterprises can be achieved both by improving their previous training and by developing new efficient equipment and technologies for biological wastewater treatment itself. Studies have confirmed the feasibility of using for pre-treatment of wastewater settling tanks-floaters, developed in NUWEE, which provide effective removal of suspended solids and fats and reduction of the organic contaminants concentration.

The choice of technology and hardware process design for the food industry enterprises biological wastewater treatment is a difficult task that requires consideration of many different factors.

Anaerobic processes have some advantages over the corresponding aerobic processes, such as low consumption of energy and low sludge production, smaller space requirements and lower overall costs, biogas production. On the other hand, aerobic treatment provides a higher removal degree of organic contaminants, nitrogen and phosphorus, have short start-up period, do not result in the occurrence of flammable and explosive conditions, unpleasant odors. These advantages emphasize the feasibility of aerobic biological wastewater treatment in the food industry enterprises.

A fundamentally new facility – an aeration tank-settler of large hydraulic height (6–10 m) with jet aeration has been developed for food industry biological wastewater treatment. Aeration tank-settler of large hydraulic height:

– multipurpose facility for biological treatment, nitrification, denitrification and sludge mix separation;

– works with increased activated sludge doses (5–7 g/dm^3) due to the large hydraulic height of the secondary settling tank flowing part;

– has a high oxidizing capacity (up to 6.8 kg BOD20 /(m^3·day)) due to the use of effective jet aeration; – due to the formation of aerobic (in the upper part) and anoxic (in the lower part) zones provides oxidizing capacity for ammonium nitrogen up to 100 g/(m^3·day) due to simultaneous nitrification-denitrification.

Keywords: food processing wastewater, aeration tanks-settlers of large hydraulic height, a simultaneous nitrification-denitrification

1. Introduction

When creating a new type of biological reactor for wastewater treatment, the following requirements and prerequisites were taken into account:
– the bioreactor must provide the required treatment degree of the food industry highly concentrated wastewater at different quantities and concentrations of contaminants (with wastewater pre-treatment);
– the biological reactor must operate at oxidizing power maximum values;
– biological nitrification-denitrification and biological/physical-chemical dephosphating should be carried out in the bioreactor;
– bioreactors must be simple in design and foolproof to operate;
– the wastewater aeration system must be highly oxidizing and reliable (Bartkiewicz at al., 2010; Rosenwinkel at al., 2005; Shifrin at al, 1981).

The developed facility is a round in plan metal tank, in the center of which is an aeration tank, separated from the peripheral secondary settling tank by a vertical cylindrical partition that does not reach the bottom (Fig. 1). Aeration of the sludge mixture is carried out by surface jet aerators inclined at an angle of 60° to the horizon. The jet aerators working liquid is selected by pumps from the aeration tank bottom part by means of the fixed devices similar on a design to sludge suck devices in radial secondary settlers. The untreated wastewater is fed to the upper part of the aeration tank, the treated wastewater is collected and removed from the secondary settling tank using a ring tray with a spillway. With the help of jet aerators there is a continuous circulation of the sludge mixture from the lower to the upper zone of the aeration tank. Together with the sludge mixture spinning in the aeration tank due to the velocity pressure of the jet inclined aerators, it creates sludge spiral downward movement (Kovalchuk at al., 2010).

In the zone of aerators jet penetration (aeration zone I) there is a three-phase system (wastewater, activated sludge, air bubbles captured by jet aerators), which turns into a two-phase (wastewater, activated sludge) in the lower part of the aeration tank. In the middle zone of the aeration tank due to biochemical processes there is a gradual decrease in the concentrations of dissolved oxygen (transition zone II), which is completely consumed before the beginning of the lower anoxic zone III. Because of this, the processes of biological oxidation of organic pollutants, nitrification and denitrification are carried out simultaneously in the aeration tank with the help of a single activated sludge.

Metal aeration tanks-settlers are manufactured in the factory and transported to the wastewater treatment facilities site in the form of rolls, or welded at the installation site from rolled metal sheets. Unlike the construction of aeration tanks from reinforced concrete, the installation of aeration tanks-settlers is performed fairly quickly, within 1–2 months. They can also be arranged by retrofitting existing metal tanks.

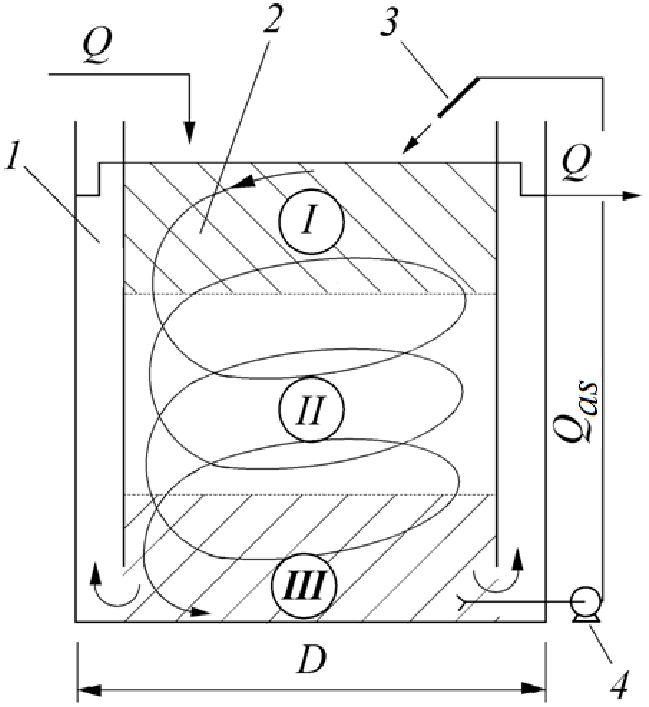

Fig. 1. Diagram of aeration tank with large hydraulic height and the surface jet aeration, combined with peripheral secondary settling tank: 1 – secondary settling tank; 2 – aeration tank; 3 – jet aerator; 4 – jet aerator pump; I – aeration zone; II – zone of reducing dissolved oxygen concentration (transitive zone); III – anoxic zone

2. Materials and Methods

The efficacy of large hydraulic height aeration tanks-settlers was studied at treatment facilities of meat processing plants (Fig. 2), dairy plants (Fig. 3), a plant for the apple juice concentrate production (Fig. 4), butter factory (Fig. 5), which are built on the developed technology. At all treatment plants, wastewater is first treated on gratings (at the plant for the production of apple juice concentrate – on arc sieves), and then in horizontal or tangential sand traps).

Fig. 2. Wastewater treatment plant of meat processing plant "Rhythm" in Chernihiv

Fig. 3. Wastewater treatment plant of dairy processing plant in Shostka

Fig. 4. Wastewater treatment plant of concentrate apple juice production plant in "Bukofruit"

At all wastewater treatment plants (except the Shostka plant) before biological treatment, wastewater was treated in a settler-flotator with a diameter of 7.2 m (Kovalchuk, 2009). Before biological treatment, nitrogen and phosphorus salts and caustic soda were added to wastewater from apple juice concentrate production.

Fig. 5. Wastewater treatment plant of Zolotonosha butter factory

Food industry wastewater biological treatment was carried out in aeration tank of the following diameter and hydraulic height respectively: 10 and 8.5 m – meat processing plant "Rhythm" in Chernihiv (discharge of treated wastewater into the municipal sewers, the plant 1 in Table 1); 10 and 8.5 m – for the Shostka milk processing plants (discharge of treated wastewater into municipal sewers, the plant 2 in Table 1); 10.0 and 9.0 m – for concentrate apple juice production plant "Bukofruit" (at the first stage, the discharge of treated wastewater into surface water, the plant 3 in Table 1); 14.0 and 8.0 m – for Zolotonosha butter factory (discharge of treated wastewater into municipal sewers, the plant 4 in Table 1).

3. Results and Discussion

During the research, the parameters and efficiency of biological wastewater treatment of the food industry in aeration tanks of large hydraulic height were determined (Table 1).

First of all, it should be emphasized that the proposed aeration tanks of large hydraulic height effectively combine biological treatment and efficient equalization of wastewater, which eliminates equalization tank from the wastewater treatment technological scheme (Kovalchuk, 2018). A two-year observation of the aeration tank-settler's operation showed that during the first year the pH values of the untreated wastewater, measured at the pumping station, fluctuated within fairly wide limits, from 2.24 to 12.46. At the outlet from the first aeration tank-settler (Fig. 6) it was already in the range 6.8–8.06 (average 7.47), and at the outlet from the second aeration tank-settler: 6.94–7.94 (average 7.50). The next year, the pH values of the untreated wastewater changed in a slightly narrower range, from 4.80 to 11.55. At the outlet from the first aeration tank, the pH was 7.30–8.06 (average 7.77), and at the outlet from the second aeration tank-settler: 7.35–7.61 (average 7.47).

As it can be seen from Figures 2–5, aeration tank-settlers are made of metal and are therefore subject to the influence of ambient air temperature, especially in winter. Capture and dispersion of cold air in the sludge mixture in winter undoubtedly leads to a decrease in its temperature, which results in decrease in the rate of oxidation of organic contaminants. On the other hand, aerobic processes occurring in the aeration zone during the biological treatment of highly concentrated food processing wastewater lead to the release of heat and, as a consequence, to an increase in the temperature of the sludge mixture.

Table 1. The results of biological wastewater treatment in the aeration tank with large hydraulic height (Kovalchuk, 2013, Kovalchuk, 2013b, Kovalchuk et al., 2015)

Parameter		**The values of wastewater pollutants concentrations for enterprises**			
		1	**2**	**3**	**4**
pH	b	6.41–7.27 6.81	4.18–6.37 5.56	4.45–5.78 5.11	4.71–7.37 6.31
	a	6.50–8.15 7.37	7.12–7.74 7.38	6.35–7.39 7.00	7.43–7.85 7.70
TSS, mg/dm^3	b	122–590 326	248–867 493	177–430 296	145–1528 586
	a	5.2–44 23	194–345 257	74–167 125	2–49 16
COD, mg/dm^3	b	637–2828 1463	910–6664 4116	2822–3205 3022	696–7330 2424
	a	85–445 248	45–739 231	129–604 312	27–108 76
BOD_{20}, mg/dm^3	b	406–1795 1040	760–4508 3547	2405–2872 2563	453–5505 1787
	a	10–104 39.8	12.5–613 58	335–542 127	118.5–246 164
Ammonia nitrogen, mg/dm^3	b	72–310 188	5.8–8.8 7.2	1.4–58 23.2	0.5–45 8.2
	a	0–30.3 14.2	0–0.87 0.48	0–5.9 2.1	0.4–13.2 4.7
Nitrate (N), mg/dm^3	a	0–39.5 20.1	–	–	0.73–23.3 11.8
Phosphate, mg/dm^3	b	36–203 118.8	49–295 210	0–125 65.1	25.4–62 45.9
	a	0–18 3.75	0–61.3 21.9	0–15 7.9	19.4–56.3 41.7
Fats, mg/dm^3	b	50–108 67	–	–	–
	a	5.3–34.3 18.4	–	–	–

Minimum and maximum value in the ranges and mean value below the ranges
b – before treatment; a – after treatment

Determination of the temperature in wastewater treatment facilities of Shostka city dairy plant for the year of operation showed the following. The average temperature of the untreated wastewater entering the pumping station was 25.4°C (ranges of changing 20.5–37°C). The average temperature of the sludge mixture in one of the aeration tank-settler was 26.8°C (20–32°C). The average temperature of the sludge mixture in the second aeration tank-settler was 25.2°C (18–32.5°C). Considering the above, one can conclude that when using metallic aeration tanks with surface jet aeration does not significantly reduce the temperature of the sludge mixture and they can be used without hindrance in winter (Kovalchuk, 2018).

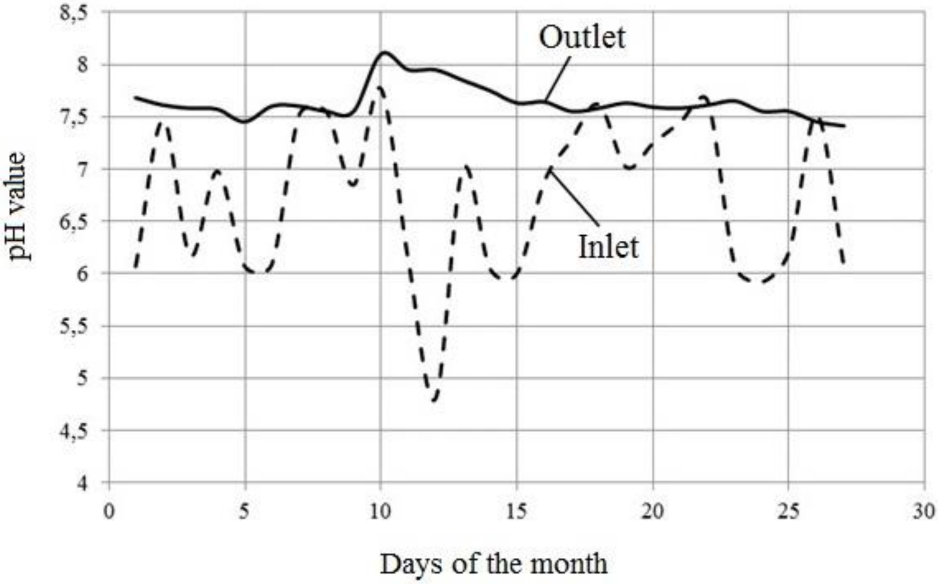

Fig. 6. The pH values at the inlet and outlet of the first aeration tank

When using aeration tanks with large hydraulic height and surface jet aeration, effective mixing of the sludge mixture should be ensured to prevent the settling of activated sludge to the bottom. Theoretical investigations on the basis of energy dissipation have shown that with the specific jet aeration capacity greater than 8 W/m^3 the sedimentation of active sludge was impossible (Kovalchuk, 2009). Experimental verification of this conclusion was performed in Shostka city dairy plant by measuring the flow rate in aeration tanks. The averaged longitudinal component of the flow velocity was measured using non-contact current meters connected with milliamperemeter – at a distance of 0.5 m from the outer constructions wall and at the middle radius aeration zone. As a result of the measurement, a decrease in the flow velocity over the height of the aeration tank from 20 to 120 sm/s (Fig. 7) was established, which is sufficient to maintain the active sludge in the suspended state (Kovalchuk, 2018).

As a result of industrial research of aeration tanks with large hydraulic height it was determined that the maximum F/M ratio at which is achieved the full biological meat processing wastewater treatment is 260 mg BOD_{20}/d per g MLVSS. For F/M ratio less than 500 mg BOD_{20}/d per g MLVSS biological treatment efficiency is 92–99%, while the big F/M ratio – reduced to 80–98%.

Dependence of work efficiency on the F/M ratio (Fig. 8) shows that in the range from 80 to 1450 mg COD/d per g MLVSS the efficiency of biological treatment dairy processing wastewater by COD is in the range of 90–98%.

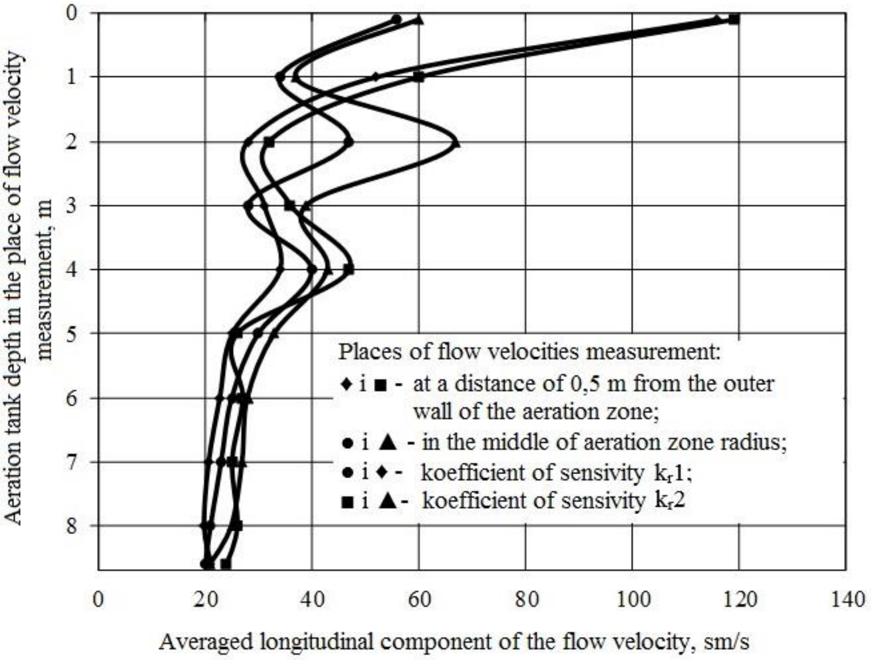

Fig. 7. Dependence of the horizontal component of the average flow velocity on the depth of the aeration tank

By increasing the F/M ratio above 400 and decreasing below 150 mg BOD_{20}/d per g MLVSS, sludge volume index increases without exceeding the value of 131 cm^3/g, which indicates its satisfactory sedimentation properties.

During the observations, the active sludge concentration in the aeration zone was within the range of 2.85–5.7 g/dm^3, and in the regenerator it was 2.6–7.4 g/dm^3. The average value of the sludge index was somewhat elevated and amounted to 150–243 cm^3/g, which, however, with elevated height of the sludge zone, did not lead to an excess of permissible concentrations of suspended solids when discharging treated sewage into the city sewage system. The oxidizing power of aeration tanks for BOD$_{20}$ was in the range of 407–2276 g/(m^3 d). The activated sludge yield in the process of biological wastewater treatment is 0.88–1.63 g per 1 g of the BOD$_{20}$ removed (Kovalchuk, 2013a).

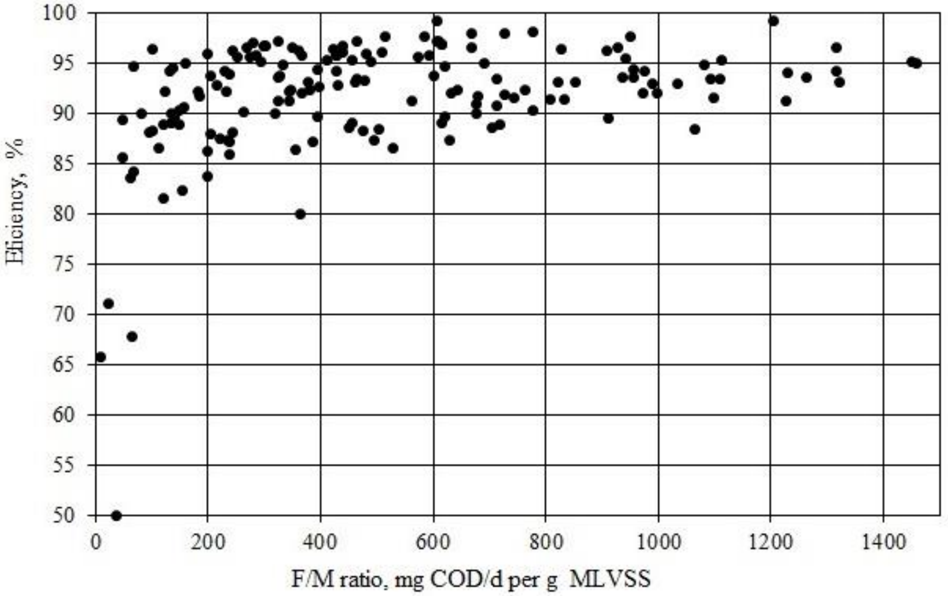

Fig. 8. Effect of F/M ratio on COD removal efficiency

Increasing the concentration of activated sludge in the aeration zone does not lead to a significant increase in the removal of sludge from secondary settling tanks. For example, increasing the concentration of activated sludge in the aeration tank of one of the meat processing plants to 7.1 g/dm^3 allowed to increase oxidizing power for BOD$_{20}$ to 6850 g/(m^3·d), and removal of sludge from secondary settling tanks does not exceed 229 mg/dm^3, which complies with the requirements for the discharge of treated wastewater into municipal sewers (Kovalchuk, 2016).

The calculation of the material balance of nitrogen in meat processing plant wastewater confirmed the possibility of implementing simultaneous nitrification-denitrification in aeration tank with large hydraulic height. It was found that in this case 22.0–71.0% of the initial content of ammonia nitrogen was removed through biological nitrification-denitrification, with total reduction of its concentration on 92.4–98.1%. When increasing F/M ratio, the efficiency of removal of ammonia nitrogen increases and reaches 90.8 g/(m^3·d). The residual concentration of ammonia nitrogen into biologically treated wastewater is 1–14.2 mg/dm^3.

The aeration tanks with large hydraulic height are being successfully implemented and used in over thirty food industry enterprises in Ukraine.

4. Summary and Conclusions

For the food industry biological wastewater treatment, the aeration tanks with large hydraulic height (6–10 m) with surface jet aeration, combined with peripheral secondary settling tanks have been developed.

Aeration tank-settlers operate at higher activated sludge concentrations (5–7 g/dm^3) and as a result have an increased oxidizing power for BOD20 to 6850 g/(m^3·d).

The food industry wastewater treatment before it is discharged into municipal sewers or use at the first stage biological treatment provides the reduction of COD – an average of 83.6% and BOD_{20} by 95.5%. The efficiency of ammonia nitrogen removal by means of simultaneous nitrification-denitrification is 84.4% or 90.8 g/(m^3·d).

The developed aeration tank-settler can be effectively applied for wastewater treatment of the various type food industry enterprises.

References

1. Bartkiewicz, B., Umiejewska, K.: Oczyszczanie ścieków przemysłowych. Warszawa: Wydawnictwo Naukowe PWN, 2010.
2. Kovalchuk, V.: To the question of the possibility of activated sludge sedimentation in the aeration zone of aeration tanks-settlers of large hydraulic height. *Bulletin of NUWEE*, 1(45), 116–121, Rivne, 2009 (in Ukrainian).
3. Kovalchuk, V., Kovalchuk, A., Samelyuk, V.: Biotechnology of food industry wastewater treatment. *Municipal economy of cities*, 93, 182–187, Kharkiv, 2013.
4. Kovalchuk, V., Kovalchuk, A.: Biological wastewater treatment in aeration tanks-settlers with jet aeration. *Installation market*, 5, 11–13, 2010.
5. Kovalchuk, V., Kovalchuk, A.: Wastewater treatment of concentrate apple juice production plants. MOTROL. *Commission of motorization and energetics in agriculture: Polish Academy of sciences. Lublin–Rzeszow*, 17(6), 53–61, 2015.

6. Kovalchuk, V.: Biological treatment intensification of food industry wastewater. In: Sobczuk H., Kowalska B. (eds.): *Water Supply and Wastewater Removal*, 78–90, Politechnika Lubelska, Lublin 2016.
7. Kovalchuk, V.: Dairy processing wastewater treatment. In: Sobczuk H., Kowalska B. (eds.): *Water Supply and Wastewater Removal*, 57–74, Politechnika Lubelska, Lublin 2018.
8. Kovalchuk, V.: High biooxidizing constructions in the meat and dairy industry wastewater treatment systems. *Construction Science Bulletin*, 60, 247–251, Kharkiv, 2013a.
9. Kovalchuk, V.: Settler-flotation units for the meat industry wastewater pre-treatment. *Installation market*, 9, 20–21, 2009.
10. Kovalchuk, V.: The technology of wastewater treatment of meat processing plants MOTROL. *Commission of motorization and energetics in agriculture: Polish Academy of sciences. Lublin-Rzeszow*, 13(6), 109–116, 2013b.
11. Rosenwinkel, K. H., Austermann-Haun, U., Meyer, H.: Environmental Biotechnology: Concepts and Applications. Chapter 2. Industrial Wastewater Sources and Treatment Strategies, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2005.
12. Shifrin, S., Ivanov, G., Mishukov, B., Feophanov, Y.: Meat and dairy industry enterprises wastewater treatment. M.: Light and food Industry, 1981.

Obtaining compost for reclamation technologies of degraded areas with use of sewage sludge as a raw material

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Abstract

Large amounts of sewage sludge (SS) generated and accumulated over decades at Ukrainian watewater treatment plamt (WWTP) pose a serious threat to the environment. The main methods of final treatment of sludge at the WWTP in Central and Western Europe today are thermal drying and incineration of sludge. At the same time, methods of drying and incineration of sludge are characterized by both high capital cost and particularly high operating costs. A resource-saving and energy-efficient alternative to the drying and incineration of mixed dewatered sludge in Ukraine is the method of aerobic biocomposting of SS to obtain an organo-mineral mixture, which, depending on its composition, can be used to solve many problems of reclamation of landfills and man-made disturbed lands. The specific capital costs for the composting of sludge are 3–5 times lower than for the drying process and 8–10 times lower than for the incineration process. SS contain a sufficient amount of nutrients necessary for plant growth and development. Numerous studies have shown that the use of organo-mineral fertilizers based on SS increases the humus content and increases crop yields. The use of composting as a mandatory stage of substrate preparation allows to get rid of pathogenic microbiota and helminth eggs. However, the optimal modes of implementation of this process to obtain substrates for a wide range of applications for different types of biological reclamation facilities remain unexplored.

Keywords*:* sewage sludge, composting, reclamation, laboratory research, compost, substrate, thermostatic unit

1. Introduction

In recent decades, the scale of generation and accumulation of industrial waste, which contains an organic component, has increased catastrophically, leading to the exclusion of new territories and environmental pollution. One of the types of such rapidly growing waste is sewage sludge generated at treatment plants in urbanized areas after the stage of biological treatment (Stefanakis et al., 2014; Feng et al., 2015; Venkatesan et al., 2014). Today the problem of their disposal and utilization is extremely acute. Uncultivated sludge has been stored for decades on overloaded silt sites, dumps, quarries, which has led to a violation of environmental safety and living conditions. Important in the disposal of sewage sludge are the processes of sludge pre-treatment, which include stabilization by adding lime, composting, aerobic or anaerobic conversion, as well as dewatering and drying processes (Christodoulo et al., 2015; Fytili et al., 2008).

The total volume of sewage sludge (SS) generated as a result of urban wastewater treatment at WWTP is 0.5–1.0% of the amount of treated wastewater at a sludge moisture content of 97–98%, respectively. Thus, an average of about 1 m^3 of sediment with a moisture content of 97% per one equivalent inhabitant is formed per year. Based on the total actual productivity of WWTP, about 40–50 million m^3 of SS with a moisture content of 97% or 1.2–1.5 million tons of sludge in terms of dry matter are generated annually in Ukraine. According to (DSTU 8727: 2017 …, 2017), the total amount of accumulated "old" sewage sludge in Ukraine is estimated at 1 billion tons. This standard proposes the use of biothermal composting as one of the most economically feasible methods of disinfection of SS, and sets requirements for the technology of preparation of organo-mineral mixture with STP for further use in agriculture and forestry. At the same time, in Ukraine there is a growing need for biological reclamation at spent industrial sites (landfills, dumps, etc.) because this process requires significant resource and financial costs, so finding ways to reduce its cost and conserve natural resources is extremely promising.

At this time, biocomposting of agricultural organic waste of animal origin has become widespread in Ukraine. The implementation of biocomposting of SS is much less common due to both the lower energy value of SS and due to the complexity of the sale of the final product due to the possible increased content of various toxic contaminants in SS. At the same time, composting of SS is widely used in many European countries (Kelessidis et al., 2012; Du et al., 2017), in particular in Hungary about 78% of sludge is treated by this technology, in the Czech Republic – 39%, in In Germany – 12%, in Poland – 9%. The possible high content of heavy metal compounds and other chemical and biological contaminants in SS makes it impossible the use of compost based on them for agricultural purposes, but opens up prospects for the use of such composts for biological reclamation of disturbed lands (used quarries, heaps, landfills, etc.). There is currently no ban on the use of SS for agricultural purposes in Ukraine.

However, according to (EU Regulation 2019/1009, 2019) on the rules of access to the EU market for fertilizers, digestate obtained from the fermentation of raw materials containing SS is prohibited for use as fertilizer in agricultural production. Therefore, the only promising areas for the future disposal of such products, which would attract the potential of plant nutrients that are part of SS, are their use for biological reclamation or in forestry.

Recycling and disposal of SS in order to prevent their negative impact on the environment is one of the important environmental issues. On the other hand, the chemical composition of SS is characterized by a high content of organic matter (about 70% by weight of sludge dry matter), significant concentrations of macro- and micronutrients, according to (Gryshko et al., 2015) on average sewage sludge contains: 1–3% nitrogen (N); 1–4% phosphorus (P); 0.2–0.7% potassium (K), however, depending on the composition of wastewater, the content of these elements may be greater or less (Ahmed et al., 2010; Dubovyy et al., 2014, Hamood et al ., 2016), as well as trace elements (cobalt (Co), iron (Fe), zinc (Zn); manganese (Mn), etc.), which in adequate concentrations are necessary for plant growth and development (Kaletnik et al., 2016; Paya et al., 2019). This gives grounds to consider this material as a component of organo-mineral fertilizers of different composition and purpose. Comprehensive disposal of SS solves not only environmental problems, but also economic ones by obtaining secondary raw materials.

As of 2021, Ukraine has already developed the main normative documents that allow extensive use of recycled SS as components of organo-mineral mixtures. In particular, it has been in force in Ukraine since 2014 (DSTU 7369: 2013 …, 2013) and since April 1, 2018 – more specialized (DSTU 8727: 2017…, 2017), which sets out the basic requirements for the preparation of SS, their processing and disinfection by the method of biothermal composting, as well as the method of calculating the allowable doses of organo-mineral mixture with SS as fertilizers for the content of pollutants.

At the same time, the facilities of biothermal composting of SS are currently extremely rarely used in the practice of Ukrainian WWTP. The task of developing more detailed scientific and practical recommendations for the use of aerobic composting for the disposal of SS remains relevant, taking into account the whole range of factors. Such factors include: humidity, chemical and bacteriological composition of SS, their age (in case of disposal of old SS accumulated on sludge sites), type and parameters of available plant raw materials, conditions of biocomposting process, type, frequency and intensity of aeration and humidification, doses and concentrations of special additives – thermophilic microorganisms to intensify the process and deepen biodegradation, as well as (if necessary) – special chemical reagents for the conversion of heavy metal ions into complex inactive compounds.

The purpose of the research is to use aerobic biocomposting methods to experimentally obtain optimal formulations of mixtures based on typical SS of large Ukrainian WWTP with the addition of the most common and economical plant material (wood chips) and recirculating active biocompost.

Performing research in controlled laboratory conditions minimizes the impact on the process of biocomposting of various environmental factors, such as sudden changes in air temperature, waterlogging by precipitation (in the case of the process in the open air).

2. Materials and Methods

Mechanically dewatered SS were taken as the main raw material for the model mixtures after centrifugation of the mixture of raw sludge and excess activated sludge in the mechanical dehydration shop of Lviv WWTP Hereinafter referred to as the new SS (SSn). In one of the raw material mixtures the influence on the process of biocomposting of old SS (SSold) was investigated. A sample of old SS was taken at the existing sludge site of Lviv WWTP; the age of the old SS according to the logbook is 2.5 ± 0.5 years.

As a plant filler in all experimental compositions used wood chips obtained by mechanical shredding of wood waste at the site of biocomposting of organic waste LLP "Green City" Lviv City Council, and for the accelerated development of the biocomposting process – recirculating active biocompost at the age of about 2 weeks, selected from the middle part of the compost piles of the biocomposting station LLP "Green City".

For laboratory composting, 4 raw material mixtures of different compositions were prepared: 3 mixtures (№–№3) with different volume fractions of SS and mixture №4 – control from active compost. The planning of the composition of mixtures №1–№3 was based on the recommendation (DSTU8727: 2017…, 2017) that in the case of using sawdust as a filler, the volume ratio "filler: SS" is from (0.5: 1.0) to (1.5: 1.0) in summer and from (1: 1) to (2.0–3.0): 1.0 – in winter. In the first approximation, the whole values of the ratio of wood chips and SS volumes were taken: 2 compositions with a ratio of 1: 1 and 1 mixture of 2: 1. To identify the impact of old SS on the biocomposting process in a mixture of №3 with a ratio of "chips: SS" = 1: 1, half of the sediment was new SS and the other half was old SS. For equality of starting conditions in the implementation of the biocomposting process in the laboratory, the initial volume of all mixtures before composting was the same and was $W_0 = 12$ dm^3. The volumes of each of the components of mixtures №1–№4 and the corresponding volume fractions of the components are given in table 1.

Table 2 shows the mass composition of mixtures №1–№4 and mass fractions of individual components of mixtures. Humidity of raw material mixtures was determined by calculation based on the results of analytical laboratory determination of humidity of all 4 components: new and old SS, wood chips and active biocompost. The content of free moisture in the substrates was determined by measuring the loss of mass as a result of drying the samples in a thermostat brand TC–80 M°C at a temperature of 68°C for 24 hours.

Table 1. Volume ratios of the components of the mixtures at the beginning of composting under laboratory conditions

№	**Volume, dm^3**					**Volume fraction**			
	SS$_n$	**SS$_{old}$**	**graft**	**active compost**	**total**	**SS$_n$**	**SS$_{old}$**	**graft**	**active compost**
1	3	0	6	3	12	0.25	0	0.50	0.25
2	4	0	4	4	12	0.33	0	0.33	0.33
3	2	2	4	4	12	0.16	0.16	0.33	0.33
4	0	0	0	12	12	0	0	0	1.00

Table 2. Masss and mass fractions of the components of the mixtures at the beginning of composting under laboratory conditions

№	**Mass, kg**					**Mass fraction**			
	SS$_n$	**SS$_{old}$**	**graft**	**active compost**	**total**	**SS$_n$**	**SS$_{old}$**	**graft**	**active compost**
1	2.76	0.00	0.94	1.71	5.41	0.51	0	0.17	0.31
2	3.68	0.00	0.62	2.28	6.59	0.55	0	0.09	0.34
3	1.84	1.84	0.62	2.28	6.59	0.27	0.27	0.09	0.34
4	0	0	0	6.84	6.84	0	0	0	1.00

To ensure proper accuracy of the results, the humidity of two samples was taken and determined for each substrate; the final value of humidity of each substrate was taken equal to the arithmetic mean of these two definitions. The initial temperature of the mixtures prepared for composting was 27.0°C. The initial humidity of the mixtures was from 60% of the mass. up to 66.2% of the mass (Table 3).

All mixtures were thoroughly mixed to homogenize their structure and intensify the composting process. Table 4 shows the distribution of the mass of DC on the components of the mixtures.

Table 5 shows the calculated masses of organic carbon and nitrogen in the 4 studied mixtures, as well as the calculated C/N ratios at the beginning of the biocomposting process. Estimated concentrations of organic carbon and nitrogen in SS and wood chips are accepted as average values according to the results of previous studies (Białobrzewski et.al., 2015, Rynk et.al., 1992):

– carbon and nitrogen content in SS: 250 g/kg DC and 31 g/kg DC (C/N ≈ 8.1);

– carbon and nitrogen content in the chips: 475 g/kg DC and 2.4 g/kg DC (C/N ≈ 200).

Mass concentrations of carbon and nitrogen in active compost, selected from the biocomposting station of LLP "Green City" (Lviv), are estimated at 300 g/kg DC and 20 g/kg DC (C/N = 15).

Table 3. The initial humidity of the mixtures at the beginning of composting under laboratory conditions

№	**Density, kg/m^3**	**Mixture's mass, kg**	**Mass of water in the mixture, kg**	**DC compound mass, kg**	**Mixture's humidity, % mass.**	**DC fraction, %**
1	451.1	5.414	3.368	2.045	62.2	37.8
2	549.2	6.590	4.365	2.225	66.2	33.8
3	549.2	6.590	4.365	2.225	66.2	33.8
4	570.5	6.846	4.108	2.739	60.0	40.0

Table 4. Distribution of dry compound of mixtures at the beginning of composting by components

№	**Mass of dry compound, g**			
	SS	**Graft**	**Active compost**	**Total**
1	607	754	685	2045
2	810	502	913	2225
3	810	502	913	2225
4	0	0	2739	2739

Table 5. Estimated ratios of the mass content of carbon and nitrogen (C/N) in mixtures before their biocomposting

№	**Carbon mass, g**				**Nitrogen mass, g**				**C/N mixture**
	SS	**graft**	**active compost**	**total**	**SS**	**graft**	**active compost**	**total**	
1	151.8	358.0	205.4	715.1	18.8	1.8	13.7	34.3	20.8
2	202.4	238.6	273.9	714.9	25.1	1.2	18.3	44.6	16.0
3	202.4	238.6	273.9	714.9	25.1	1.2	18.3	44.6	16.0
4	0.0	0.0	821.6	821.6	0.0	0.0	54.8	54.8	15.0

The unit for biocomposting of organ-containing mixtures in laboratory conditions consists of a thermostated device of TCP 0105 brand, equipped with a tubular electric heater (TEH) with a maximum power of 3.0 kW, temperature controller, stirrer and resistance thermocouple. The volume of the working space of the thermostat is 250 dm^3. Internal dimensions of the thermostated capacity – 1080 × 810 × 320 (280) mm. Overall dimensions (maximum): 1200 × 900 × 550 mm. Inside the thermostated device there are 4 identical containers (standard plastic buckets with a nominal volume of 20 dm^3), partially filled with the studied organo-containing mixtures.

The thermostated tank is applied in the housing of the unit and is covered with a special fastener for fixing the tanks with the studied substrates in the submerged position. In addition to the heating element and the stirrer, a platinum resistance thermocouple is attached on top, which is electrically connected to the regulator. Automatic maintenance of the set temperature of water in the thermostat is carried out by means of the temperature regulator by change of the power given on a heater of the thermostated capacity. A platinum resistance thermocouple is connected to the regulator input and a triac to the output. To equalize the temperature field in the tank is a stirrer – impeller mounted on the axis of the motor.

Temperature and humidity sensors are applied in the inner part of the tank lids. The latter are connected by a cable with a digital eight-channel temperature and humidity meter VTV 118–4 (four channels for temperature and humidity). Temperature measurements in the thermostat are performed using a built-in temperature controller with a resistance thermocouple. The thermostat controller TCP-0105 has a digital display and buttons for setting the required values of water temperature in the thermostat vessel.

The aerobic composting experiment (Fig. 1) was performed for 60 days in four plastic bioreactors 1 with a capacity of 20 dm^3, which are tightly closed with lids. The initial volume of compost mixtures in each bioreactor is 12 dm^3, which is 60% of their nominal volume.

To reduce heat consumption during composting, four reactors were placed in a thermostated tank 8 filled with water, the temperature of the water bath was controlled by a temperature controller, to equalize the temperature field in the tank installed a stirrer 4. In the inner part of the bioreactor lids built-in temperature and humidity sensors 3. The latter are connected by cable to a digital eight-channel temperature and humidity meter VTV-118-4. Using a hand drill on the lids of the bioreactor drilled two equidistant from the center holes 2 with a diameter of 5 mm for air circulation inside the bioreactor. A mounting frame is used to completely immerse the test objects in the liquid thermostat TCP-0105-BEI. For aeration, the compost in the reactors was stirred vigorously once a day for 20 C by pouring the compost mixture into a larger container and mechanically stirring with a 1700 W hand-held construction mixer, then pouring the mixture back into the bioreactor and placed inside a thermostated container. The composting process was carried out with the window open to provide natural aeration.

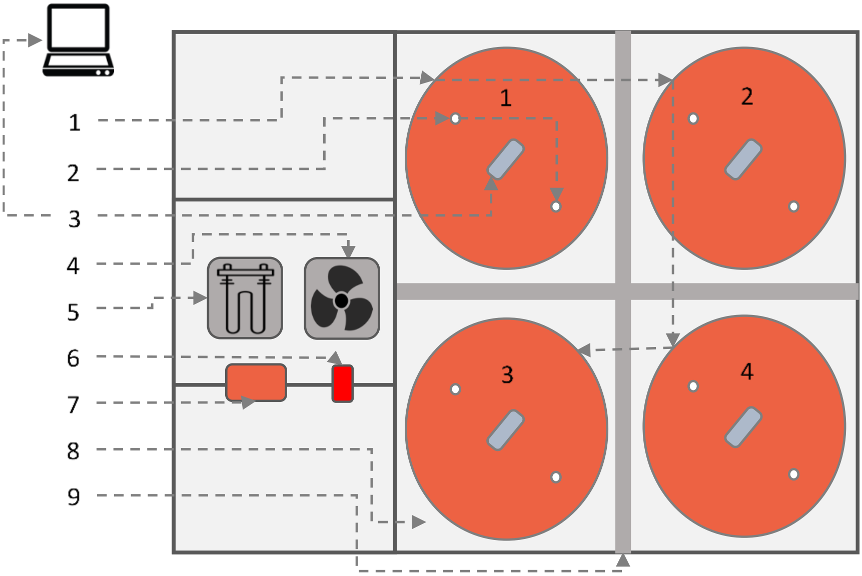


Fig. 1. Schematic diagram of the process of aerobic composting of organ-containing mixtures: 1 – bioreactor; 2 – openings; 3 – sensors of temperature and humidity; 4 – wing stirrer; 5 – TEH; 6 – power button; 7 – platinum resistance thermocouple with temperature regulator and triac; 8 – thermostated capacity; 9 – mounting bioreactors

Temperature measurements of compost mixtures were performed once a day, immediately after measuring the composition of the gas mixture, inserting the thermometer inside the mixture to the same depth from the bottom of the bioreactor. Laboratory thermometers TL-4 and TGL 11998 with temperature measuring ranges 0–55ºC and 50–100ºC, respectively, were used to measure the temperature of compost mixtures. Maximum absolute error of temperature measurement ± 0.1ºC.

To avoid a rapid decrease in temperature observed in small-volume reactors (Petric et al, 2009), a set temperature was set for thermophilic composting, simulating the corresponding temperature dynamics inside the full-scale compost pile. The thermophilic regime of biocomposting lasted for 5–7 days, which is enough to destroy most pathogens, and then the temperature was gradually reduced. The temperature control procedure allows to model the thermodynamic regime of the composting process, which will determine many other parameters of composting, such as humidity, biological activity, population dynamics of microorganisms (Mason et al, 2005).

The chemical composition of gas in bioreactors was measured once a day using a five-component gas detector-analyzer DOZOR-S-M-5, which allows to determine the content of five gases in the air: oxygen (O_2), methane (CH_4), carbon dioxide (CO_2), ammonia (NH_3) and hydrogen sulfide (H_2S). The content of oxygen, methane and carbon dioxide is determined in volume percentages (% vol.), And the content of ammonia and hydrogen sulfide – in mg/m^3. Measurement time for measuring channels: ammonia, hydrogen sulfide – 3 minutes; carbon dioxide, oxygen, methane – 1.5 minutes. To determine the oxygen content, its minimum value was recorded in bioreactors to ensure the necessary conditions for aerobic composting. It is believed that for the composting process the oxygen concentration should be within 15–20%. Adequate aeration at an early stage of composting reduces the process time, leading to the oxidation of carbon (C) to carbon dioxide (CO_2) and the reduction of methane emissions (Awasthi et al., 2014). The value of carbon dioxide was recorded at the maximum during the measurement.

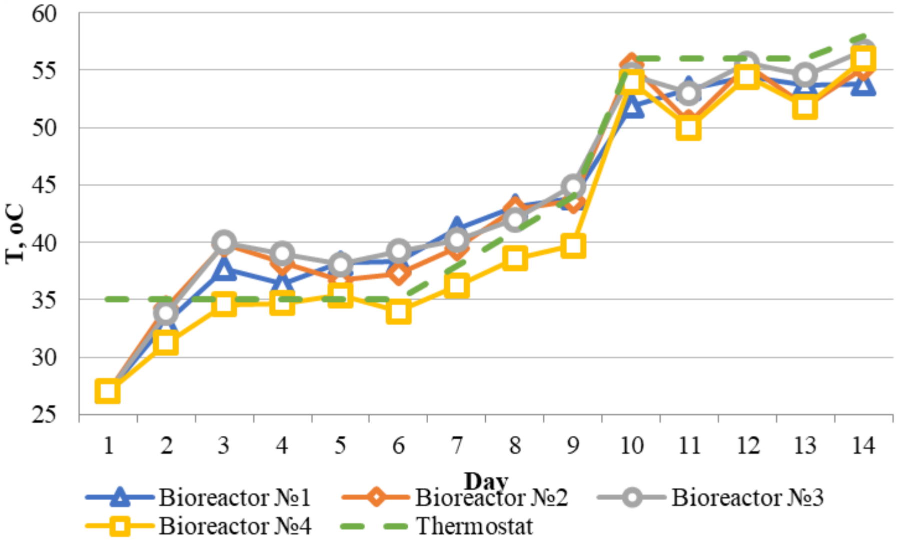
3. Results and discussion

3.1. Temperature profiles

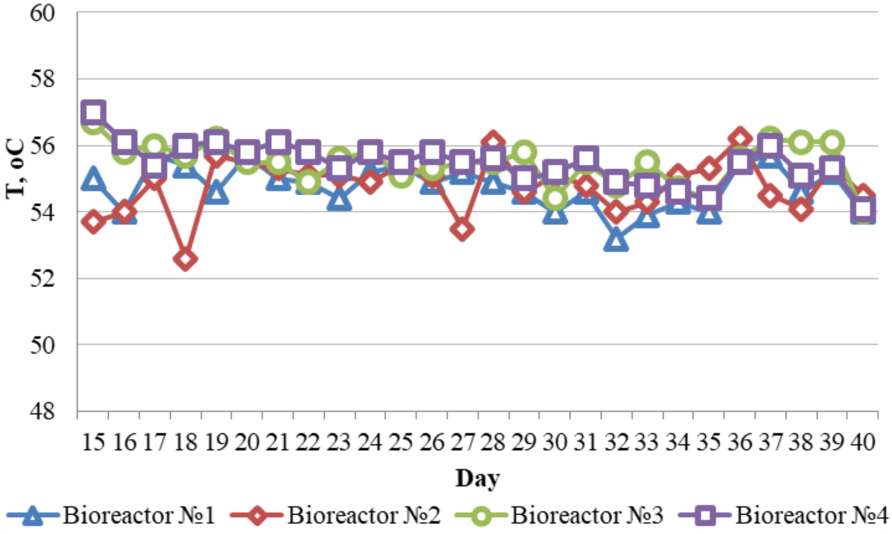
Temperature is one of the main parameters of the anaerobic composting process, which characterizes the intensity of decomposition of organic matter by aerobic microorganisms and is subject to monitoring. The initial temperature of all four compost mixtures is 27ºC. Temperature graphs for the studied compost mixtures in four bioreactors are presented in Fig.1. The study was started at a water temperature in a thermostated tank of 35ºC, which corresponds to the average temperature of mesophilic aerobic composting.

Directly at the beginning of the experiment the temperature of compost mixtures was significantly lower than the temperature in the thermostat, but since the second day of research the temperature of the studied mixtures (№1, №2 and №3) was higher than the water temperature in the thermostat, which is evidence of the rapid activation of the decomposition of organic raw materials by aerobic microorganisms, accompanied by intense local heat release. For example, 2 days after the start of a series of studies, the temperature inside the compost mixtures was: in the mixture №1 – 37.7ºC; № 2 – 39.8ºC; № 3 – 40.0ºC; № 4 – 34.6ºC, which corresponds to a significant positive temperature difference ΔT in mixtures №1 – №3 ($\Delta T1$ = +2.7ºC; $\Delta T2$ = +4.8ºC; $\Delta T3$ = +5.0ºC) and only in control capacity №4 with active compost, the temperature difference was negative ($\Delta T4$ = -0.4ºC) Fig. 7, which is an indirect indication that the most intense phase of aerobic composting in the control active compost has already taken place in kind, in the biocomposting station.

On the seventh day of research, the temperature of water in a thermostated tank began to increase, reproducing the gradual transition of the composting process from mesophilic to thermophilic mode in laboratory thermostated conditions. The change in temperature of compost mixtures in bioreactors is presented in Fig. 2 (a, b).



a)



b)

Fig. 2. Change in temperature of compost mixtures in bioreactors: a) from 1–14 days; b) from 15 to 40 days

From the 13th day, the temperature of the compost mixture in all bioreactors stabilized at 2–5 less than the water temperature in the thermostat, which indicates a decrease in the intensity of biodegradation and the transition to the stage of maturation of compost mixtures.

3.2. Oxygen content in biocompost mixtures

The minimum concentration of O_2 in biocompost mixtures decreased slightly in the first week.

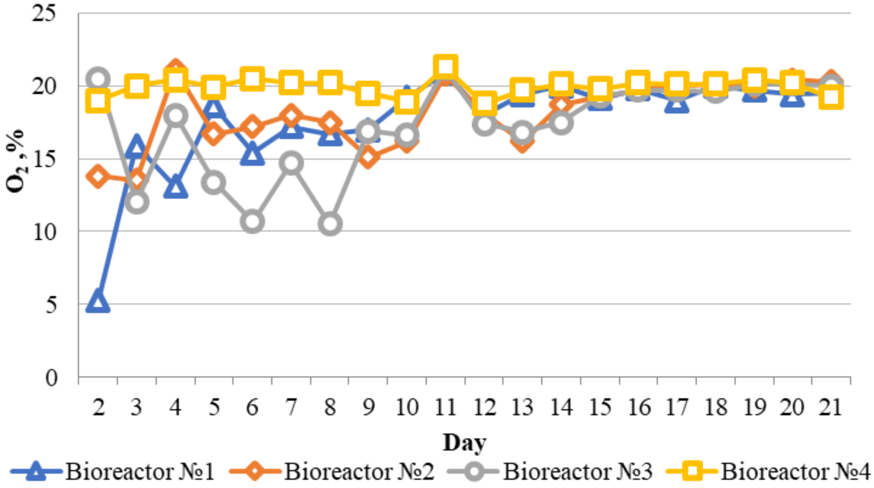


Fig. 3. Changes in the time of the volume fraction of oxygen in the gaseous medium of bioreactors

3.3. The content of carbon dioxide in biocompost mixtures

Since CO_2 is the main gas formed due to microbial degradation of organic matter, the rate of CO_2 emissions reflects the rate of decomposition of organic matter and microbial activity in the process of anaerobic composting of organo-containing mixtures (Awasthi et al, 2014). The change in CO_2 content (% vol.) inside the bioreactors №1 − (4 is presented in Fig. 4. In the first bioreactor with the highest wood chip content, the maximum CO_2 content is 6.7% vol. observed in the period from 1 to 5 days of research. In the bioreactor № 2 the maximum CO_2 content is 6.7% vol. observed the first 3 days.

From the 15th day, stable values of CO_2 content were observed in all bioreactors in the range of 0.5–1.5% vol. CO_2,% vol.

3.4. Ammonia content in biocompost mixtures

As shown in Fig. 5, the NH_3 content in the middle of bioreactors increased: in bioreactors №2 and №1 on the 7th and 9th day of composting, respectively, and reached a maximum on the 15th day. The increase in NH_3 content showed that the decomposition of organic nitrogen compounds occurred at the initial stage of composting. After reaching the maximum, the entire NH_3 content began to decrease. NH_3 content was not recorded in bioreactors №3 and №4. No NH_3 content was detected compared to control mixture №4 (active compost) and mixture №3 with the combined addition of SS_{old} and SS_n. That is, the addition of wood chips and active compost stimulates the absorption of ammonia, improves the structure and porosity of the composting mixture and free air space, which affects the ventilation and conversion of nutrients.

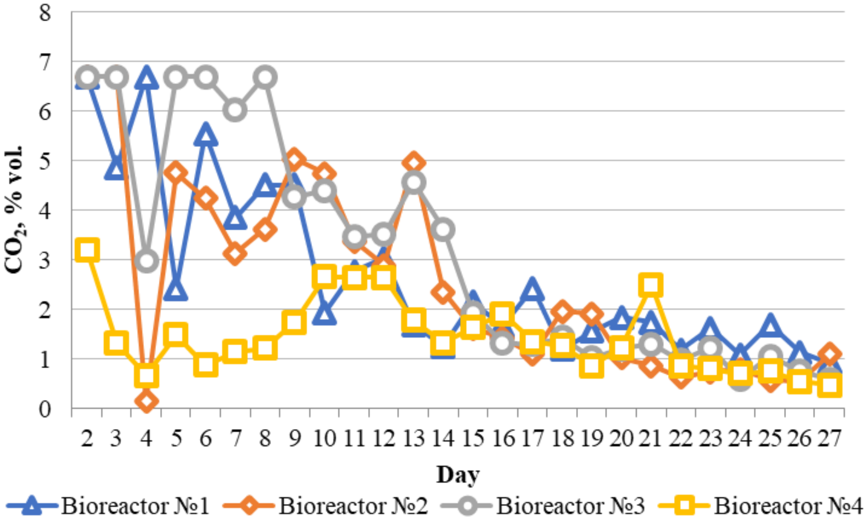


Fig. 4. Changes in CO_2 content inside bioreactors

3.5. Moisture content of compost mixtures

Moisture content is usually reduced due to a combination of high levels of temperature and aeration during the thermophilic phase. The initial moisture content (68% of the wet mass) decreased, so the practical method was used to determine the level of water evaporation in bioreactors (drying of samples in a thermostat) and periodic watering was carried out to maintain optimal humidity of the composting mixture.

4. Summary and Conclusions

The results of research on biocomposting of organo-containing mixtures in the laboratory proved the viability of sewage sludge in the raw material composition, and also showed that the addition of wood chips and active compost stimulates the absorption of ammonia, microbial nitrification improves structure, porosity of composting mixture and free air ventilation and conversion of nutrients.

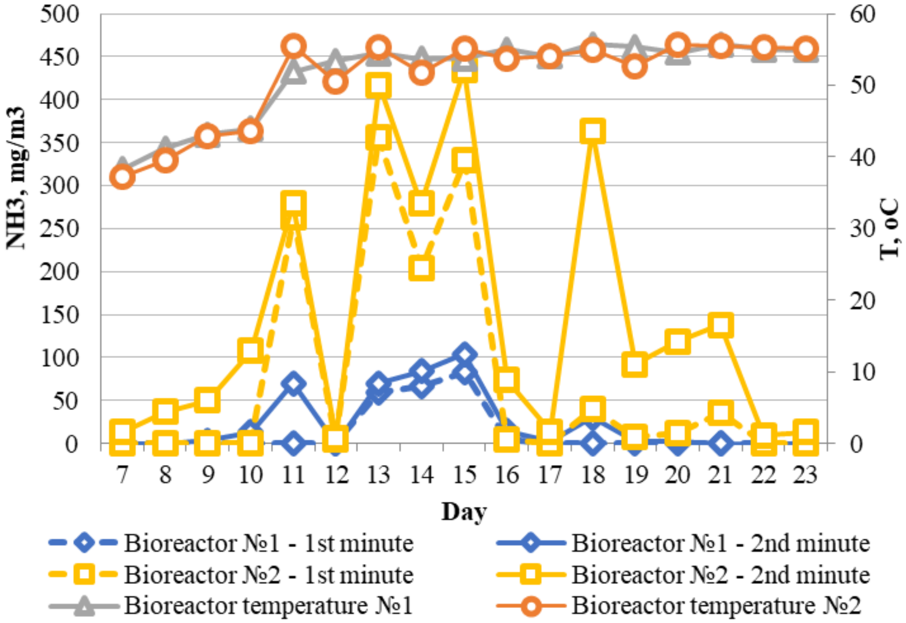


Fig. 5. Changes in NH_3 content in bioreactors №1 and №2

Acknowledgement

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References

1. Awasthi, M.K., Pandey, A.K., Khan, J., Bundela, P.S., Wong, J.W., Selvam, A.: Evaluation of thermophilic fungal consortium for organic municipal solid waste composting Bioresour. *Technol*., 168, 214–221, 2014.
2. Białobrzewski, I. et al.: Model of the sewage sludge-straw composting process integrating different heat generation capacities of mesophilic and thermophilic microorganisms. *Waste Management*, 43, 72−83, 2015.
3. Rynk, R.: On-Farm Composting Handbook. Northeast Regional Agricultural Engineering Service. Cooperative Extension Ithaca, NY 1992.

4. DSTU 7369:2013: Stichni vody. Vymohy do stichnykh vod i yikhnikh osadiv dlia zroshuvannia ta udobriuvannia. (Sewage. Requirements for wastewater and its sediments for irrigation and fertilization.). Minekonomrozvytku Ukrainy, Kyiv 2014 (in Ukrainian).
5. DSTU 8727:2017: Osad stichnykh vod. Pidhotuvannia orhano-mineralnoi sumishi z osadu stichnykh vod. (Sewage sludge. Preparation of organo-mineral mixture from sewage sludge.). DP "UkrNDNTS", Kyiv 2017 (in Ukrainian).
6. Mason, I.G., Milke, M.W.: Physical modelling of the composting environment: a review. Part 1: reactor systems. *Waste Management*, 25, 481–500, 2005.
7. Regulation (EU) 2019/1009 of the European Parliament and of the Council https: *Laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003*//eur-lex.europa.eu/legal-content/EN/TXT/?uri= CELEX%3A32019R1009.
8. Petric, I., Sestan, A., Sestan, I.: Influence of initial moisture content on the composting of poultry manure with wheat straw. *Biosystems Engineering*, 104, 125–134, 2009.
9. Stefanakis, A., Akratos, C.S., Tsihrintzis, V.A.: General Aspects of Sludge Management. *Vertical Flow Constructed Wetlands*, 181–189, 2014.
10. Feng, L., Luo, J., Chen, Y.: Dilemma of sewage sludge treatment and disposal in China. *Environmental Science & Technology*, 49(8), 4781–4782, 2015.
11. Venkatesan, A.K., Done, H. Y., Halden, R.U.: United States National Sewage Sludge Repository at Arizona State University – a new resource and research tool for environmental scientists, engineers, and epidemiologists. *Environmental Science and Pollution Research*, 22(3), 1577–1586, 2014.
12. Christodoulou, A., Stamatelatou, K.: Overview of legislation on sewage sludge management in developed countries worldwide. *Water Science and Technology*, 73(3), 453–462, 2015.
13. Fytili, D., Zabaniotou, A.: Utilization of sewage sludge in EU application of old and new methods – A review. *Renewable and Sustainable Energy Reviews*, 12(1), 116–140, 2008.

14. Kelessidis, A., Stasinakis, A.S.: Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. *Waste Management*, 32(6), 1186–1195, 2012.
15. Du, H., Li, F.: Characteristics of dissolved organic matter formed in aerobic and anaerobic digestion of excess activated sludge. *Chemosphere*, 168, 1022–1031, 2017.
16. Hryshko, V.M., Korinovska, O. M.: Vplyv orhano-mineralnykh dobryv na osnovi osadiv stichnykh vod na tsenoz mikromitsetiv (Influence of organo-mineral fertilizers based on sewage sludge on the coenosis of micromycetes). *Gruntoznavstvo*, 16(1–2), 75–81, 2015.
17. Ahmed, H.Kh., Fawy, H.A., Abdel-Hady, E.S.: Study of sewage sludge use in agriculture and its effect on plant and soil. *Agriculture and Biology Journal of North America*, 1(5), 1044–1049, 2010.
18. Dubovyi, V.I., Tabakaieva, M.H.: Vplyv osadu stichnykh vod na produktyvnist i yakist zerna pshenytsi (Influence of sewage sludge on wheat grain productivity and quality). *Zbalansovane pryrodokorystuvannia*, 3, 127–131, 2014.
19. Hamood, A., Khatib, J.: Sustainability of sewage sludge in construction. *Sustainability of Construction Materials*, C, 625–641, 2016.
20. Kaletnik, H.M., Honcharuk, T.V.: Perspektyvy vykorystannia stichnykh kanalizatsiinykh vod m.Vinnytsi dlia pidzhyvlennia polovykh kultur: vitchyznianyi ta zarubizhnyi dosvid (Prospects for the use of sewage in Vinnytsia for fertilization of field crops: domestic and foreign experience). *Zbalansovane pryrodokorystuvannia*, 3, 42–47, 2016.
21. Paya, J., Monzo, J., Borrachero, M.V., Soriano, L.: Sewage sludge ash New trends in Eco-Efficient and Recycled Concrete. *Woodhead Publishing Series in Civil and Structural Engineering*, 121–152, 2018.

Methods of hydrological and hydraulic modelling of the first flush of stormwater runoff from urban catchments: the analysis of Ukraine experience

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Abstract

New detailed analysis of actual data on the problem of flooding of urbanized areas in Europe is performed. The analysis of methods of hydrological and hydraulic modelling, as well as modelling of the qualitative composition of the first flush of stormwater from urban runoff basins, is presented with special emphasis on the approaches used in Austria and Ukraine. Using a rational method, as well as the results of large-scale interdisciplinary surveys and studies of the Baltic Sea catchment within the city of Lviv, the estimated maximum daily stormwater runoff flow rates at the inlet of Lviv wastewater treatment plant (WWTP) were obtained as a function of the return period and should be recommended for use in the implementation of the feasibility study of the reconstruction and modernization of Lviv WWTP.

Keywords: first flush, rainfall intensity, runoff hydrograph, stormwater runoff

1. Introduction

The problem of flooding of urban areas and the first flush discharge of highly polluted stormwater runoff into natural reservoirs has become more acute in recent decades (Bayazit et al., 2021; Bellos et al., 2020; Di Modugno et al., 2015). Therefore, it is important today to develop and implement advanced methods of modelling stormwater, taking into account the specifics of urban basins, using modern technical capabilities for monitoring, collection and analysis of diverse connected data sets and using the latest software (Cristiano et al., 2017; James and Rossman, 2010; Zhuk et al., 2021a). Scientifically based modelling and estimation of stormwater runoff parameters are important from both economic and social and environmental points of view. In recent decades, most countries around the world have seen a sharp increase in the frequency of heavy rainfall, which, together with intensive urbanization, leads to increased flooding of human settlements, causing significant economic damage and social problems (Dottori et al., 2018; Salvadore et al., 2015).

The results of the long-term analysis presented by (Blöschl et al., 2020) indicate that the last three decades are one of the four periods with the largest floods in Europe in the last 500 years, and the current period differs from other similar periods in the past, such as 1560−1580 in Western and Central Europe, 1760−1800 – in most of Europe, 1840−1870 – in Western and Southern Europe. All previous periods of large-scale flooding took place against the background of temporary periods of cooling, during which the average air temperature was about 0.3ºC lower than the temperature in the inter-flood periods (Blöschl et al., 2020), while the current flood wave, which began around 1990 and continues to this day, accompanied by large-scale warming, which is currently continuing to increase. Official data from the World Meteorological Organization indicate, for example, that 2020 was among the three warmest in the history of meteorological observations, 2015–2020 was the warmest six-year period for the entire observation period, and the average surface temperature in 2020 exceeded preindustrial by more than 1ºC level (State of the Global Climate 2020, 2021).

The purpose of the work is a review of actual tendencies of changing the rainfall parameters in Central and Eastern Europe and analysis of methods of the hydrologic and hydraulic modelling of the first flush of stormwater runoff from urban catchments.

2. Flooding in Europe: Trends and New Cases

Analysis of the results of large-scale long-term observations at about one hundred meteorological stations in Europe in 1946–1999 showed an overall increase in the average annual precipitation height of 0.76 mm/year and an increase in the number of days with precipitation of 0.04 year^{-1} (Klein Tank et al., 2002).

In 2018, a team of experts from the Joint Research Center, the EU and the world's leading scientists, using a multifactor modelling system, assessed potential human casualties, direct economic losses, and subsequent indirect losses (so-called decline in welfare) caused by river floods, increasing global average temperature on the planet at 1.5˚C. It is established that in the absence of measures to adapt to climate change, depending on the socio-economic scenario, human losses from floods can increase by 70–83% of current, direct losses – by 160–240%, and a relative decline in welfare – by 0.23–0.29% (Dottori et al., 2018).

2.1. Large-scale flooding in Western and Central Europe in 2021

The most recent events of the summer of 2021 in Central Europe confirm the concept of increasing the intensity of the most powerful showers. In July 2021, a series of floods caused by cyclone Bernd were observed in seven European countries (Austria, Belgium, Great Britain, Italy, the Netherlands, Germany, France, and Czech Republic). Thus, in Germany, on July 12–15, 2021, the monthly norm (about 150 mm) was observed, and in some cases even more than the monthly precipitation norm (over 200 mm). For some regions, this level of precipitation has become the highest in the last 1.000 years, and the floods themselves have been called the greatest natural disaster of the last century. After a series of heavy rains in late June 2021, heavy storms in the first half of July caused small flowing lakes and sudden local floods to overflow, followed by medium and large rivers in western Germany, leading to massive flooding from the Eiffel National Park, the federal state of Rhineland-Palatinate up to South Westphalia (Germany) and further to the south.

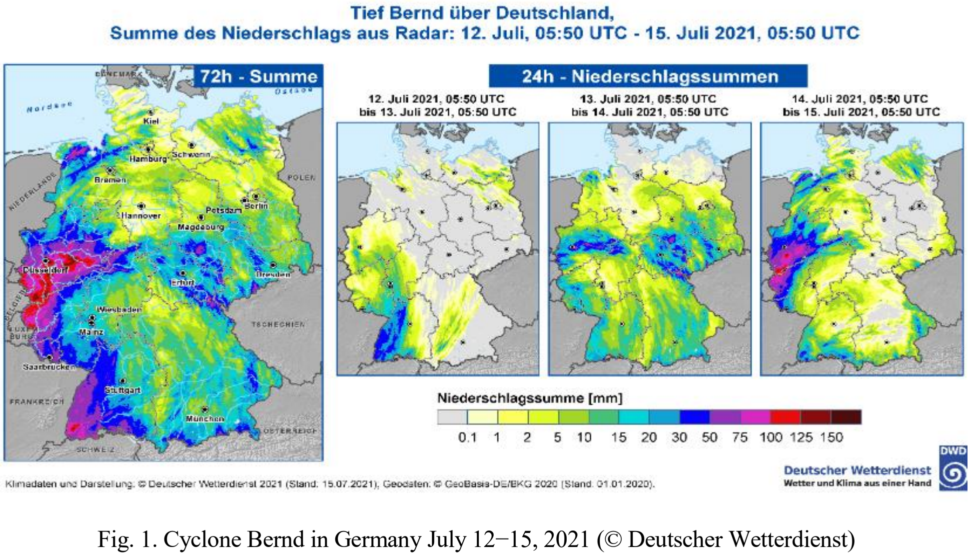

Fig. 1. Cyclone Bernd in Germany July 12−15, 2021 (© Deutscher Wetterdienst)

On July 12, 2021, the centre of the low-pressure area moved from south-western Europe to Germany, causing precipitation of 20 mm per day in the federal states of Hesse and Saarland to more than 50 mm per day in the federal state of Baden-Württemberg (Fig. 1). On July 13, the peak of precipitation fell in central Germany. In the Marienberg and Upper Franconia districts, precipitation levels of 43 mm were observed in 30 minutes, up to 88 mm in 120 minutes. The cities of Solingen, Hagen, and Wuppertal (North Rhine-Westphalia in western Germany) suffered the most. More than 241 mm of precipitations was recorded at the station of the State Administration for Nature, Ecology and Consumer Protection of North Rhine-Westphalia in Hagen in 22 hours (https://www.lanuv.nrw.de). On July 14 and the morning of July 15, the centre of activity of Cyclone Bernd was in the territory of western Germany from Dortmund through Cologne to Trier. Continuous rains were intensified by storms, more than 150 mm of precipitation per day were recorded.

Excessive rainfall, significant soil moisture, and geographical location have led to significant human losses and destruction. In the valley of the river Ahr, cyclone destroyed numerous residential buildings and infrastructure: roads and part of the railways were blurred, many bridges were completely destroyed (Fig. 2) (https://www.swr.de/swraktuell/rheinland-pfalz/koblenz).

Fig. 2. The valley of the river Ahr before and after the flood in July 2021 (https://www.swr.de/swraktuell/rheinland-pfalz/koblenz)

The SWR website (Regional Public Broadcasting Corporation serving south-western Germany, including the federal states of Baden-Württemberg and Rhineland-Palatinate) has created a map of all local communities affected by this natural disaster (Fig. 3–4) (https://www.swr.de/swraktuell/rheinland-pfalz/rlp-hochwasser).

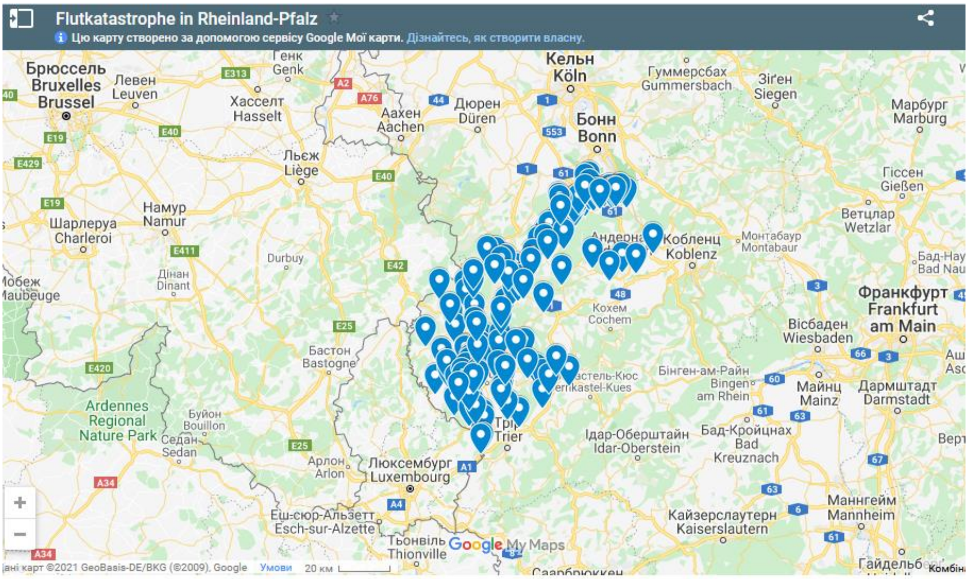

Fig. 3. Map of affected communities in southwestern Germany in July 2021,
(© SWR https://www.swr.de)

In Austria in July 2021, significant flooding was observed in Vienna, Salzburg, Graz, and the city of Galline. In Vienna on July 17−18, a large part of basements, underground parking lots, and passages were flooded. Due to heavy rains, there was an emergency power outage. To overcome the consequences, fire brigades were involved, 1.200 rescue operations were carried out (https://www.diepresse.com).

The town of Galline, located near the German border, suffered the most in Austria. Due to the flooding of its city centre, as well as the threat of landslides, civil defence alerts were used, and residents were evacuated for fear of casualties among the population (https://www.kleinezeitung.at). The precipitation depth in this region for one and a half days (July 17–18, 2021) reached 135 mm, the situation was aggravated by floods in the neighbouring region of Germany (https://www.dwd.de).

In Graz (Austria) on July 30, 2021 about 160 mm of precipitation fell. This caused flooding of many streets. However, the Graz Security Service noted that numerous stormwater storage tanks (SWST) saved the city from the devastating effects of bad weather (https://kurier.at).

Cyclone Bernd also passed over the Benelux countries, Great Britain, France, Switzerland, Poland and weakened to the Balkans (Fig. 5). In the United Kingdom, particularly in London, isolated torrential rains with a precipitation height of more than 24 mm/day were recorded, and central streets and roads of regional importance were flooded.

Fig. 4. Flooded streets of Rayland Palatinate (Germany), July 2021 (https://kurier.at)

In the Netherlands, the Limburg region was hit by floods, a motorway was partially flooded, and an army was used to evacuate the victims. The east of Belgium has been hit by heavy rains, rail services have been suspended, flooding of up to 2 meters has been recorded on some streets in the provinces of Namur and Luti, and 2.000 residents have been evacuated. In Luxembourg, the height of the precipitation layer exceeded 79 mm in 24 hours, which is much higher than the July average.

France was also covered by rains, which were equal in intensity to the amount of precipitation for 2 months. During July 12–15, an average rainfall of 100 mm was recorded in the east, sometimes up to 150 mm (https://meteofrance.com).

In Switzerland, with an average rainfall of 112 mm per month in July, only 10 minutes. on the night of July 12–13, 2021, 27 mm of precipitation was recorded. Gusts of wind and torrential rains led to falling trees, damage to cars and houses, massive landslides. In the first 14 days of July, 300 mm of precipitation was recorded at Sedrun station, which is twice the maximum for the last 60 years (https://www.meteoschweiz). By July 13, 2021, Cyclone Bernd reached northern Italy, where it caused severe thunderstorms with hail precipitation of up to 7 cm and heavy rainfall of about 83 mm in 30 minutes. Many houses and plantations were affected (https://www.eswd.eu).

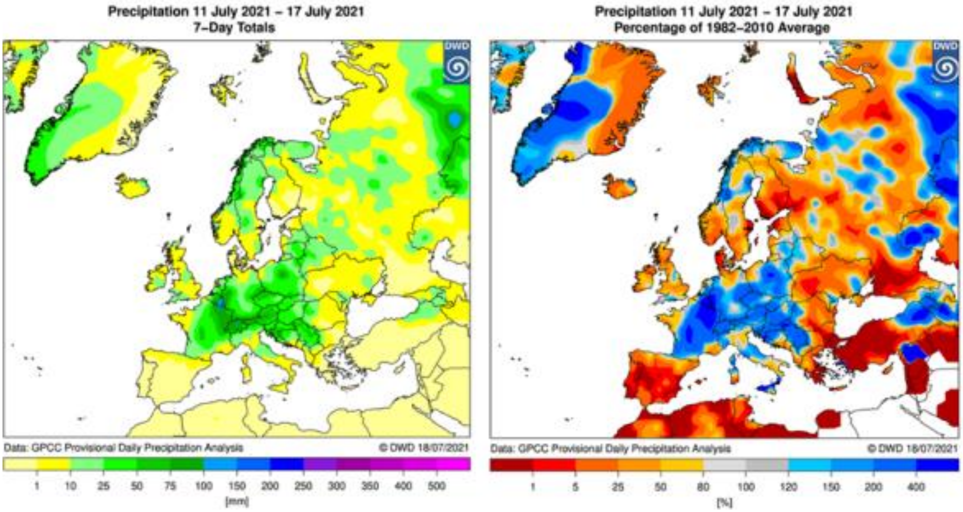

Fig. 5. The amount of precipitation during 11−17.07.2021 in Europe is absolute (left) and as a percentage of the average value for 1982−2010 (right), (https://www.dwd.de)

2.2. Flooding of urban areas in Ukraine

The results of meteorological observations show that the climate in Ukraine has been actively changing in recent decades. There is a sharp temporal and spatial variability of precipitation distribution in Ukraine in the period from 2002 to 2011 (Kulbida et al., 2013). A large-scale analysis of changes in rainfall parameters in Ukraine in 1991–2013, presented in (Tatarchuk and Tymofeiev, 2015), showed that 36 of the 40 hydrometeorological stations studied during this period exceeded the long-term maximum monthly altitudes of the precipitation layer. There is a high probability of the continuing trends of recent decades, namely − an increase in the amount of rain, especially with high intensity, as well as increasing the irregularity of precipitations during the year.

The last three decades have seen a sharp rise in average air temperatures throughout Ukraine. For example, in Kyiv during this period the temperature of the surface air layer increased by almost 2ºC, and climate modelling predicts the continuation of such rapid growth in the current century (Osadchyi, 2021) (Fig. 6).

Similar temperature rising trends are typical of all major cities in Ukraine. For example, according to the Ukrainian Hydrometeorological Center, the average annual air temperature in Lviv has been growing at a rate of about 0.016ºC/year in recent decades (Fig. 7), which corresponds to a century above the first critical indicative value of 1.5ºC. Despite the same trend throughout Ukraine to increase the average air temperature, trends in precipitation in different cities differ slightly. For example, in Kyiv there is a decrease in the average annual height of the precipitation layer, while in Lviv – on the contrary, an increase (Zhuk et al., 2021a).

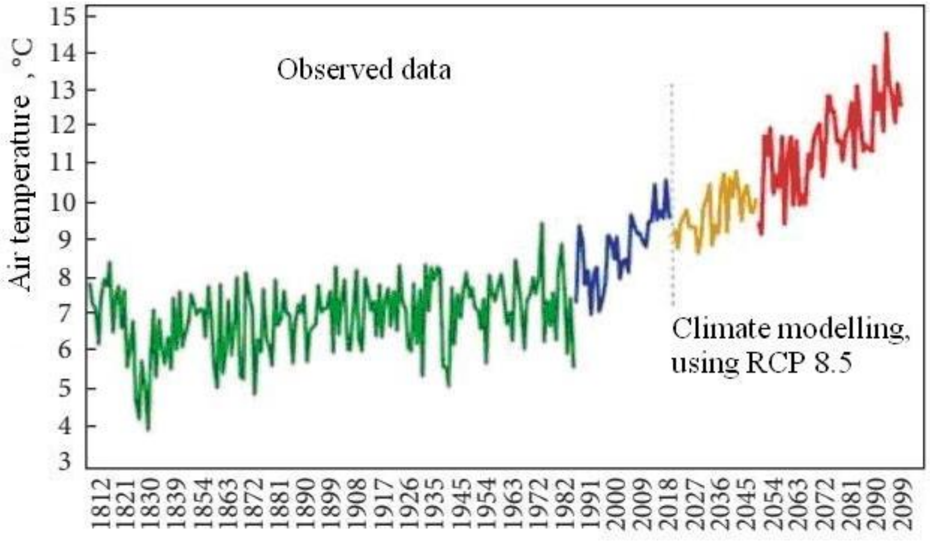

Fig. 6. Actual and projected long-term changes in the surface air temperature in Kyiv (according to Osadchyi, 2021)

This confirms the general global trend regarding the diversity of changes in average precipitation parameters, even within one geographical region (State of the Global Climate 2020, 2021). On the other hand, as in the countries of Western and Central Europe, the frequency and capacity of the most intense rains in the cities of Ukraine is increasing, which leads to an increase in the frequency and scale of flooding of urban areas. Similar consequences with the flooding of urban areas after heavy rains occur every year in most regional centres of Ukraine.

Given the above, improving the methods of hydrological modelling of water runoff in climate change is today one of the priority areas of research in water management in Ukraine (Osadchyi, 2021), and integrated stormwater runoff management in urban areas − an important element of practical adaptation to global climate change.

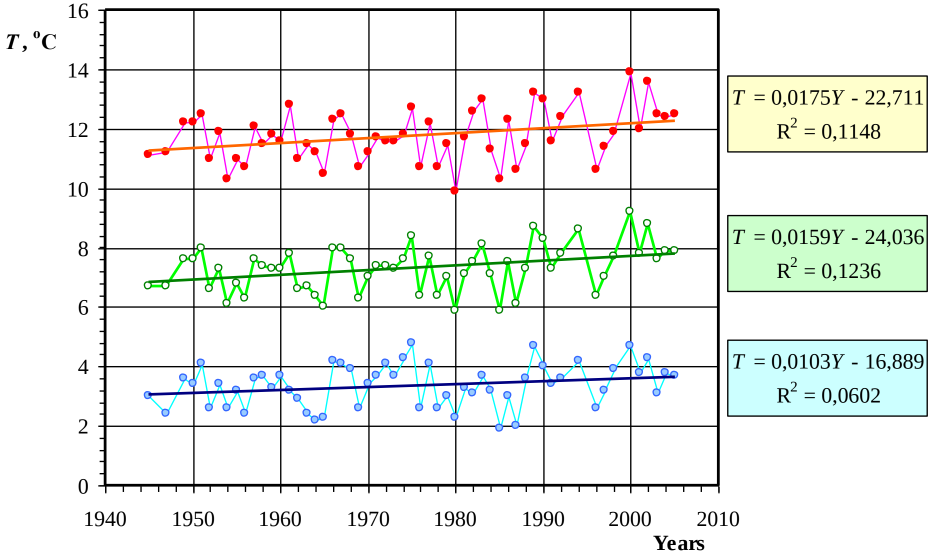

Fig. 7. Average annual maximum, average and minimum air temperatures in Lviv (data of Ukrhydrometeocenter)

3. Features of the first flush discharge of surface runoff from urban areas

Today, progressive urbanization is becoming one of the key factors of negative impact on the environment. It causes a number of problems, including in terms of stormwater management. These problems are complicated by the lack of an integrated approach to the design of municipal infrastructure, including sewerage systems (Bayazit et al., 2021; Tkachuk and Zhuk, 2012).

The first flush discharge of surface stormwater from urban areas poses a special threat to the normal operation of both the sewerage network and wastewater treatment plants (Di Modugno et al., 2015). During this phase of the runoff hydrograph, the most concentrated part of the surface runoff from the territories characterized by a high proportion of impervious surfaces enters the drainage network. Simultaneously with high concentrations of pollutants, the first flush discharge is characterized by a sharp increase in volumetric flow, which causes a complex peak load on the drainage system, both in terms of quantitative parameters of surface runoff (maximum volumetric costs) and in terms of maximum concentrations and mass consumption of pollutants. The first discharge can indeed be considered a flush if at least 70–80% of the total mass of pollutants is transported in the initial 25–30% of the volume of stormwater runoff (Bertrand-Krajewski et al., 1998).

Identifying the nature and characteristics of the phenomenon of the first flush discharge is especially important for the implementation of stormwater quality management practices (Deng et al., 2005). An alternative methodology for detecting the first flush discharge is the mass factor of the first flush. A number of researchers have established in practice that the first flush release is present only for part of the analyzed rains. Thus, less than half of the rains in the study (Bertrand-Krajewski et al., 1998) showed more than 40% of the total mass of pollutants in the first 20% of the total volume of runoff.

Another disadvantage of the traditional approach of determining the first flush discharge is the immensity of the key parameters, which does not allow to take into account the influence of the absolute value of the surface runoff. The total amount of runoff due to light rain may be equal to the volume of the first 20% of heavy rain, and therefore may be completely within its first flush discharge. Two types of pollutant sources are identified in urban runoff basins:

– short-term pollution accumulated during the period of dry weather, which is completely washed away from the surface of the runoff basin, if the rain is sufficiently intense and prolonged;

– long-term pollution that corresponds to the background level of pollution for a given runoff basin and that cannot be completely washed away by rain of arbitrary duration and intensity.

If a short-term source of contaminants is not exhausted as a result of rainfall with a low layer height, the concentration of the pollutant will be consistently high. This explains the results of studies in which the effect of the first flush was much weaker and less frequent for rains with a low height of the precipitation layer.

Lee at al. (2004), presented an improved technique, which relates the first discharge to the absolute volume of runoff and allows you to simulate changes in the mass of contaminants over several rains over a sufficiently long period of time, presented. Continuing this direction, Bach et al. (2010), presented a new approach to the definition of the first flush discharge, which corrects a number of shortcomings of the traditional approach, including the use of actual values of runoff compared to dimensionless fractions of the total volume, more accurate definition of the first flush, as a function of the characteristics of the catchment, rather than a separate estimated rain.

4. Maximum daily flow rates of the stormwater runoff at the inlet of Lviv WWTP

Scientifically based modelling of stormwater drainage systems should be based on the maximum possible consideration of climatic, topographic, hydrological, hydrogeological, hydraulic and urban planning parameters of the object (James, 2005; Tkachuk and Zhuk, 2012). Stormwater modelling involves solving a set of stochastically determined non-stationary hydrodynamic and mass transfer equations, and the quality of the model depends on the completeness and relevance of the original data, which can be obtained only with multidisciplinary approaches and the widespread introduction of specialized computer programs (Bell and Moore, 2000; Maier et al., 2020; Zhuk et al., 2021b). The following is an example of a multidisciplinary study performed to determine the maximum daily surface runoff flow rates at the inlet of Lviv wastewater treatment plants (WWTP).

The peculiarity of the geographical location of Lviv is that the territory of the city is almost equally divided by the line of the Main European watershed onto the Baltic Sea catchment and Black Sea catchment (Fig. 8).

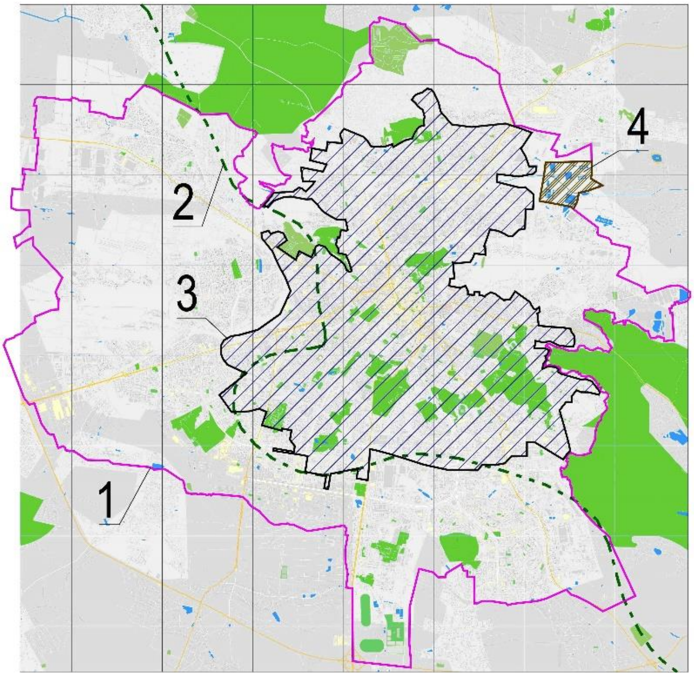

Fig. 8. Plan-scheme of Lviv city: 1 – official city boundaries; 2 – the main European watershed (geographical watershed); 3 – technical watershed of the Baltic Sea catchment, 4 – territory of Lviv WWTP

Poltva River, which originates in the city, is the main sewer collector of the general-alloy sewerage system, which collects domestic and industrial wastewater from the whole city, as well as surface wastewater from the Baltic Sea runoff basin and underground river runoff Poltva and delivers wastewater to Lviv WWTP. From the territory of the Black Sea runoff catchment, only heavily polluted part of stormwater and snowmelt runoff, which enters the combined sewerage network through the separation chambers, and an insignificant part of runoff, which enters the network due to leaks of sewage system elements, enters Lviv WWTP. The area of the Baltic runoff catchment within the official boundaries of the Lviv city is about 59.5 km^2, and the area of the Black Sea runoff catchment equal to 62.1 km^2 (Zhuk et al., 2021c). As of 2021, Lviv WWTP is in a rather problematic technical condition and needs large-scale reconstruction and modernization.

Estimated maximum daily volumes of stormwater runoff of different return periods, that enter the combined sewerage system of Lviv city and flow to the Lviv WWTP, can be found using a rational method (Urban hydrology for small watersheds, 1986), which is most often used to solve similar problems both in Ukraine and abroad:

$$W_{d.max,P} = (\Sigma\ \psi_{\mathrm{i,P}}\ F_i\ )\ h_{d.max.P} / 1000, \tag{1}$$

where: $\psi_{\mathrm{i,P}}$ – calculated values of runoff coefficients for pervious and impervious surfaces in Lviv, as a function of the return period P; $h_{d.max.P}$ – maximum daily depth of the precipitation layer in Lviv, as a function of the return period P; F_i – area of different types of coverage of the Baltic Sea catchment of Lviv.

The total area of the Baltic Sea catchment within the technical watershed was defined by processing and analyzing a map of the main sewers of Lviv, made at a scale of 1:2000, as well as satellite photographs of the city with the current state of development. The total area of the Baltic Sea catchment, determined by an analytical method, is equal to F = 40.79 km^2.

To estimate the share of water impervious surfaces, a statistical sample analysis of 20.000 elementary cells of the high definition satellite photographic image of the Baltic Sea runoff catchment within the city of Lviv was performed. An example of identification of cover types is shown in the fragment presented in Fig. 9.

Among the 20.000 analyzed cells measuring 2 × 2 m, the number of water impervious cells was equal to 10.157 units. Thus, the use of the method of simple statistical sampling for the Baltic basin of the city of Lviv, allowed to determine the share of total impervious covers at 50.8% (p_{tot} = 0.508). The relative error of this value is ±0.9% with a confidence interval of 99% or ±0.7% with a confidence interval of 95%.

To find the relationship between the share of total impervious covers and the share of effective impervious covers within the Baltic Sea catchment of Lviv, the results of sample field studies of the territory of 75 quarters in six administrative districts of Lviv with a total area of over 1000 hectares were analyzed. Table 1 shows a summary of the areas of all 75 studied quarters of the Baltic Sea catchment within the city of Lviv.

Fig. 9. Fragment of a satellite image of the city of Lviv with examples of determining the types of coverage: blue (dark) cells − impervious surfaces; yellow (light) cells − water-pervious surfaces

Table 1. Summary of the surveyed areas of 75 quarters within the Baltic Sea catchment of the Lviv city

#	**Type of surface cover**	**Area**		***p*, %**
		m^2	**ha**	
1	Directly connected impervious areas	5518094	551.81	55.12
2	Non-connected impervious areas	666536	66.65	6.66
3	Pervious areas	3808196	380.82	38.04
4	Water bodies	17723	1.77	0.18
5	Impervious	6184630	618.46	61.78
	Total:	10010549	1001.05	100.00

Mathematical processing of field sample data revealed a statistically significant relationship between the dimensionless total imperviousness and the effective imperviousness in the Lviv Baltic Sea catchment (Fig. 10):

$$P_{ef} = P_{tot}^{1.318}, \tag{2}$$

Applying the dependence (2) for the entire Baltic Sea catchment at $p_{tot} = 0.508$ gives the calculated value of the effective imperviousness equal to $p_{ef} = 0.410$, surface runoff from which directly enters the sewer system through a network of gullies, drains, stormwater inlets, etc. The maximum relative error in converting the share of total to the share of effective impervious covers for the Baltic Sea catchment is ±1.32%.

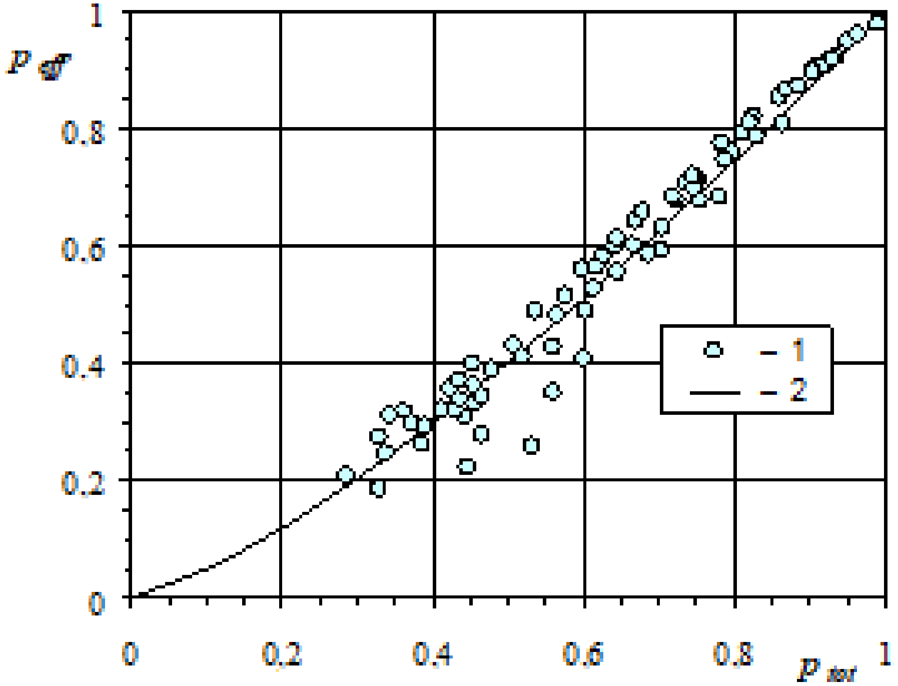

Fig. 10. Relationship between the shares of effective and total impervious covers at the territory of the Baltic Sea catchment of the Lviv city: 1 – results of the survey of 75 quarters; 2 – power-law function (2)

Ranking and statistical processing of the highest rainfalls in Lviv for the period from 1984 to 2019 revealed the dependence of the maximum daily rainfall depth on the return period P in the form of Weibull function:

$$h_{d.max} = 72.1 - 67.5e^{-0.765 \cdot P^{0.667}}, \tag{3}$$

Estimation of runoff coefficients for different types of surfaces in Lviv (Table 2) were done using the Curve Number method, which is most often used today in US engineering practice (Urban hydrology, 1986) and around the world.

Table 2. Estimated values of runoff coefficients ψ by the Curve Number method of the (Urban hydrology, 1986) for the city of Lviv

Return period P, years	**Rainfall depth $h_{d.max}$, mm**	**Runoff coefficient ψ**	
		impervious surfaces	**pervious surfaces**
0.1	14.85	0.677	0.040
0.25	22.27	0.767	0.0001
0.5	30.41	0.821	0.016
1	42.24	0.867	0.067
2	56.23	0.897	0.135
3	63.46	0.908	0.168
4	67.43	0.913	0.186
5	69.69	0.916	0.196

The maximum daily flow rates of the stormwater runoff of different return periods, estimated by the rational method, are given in Table 3.

Table 3. Estimated maximum daily flow rates of the stormwater runoff at the inlet of Lviv WWTP and corresponding relative errors

Return period P, years	**Rainfall depth $h_{d.max}$, mm**	**Maximum daily flow rates $W_{d.max}$, th. m^3/day**	**Errors**	
			$+\delta W_{max}$, %	**$-\delta W_{max}$, %**
0.1	14.85	182.42	2.34	2.31
0.25	22.27	285.55	2.50	2.47
0.5	30.41	428.96	2.45	2.42
1	42.24	680.06	2.30	2.27
2	56.23	1026.0	2.13	2.11
3	63.46	1220.8	2.06	2.04
4	67.43	1331.8	2.03	2.01
5	69.69	1396.1	2.01	1.99

5. Summary and Conclusions

New detailed actual data on the problem and tendencies of the flooding of urban areas in Central and Eastern Europe were obtained.

The analysis of methods of hydrological and hydraulic modelling of the first flush discharge of stormwater runoff from urban catchments was presented with special emphasis on the approaches used in Ukraine.

Using a rational method, as well as the results of large-scale interdisciplinary surveys and studies of the Baltic Sea catchment within the territory of the Lviv city, the maximum daily stormwater runoff flow rates at the inlet of Lviv WWTP were estimated as the function of return period, that should be recommended for using in the implementation of the feasibility study of the reconstruction and modernization of Lviv WWTP.

References

1. Bach, P.M., McCarthy, D.T., Deletic, A.: Redefining the stormwater first flush phenomenon. *Water Research,* 44(8), 2487–2498, 2010.
2. Bayazıt, Y., Koç, C., Bakış, R.: Urbanization impacts on flash urban floods in Bodrum Province, Turkey. *Hydrological Sciences Journal*, 66(1), 118−133, 2021.
3. Bell, V.A., Moore, R.J.: The sensitivity of catchment runoff models to rainfall data at different spatial scales. *Hydrology and Earth System Sciences,* 4, 653–667, 2000.
4. Bellos, V., Papageorgaki, I., Kourtis, I. et al.: Reconstruction of a flash flood event using a 2D hydrodynamic model under spatial and temporal variability of storm. *Natural Hazards*, 101, 711–726, 2020.
5. Bertrand-Krajewski, J.L., Chebbo, M.G., Saget, A.: Distribution of pollutant mass vs volume in stormwater discharges and the first-flush phenomenon. *Water Resources,* 32(8), 2341–2356, 1998.
6. Blöschl, G., Kiss, A., Viglione, A. et al.: Current European flood-rich period exceptional compared with past 500 years. *Nature,* 583, 560–566, 2020.
7. Cristiano, E., ten Veldhuis, M. C., van de Giesen, N.: Spatial and temporal variability of rainfall and their effects on hydrological response in urban areas − A review. *Hydrology and Earth System Sciences,* 21, 3859–3878, 2017.
8. Deng, Z.Q., de Lima, J.L., Singh, V.P. Fractional kinetic model for first flush of stormwater pollutants. *Journal of Environmental Engineering,* 131(2), 232−241, 2005.
9. Di Modugno, M., Gioia, A., Gorgoglione, A., Iacobellis, V., La Forgia, G., Piccinni, A.F., Ranieri, E.: Build-up/wash-off monitoring and assessment for sustainable management of first flush in an urban area. *Sustainability,* 7(5), 5050−5070, 2015.
10. Dottori, F., Szewczyk, W., Ciscar, M.J.C., et al.: Increased human and economic losses from river flooding with anthropogenic warming. *Nature Climate Change,* 8, JRC111224, 781–786, 2018.
11. https://www.lanuv.nrw.de/umwelt/wasser/niederschlag/niederschlag-online.

12. https://www.swr.de/swraktuell/rheinland-pfalz/koblenz/bad-neuenahr-ahrweiler-nach-dem-hochwasser-100.html.
13. https://www.swr.de/swraktuell/rheinland-pfalz/rlp-hochwasser-2021-uebersicht-karte-100.html.
14. https://www.diepresse.com/6009677/1200-feuerwehreinsatze-in-wien-mehrere-stromausfalle.
15. https://www.kleinezeitung.at/oesterreich/6009570/Hochwasser-in-Oesterreich_Wetterberuhigung-soll-nun-Entspannung].
16. https://www.dwd.de/DE/leistungen/besondereereignisse/niederschlag/20210721_bericht_starkniederschlaege_tief_bernd.pdf;jsessionid=0727186698CDF5A64A9F389EE24EF716.live21063?__blob=publicationFile&v=10.
17. https://kurier.at/chronik/niederoesterreich/ueberschwemmungen-und-historische-regenmengen-in-graz/401459287.
18. https://meteofrance.com/actualites-et-dossiers/actualites/climat/ inondations-catastrophiques-en-allemagne-et-belgique.
19. https://www.meteoschweiz.admin.ch/home/aktuell/meteoschweiz-blog.subpage.html/de/data/blogs/2021/7/heftige-gewitter-und-intensiver-regen.html.
20. https://www.eswd.eu/.
21. James, W.: Rules for responsible modelling. 4th ed. CHI Catalog Number: R184, 304, 2005.
22. James, W., Rossman, L.: Water systems models. User’s guide to SWMM 5, 13th ed., CHI Press Publication, Ontario, Canada, 905, 2010.
23. Klein, T.A.M.G., Wijngaard, J.B., Können, G.P. et al.: Daily dataset of 20th-century surface air temperature and precipitation series for the European Climate Assessment. *International Journal of Climatology: A Journal of the Royal Meteorological Society*, 22(12), 1441−1453, 2002.
24. Kulbida, M.I., Oliinyk, Z.Ia., Palamarchuk, L.V., Halytska, Ye.I.: Analiz rezhymu opadiv na terytorii Ukrainy za desiatyrichchia 2002−2011. *Fizychna heohrafiia ta heomorfolohiia*, 1(69), 127−138, 2013.
25. Lee, H., Lau, S., Kayhanian, M., Stenstrom, M.K.: Seasonal first-flush phenomenon of urban stormwater discharges. *Water Research*, 38, 4153–4163, 2004.
26. Maier, R., Krebs, G., Pichle,r M., Muschalla, D., Gruber, G.: Spatial rainfall variability in urban environments − high-density precipitation measurements on a city-scale. *Water*, 12(4), 1157, 2020.

27. Osadchyi, V.I.: Klimatychna prohrama Ukrainy yak osnova tsilisnoi ekolohichnoi polityky derzhavy v umovakh zminy klimatu. *Visnyk NAN Ukrainy,* 6, 81–84, 2021.
28. Salvadore, E., Bronders, J., Batelaan, O.: Hydrological modelling of urbanized catchments: A review and future directions. *Journal of Hydrology,* 529(1), 62–81, 2015.
29. State of the Global Climate 2020. WMO-No.1264. *World Meteorological Organization,* 38, 2021.
30. Tatarchuk, O., Tymofeiev, V.: Kharakterystyka naibilshoi misiachnoi kilkosti opadiv na terytorii Ukrainy v umovakh suchasnoho klimatu. Visnyk Kyivskoho natsionalnoho universytetu im. T. Shevchenka. *Heohrafiia,* 1(63), 33–37, 2015.
31. Tkachuk, S.H., Zhuk, V.M.: Rehuliuvannia doshchovoho stoku v systemakh vodovidvedennia: monohrafiia. Lviv: Vydavnytstvo Lvivskoi politekhniky, 216, 2012.
32. Urban hydrology for small watersheds. United States Department of Agriculture. *Technical Release* 55, 164, 210-VI-TR-55, 2 ed., 1986.
33. Zhuk, V.M., Malovanyi, M.S., Mysak, I.V., Tymchuk, I.S., Mushalla, D., Pikhler, M.: Chasova ta prostorova nerivnomirnist vypadannia doshchiv pry modeliuvanni poverkhnevoho stoku z urbanizovanykh terytorii. *Naukovyi visnyk NLTU Ukrainy*, 31(5), 67−73, 2021a.
34. Zhuk, V.M., Malovanyi, M.S., Mysak, I.V., Tymchuk, I.S., Mushalla, D., Pikhler, M.: Mizhdystsyplinarni pidkhody pry modeliuvanni doshchovoho stoku na zabudovanykh terytoriiakh. Zbirnyk materialiv II Mizhnarodnoi naukovo-praktychnoi konferentsii "Ekolohiia. Dovkillia. Enerhozberezhennia", prysviachenoi 203-richchiu Natsionalnoho universytetu "Poltavska politekhnika imeni Yuriia Kondratiuka" (2-3 hrudnia 2021 roku). Poltava: NUPP, PP "Astraia", 143−145, 2021b.
35. Zhuk ,V., Vovk, L., Matlai, I., Popadiuk, I.: Maximum daily stormwater runoff flow rates at the inlet of the Lviv WWTP based on the results of systematic hydrologic observations of the catchment. Lecture Notes in Civil Engineering: *Proceedings of 2nd International scientific conference on EcoComfort and current issues of civil engineering EcoComfort 2020,* 100, 514–521, 2021c.

On the issue of sanitary and hygienic condition of the river network of the Pokutsko-Bukovynian Carpathians

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Abstract

The sanitary-hygienic and microbiological condition of surface waters of the river network of the Pokutsko-Bukovynian Carpathians is analyzed. As a benchmark for comparing the impact of anthropogenic activities on the state of mountain ecosystems, we have chosen the protected areas of the Vyzhnytskyi National Nature Park (hereinafter NNP), where for more than two decades a specific ecosystem has been formed related to environmental protection.

The main risks to the ecological safety of the hydrosphere of the studied region have been identified. Two types of ecological threats have been identified: microbiological pollution of streams and watercourses by domestic effluents and washes of polonyn farms and pollution of the hydrosphere by effluents of processing enterprises. Contamination of surface waters with organic residues is accompanied by a change in their hydrochemical composition and the level of contamination of indicative forms of bacteria. Based on the monitoring studies of the hydrosphere, the main threats were identified and engineering and technical and management solutions were developed to minimize the level of ecological danger of the mountain ecosystem.

In order to improve the quality of surface waters of the river network, the use of special structures "ViKa", mounted on the basis of wooden structures of pulp and fibrous carrier "Via", as well as the use of a modified method of obtaining pellets and wood waste from adjacent loggers based on lignin soap. To reduce the inflow of discharges into the river network of alcohol enterprises, in the absence of centralized treatment facilities in the region, the method of waste treatment using a reagent method based on sodium hypochlorite was quite effective.

It is shown that one of the ways to reduce the loss of the river network by wood waste may be the creation of facilities for the production of fuel pellets and briquettes in traditional economic landscapes.

Keywords: surface waters, river network, organic pollution, water quality, protected areas, engineering and technical solutions, Pokutsko-Bukovynian Carpathians

1. Introduction

A lot of research has been done to determine the quality of surface water, which proves the urgency of this issue in connection with the exacerbation of the problem of drinking water on the planet. Assessing surface and groundwater quality remains a major public interest in the developed world fecal contamination of water and thus to assess health hazards (Ince et al., 2011; Rylskkyi and Masikevych, 2012; Pall et al., 2013). Identification of pathogenic bacteria in water, according to a number of researchers, is one of the main problems in assessing the safety of the environment for human health and the ecosystem in general. Microbiological contamination of E. coli is one of the specific indicators of fecal contamination in tropical and temperate regions. The study of bacterial water density can provide an approach to assessing the reliability of monitoring darta. Fecal indicator bacteria, such as total coliform forms, fecal coliforms (themotolerant coliform forms), Escherichia coli and intestinal enterococci (fecal streptococci), are released by humans and warm-blooded animals into wastewater in large quantities, and these bacteria retain longevity and longevity (Megan et al., 2020; Srivastava, 2020). In order to study the differential detection and quantification of the viability of Escherichia coli cells in recent years, in addition to traditional methods of culture on nutrient media, use quantitative polymerase chain reaction (Deshmukh et al., 2021), flow cytometry, inclusion and sequencing of the 16S rRNA gene (Kirschner et al., 2021).

Pathogens themselves are normal components of natural ecosystems, but the growth of fecal bacteria due to anthropogenic activity is a very important problem of the river network of the Carpathians and in particular the Danube basin (Kirschner et al., 2021 Mayr et al., 2021; Pekarova et al., 2021). Studies conducted by the authors have shown that the Danube Delta, where the biosphere reserve is located, has become one of the most vulnerable ecosystems. The Danube is one of the most important rivers in Europe and the world. To preserve its ecosystem in 1991 in the river delta created a biosphere reserve. Despite this, the water areas of the Danube are subject to severe physical, chemical and biological pollution. The river network of the Pokutsko-Bukovynian Carpathians is a component of the Danube basin (its upper part), where intensive anthropogenic activity is developing. Bacteria turned out to be ideal markers of microbial contamination of surface waters due to their rapid response to environmental changes.

Fecal coliforms and intestinal enterococi are good indicators for assessing fecal emissions and the potential presence of pathogens, which are mainly due to untreated wastewater from agricultural lands and pastures. However, the low concentration of bacteria in surface waters, high costs and long-term detection technologies create certain methodological limitations in this way.

Therefore, the search for simple and affordable technologies for detecting minor amounts of pathogens remains relevant today. It should be noted that the use of sanitary-microbiological indicators to assess the condition of protected areas is now episodic and does not apply to specific functional areas of these areas (Mudrak, 2012; Patyka and Symochko, 2013).

2. Materials and Methods

2.1. Object and concept of research

The object of the study was the sanitary-hygienic and microbiological indicators of surface waters in the region of Pokutsko-Bukovynian Carpathians. The aim of the research was to investigate the ecological condition and to develop a system of engineering measures to minimize the ecological danger to the river network. The defining point of the research was the monitoring of pollution in the Pokutsko-Bukovynian Carpathians. The hydrological grid of the research region is presented in Fig.1.

As a benchmark for comparing the impact of anthropogenic activities on the state of the river network of mountain ecosystems, we chose protected areas located in the Pokutsko-Bukovynian Carpathians, in particular the Vyzhnytskyi National Nature Park (hereinafter NNP). To prevent microbiological contamination of streams and watercourses, we used a fibrous carrier type "Vija" (TU (995990), made of textured plait thread (TU 6-06-C116-87, tex 350). Earlier, a number of authors (Hvozdiak, 2003) found that the fibrous carrier "Vija" can be successfully used for the construction of "bioreactors" for surface degree of purification. The reliability of the results is ensured by laboratory control of errors in the composition of the samples and mathematical verification of data for a statistically significant relationship using rank correlation coefficients. The validity and reliability of the conclusions and recommendations are confirmed by the close connection of theoretical and experimental data. water treatment. Invertebrates, where they are able to accumulate, which is the basis of water treatment. In addition, some bacteria become part of the food chain and serve as food for invertebrates trophic chains on the second. To minimize the environmental risk of pollution of the hydrosphere by effluents of processing industries used a reagent method of contamination (use of sodium hypochlorite solution), which is effective, reliable, allows to provide the required.

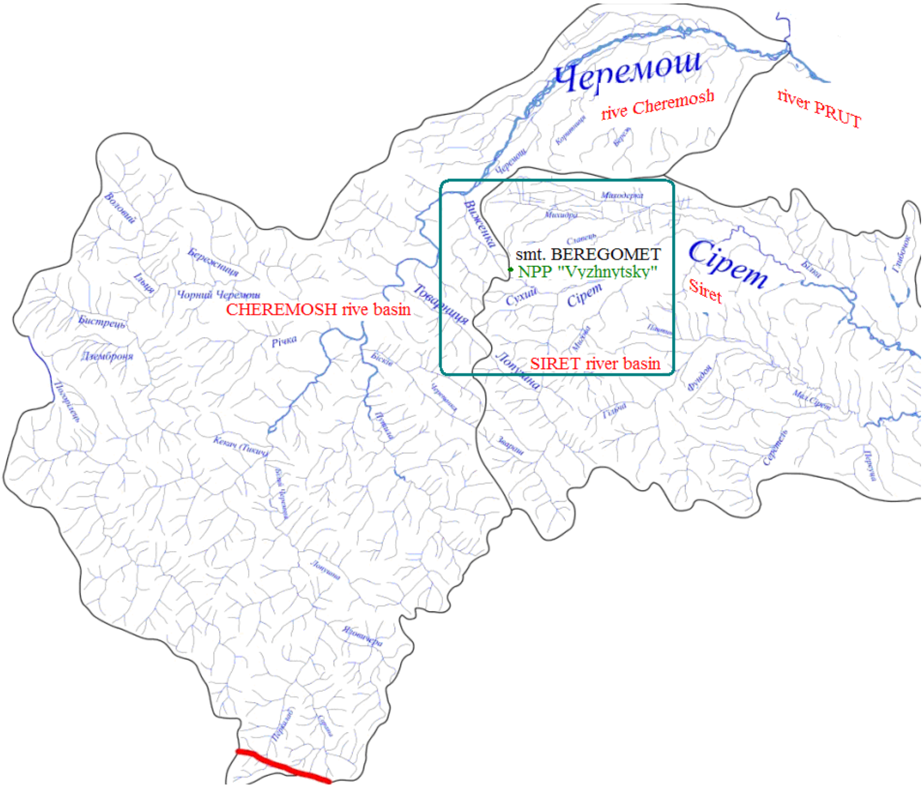

Fig.1. Hydrological network of the Pokutsko-Bukovynian Carpathians

2.2. Methods for determining the sanitary and hygienic indicators, chemical composition and pH of the aquatic environment

Determination of chemical oxygen consumption (COC) determined by the dichromate method according to the method in the presence of phenylanthranilic acid as a redox indicator of orange green (MVV 081/12-0019-01). The value of chemical oxygen consumption (COC, mg O_2/dm^3).

The biochemical oxygen consumption (BOC-5) index was determined by the method (MVV 081/12-0014-01).

Determination of the pH of the aqueous medium. The pH of the aqueous medium was determined by electrometric method, according to DSTU 4077–2001. "Water quality. Determination of pH" and instructions for the device Ionomer laboratory I-160 MI.

Water sampling was carried out in the Cheremosh and Siret river basins, which flow into the Pokutsko-Bukovynian Carpathians and are part of the Ukrainian part of the Danube basin. The research was conducted during the summer season of 2013–2020. Water sampling (23–25ºC) was carried out by watercourses of various functional zones of the protected object of national importance (Vyzhnytskyi National Nature Park) and territories of landscapes with intensive economic activity. Coli-index, total microbial count was determined by generally accepted methods in accordance with methodological guidelines (Nakaz MOZ Ukrayiny 284, 2007).

To confirm the morphological and other properties of the culture of microorganisms used the method of microscopy with subsequent identification according to the determinant of Bergi (Khoult et al., 1997).

3. Results and discussion

3.1. Sanitary and microbiological condition of surface waters

The obtained results show that downstream of the studied watercourses in the territories of the NNP (at the transition from the protected to the economic zone), the nitrate content increases in the water, the BOC indicator increases and the dissolved oxygen decreases. It is established / that there is an increase in pollution of the river network with organic residues, in particular they may be fecal compounds of the economic zone, where there are no active treatment facilities. Studies of sanitary and hygienic indicators of the part of the river network adjacent to the Vyzhnytskyi National Park and not part of it, showed a significant increase in the content of suspended solids in water (mainly sawdust – wood processing waste), compared with the reference "protected" area of the NPP (Table 1). The increase in the content of suspended solids is accompanied by a decrease in free oxygen in the water and an increase in the value of BOC, COC, total oxidation. At the same time, the content of chlorides and nitrites (salts of hydrochloric and nitric acids) in water increases, which leads to acidification of the river network (pH = 5.8, below the norms (San PiN 4360-88; Surface Water Directive). It also turned out that the river network of territories with traditional management in terms of sanitary and hygienic indicators is inferior to the quality of water samples taken from the watercourses of the "economic zone" of the NNP (Fig. 2).

In addition, we conducted a study of the microbiological state of water of all these objects. Indicators include coli index, coli titer, and microbial count. In most cases, there is a direct correlation (r = 0.95) between the indicators of biological BOC, COC and the value of microbiological indicators. Studies have shown that the values of sanitary-microbiological indicators increase downstream in all these watercourses. This was especially true of the increase in the number of lactose-positive Escherichia coli (E. coli) per 1 liter of water (coli-index). It should be noted that Escherichia coli is a sanitary indicator and indicates fecal contamination in this case of water bodies.

Comparing the coli-index in the river water samples of the protected area and the selected water samples in the economic zone, we found an increase in the coli-index on average by 2 times (Table 1).

The total microbial count (CFO/dm^3) was 2–4 times higher than the normative indicators adopted in the EEC countries (Surface Water Directive: 75/440 EEC) and was 1500–1700 (for the protected area), 2300–3500 (for the stationary recreation area) and more than 5000 (for the economic zone).

A comparative analysis of microbiological indicators of surface water bodies of the NNP economic zone and traditional management areas adjacent to the protected object is shown in table 1, which shows that there is a significant difference in water quality in the river network between these areas.

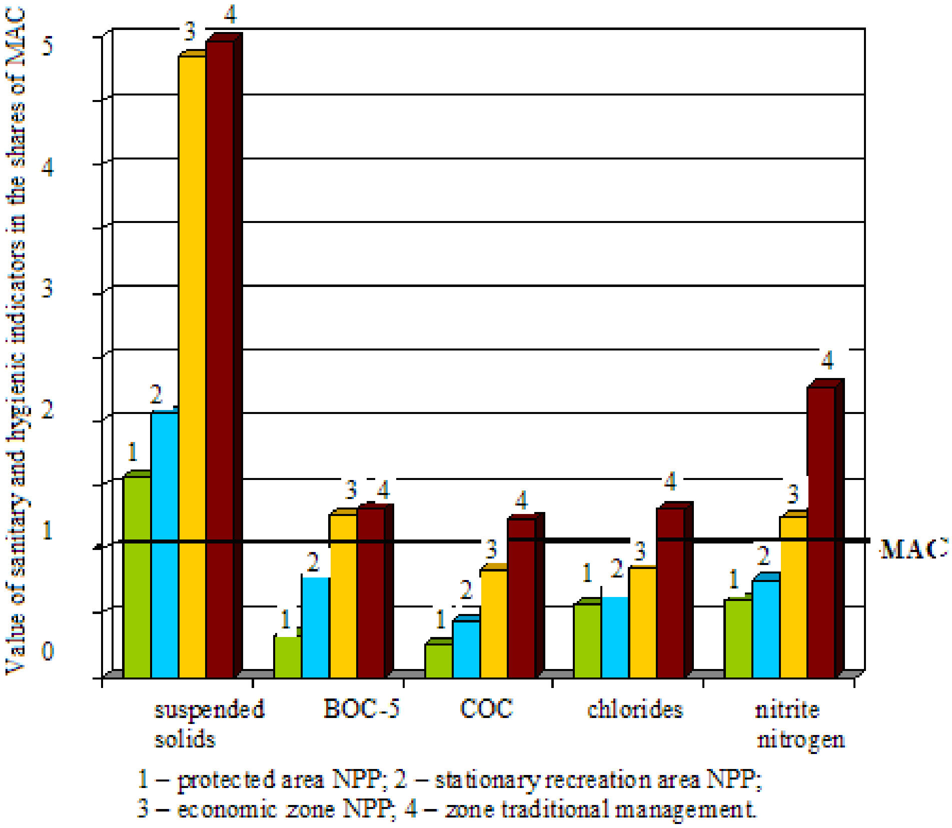

Fig. 2. Sanitary and hygienic indicators of surface waters of Pokutsko-Bukovynian Carpathians in shares of maximum allowable concentration (MAC)

Table 1. Comparative analysis of sanitary-microbiological indicators of surface waters of the economic zone of NPP "Vyzhnytskyi" and adjacent to the NPP areas of traditional management

N	**Sanitary-micro-biological indicators**	**economic zone**	**adjacent areas NPP**	**(±), в %**	**San PiN 4630-88**	**EEC Water Directive**
1	Coli Index (CFO/dm^3)	107.5 ±13.5	122 ±10.2	+13.5		
2	Total microbial count (CFO/dm^3)	5350 ±270	6500 ±310	+21.5	<5000	<5000

- CFO – colonies forming organisms

Figures 3 show the dynamics of the main microbiological indicators of the aquatic environment of different functional load and conservation status of the Pokutsko-Bukovynian Carpathians over the past 10 years.

Based on monitoring observations, it can be stated that there is a progressive trend of pollution of the river network in the territories of traditional economic landscapes, which are outside the protected areas and where there is active anthropogenic activity. At the same time, the relative stability of the studied indicators of the hydrosphere is preserved within the protected areas, despite the existing some annual fluctuations.

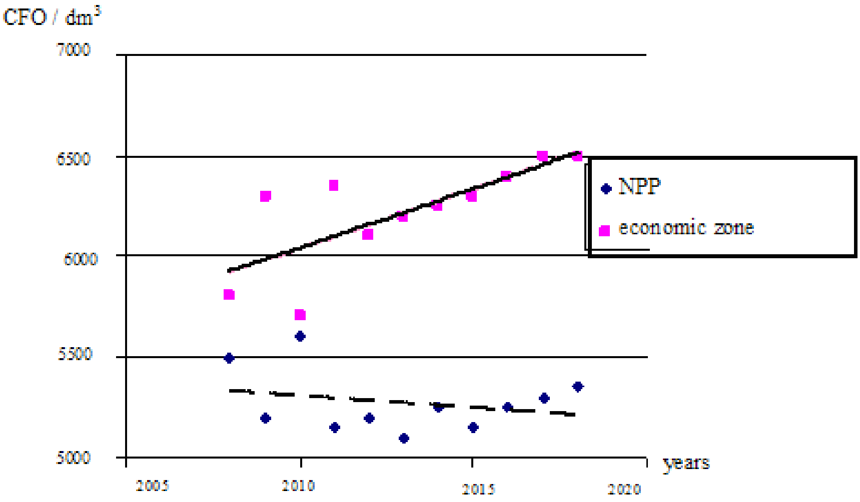

Fig. 3. Dynamics of the total microbial number of surface waters of the river network of the Pokutsko-Bukovynian Carpathians; CFO – colonies forming an organism/dm^3; the difference is significant at $p < 0.05$

3.2. Technical measures are aimed at improving surface water quality

Research to reduce the level of organic and microbiological pollution of watercourses. In order to improve the quality of surface waters of watercourses, we used a fibrous carrier type "Via" (TU (995990), made of textured plait thread (TU 6-06-C116-87, tex 350). Previously, a number of authors (Hvozdiak, 2003; Rylskyi and Masikevych, 2012) established that the fibrous carrier "ViKa" can be successfully used for the construction of "bioreactors" for surface water treatment, for saturation of streams with oxygen. This design is presented in Fig. 4.

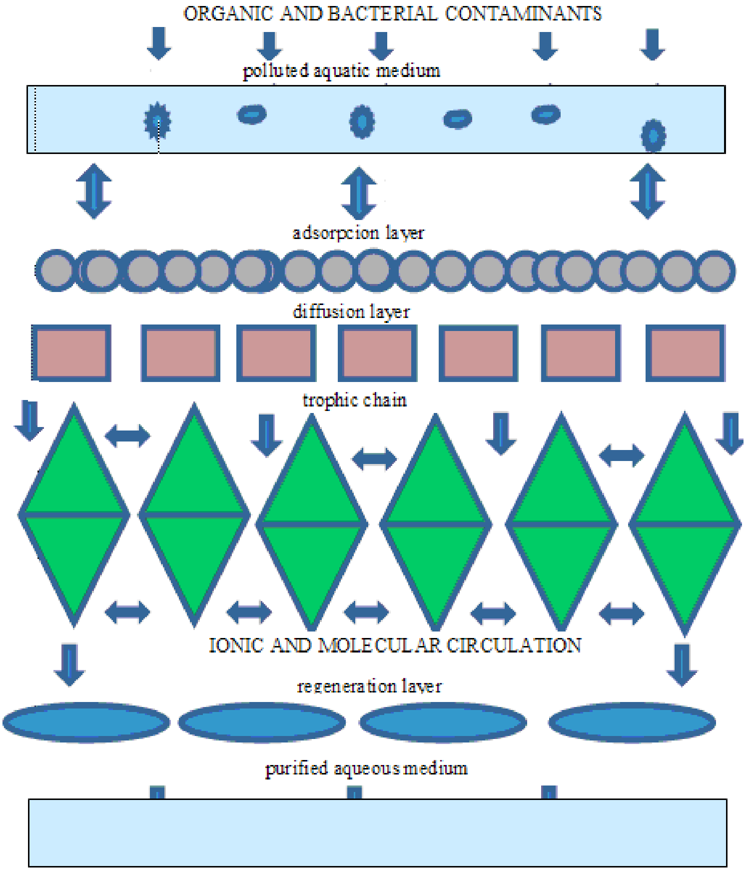

Fig. 4. Schematic representation of the processes occurring in the "bioreactor – ViKa"

During the season, "Vija" is overgrown with invertebrates (the so-called periphyton is created). Bacteria and algae also accumulate on the eyelashes. As can be seen from Figure 5, "Vija" is capable of almost 15–fold accumulation of bacteria and aquatic organisms.

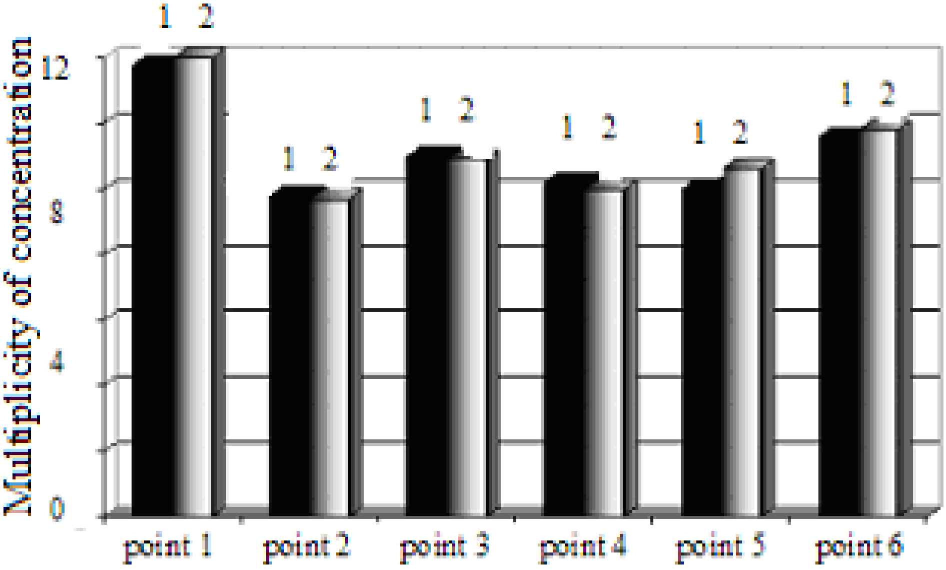

Fig.5. Accumulation of bacteria and aquatic organisms on a fibrous carrier type "Vija":
1 – temperature 23ºC, 2 – temperature 6ºC

A specific "biofilter" is formed on fibrous media in the form of an artificially created microecosystem. In it, such a carrier serves as a kind of "home" for microorganisms, plant and invertebrates, where they are able to accumulate, which is the basis for water treatment. In addition, some bacteria become part of the food chain and, consequently, food for invertebrates. Thus, the purification of reservoirs is observed in two stages: due to adsorption on a synthetic carrier on the first and a trophic chain on the second. The mounted cleaning device "ViKa" ("Vija" + "Kashytsia") works on the principle of a bioconveyor, which was once described by P. I. Hvozdyak (Hvozdiak, 2003). In fact, the proposals and arguments presented by the author became both a theoretical and methodological basis for the creation of the treatment plant "ViKa". The "ViKa" bioconveyor accumulates a significant amount of BECG (Escherichia coli bacteria), forming a spatial succession of microorganisms, as well as a trophic chain of aquatic organisms, which includes representatives of eight systematic groups: see section 3). In terms of numbers, the studied microperiphyton was dominated by ciliates (510 specimens/100 cm^2), rotifers accounted for 33% of the total number of fouling biocenosis. Both prokaryotes (aerobic and anaerobic microorganisms) and eukaryotes (filters and predators of different trophic levels) take part in the water purification process. The advantages of the proposed scheme of natural water treatment are that the biomass accumulated on "Via" is consumed and mineralized in the trophic chain, as evidenced by the indicators of BOC, COC, the amount of suspended solids in the water. For comparison, we note that during the treatment of wastewater with activated sludge involved in the process only protozoa and bacteria (others can not survive in the toxic fluid of collectors), while in the case of treatment plant "ViKa" also involved more complex aquatic organisms (consumers II tv. III order), forming a more complete trophic chain. In nature, a priori, there is no organism that could dispose of all types of pollution and even yourself. On the contrary, there are many organisms in the biosphere that form complex hydrobiocenoses and that are able to work on the principle of "bioconveyor". There are many examples when treatment plants based on synthetic fiber "Via", arranged for direct-flow biotechnology, have become very efficient, easy to maintain, environmentally friendly, low-cost facilities that have been operating for decades. Thus, we can assume that the fibrous carrier "Via" (which is similar in structure to man-made fibers) not only serves as a substrate where BGKP and a number of aquatic organisms accumulate, but also is a hiding place from predators and a source of food because it retains particles gross detritus. The results obtained by us fully confirm the opinion (Hvozdiak, 2003) that "the future of biotechnology to protect the environment, in particular water, from chemical and biological pollution – in the use of as much diversity as possible in these technological processes."

Wastewater treatment of an alcohol enterprise by the reagent method.

Pollution of the hydroecosystem of the Pokutsko-Bukovynian Carpathians and Precarpathians by effluents of small processing enterprises, which contain mostly organic pollutants, can be minimized, in our opinion, by an effective reagent method that allows for effective treatment. The most available, safe, and cheapest reagent that can be used to oxidize organic compounds is sodium hypochlorite, a multi-ton production waste.

Indicators such as COC and dry residue were used as criteria for cleaning efficiency. The protocol of sewage tests of Vashkivtsi distillery showed an increase in wastewater, the concentration of nitrates, sulfates, suspended solids and indicators of COC and BOC, which suggests the presence in the discharges of proteins, fats and carbohydrates and the process of biodegradation of organic pollutants. The results of experimental studies are presented in Fig. 6.

As can be seen from Figure 6, it is optimal to use hypochlorite for sewage treatment in the ratio of 0.5 L/m^3 of the effluent to be treated. This ratio is recommended for the introduction of industrial wastewater treatment technology at the Vashkivtsi distillery.

Improving the technology of wood waste disposal. We studied the technology of utilization of wood processing waste by creating fuel pellets and briquettes using as a binder waste pulp – paper production – sulfate soap, the main component of which is lignin. This approach allows to significantly reduce the working pressure in the equipment where the pellets are formed, and to involve in the production of low-grade wood waste. In the process of extrusion method of obtaining granules, to improve their quality, we used a lignin binder. In Fig. 7 shows the results of experiments to determine the static strength of the briquette with the addition of different concentrations of binder.

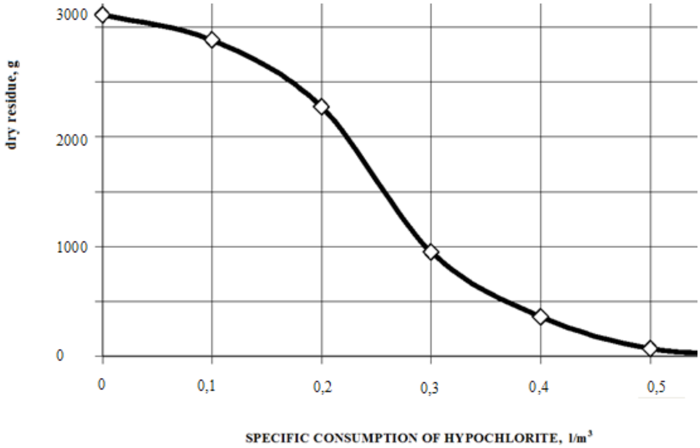

Fig. 6. The dependence of the mass of the dry residue on the specific consumption of hypochlorite

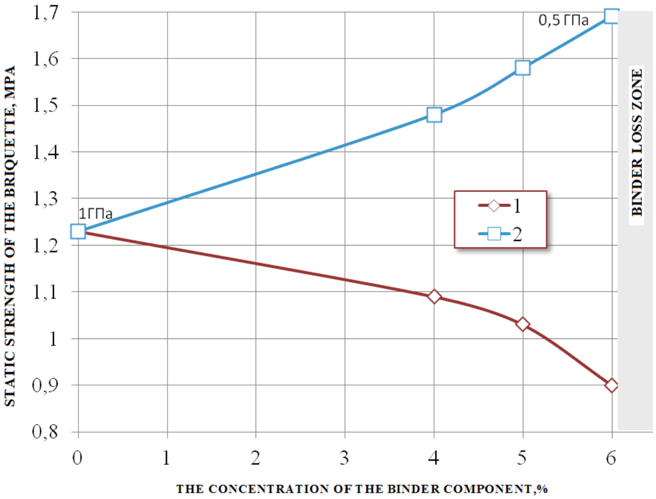

Fig. 7. Change in the static strength of the briquette with different concentrations of binder depending on the pressure: 1 – supply of the binder component in the center of the mixture, 2 – mixing of the binder component with wood waste

From fig. 7 shows that the static strength increases in those briquettes in which the binder was mixed with wood waste. This is due to the better distribution of the binder within the volume of the briquette with the formation of a reinforcing frame of wood, and the binder did not allow it to disintegrate.

4. Summary and Conclusions

As a result of research, 2 types of environmental threats to surface waters of the region were identified: microbiological pollution of streams and watercourses and pollution of the hydrosphere by effluents of processing enterprises, which are a common industry in the study region. The prospects of the method of biological purification from organic and microbiological pollution of watercourses of the hydroecosystem of the Pokutsko-Bukovynian Carpathians and minimization of ecological danger from their negative impact on the hydrosphere by using a fibrous carrier type "Via" are proved. A method of wastewater treatment of processing enterprises from organic pollutants by oxidation of them with sodium hypochlorite has been developed. The proposed method does not require a radical restructuring of existing treatment facilities and significant material costs to create new ones based on our proposed technology. Failure to comply with the requirements for the formation of protected areas on the watershed principle leads to significant contamination of soils and river network with sawdust, bark and other wood waste requires the introduction of urgent measures for the disposal of this type of waste. Grinding of wood waste and their preparation do not require large costs, and lignin-binding substance requires proper disposal.

References

1. Ince, B.K., Cetecioglu, Z., Ince, O.: Pollution Prevention in the Pulp and Paper Industries. *Environmental Management in Practice,* 2011. DOI:10.5772/23709.
2. Rylskyi, O.F., Masikevych, Yu.H.: Mikrobiolohichna bioindykatsii dovkillia zabrudnenoho vazhkymy metalamy ta inshymy ksenobiotykamy. *Visnyk Zaporizkoho natsionalnoho un-tu*, 3, 139–147, 2012.
3. Páll, E., Niculae, M., Kiss, T., Şandru, C.D., Spînu, M.: Human impact on the microbiological water quality of the rivers. *Journal of Medical Microbiology*, 62, 11, 2013. DOI:10.1099/jmm.0.055749-0.

4. Brauwere, A., Ouattara, N.K., Servais, P.: Modeling Fecal Indicator Bacteria Concentrations in Natural Surface Waters: A Review. *Critical Reviews in Environmental Science and Technology,* 44–21, 2380–2453, 2014. DOI:10.1080/10643389. 2013. 829978.

5. Devane, M.L., Moriarty, E., Weaver, L., Cookson, A., Gilpin, B.: Fecal indicator bacteria from environmental sources; strategies for identification to improve water quality monitoring. *Water Research,* 185(3), 116204, 2020. DOI:10.1016/j.watres.2020.116204.

6. Deshmukh, R., Bhand, S., Roy, U.: BCIG-SMAC medium and PMA-qPCR for differential detection of viable *Escherichia coli* in potable water. *Iranlan Journal of Microbiology,* 13(5), 624–631, 2021. DOI:10.18502/ijm.v13i5.7427.

7. Kirschner, A.K.T., Lindner, G., Jakwerth, S., et al.: Assessing biological stability in a porous groundwater aquifer of a riverbank filtration system: combining traditional cultivation-based and emerging cultivation-independent *in situ* and predictive methods. *Österr Wasser- und Abfallw* 73, 490–500, 2021. DOI:10.1007/s00506-021-00801-0.

8. Mayr, M.J., Besemer, K., Sieczko, A., Demeter, K., Peduzzi, P.: Bacterial community composition and function along spatiotemporal connectivity gradients in the Danube floodplain (Vienna, Austria). *Aquatic Sciences,* 82–28, 2020. DOI:10.1007/s00027-020-0700-x.

9. Pekarova, P., Mészáros, J., Miklánek, P., Ilic, A.: Long-Term Runoff Variability Analysis of Rivers in the Danube Basin. *Acta Horticulturae et Regiotecturae,* 24, 37–44, 2021. DOI:10.2478/ahr-2021-0008.

10. Mudrak O.V.: Zbalansovanyi rozvytok ekomerezhi Podillia: stan, problemy, perspektyvy. *Vinnytsia,* 914, 2012.

11. Patyka, V.P., Symochko, L.Yu.: Mikrobiolohichnyi monitorynh gruntu pryrodnykh ta transformovanykh ekosystem Zakarpattia Ukrainy. *Mikrobiolohichnyi zhurnal*, 75, 2, 21–31, 2013.

12. Hvozdiak, P.: Za pryntsypom biokonveiera. *Visnyk NAN Ukrainy,* 3, 29–36, 2003.

13. MVV 081/12-0019-01. Poverkhnevi vody. Metodyka vykonannia vymiriuvan khimichnoho spozhyvannia kysniu (KhSK) okyslenniam dykhromatu (5–100 mh O_2/dm^3). URL:http://online.budstandart.Com/ua/catalog/doc-page.html?id_ doc=76354.

14. MVV 081/12-0014-01. Poverkhnevi vody. Metodyka vykonannia vymiriuvan biokhimichnoho spozhyvannia kysniu (BCK5) (0.5–15 mh O_2/dm^3). URL: http://online.budstandart. com/ ua/catalog/doc-page.html?id_doc=76349.

15. DSTU 4077-2001 Yakist vody. Vyznachennia rN: Zatverdzheno: nakaz Derzhstandart vid 12.03.2002 r. № 146. URL: http://document.ua/jakist-vodi_-viznachannja-rn-std2236.html.

16. Sanitarno-virusolohichnyy kontrol' vodnykh ob"yektiv: metod. vkazivky MV 10.2.1-145-2007. Pro zatverdzhennya metodychnykh vkazivok. Sanitarno-virusolohichnyy kontrol' vodnykh ob"yektiv. Nakaz MOZ Ukrayiny N 284 vid 30.05.2007 r. Dodatok 1. Rezhym dostupu: http://www.moz.gov.ua/docfiles/8203_dodatok.rar.

17. Dzh, K., Krig, N., Smit, P., Dzh. St., Uill`yams, S. Opredelitel` bakterij Berdzhi. Devyatoe izdanie v 2-kh tomakh.; Perevod s anglijskogo *G.A. Zavarzina Moskva,* 1–2, 800,1997.

18. SanPiN 460-88.

19. Surface Water Directive: 75/440 EEC.

Radon its occurrence and effects on various aspects of human life

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Abstract

Radon is a chemical element that belongs to the group of noble gases on the periodic table. It is a colorless gas and has radioactive properties. During decay it emits alpha radiation, and also beta radiation only to a much lesser extent. It is an element with low penetrability but high ionizing ability. It has a high atomic mass of 222u which makes it a stable isotope (Przylibski, 1999). It dissolves well in water, but also in other liquids. Its half-life is 3.8 days while forming a number of short-lived derivatives such as isotopes of polonium, bismuth and lead, which also have radioactive properties (Hrynkiewicz, 2001). So far, radon and its properties have been studied, among others, by Tadeusz Przylibski in his work entitled "Radon – a specific component of therapeutic waters in the Sudety Mountains". The author characterized radon as an element; its genesis, migration and accumulation in the in the lithosphere, examining the geological structure of the Sudety Mts. and attempting to present potentially therapeutic radon waters (2005); Jadwiga Mazur – "Dynamics of radon exhalation from soil, meteorological parameters and soil properties". The author discussed such issues as radon in health aspect; radon in soil including transport, emanation and exhalation (2008); Mirosław Janik Mirosław Janik in his doctoral thesis entitled: "Radon penetration from soil to building. Computer modelling and verification in residential buildings", presented radon in relation to ionizing radiation and its effects, as well as radon sources in soil, a model of radon penetration from soil into a building and a scharacteristic model of radon from the ground to the building, and characterized the permeability of the ground to radon (2005); Jakub Nowak developed the topic: "Natural radioactivity of thermal waters of the Polish Carpathians" taking into account the correlation of natural radioactivity of thermal waters of selected countries in the world, including Poland with the concentration of radon 222Rn, which appears in water supply networks (2013). Taking a close look at the above-mentioned work, as well as using other sources, in the first part radon will be characterized in terms of its occurrence, impact on human health and life, and then after preliminary studies of 222Rn activity activity in water to determine if and in what quantities it appears in waters used in everyday life.

Keywords: radon activity in water, radioactivity, radon health effects

1. Introduction

Radon studies in water are conducted in Poland on a regular basis only for spa waters in the Sudety Mountains (Pochocki et al. 2001). Radon is a colorless, odorless, tasteless, non-flammable, monatomic gas. The density of radon under normal conditions is 9.82 kg/m^3 in the liquid state – 6600 kg/m^3, in the solid state – 8040 kg/m^3. It belongs to the group of helihydrides therefore its properties resemble other elements from this group. It dissolves in water as shown in Figure 1 and in organic solvents. During discharges in a rarefied atmosphere it shines with white light. When cooled down below the freezing point it shines with an intense brilliant-blue light (Miliszkiewicz, 1978).

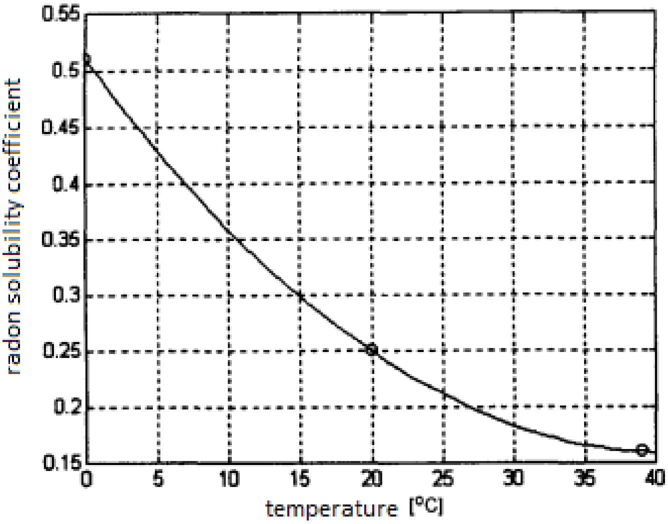

Fig. 1. Solubility coefficient of radon in water as a function of water temperature (Nazaroff, Nero; 1988)

The melting point is – 71ºC, while the boiling point is – 61.7ºC. Radon, as a noble gas, is chemically inactive. Even after excitation it does not react with oxygen, magnesium, hydrogen, sodium or sulfur. It forms clathrates (wider groups) and so, for example, with fluorine it forms fluorides and with chlorine – chlorides. Reacts with fluorides: CIF_3, BrF_3, BrF_5. There are 33 isotopes of radon known with mass numbers from 196 to 229. Radon is represented in nature by four natural radioactive isotopes: ^{222}Rn (radon), ^{220}Rn (thoron), ^{219}Rn (actinone), 218Rn. Their names were formed from the name of the radioactive series in which each radon isotope is formed. The isotope with mass number 222 has the longest half-life; the other isotopes are short-lived (Janik, 2005). As a natural radioactive element, it accounts for more than 50% of the contribution to the total dose absorbed by the population from all possible sources of ionizing radiation. In the lithosphere, its occurrence is not limited only to uranium and thorium minerals, which are its sources. In very small amounts, however, it appears in all soils and rocks. In typical soil air, ^{222}Rn concentrations range from 4 to 40 kBq·m^{-3} (Lorenc et al., 2005). In the compact, gas-free lithosphere, radon ^{222}Rn is in radioactive equilibrium with its parent element, radium ^{226}Ra. Radium rarely occurs alone in the environment. All geologically old rocks and minerals contain measurable amounts of this element. In rocks, radium isotopes are in equilibrium with their parent isotopes, i.e. ^{238}U, ^{235}U and ^{232}Th, unless environmental factors such as weathering, hydrological activity or biological processes disturb this equilibrium. The highest radium content is found in granitic rocks, metamorphosed magmatic rocks, and shales, where the average concentration is about 50 Bq·kg$^{-1.}$ (Podgórka et al., 2020).

Radon enters waterways primarily from soil, building materials, ^{222}Rn migration from rocks and soils, and from natural gas, or air. If you are dealing with drinking water with high concentrations of radon, there is a risk of transferring large quantities of the gas to the air inside the dwelling. The penetration of radon into the air is mostly through the same pathways as into water. Radon dissolves well in water (at 0°C it is 510 cm^3/ to 130 cm^3 but also in other liquids. Its half-life is 3.8 days and it forms a number of short-lived derivatives such as isotopes of polonium, bismuth and lead, which also have radioactive properties. Having a very high solubility it can appear in drinking water (Bogacz et al., 2001). In Poland there are clearly defined standards for the quality of water intended for human consumption. The Regulation of the Minister of Health of 7 December 2017 assumes for radon in drinking water as a reference level of 100Bq/L (Regulation, 2017). According to the US Environmental Protection Agency (EPA), the limit for radon in water is only 11 Bq/L (EPA, 2021; El-Badry et al., 2020). Water exceeding 74 Bq/L has medicinal properties. The activity concentrations of ^{226}Ra and ^{228}Ra are significantly affected by the desorption/adsorption characteristics of the waters. When groundwater has similarities in terms of: age, physical conditions, uranium and thorium activity concentration ratios in the aquifer formation, and is characterized by low flow (up to a few mer per year), radium isotope concentrations and their ^{226}Ra/^{228}Ra activity ratios increase with increasing desorption rates and decrease with increasing adsorption rates. In groundwater systems, sulfate waters have relatively low desorption and high adsorption coefficient, and radium isotope concentrations are relatively low. In contrast, high desorption rates and low adsorption coefficients lead to relatively high radium contents, where the ^{226}Ra/^{228}Ra activity ratio exceeds 1 and this is typical of chloride waters. Bicarbonate waters show intermediate properties (Chau et al., 2011; Chau et al., 2016). Reduction of radium isotope content in water may also result from their precipitation from water to the rock surface, e.g. in the Polish Carpathians, where radium activity concentration decreases with increasing sulfate concentration in water. A schematic of the behavior of the isotopes ^{226}Ra and ^{222}Rn after escape from the rock in soil is shown in Figure 1 (Mazurek-Rudnicka).

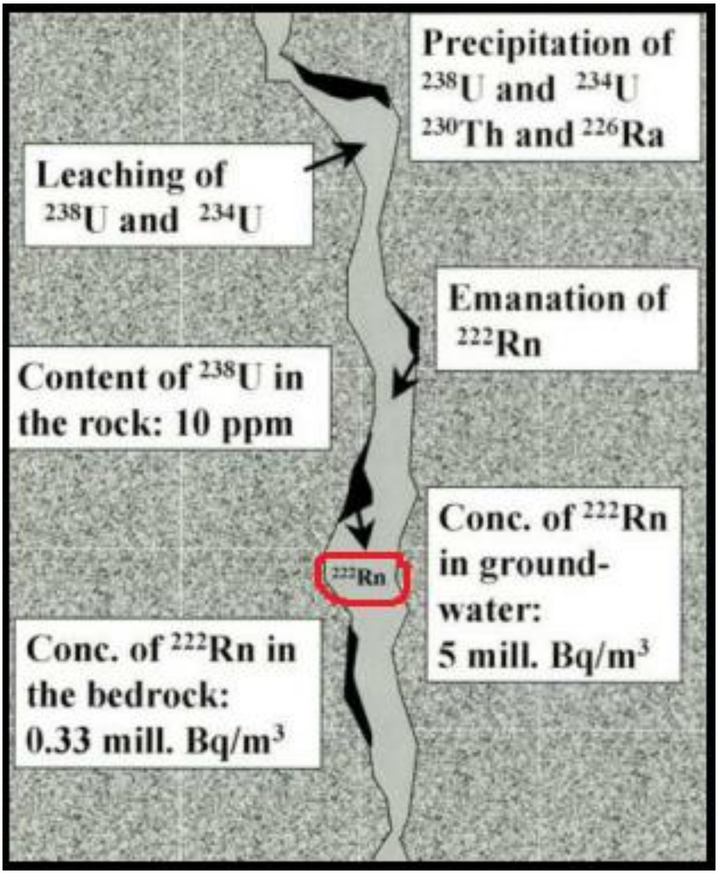

Fig. 2. Radium and radon precipitation into the water layer (Suleiman et al., 2013)

Water intended for drinking should meet the highest quality standards, including acceptable levels of radioactive elements. Radon is a well-documented risk factor for cancer induction. In recent years, there has been an increased interest in population exposure to radon and radon-related products. Attempts are being made to assess the risk of lung cancer from indoor exposure to radon and its derivatives (Muras, 1995). The results so far are inconclusive, probably because it is the effect of low doses of radiation that are interfered with by other factors with carcinogenic effects, such as cigarette smoke and irritants. Other factors that affect these ratings to varying degrees are social problems, lifestyle habits, and industrialization, which has been linked with the occurrence of lung cancer (Bilska, 2016). As early as 1988, radon was recognized as a class I carcinogen by the International Agency for Research on Cancer. Miners are the most vulnerable to harmful effects. In addition to exposure to radon concentration, smoking is an additional factor exacerbating this condition. In Poland, apart from this social group, studies have not revealed high mortality rates due to exposure to radon. It is worth adding that there are opinions on the positive influence of radon on human health. We are talking here about the phenomenon of radiation hormesis. Therefore, radon waters are used for therapeutic purposes for such ailments as coronary insufficiency, primary bronchial asthma or male infertility. In addition, radon has a beneficial effect on diseases of the locomotor system and strengthens the immune system. Waters containing radon are used in therapeutic baths, drinking cures and inhalations. In summary, the effect of radon is difficult to classify as harmful. Its impact on human health and life depends on the dose received (Strupczewski, 2005). Increasing public awareness about radon and other harmful elements emitted to water and the environment is very important. For this purpose, the activity of radon was analysed in water from the intakes of the water supply network.

The results of studies on radon activity in waters of Wielkopolska Province, studied in a doctoral dissertation by Daria Mazurek-Rudnicka titled: "Radiological exposure of the population related to the presence of natural radionuclides in drinking waters from the southern Wielkopolska region" were compared.

2. Materials and methods

The first very important thing to study radon activity in water is proper sampling. The water was taken into 1.5 L PET bottles after free flowing water from the tap. It was poured full (under the cork) to prevent the formation of air bubbles. It was then transported to the laboratory. Tests for ^{222}Rn activity in water are conducted using specialized AquaKIT equipment (manufactured by Genitron GmbH) connected to AlphaGUARD PQ200PRO ionization chamber shown in Fig. 2. In order to obtain correct test results, it must be remembered that half-life of radon – ^{222}Rn is only 3.825 days. Therefore, the collected water sample must be taken to the laboratory as soon as possible. The water in the water in the water supply network was taken for measurement of radon activity after a few minutes of free flowing. Two samples each were taken from 3 different intakes in Kielce district; in 1.5 L PET bottles. The first samples were taken from domestic taps, while the second from outdoor taps after different time of free flow of water from the pipes supplying it (after 6 and 9 min). The samples were transported to a specialist laboratory equipped with the equipment discussed above and tested for radon content. The results are shown in Figure 3.

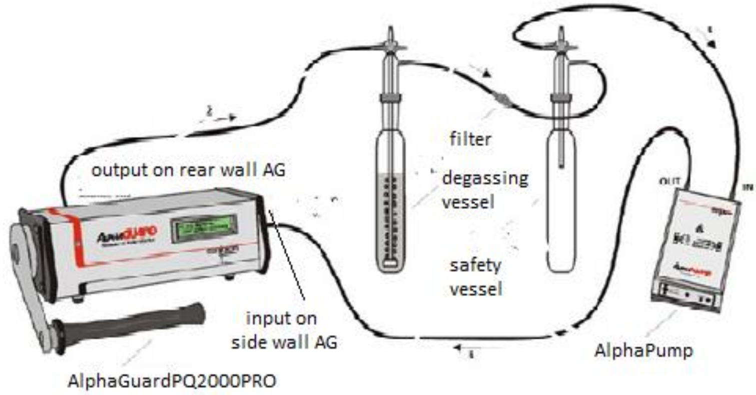

Fig. 3. Kit for measuring ^{222}Rn concentration in water samples (Przylibski, 2003)

The kit for measuring ^{222}Rn concentration in water samples shown in Figure 3 consists of a portable radon monitor (AlphaGUARDTM); a gas-tight pump with a step-regulated gas flow rate from 0.03 to 1.0 $dm^3 \cdot min^{-1}$ (AlphaPUMPTM) and a gas-tight kit for degassing the water sample and, most importantly, for releasing the dissolved radon. These components are connected in a hermetically sealed circuit. The measuring station also includes an immersion thermometer (measures the temperature of the water during the measurement); a stopwatch measuring the exact time of measurement; a "docker" (thanks to it it is possible to connect a syringe with a taken water sample to the system, as well as a syringe included in the AquaKITTM set with a volume of AquaKITTM with a volume of 100 cm^3. Thanks to the connection of the AlphaGUARDTM monitor with a computer, all the data from the measurement are transmitted and collected, and then the necessary calculations are performed. This monitor is the basic instrument on the test bench because it performs the actual measurement of ^{222}Rn concentration. The measurement takes place in an ionization chamber equipped with filters to contain radioactive radon decay products as well as contaminants. Radon enters the chamber with ambient air via the AlphaPUMPTM pump. Before entering the chamber, the air is pumped through a glass vessel to degas the water sample, and then through a containment vessel called a desiccant, The water sample is placed directly into the degassing vessel by connecting a syringe to the "docker" and gently injecting water in such a way that no turbulent flow is induced which could cause partial escape of radon. Immediately after the 100 cm^3 water sample is introduced into the degassing vessel, the valves in this vessel and in the assurance vessel are closed to hermetically seal the measurement system. After transferring a water sample After a 100 cm^3 water sample has been transferred into the measuring system and it is hermetically sealed, and the AlphaGUARD™

is turned on in a one-minute measurement cycle, in flow-through mode, the actual measurement of radon concentration in the water sample, or rather in the air of the ionization chamber into which ^{222}Rn has been extracted from the water, takes place. During the first 10 minutes of the measurement, the AlphaPUMP™ operates by pumping 0.3 $dm^3 \cdot min^{-1}$ of air in a closed circuit: AlphaPUMP™-AlphaGUARD™-AquaKIT™. After 10 minutes of measurement, the pump is turned off and measurements are continued, for another 20 minutes. After 30 minutes from the start of the measurement (pump on), AlphaGUARD™ is turned off, ending the measurement. AlphaEXPERT™ software is used to process the acquired data. This software also provides pre-processing of the data, including reading of the mean ^{222}Rn concentration values and uncertainty of its determination for each 30-minute measurement. Mean ^{222}Rn concentration and uncertainty are given in $Bq \cdot m^{-3}$. Converting this value to ^{222}Rn concentration in water sample is possible using the equation proposed by the kit manufacturer (Koza, 2003).

For the results shown in Figure 4, for each drinking water intake in the study area, samples of raw and treated water were taken into 5 L PET bottles after a few minutes from the moment the tap was turned on and water was flowing freely from the water supply pipes. At four points in the vicinity of each of the studied water intakes, radon ^{222}Rn was extracted from ground air into a scintillator solution to determine the activity concentration of this radionuclide in soil air (Mazurek-Rudnicka, 2020).

3. Results and Discussion

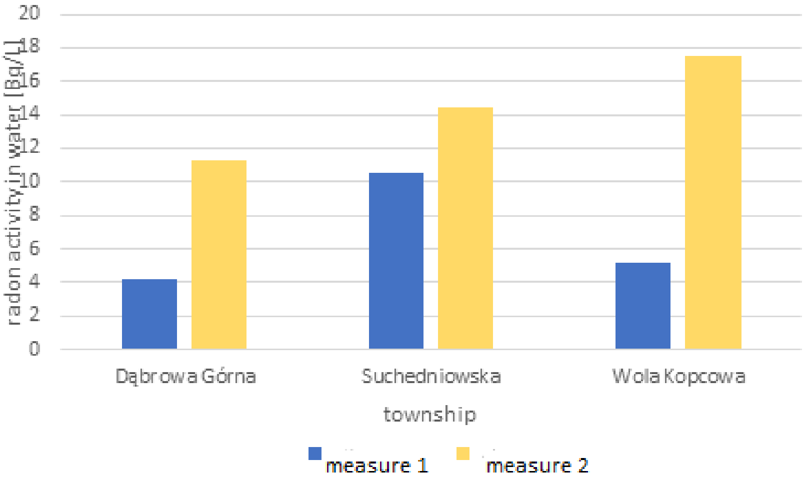

Fig. 4. Results of ^{222}Rn activity determinations in water from the water supply network for selected intakes in Świętokrzyskie voivodeship

Figure 4 shows the results of preliminary studies on radon activity in water in Kielce County. Samples of water were taken from 3 different water intakes: Dąbrowa Górna and Suchedniowska belonging to one commune and Wola Kopcowa located about 15 km away from the others. For the studied intakes there is a clear difference between the concentration of ^{222}Rn activity in domestic water and that from the external tap. The reason may be that the outdoor water is not treated there. The values are for Dąbrowa Górna and Wola Kopcowa intakes almost three times higher than for treated water. The results presented in the figure above are the first values of radon activity in water for intakes in the Kielce region. Its appearance in water may be due to the fact that it penetrates from the ground and dissolves in it very well. Assuming quite strict norms according to which water intended for consumption should not exceed the permissible concentration of 11Bq/L for each of the examined intakes, in the case of water coming from the external tap this norm was exceeded. It is worth noting that fast half-life of radon and the fact that it is absorbed from a liquid into the air make that with time its amount in the intake water will decrease.

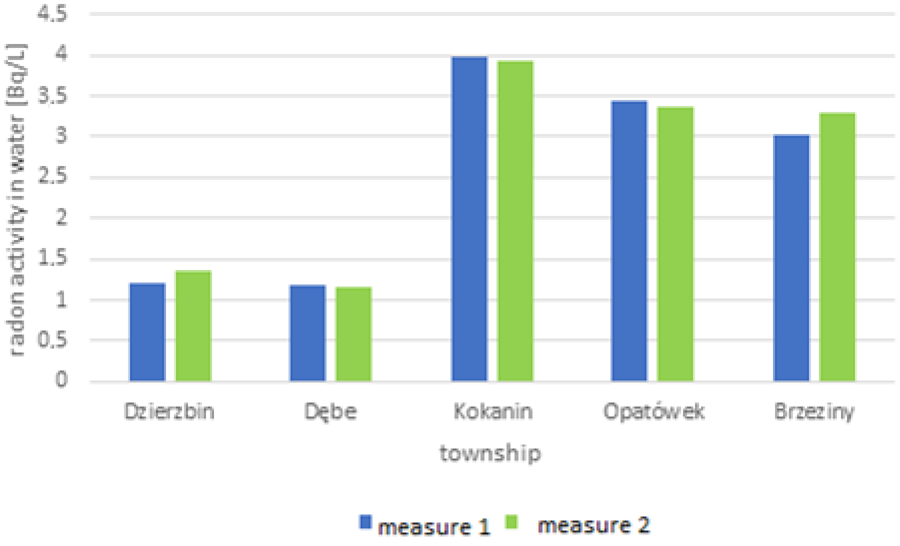

Fig. 5. Results of ^{222}Rn activity determinations in water from the water supply network for selected intakes in Wielkopolska voivodeship (Mazurek-Rudnicka, 2020)

The above graph shows the results of activity of radon ^{222}Rn in water for selected intakes in Wielkopolska region. The results were presented in her PhD thesis by Daria Mazurek-Rudnicka. The author compared these results with radon activity in raw water, where the concentrations were generally higher than in treated water. Water treatment plants make the most of aeration and filtration processes. These activities promote the reduction of radon content in waters. The author showed that concentrations in treated waters are almost twice lower than in raw waters which gives an average value of 2.61 µg/L, which is also close to the average concentration of ^{222}Rn activity in water intended for consumption by the public living in the southern Wielkopolska region. This relation can be seen in the table below.

Table 1 shows the average results of ^{222}Rn activity values in treated and raw water for the intakes in Wielkopolska County. In this comparison the difference of values is visible, which are higher for raw water. After preliminary studies conducted for the intakes in Kielce district, a similar relationship can be observed by referring to Figure 4.

Tab. 1. Average values of activity of ^{222}Rn in water for selected intakes in Wielkopolska province for raw and treated waters (Mazurek-Rudnicka 2020)

Intake	**Average value for treated waters [Bq/L]**	**Mean value for raw water [Bq/L]**
Dzierzbin	1.29	2.53
Dębe	1.17	1.98
Kokanin	3.95	4.65
Opatówek	3.41	4.44
Brzeziny	3.15	4.67

4. Summary

Analyzing the theoretical part about radon and the part with the results and their analysis, the following conclusions were made:

– radon concentrations in the air that the average person breathes when exceeded as well as in water can harm health and lead to cancer;

– radon entering the air from water leads to worse health effects than that which we consume by drinking water;

– studies on radon content in water were conducted e.g. for therapeutic waters, where no harmfulness was found, assuming that water having of ^{222}Rn activity above 74 Bq/L has therapeutic properties;

– radon concentrations for drinking water are still not clearly defined. In Poland a reference level of 100 Bq/L is assumed for radon in drinking water. According to the US Environmental Protection Agency (EPA) the limit for radon in water is only 11 Bq/L. Precise studies on the concentration limit are still open;

– radon levels in buildings are dependent on many factors, e.g. what the building is made of; the time of year and time of day are also important for the level of concentration; the higher the floor of the building, the lower the radon concentration will be, because it penetrates most from the building floor;

radon penetrates residential buildings to a large extent from the ground, but also from water;

– preliminary studies of radon activity in water conducted in Kielce County for 3 different intakes: Dabrowa Górna, Suchedniowska and Wola Kopcowa showed that it appears in these waters in small amounts. Figure 3 shows that for waters coming from external taps the concentration of radon activity is much higher in water flowing from external taps;

– the presented results from Daria Mazurek-Rudnicka's PhD thesis showed a similar relationship for the regions of southern Wielkopolska. The author first examined raw water and then treated water. Analyzing the results she came to unequivocal conclusions that raw water has twice the concentration of ^{222}Rn activity in water. She argued for lower activity of this radioactive element in waters treated with aeration and filtration during treatment, where radon activity in water is reduced.

References

1. Bartak, J., Machaj, B., Pieńkos, J.: Apparatus for measuring radon concentration in air Institute of Chemistry and Nuclear Technology, Warsaw.
2. Bilska, I.: Impact of radioactive radon and its derivatives on human health. *Medycyna Środowiskowa – Environmental Medicine*, 19(1), 51–56; 2016.
3. Bogacz, J., Mazur, D., Swakoń, J., Janik, M.: The calibration of activated charcoal detectors in a small 222 Rn exposure chamber, *Radiation Measurements*, 33, 873–878, 2001.
4. Chau, N.D., Duliński, M., Jodłowski, P., Nowak, J., Różański, K., Śleziak, M, Wachniew, P.: Natural radioactivity in groundwater – a review. *Enveromential and Health Studies*; 47(4), 415–433, 2011.
5. Chau, N.D., Rajchel, L., Nowak, J., Jodłowski, P.: Radium isotopes in the Polish Outer Carpathian mineral waters of various chemical composition. *Journal of Eviromental Radioactivity*; 112, 38–41, 2016.
6. Data obtained from the Environmental Protection Agency, https://www.google.com/search?q=enviomental+protection+agency+information+about+radon&ei=Pyw7YcDCA4SSwPAPh8akAU&oq=enviomental+protection+agency+information+about+radon&gs_lcp=Cgdnd3Mtd2l6EANKBAhBGABQg6QCWMuHBGD3iQRoBXACeACAAdgBiAGxG5IBBzE5LjE0LjGYAQCgAQHAAQE&sclient=gwswiz&ved=0ahUKEwiA3pS_kvTyAhUECRAIHQcjCV8Q4dUDCA4&uact=5 (June 2021).

7. Journal of Laws Item 2294 Decree of the Minister of Health dated December 7, 2017.
8. El-Badry, B., Al-Naggar, T., Khouqeer, G.: Monitoring the levels of radon and toxic element pollutants in bottled drinking water. *International Journal of Radiation Research*, 428, 2020.
9. Hrynkiewicz, A. et al.: Man and ionizing radiation. PWN, 16, 2001.
10. Janik, M.: Radon transfer from soil to building. *Computer modelling and verification in residential buildings*, 7, 9, 2005.
11. Koza, W., Skowronek, J., Chałupnik, S.: Radon exhalation rate chamber; *Research Repootrs Mining and Environment*, 3, 83–87, 2003.
12. Kozak, K, Mazur, J.: Techniques for decreasing of indoor radon concentration (in Polish), Radon in the Environment of Living, Work and Study of Lower Silesia Inhabitans, Polski Klub Ekologiczny, Okręg Dolnośląski, ISBN: 978-83-89983-10-7, Wrocław, 2006.
13. Lorenc, A., Goldsztejn, P.: Distribution of radon concentrations in underground waters of the Ladek – Śnieżnik metamorphic area. *Prace Naukowe Instytutu Górnictwa Politechniki Wrocławskiej, Studnia i materiały*, 113, Wrocław, 2005.
14. Mazur, J.: Report No. 2014/AP Dynamics of radon exhalation process from soil, and meteorological parameters and soil properties, Cracow, 2008.
15. Mazur, J., Kozak, K., Horwacik, T., Haber, R., Zdziarski, T.: Influence of meteorological conditions on radon measurements in soil – preliminary results. *GIG Mining & Environment, Research Report*, NORM IV Conference Szczyrk, Poland, 59, 2004.
16. Miliszkiewicz, A.: Radon, PWN, Wrocław, 1978.
17. Muras, K.: Uranium mining in Poland in 1948–63. The problem of threats to humans and the environment. *Bezpieczeństwo Jądrowe i Ochrona Radiologiczna*, 23, 41–52, 1995.
18. Nazaroff, W.W., Nero, A.V.: Radon and its decay products in indoor air. John Wiley & Sons, 1988.
19. Nowak, J.: Natural radioactivity of thermal waters in the Polish Carpathians. Krakow, 2013.
20. Podgórka, Z., Słonecka, I., Koszuk, Ł.: Radon and its sources. *Guidebook of a young explorer*, Warsaw, 2020.

21. Przylibski, T.A., Adamczyk, A.: New stand for measurements of concentrations of radon 222Rn in water in the Hydrogeological Laboratory at the Faculty of Mining, Wrocław University of Technology. *Prace Naukowe Instytutu Górnictwa Politechniki Wrocławskiej*, 103, Seria: *Conferences*, 36, 329–343, 2003.
22. Przylibski, T.A.: Radon concentration changes in the air of two caves in Poland. *Journal of Environmental Radioactivity*, 1999.
23. Przybilski, T.: Radon specific component of therapeutic waters of the Sudety Mts; 3–4, Wrocław, 2005.
24. Przylibski, T., Gorecka, J., Kowalska, A., Fijałkowska-Lichwa, L., Zagożdżon, K., Zagożdżon, et al.: 222Rn and 226Ra activity concentrations in groundwaters of southern Poland: New data and selected genetic relations. *J. Radioanal. Nucl. Chem*., 301, 757–764, 2014.
25. Pachocki, K., Gorzkowski, B., Różycki, Z., Wiejczyk, J., Smoter, J.,: Radon-222 in drinking water from Jelenia Góra, 2001.
26. Suleiman, A., Tukura, Z., Funtua, I., Abdullah, M., Kurowska, E., Suleiman, M.: Radon dynamics, activity concentration and radiological hazards associated with groundwater around the quake-prone Federal Capital Territory o environs, north-central Nigerial. *Arabian Journal of Geosciences*, 2479, 2021.
27. Atomic Laws Act, 2019, item 1792.

Prognosis models of surface water status

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Abstract

The problem of the state of surface waters is one of the key challenges of humanity. In accordance with the goals of sustainable development for Ukraine, where more than 70% of all water using falls on surface waters, the issues of assessing the state of water resources, their monitoring are very relevant. The main global challenges in the field of water safety are a careful study of the patterns of impact of climate change on the state of water resources, rational integrated water management and more. Two of the 17 global sustainable development goals are directly related to the environmental security of water resources.

The main problems regarding the rational use and protection of water resources of Ukraine are: pollution of water bodies with harmful emissions and insufficiently treated industrial and domestic wastewater; moral aging of fixed assets for water supply and water protection purposes, low productivity of treatment facilities; insufficient self-healing and self-cleaning ability of aquatic ecosystems; unbalanced management system, characterized by high volumes of water resources in the economy and high water content of products.

The hydrochemical parameters dynamics of river surface waters is analyzed. Based on the analysis of extensive time monitoring data, a forecast of integrated hydrochemical parameters was made.

The aim of the work was to assess the state of the surface water by integrated hydrochemical parameters and their regression analysis. On the basis of regression analysis, mathematical models of oscillations of the studied integrated indicators (pH, suspended solids, dissolved oxygen, BOD_5) were created during 2008–2020.

The object of the study – integrated hydrochemical indicators of the water status of the river Inhul at the observation point Sofiyivske Reservoir (drinking water intake of Novy Buh) during 2008−2020.

The method of regression analysis through the software of the Windows Excel CurveExpert environment was used to determine empirical dependencies and search for connections.

Based on the obtained functions, prognoses for 2021−2030 based on average annual averages have been developed. The main anomalous values of measurements of 2008−2020, as deviations from the specified function, are determined and the causes of such anomalies, which have anthropogenic origin due to the activity of communal and agricultural sectors of the economy, are determined. The determined sinusoidal dependences of the integrated water quality indicators allowed outlining the average time of fluctuations in the processes of self-organization of river waters, which is about 6 years, and confirms the theory of "waves of life".

Keywords: surface water quality, water security, hydrochemical indicators, regression analysis, the prognosis of the environment state

1. Introduction

Water infrastructure is the basic infrastructure that is a component of economic developed countries, urban and rural development, the source of life in the literal sense of the word. However, as if realizing the importance of water in life, our society is treated too carefree on water issues. Year after year, the situation is slowly worsening, cities and communities are increasingly facing water scarcity, poor quality, pollution and drying of water bodies (Mitryasova et al., 2017; Chugai et al., 2020; Jepson et al., 2017; Mitryasova et al., 2018). The main global challenges in the field of water security are a careful study of the patterns of climate change impact on water resources, rational integrated water management, etc. Among the 17 global sustainable development goals, two are directly related to water security (Staddon et al., 2017; NRDC, 2013; Butler et al., 2016; Mitryasova et al., 2020; Gersonius et al., 2013; Ward et al., 2019).

In 2014, Ukraine signed the agreement on EU-Ukraine association: we recognized that the soviet or post-soviet water management system has exhausted and should move to the European model, which is more successful and understandable to our strategic partners. European legislation gives the EU board of directors 10 years to implement the agreement phased implementation.

The main problems regarding the rational use and protection of water resources of Ukraine are pollution of water bodies with harmful emissions and insufficiently treated industrial and domestic wastewater; moral aging of fixed assets for water supply and water protection purposes, low productivity of treatment facilities; insufficient self-healing and self-cleaning ability of aquatic ecosystems; unbalanced management system, characterized by high volumes of water resources in the economy and high water content of products (Yurasov et al., 2012; Vasenko et al., 2017; Mitryasova et al., 2020).

The growth of anthropogenic activity leads to excessive pollution of water resources (Petrov et al., 2020, Mitryasova et al., 2017, Wang et al., 2018). Assessment of surface water quality takes into account in time and space the state of the water body, which allows identifying trends in water quality, helps to determine the anthropogenic pressure and the consequences of water conservation measures (Bezsonov et al., 2017; Abbasi et al., 2012; Barakat et al., 2011; Casal-Campos et al., 2015).

A negative factor limiting the use of water resources is the deterioration of water quality due to the discharge of wastewater into water bodies, as a result of which water is polluted, loses its useful qualities, and often becomes unusable (Soboleva et al., 2020; Birk et al., 2021). A significant problem of reservoirs of the Mykolaiv area (Ukraine) is dumping of the polluted sewage. Sewage is discharged by 66% of water users, of which 40% discharges contaminated wastewater (Lykhovyd et al., 2018; Shakhman et al., 2017; Bashynska 2018; Mitryasova et al., 2021).

The Black Sea river basin covers about 60% of the area of all river basins in the region and currently the Regional office of water resources monitors the water bodies condition, assesses irrigated lands, agricultural lands and settlements that are flooded, and hydrochemical and radiological control of border water bodies by agreement between the governments of neighboring countries (Ignatowicz 2020; Vlasov and Hryshchankava, 2014).

Surface water monitoring is the basis for prognosis the state of aquatic ecosystems, prevention of environmental crises, sustainable use of water resources to achieve sustainable development goals (Fernandez et al., 2012; Meyer et al., 2019).

The main feature of this study is the temporal analysis of the dependences of the integrated hydrochemical parameters of the Inhul River on temperature, which allows for the creation of forecasts of long-term dynamics and a detailed study of the relationships between chemicals and temperature changes.

A purpose of the study is assessment of the river’s water state by integrated hydrochemical parameters and their regression analysis.

The object of the study – integrated hydrochemical indicators of the water status of the river Inhul at the observation point Sofiyivske Reservoir (drinking water intake of Novy Buh) during 2008−2020.

To achieve the purpose there was a need for a detailed reseach of the water’s characteristics. Based on the regression analysis mathematical models of fluctuations of the studied waters indicators of the Inhul River during 2008−2020 have been studied.

2. Materials and Methods

For mathematical interpretation of data, Microsoft Exel software packages were used - to build graphs of dynamics and point graphs of fluctuations of the studied indicators; CurveExpert – for automatic selection of correlation functions of time and temperature, as well as cross-correlations of BSC5, dissolved oxygen concentrations and suspended solids. Automation of regression analysis of the obtained functions allowed obtaining predictions with an accuracy of 60–80%. The CurveExpert software package was used instead of the Korel software package, as in the automatic analysis of the data set of quarterly dynamics of indicators – it gave critical errors, and the obtained graphs of correlation of hydrochemical parameters with temperature. A figure 1 shows the research stages.

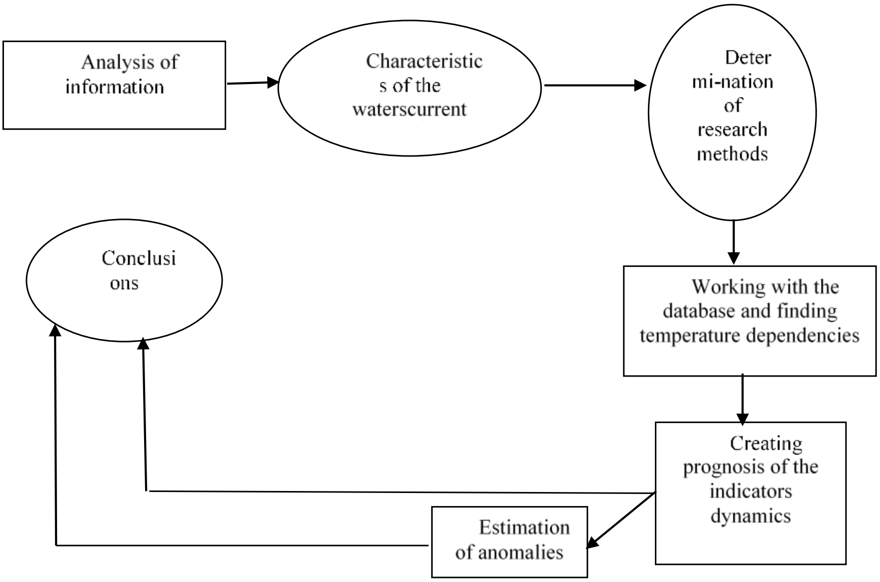

Fig. 1. Research stages

To assess the adequacy of the model used the criterion of significance, or Fisher (formula 1). To determine the significance of the function coefficients, Fisher distribution tables (a = 0.10, a = 0.05) for 120 degrees of freedom and critical Fisher distribution points for 12–17 degrees of freedom (a = 0.01, a = 0.05) are used.

$$F = \frac{R^2}{1-R^2} \cdot \frac{n-m-1}{m}, \tag{1}$$

where: R is the regression coefficient (determination), n is the number of observations, m is the number of factors in the regression equation.

The regression coefficient (determination) is a fraction of the variance of the dependent indicator, which is explained by the obtained function (formula 2).

$$R^2 = 1 - \frac{\sigma^2}{\sigma(y)^2}, \tag{2}$$

where: $\sigma^2(y) = D[y]$ – the variance of the random variable obtained from the measurements; $\sigma^2 = D[y|x]$ – conditional variance depending on the exponent x in the function for which the regression coefficient is located.

The method of estimating the correlation level involves the possibility of direct use of the determination coefficient as a number describing the degree of deviation of the estimated values from the values of the function, and then the qualitative analysis of the correlation degree is carried out in a table 1.

Table 1. Cheddock scale of regression coefficient (determination)

Value	**Interpretation**
R < 0	Inverse correlation
0 < R < 0.2	Very weak
0.2 < R < 0.5	Weak
0.5 < R < 0.7	Average
0.7 < R < 0.9	High
0.9 < R	Very high

The quantification also determines the level of the standard error of rank correlation (formula 3) and builds a balance chart, which in the CurveExpert software package occurs automatically.

$$S = \sqrt{\frac{1 - R^2}{n - 2}}. \tag{3}$$

3. Results and Discussion

To assess and prognosis the state of the aquatic ecosystem, four hydrochemical indicators were analyzed, as well as the water temperature indicator over time.

The integrated indicators were selected, namely:

– pH;
– dissolved oxygen;
– BOD_5;
– suspended solids.

It was decided that for completeness of results it is necessary to cover both the general dynamics of averages by years, and their highs and lows, as well as quarterly maximum, average and minimum values.

During the study, a regression analysis of the dynamics of annual averages and their seasonal quarterly dynamics during 2002–2020 was performed (data from the laboratory of water and soil monitoring of the Regional Office of Water Resources of Mykolaiv region (Ukraine) (Law of Ukraine, Regional report). The recurrence of the studied indicators indicates the cyclical nature of natural and man-made processes that generate them.

The main indicator around which the analysis was carried out is the water temperature. This factor directly affects the biological and chemical processes, as well as the solubility of substances. Analysis of changes in water temperature (Fig. 2), despite the well-known facts of global warming, shows harmonic periodic fluctuations and even some decrease in temperature.

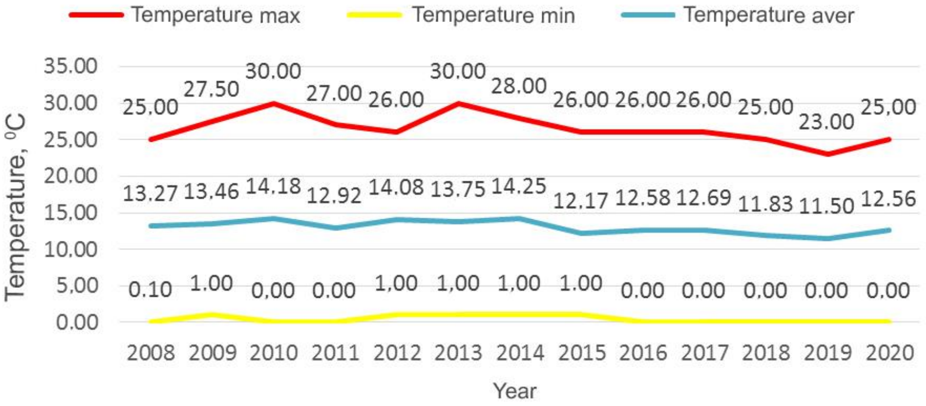

Fig. 2. Changes in temperature

The red line indicates the maximum values of measurements, the blue – the average, the yellow – the minimum. For the maximum measured data (red line), the peak values in 30ºC fall in 2010 and 2013, and the minimum 23ºC – in 2019. For the minimum values (yellow line) the stable mark in 0ºC remains excepting for 2009 and the period from 2012 to 2015, when the minimum values were 1ºC. For average values, which are taken as a basis for further calculations, the peak values fall on 2010 (14.18ºC), 2012 (14.08ºC) and 2014 (14.25ºC).

The graph shows that 2010 was the warmest, while temperature fluctuations in 2012 gave high values of average (14.08ºC) and minimum (1ºC) temperatures, but low for maximum temperature (26ºC). 2013 and 2014 were more balanced in this respect and 2014 saw the middle of the decline in maximum temperatures (28ºC) and the peak for the growth of averages (14.25ºC). The gradual decline of maximum (from 30–26ºC to 26–23ºC), average (from 13–14ºC to 12–13ºC) and minimum temperatures (from 1 to 0ºC) may indicate both a drop in temperature and fluctuations, as part of the cycle.

To determine whether this decline was due to cooling or part of a multi-year cycle, a regression analysis of the mean temperature (blue line) of the research year was performed on the measured 12-year interval. Approximating the obtained data by average temperatures, we obtain a sinusoidal graph with a regression coefficient of 0.81 and a period of oscillation of about 6 years. The obtained function demonstrates harmonic temperature fluctuations.

In the process of constructing a regression dependence, their numbering was adopted, where 2008 is the first year of the study, 2009 is the second, and so on by 2020, which is the twelfth. The same principle is used in subsequent Curve Expert graphs, as it better conveys the sequence of processes.

Deviations were recorded only of the maximum temperatures of 2010 and 2013. The values of average temperatures have been predicted for the next 10 years (Fig. 3).

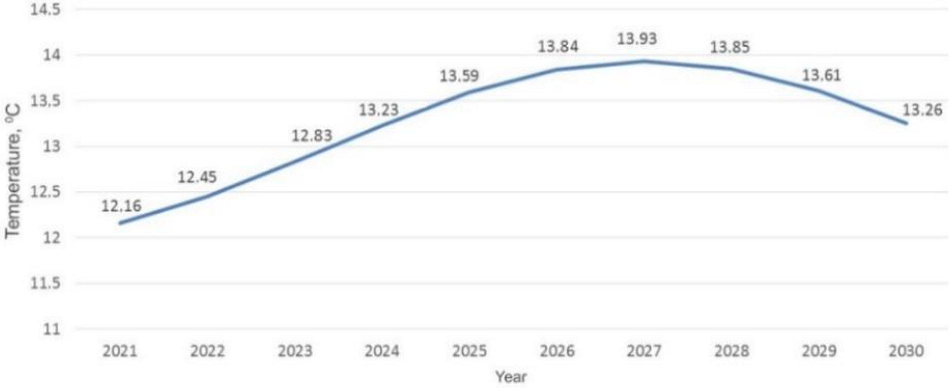

Fig. 3. Water temperature prognosis until 2030 years

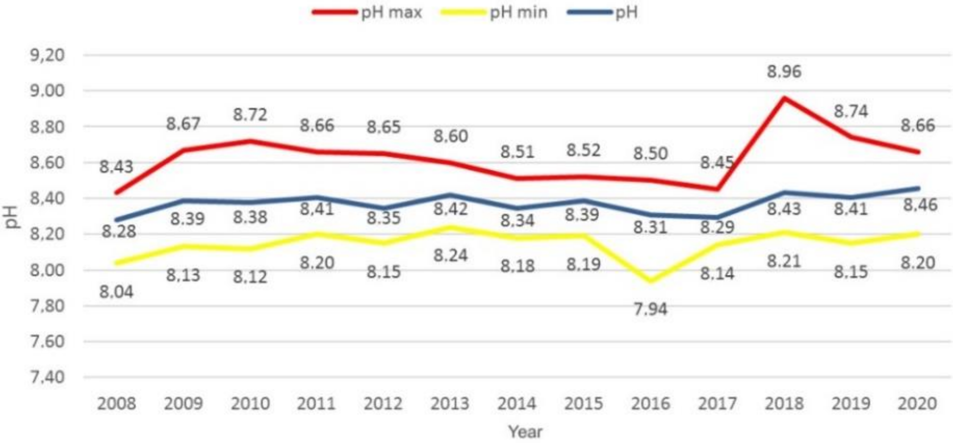

Fig. 4. Changes in the pH

The next indicator, which has been researched was the hydrogen index as one of the main integrated factors (Fig. 4). The value of the indicator is influenced by all physicochemical parameters of the aquatic environment. The minimum was observed in 2016 (7.94), possibly due to precipitation, or due to acid contaminants. The maximum was 8.96 in 2018 when due to the gradual increase during the year, the maximum concentration limit was exceeded (MPC = 6.5–8.5) and the water became alkaline. Also, the excess of the MPC by a small amount of 0.1 was observed.

Values from 2008 to 2020 studies show a average level of correlation with the regression coefficient R = 0.68 (table 1). Approximation of the obtained data shows the same harmonic fluctuations as temperature, but with a lower regression coefficient. We have obtained fluctuations during the 6-year period of a sinusoid (Fig. 5).

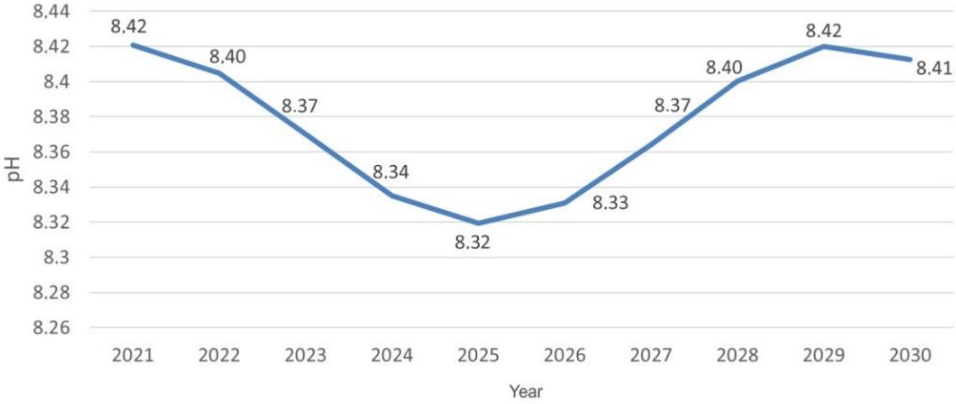

Fig. 5. pH prognosis until 2030 years

Oxygen dissolved in water (Fig. 6) is a key indicator for the activity of aerobic living organisms. There is no maximum concentration limit for this indicator, but at least 4 mg/dm^3 of oxygen is required for the survival of higher living organisms. The minimum figure of 2.8 mg/dm^3, recorded in 2020. This figure is below the subsistence level and well below the summer norm of 6 mg/dm^3. It is caused, apparently, by eutricification of the river waters due to discharges of utilities. Which, in turn, led to the mass extinction of fish in river.

The oxygen content in water is affected by atmospheric pressure, precipitation, mineralization, temperature. The supply of oxygen to the reservoir occurs through the processes of adsorption, photosynthesis, as well as inflowing rainwater, and melt water. The content of soluble oxygen is important for assessing the environmental and sanitary condition of the river ecosystem. The oxygen content must be at a sufficient level necessary for the respiratory processes of aquatic organisms. Soluble oxygen is also necessary for the processes of self-purification of reservoirs, as it participates in redox reactions of organic and mineral substances.

During the study period the content of soluble oxygen ranges from 2.8 mg/dm^3 to 29.06 mg/dm^3 and is subject to seasonal and daily changes (Fig. 6). Reducing the oxygen concentration to 3 mg/dm^3 causes the mass death of aquatic organisms. Of course, it depends on the scale and type of organisms. For the natural functioning of the aquatic ecosystem, the oxygen content must be at least

4 mg/dm^3, and for fish ponds – 6 mg/dm^3. In general, the oxygen content is a very unstable component of the chemical composition of water. The prognosis results are presented in Fig. 7.

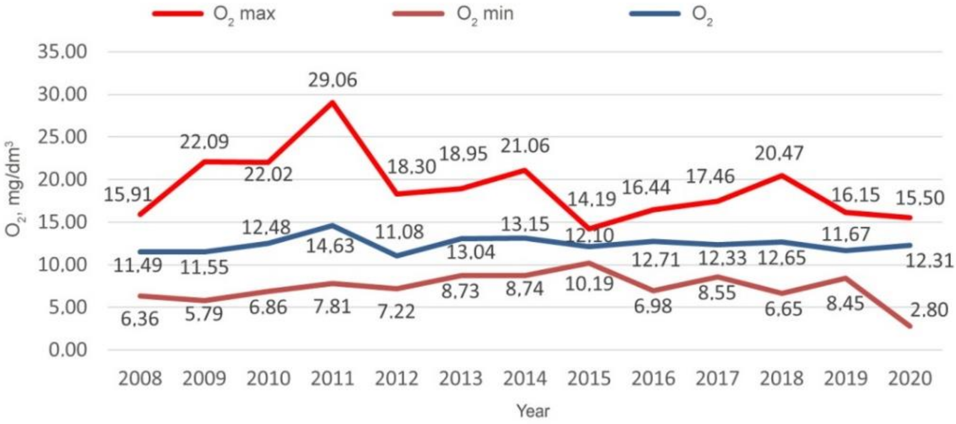

Fig. 6. Changes in the dissolved oxygen

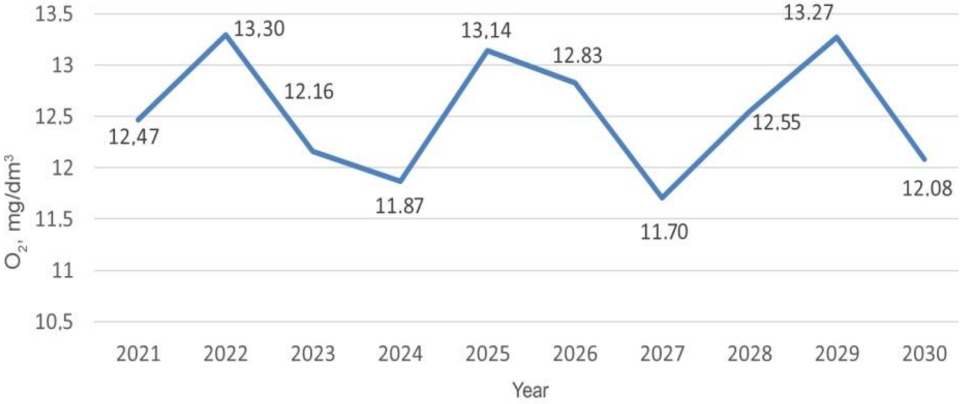

Fig. 7. The dissolved oxygen prognosis until 2030 years

Possible organic pollutants may include phenols, aromatic compounds, petroleum and petroleum products, sulfur-containing organic compounds. Some organic compounds have a toxic effect. BOD$_5$ determines the consumption of oxygen for the oxidation of organic pollutants present in the reservoir. This is one of the most important integrated indicators of water purity. The natural sources of such organic compounds may be the remains of living organisms, but the bulk of organic compounds are the result of anthropogenic activity. The MPC for the indicator is 3 mg/dm^3. The dynamics of change of BOD$_5$ is presented in Fig. 8.

Peak values of 3.3–3.5 are higher than the MPC, which means strong organic pollution. Exceeding the indicator of 3 mg/dm^3 indicates the presence of significant anthropogenic impact from utilities, agricultural production, and river transport. So, we have obtained a prognosis for the next 10 years (Fig. 9).

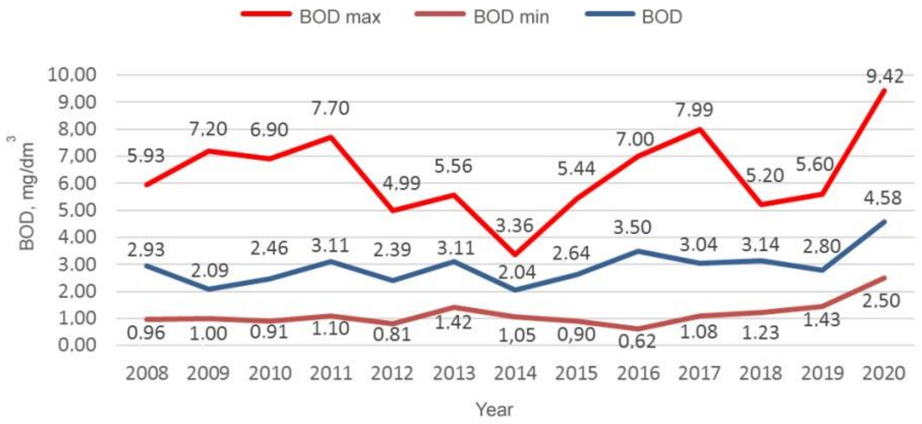

Fig. 8. Changes in the BOD5

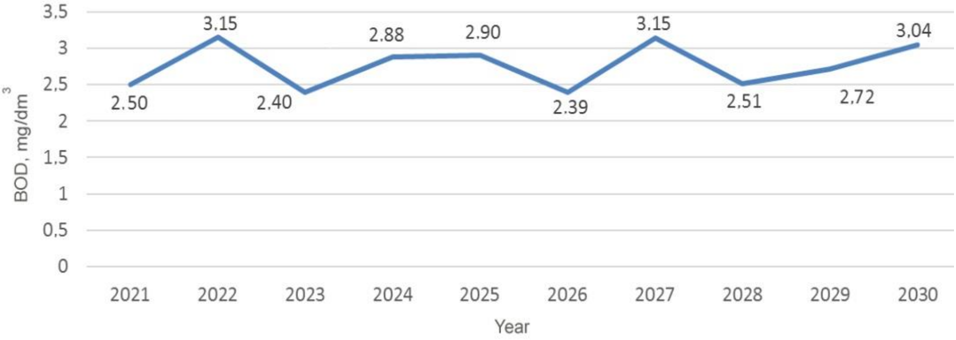

Fig. 9. The BOD$_5$ prognosis until 2030 years

The dynamics of the content of suspended solids over 12 years is shown in Fig. 10. The content of suspended solids should not exceed 500 mg/dm^3. However, there is also a norm of wastewater treatment. Wastewater is considered if the content of suspended particles does not exceed 60 mg/dm^3.

The prognosis on the basis of this function gives the dynamics of the content of suspended particles for the next 10 years. Regression analysis (Fig. 11) indicates a period of sinusoids of 10 years. A significant deviation in the direction of decline in 2017 falls somewhat out of these statistics, which gives a regression coefficient of 0.73 instead of close to 1.

Fig. 10. Changes in the suspended solids

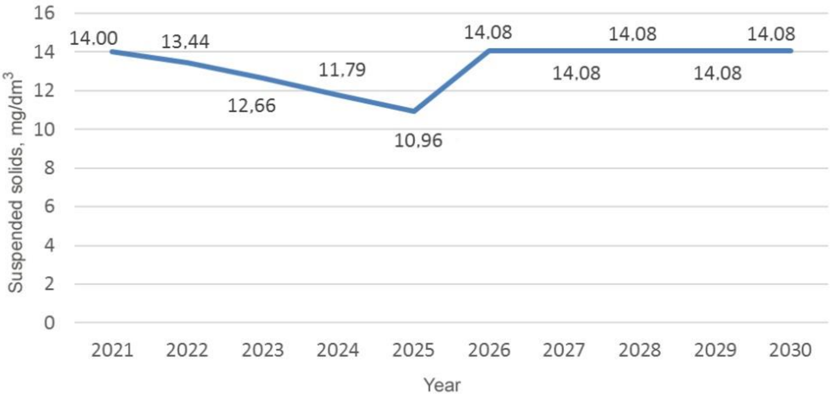

Fig. 11. The suspended solids prognosis until 2030 years

4. Summary and Conclusions

Based on the obtained functions, prognoses for 2021–2030 based on average annual averages have been developed. The main anomalous values of measurements of 2008–2020, as deviations from the specified function, are determined and the causes of such anomalies, which have anthropogenic origin due to the activity of communal and agricultural sectors of the economy, are described. The determined sinusoidal dependences of the integrated water quality indicators allowed outlining the average time of fluctuations in the processes of self-organization of river waters, which is about 6 years, and confirms the theory of "waves of life".

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References

1. Abbasi, T., Abbasi, S.A.: Water quality indices. Amsterdam: Elsevier Science Ltd. 384, 2012.
2. Barakat, M.A.: New trends in removing heavy metals from industrial wastewater, Arab. *J. Chem*., 4, 361–377, 2011.
3. Bashynska, I.L.: Ekolohichna otsinka efektyvnosti ochyshchennia pytnoi vody na vodoprovidnykh sporudakh komunalnoho pidpryiemstva «Zhytomyrvodokanal» (Environmental estimation of efficiency of drinking water purification on plumbing of UC «Zhytomyrvodokanal»). *Naukovi horyzonty (Scientific horizons*), 7–8(70), 50–58, 2018 (in Ukrainian).
4. Bezsonov, Ye., Mitryasova, O., Smyrnov, V., Smyrnova, S.: Influence of the South-Ukraine electric power producing complex on the ecological condition of the Southern Bug River. *Eastern-European Journal of Enterprise Technologies*, 4/10 (88), 20–28, 2017.
5. Birk, S., Bonne, W., Borja, A., Brucet, S., Courrat, A., Poikane, S., Solimini, A., W. van de Bund, N. Zampoukas & D. Hering: Three hundred ways to assess Europe’s surface waters: An almost complete overview of biological methods to implement the Water Framework Directive. *Ecological Indicators*, 18, 31–41, 2012.
6. Butler, D., Ward, S., Sweetapple, C., Astaraie-Imani, M., Diao, K., Farmani, R. and Fu, G.: Reliable, Resilient and Sustainable Water Management: The Safe and SuRe Approach. *J. Global Challenges*, 1(1), 63–77, 2016.

7. Casal-Campos, A., Butler, G. Fu, D., Moore, A.: An Integrated Environmental Assessment of Green and Grey Infrastructure Strategies for Robust Decision Making. *J. Environmental Science and Technology,* 49(14), 8307–8314, 2015.
8. Chugai, A., Safranov, T.: Assessment of Technogenic Loading on the Surface Water Bodies of the Separate Regions of the North-Western Black Sea. *Journal of Ecological Engineering*, 21(5), 197–201, 2020.
9. Fernandez, N., Ramirez, A., Solano, F.: Revista Busta Physico-chemical Water Quality Indices. A Comparative Review, URL: http://www.academia.edu/193200/ physico-chemical_water_quality_indices, 2012.
10. Gersonius, B., Ashley, R., Pathirana, A., Zevenbergen, C.: Climate change uncertainty: Building flexibility into water and flood risk infrastructure. *Clim. Change*, 116(2), 411–423, 2013.
11. Ignatowicz, K.: Removal of Pesticides from Wastewater by the Use of Constructed Wetlands. *Journal of Ecological Engineering,* 21(1), 210–218, 2020.
12. Jepson, W., Budds, J., Eichelberger, L., Harris, L., Norman, E., 'Reilly, K., Young, S.: Advancing human capabilities for water security: A relational approach. *J. Water Security*, 1, 46−52, 2017.
13. Lykhovyd, P.V., Kozlenko, Ye.V.: Assessment and forecast of water quality in the River Ingulets irrigation system. *Ukrainian Journal of Ecology*, 8(1), 350–355, 2018.
14. Meyer, A.M., Klein, C., Fünfrocken, E., Kautenburger, R., Beck, H.P.: Real-time Monitoring of Water Quality to Identify Pollution Pathways in Small and Middle Scale Rivers. *Science of the Total Environment*, 651, 2323–2333, 2019.
15. Mitryasova, O., Pohrebennyk, V.: Integrated Environmental Assessment of the Surface Waters Pollution: Regional Aspect. International Multidisciplinary Scientific GeoConference SGEM, Vienna, Austria, 27 November – 29 November 2017, 33(17), 235–242, 2017.
16. Mitryasova, O., Pohrebennyk, V., Kardasz, P.: Hydrochemical Aspects of Surface Water Quality Assessment. 18th International Multidisciplinary Scientific Geoconference SGEM 2018, Albena, Bulgaria. 30 June–9 July 2018, 5.2.(18), 513−520, 2018.
17. Mitryasova, O., Koszelnik, P., Gruca-Rokosz, R., Smirnov, V., Smirnova, S., Bezsonov, Ye., Zdeb, M., Ziembowicz, S.: Features of Heavy Metals Accumulation in Bottom Sediments of the Southern Bug Hydroecosystem. *Journal of Ecological Engineering*, 21(3), 51–60, 2020.

18. Mitryasova, O., Cieśla, M., Nosyk, A., Mats, A.: Hydrochemical Indicators Dynamic in Surface Water, *Journal of Ecological Engineering*, 2021, 22(8), 111–122, 2021.

19. NRDC. Climate Change and Water Resource Management, 2013, https://www.nrdc.org/resources/climate-change-and-water-resource-management.

20. Petrov, O., Petrichenko, S., Yushchishina, A., Mitryasova, O., Pohrebennyk, V.: Electrospark Method in Galvanic Wastewater Treatment for Heavy Metal Removal. *Applied Sciences, Determination and Extraction of Heavy Metals from Wastewater and Other Complex Matrices*, 10(15), 5148, 2020.

21. Shakhman, I. A., Bystriantseva, A. N.: Assessment of Ecological State and Ecological Reliability of the Lower Section of the Ingulets River. *Hydrobiological Journal*, 53(5), 103–109, 2017.

22. Soboleva, O.A., Anischenko, L.N., Shchetinskaya, O.S., Dolganova, M.V., Demichov, V.T.: Assessment of the ecological and chemical state of springs in urban and rural settlements of the bryansk region based on monitoring data for 2012–2020. *J. Siberian Journal of Life Sciences and Agriculture,* 12(5), 128–149, 2020.

23. Staddon, C., Sarkozi, R., Langberg, S.: Urban Water Governance as a Function of the “Urban Hydrosocial Transition. In E. Karar (Ed.), Freshwater Governance for the 21st Century. edited by E. Karar. Springer, 81–102, 2017.

24. Vasenko, O.G., Rybalova, O.V., Korobkova, G.V.: Ekolohycheskoe normyrovanye kachestva poverkhnostnykh vod s uchetom rehyonalnykh osobennostei (Ecological Rationing of Surface Water Quality Taking into Account Regional Features). *Hydrology, hydrochemistry and hydroecology*, 1(44), 21–33, 2017 (in Ukrainian).

25. Wang, X., Daigger, G., Lee, D. J., Liu, J., Ren, N., Qu, J., Liu, G., Butler, D.: Evolving Wastewater Infrastructure Paradigm to Enhance Harmony with Nature. *Sci. Adv.*, 4, 1–10, 2018.

26. Ward, S., Borden, D. S., Kabo-Bah, A., Fatawu, A.N., Mwinkom, X.F.: Water resources data, models and decisions: International expert opinion on knowledge management for an uncertain but resilient future. *Journal of Hydroinformatics*, 21(1), 32–44, 2019.

27. Yurasov, S.M., Safranov, T.A., Chugai, A.V.: Otsinka yakosti pryrodnykh vod (Assessment of Natural Water Quality). *Odessa: Ecology*, 168, 2012. (in Ukrainian).

Influence of green architecture and permeable pavements application on water balance of public utility facility catchment – modeling study

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Abstract

This paper presents the comparative numerical analysis of changes in stormwater outflow volumes and patterns for the urbanized catchment of a public facility i.e. school complex of total area 4.66 ha. This study was based on assumed variable partial replacement of sealed surfaces by green roofs and permeable pavements allowing to delay and reduce surface runoff. The numerical studies were performed in SWMM, EPA, USA software for the three selected rainfall events of various intensity. Variable permeable concretes, of different permeability and infiltration ratio were selected to replace the traditional sealing materials i.e. asphalt and concrete bricks. The required input data concerning infiltration and retention characteristics of green roofs and studied permeable pavements were accepted after literature. The obtained results allowed assessment of possible influence of green architecture and permeable pavements application on time-related reduction in surface runoff volume.

Keywords: LID, rainwater, catchment, SWMM, runoff

1. Introduction

The intense urbanization of urban areas observed in the recent years, related to the construction of new buildings, roads, pavements and parking lots, has a negative impact on the water balance of the catchment area. The increase of impermeable surfaces contributes to the intensification of surface runoff, changes in soil and hydrological conditions, deterioration of the air and water quality. In addition, urbanization intensifies human activities that directly affect climate changes, i.e. the diversity of rainfall patterns (Karamouz et al., 2010; Varotsos et al., 2013; Sabat et al., 2021) and the increase in the frequency and intensity of storms (Dong et al., 2017). Sealing the surface of the catchment area in the range of 70–100% leads to an increase in surface runoff to the amount of 55% of the precipitation volume and a decrease in evapotranspiration and infiltration to the value of 30% and 15% of the precipitation volume, respectively (TU1206-WG2.0-001). The use of traditional rainwater drainage systems in conditions of changing frequencies and patterns of rainfall events may lead to the occurrence of local flooding. The climate changes observed in recent years have already caused a change in the approach to the design and operation of drainage systems (Semadeni-Davies et al., 2008; Houng and Pathirana, 2013). Currently, the additional aspects of water management in cities, such as the quality of runoff, visual values, recreational values, environmental protection and various uses of rainwater are taken into account (Ellis and D’Arcy, 2002; Zhou, 2014). Hence, many countries are implementing techniques for sustainable stormwater drainage systems, such as Low-Impact Development (LID) (Dietz, 2007; Elliot and Trowsdale, 2007), which main goal is to manage urban floods by controlling the source of rainwater runoff (Dietz, 2007; Ahiablame et al., 2012; Khan et al., 2012; Kaykhosravi et al., 2018). The LID activities reduce the risk of flooding through a number of non-structural and structural measures, i.e. increasing the permeability of the catchment area by using permeable materials (Abdollahian et al., 2018), reducing runoff by green infrastructure (green roofs, green walls) (Gaffin et al., 2009; Gdela et al., 2019; Ascione et al, 2020), bioretention systems or retention reservoirs application (e.g. Sijanec Zavrl and Zeren, 2010; Kaykhosravi et al., 2018; Wang et al., 2019).

Numerous studies (Pereira et al., 2020), (Bressy et al., 2014), (Demuzerea et al., 2014) confirm that LID activities consisting in implementing green infrastructure lead to a significant reduction in surface runoff and reduction of its peak flows. The results of the research conducted by Stovin et al. (2012) indicate that using cumulative retention in the form of green roofs, it is possible to reduce peak stormwater runoff by 60%. Which suggests that green roofs can make a significant contribution to mitigating runoff.

Sustainable rainwater drainage systems are very often oriented also on the increased infiltration of rainwater into the soil, and thus the improvement of the disturbed water balance. As part of Low Impact Development, classic surfacing materials with slots or water-permeable materials (including permeable concrete or asphalts) are used to reduce the volume of runoff and increase the degree of infiltration (Timm et al., 2018; Boogaard and Lucke, 2019; Zhu et al., 2019). Research conducted by Timm et al. (2018), showed that the use of paving slabs in place of traditional asphalt covers allowed to increase the amount of infiltration from 6–9% to 38–53% of the precipitation height. And in the case of using pebbles, bricks or cobblestones, it allowed for an increase in infiltration to the level of over 70% of the precipitation value.

The paper presents the modeling results of the rainwater drainage network operation under the conditions of three different rainfall events, characterized by variable duration and intensity, carried out for four different variants of land cover (actual catchment, application of green roofs, permeable surfaces and the simultaneous use of green roofs and permeable surfaces).

2. Materials and Methods

2.1. Object of the study

The 4.2 ha urbanized catchment located in Krasnik, Lublin Voivodship, Poland was selected to our studies (see Fig. 1). The surface sealing of the catchment were divided as impervious, including roofs, sidewalk, parking lots, roads and previous, such as grass, football pitch and high vegetation.

Fig. 1. Studied catchment

The share of each surface area, sealing degree and values of assumed runoff coefficients are presented in Tab. 1.

Table 1. Surface sealing characteristics

Sealing	**Subcatchment type**	**Areas [ha]**	**Sealing degree [%]**	**Runoff coeff., ψ [-]**
Impervious	Roof	0.962	99	0.90
	Asfalth	0.085	95	0.90
	Sidewalk, pavement	0.53	85	0.80
Pervious	Football pitch	1.18	25	0.35
	Grass	0.72	10	0.20
	High vegetation	0.76	3	0.10

Rainwater from the studied catchment are collected and delivered to the local stormwater system. The designed stormwater collection system consists of PVC-U pipelines of diameters 315–500 mm. The total length of pipelines equals 4200 m (d = 315mm – 1928.94 m; d = 400 mm – 267.75 m; d = 500 mm – 48.75 m). The percentage share of each diameter length in the total length of designed system is presented in Fig. 2.

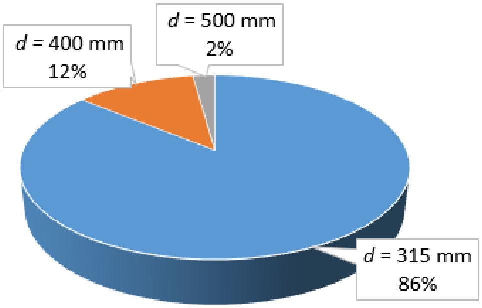

Fig. 2. Percentage of pipe diameters in the total network length

2.2. Hydraulic model

The modeling studies were performed in SWMM 5.0 (EPA, USA) software. The physical characteristics of the stormwater system, including material, diameters, lengths, depth, inclination and type of surface cover were obtained basing on the technical documentation of the network.

The developer model covered 30 subcatchments, 27 nodes, 27 pipelines (links) and outflow. The partition of catchment to subcatchments was performed basing on sealing degree of each cover. For separate subcatchments the runoff strip width (*W*) was determined using equation:

$$W = \frac{A_{red}}{L_d}, \tag{1}$$

where: A_{red} – reduced catchment area [m^2], L_d – calculation length of flow path from partial catchment area [m].

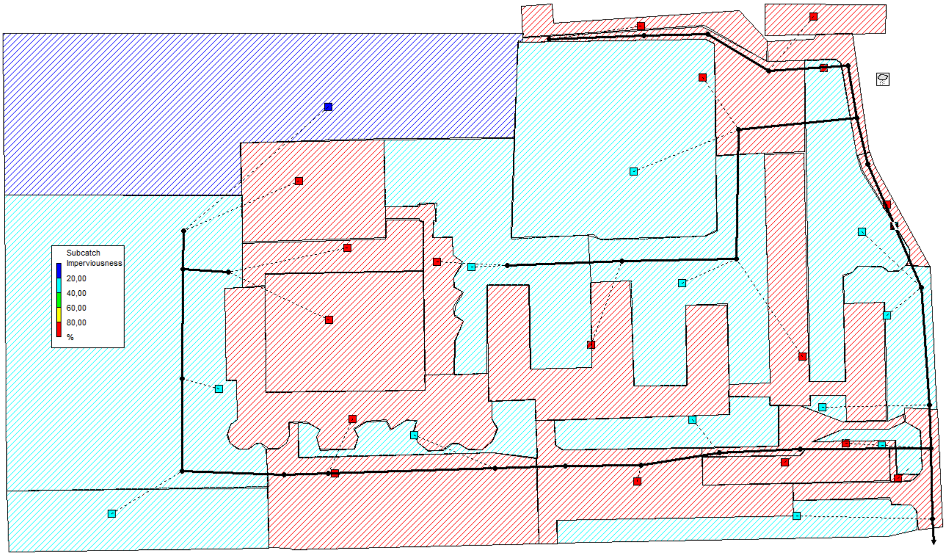

Fig. 3. Scheme of developed model

The calculated values of runoff strip width, slopes inclination and catchments characteristics such as Manning's roughness coefficient for impervious and pervious surfaces, retention depth determined after literature studies are presented in Tab. 2.

Table 2. Catchment characteristics

Parameter	**Unit**	**Value**
Catchment slope	[%]	0.1–15.5*
Catchment width	[m]	2.57–97.1*
Infiltration intensity ratio	[h^{-1}]	4
Manning's roughness for impervious surface	[-]	0.012
Manning's roughness for pervious surface	[-]	0.15
Retention depth for impervious surface	[mm]	0.5
Retention depth for pervious surface	[mm]	2.0

*– calcluladed values

Table 3 presents input data for the modeling calculations, including maximal and minimal infiltration ratio for each studied cover type assumed, after literature studies.

The performed simulation studies covered four different variants of calculations:

– variant A – existing sealing surface cover;
– variant B – green roofs application;
– variant C – permeable pavements application;
– variant D – combined green roofs and permeable pavements application.

Table 3. Infiltration ratio

Surface type	**Maximal infiltration ratio [mm·h^{-1}]**	**Minimal infiltration ratio [mm·h^{-1}]**
Roof	0.12	0.04
Parking	5.00	1.00
Asphalt	3.00	0.50
Football pitch	20.00	2.10
Grass	50.00	4.00
High vegetation	100.00	4.00
Green roof	4.08	2.06
Permeable	30.83	18.96

Table 4 contains area values assigned for each of the available surface sealing type in each tested variant of calculations.

Table 4. Surface sealing types for each variant of stormwater management

Type of surface	**Variant A**	**Variant B**	**Variant C**	**Variant D**
	Area [ha]			
Roof	0.96	0.06	0.96	0.06
Parking	0.53	0.53	0.03	0.03
Asphalt	0.08	0.08	0.08	0.08
Football pitch	1.18	1.18	1.18	1.18
Grass	0.72	0.72	0.72	0.72
High vegetation	0.76	0.76	0.76	0.76
Green roof	0.00	0.90	0.00	0.90
Permeable	0.00	0.00	0.50	0.50

Each applied variant of surface sealing was analyzed for three real rainfall events of variable intensity and duration (see Table 5), observed in the vicinity of approx. 30 km from the tested location. The Chicago model of time-related rainfall distribution was assumed to our calculations, see Fig. 4.

Table 5. Assumed rainfall characteristics

Variant	**Rainfall duration [h]**	**Rainfall intensity [mm/h]**	**Rainfall depth [mm]**
Rainfall No. 1	6.4	4.08	26.10
Rainfall No. 2	3.1	12.13	37.60
Rainfall No. 3	0.6	32.30	19.40

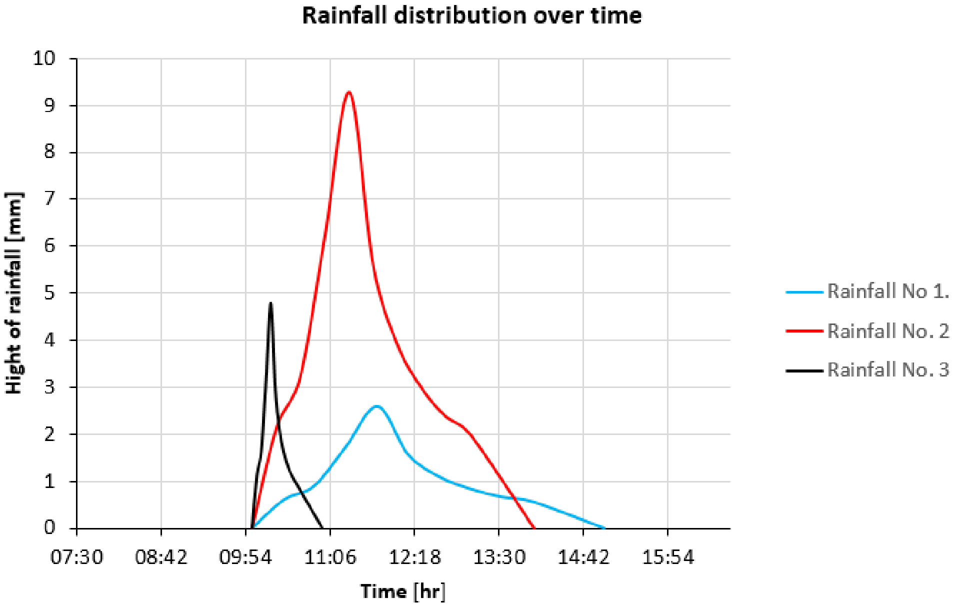

Fig. 4. Time-related rainfall distributions applied to numerical calculations, Chicago model

The numeric calculations in SWMM of runoff and rainwater flow inside the sewers software were based on:

– dynamic wave model;

– outflow type OUTLET (the runoff is realized from both types of catchments, impervious and previous, directly to the stormwater system);

– infiltration of rainwater into soil according to Horton’s model;

– duration of the simulation – 48 hours.

The obtained results were statistically assessed by the standard procedures. The normality of variables was tested by Shapiro-Wilk test and, according to the obtained results, the required variance test was applied.

3. Results and Discussion

Figure 5 shows determined time-related stormwater volumetric flow rate distribution, observed for pipeline, calculated for various rainfall event and variants of LID application. The highest peak values of volumetric stormwater flow were noted for the existing catchment, without any LID application, i.e. 85.87 dm^3/s, 205.07 dm^3/s and 237.90 dm^3/s for rainfall events 1, 2 and 3, respectively. The highest reduction in peak volumetric flow for all tested rainfall events was noted for variant assuming combined application of green roofs and permeable pavements. The values of calculated reduction in peak flow, presented in Tab. 6, shows, that green roofs application allowed limiting the peak flow by 33% and 6%, respectively. Application of permeable concrete pavements allowed the similar reduction in peak rainwater outflow for rainfall 1 and 3, 8 and 7%, respectively. The combined application of green roofs and permeable pavements allowed reduction in the peak outflow in 42% and 21%, for rainfall events 1 and 3, respectively. No rainwater peak flow reduction was observed in case of rainfall event No. 2.

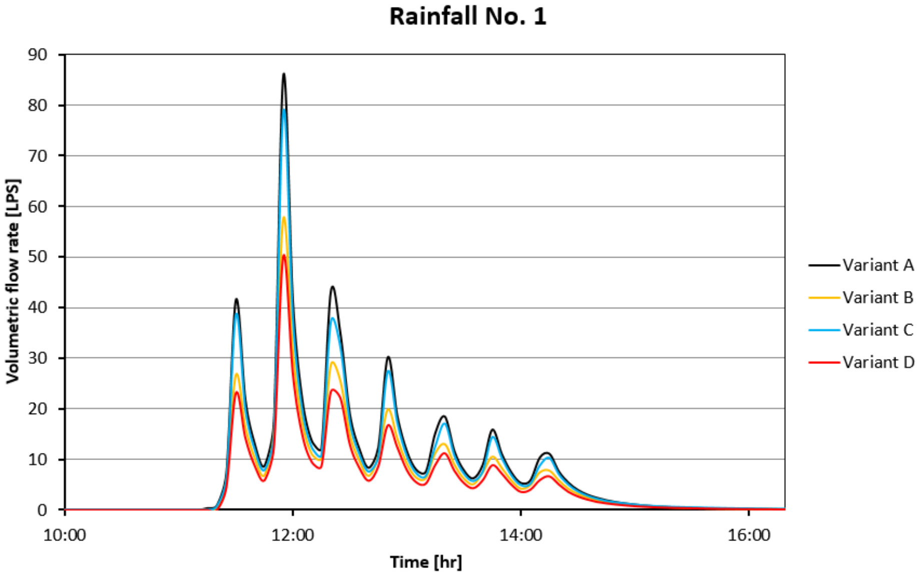

Fig. 5a. Volumetric flow rate for rainfall No. 1 for variants A, B, C, D

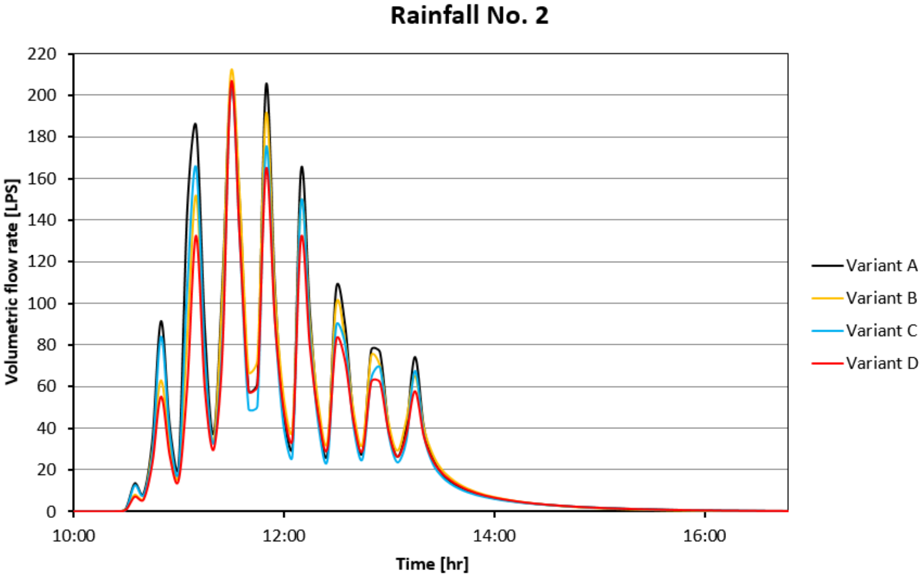

Fig. 5b. Volumetric flow rate for rainfall No. 2 for variants A, B, C, D

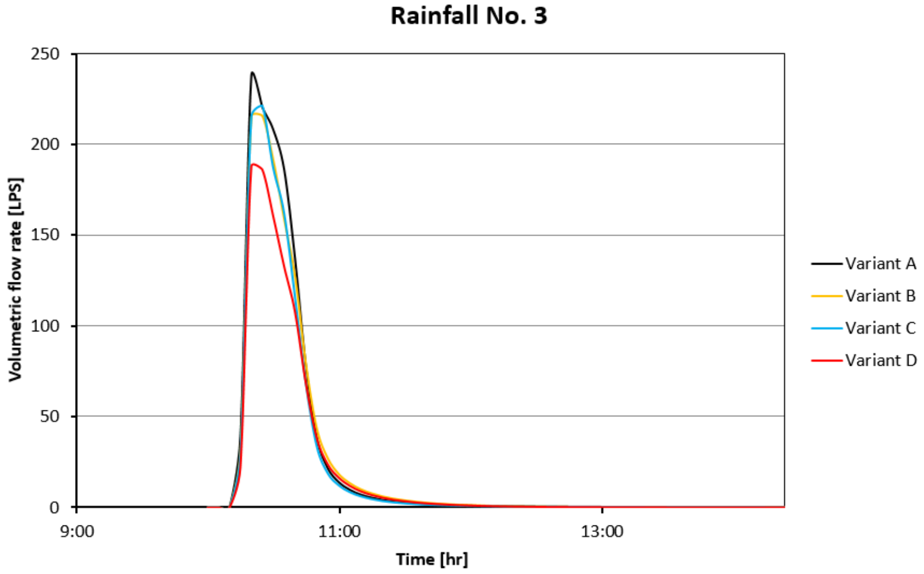

Fig. 5c. Volumetric flow rate for rainfall No. 3 for variants A, B, C, D

Table 6. Total peak flow reduction

Variant	**Peak flow [LPS]**						
	Rainfall No. 1	**Rainfall No. 2**	**Rainfall No. 3**	**Variant**	**Rainfall No. 1**	**Rainfall No. 2**	**Rainfall No. 3**
A	85.87	205.07	237.90				
B	57.65	211.66	215.63	B	–33%	3%	–9%
C	78.92	204.99	221.25	C	–8%	0%	–7%
D	50.18	205.74	187.70	D	–42%	0%	–21%

Figure 6 presents obtained values of accumulated rainwater volume discharged from the studied catchment to the receiver for all studied rainfall events and variants of LID application. For all studied rainfall events the highest calculated reduction of runoff volume was determined for the combined application of green roofs and permeable pavements. Taking into account the individual application of studied LID manners, green roof showed significant efficiency only in case of rainfall event No. 1, of the longest duration and the lowest intensity. The sole application of permeable concrete as surface sealing allowed higher reduction of runoff volume in case of rainfall events No. 2 and 3.

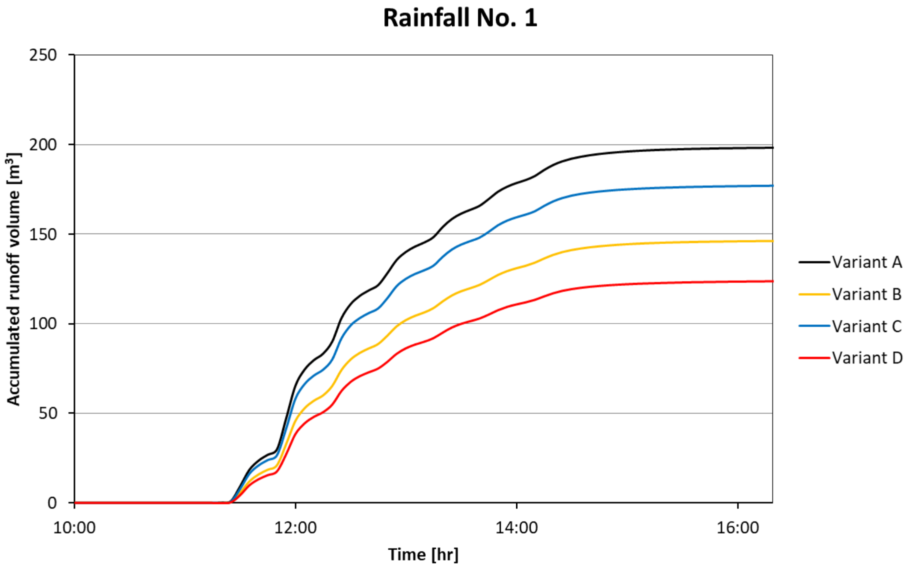

Fig. 6a. Runoff volume rate for rainfall No. 1 for variants A, B, C, D

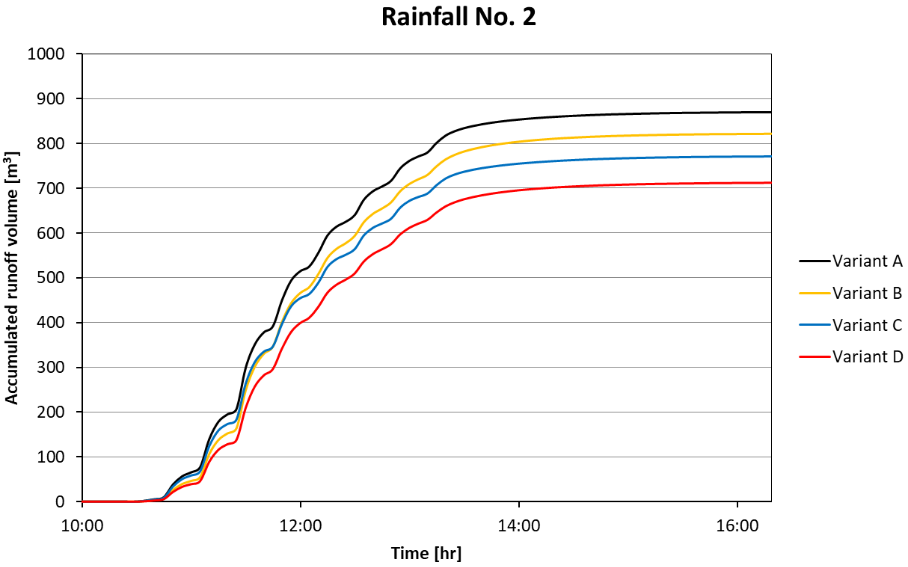

Fig. 6b. Runoff volume rate for rainfall No. 2 for variants A, B, C, D

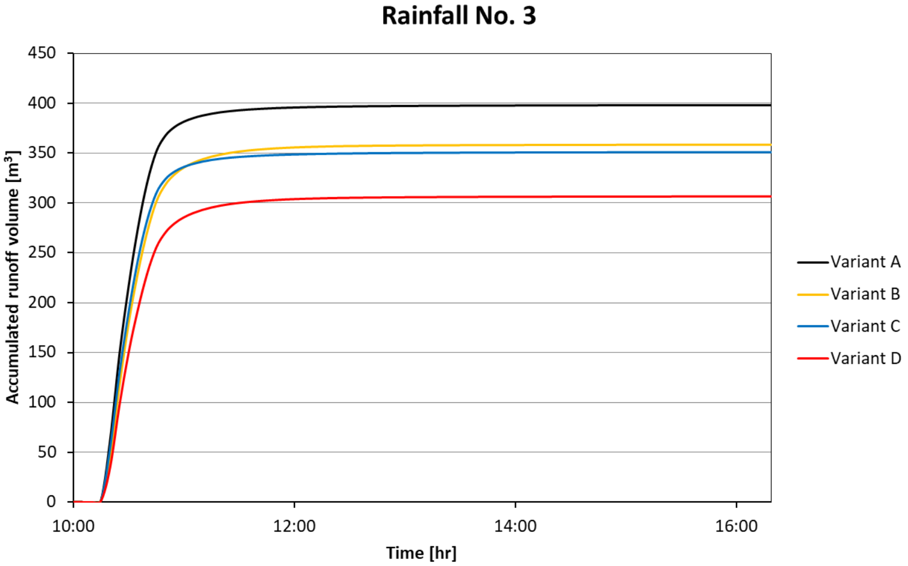

Fig. 6c. Runoff volume rate for rainfall No. 3 for variants A, B, C, D

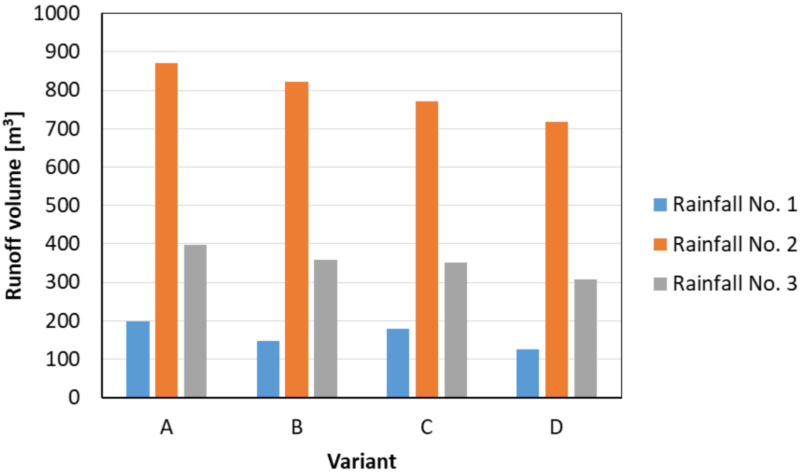

Fig. 7. Runoff volume comparison

The comparison of runoff volume for all tested LID variants and different rainfall events, presented in Fig. 7, shows that the combined application of green roofs and permeable concrete pavements significantly affects volume of surface runoff discharged to the receiver. The degree of runoff reduction, presented in Tab. 7, shows that in case of Variant C (permeable pavements) the comparable reduction was determined for each tested rainfall, i.e. 10.7%, 11.3% and 11.8% for rainfall No. 1, 2 and 3, respectively. Generally, the studied possible LID applications showed the best efficiency for rain of the longest duration and the lowest intensity. To the contrary, the determined efficiency in rainwater runoff reduction was the lowest for rainfall of the highest depth (37.6 mm) and significant duration i.e. 3.1 h.

Table 7. Runoff volume reduction

Runoff volume reduction							
Variant	**Rainfall No. 1**	**Rainfall No. 2**	**Rainfall No. 3**	**Variant**	**Rainfall No. 1**	**Rainfall No. 2**	**Rainfall No. 3**
A	198.92	870.60	398.26				
B	146.86	822.31	358.60	B	26.2%	5.5%	10.0%
C	177.70	771.84	351.11	C	10.7%	11.3%	11.8%
D	124.38	717.96	306.70	D	37.5%	17.5%	23.0%

The performed statistical analysis of the obtained results, based on one-way Kruskal-Wallis ANOVA, showed that in all cases the result of the test was statistically significant ($p < 0.05$) thus the observed differences among all calculated rainwater volumetric outflow are also statistically significant. The performed post-hoc pairwise comparison (see Tab. 8) allowed the conclusion that the above observation is related mainly to differences caused by outflow values for the Variant D, combining green roofs and permeable pavements application.

Table 8. Determined *p* values for post-hoc pairwise comparison

Rainfall No. 1				
Variant	**A**	**B**	**C**	**D**
A		0.001	0.463	0.000
B	0.001		0.273	0.289
C	0.463	0.273		0.000
D	0.000	0.289	0.000	
Rainfall No. 2				
Variant	**A**	**B**	**C**	**D**
A		0.321	0.001	0.000
B	0.320		0.338	0.001
C	0.001	0.338		0.277
D	0.000	0.001	0.277	
Rainfall No. 3				
Variant	**A**	**B**	**C**	**D**
A		0.012	0.000	0.000
B	0.013		0.058	0.000
C	0.000	0.058		0.012
D	0.000	0.000	0.012	

4. Summary and Conclusions

The performed numerical calculations allowed the following conclusions:

– application of green architecture and permeable surface sealings alerts water balance of urbanized catchment;

– the best results of runoff reduction were obtained in case of the combined application of green roofs and permeable Surface for parking lots, roads and pavements;

– separately applied, under conditions of the tested catchment, green roofs performed better than permeable sealings only for rainfall No. 1, with the lowest rain intensity;

– performance of the studied permeable surface covers was comparable for each tested rainfall event;

– the performed statistical analysis of the obtained results showed that the observed differences are statistically significant.

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References

1. Abdollahian, S., Kazemi, H., Rockaway, T., Gullapalli, V.: Stormwater Quality Benefits of Permeable Pavement Systems with Deep Aggregate Layers. *Environments,* 5(6), 68, 2018.
2. Ahiablame, L.M., Engel, B.A., Chaubey, I.: Effectiveness of low impact development practices: Literature review and suggestions for future research. *Water, Air, & Soil Pollution,* 223, 4253–4273, 2012.
3. Ascione, F., Francesca De Masi, R., Mastellone, M., Ruggiero, S., Vanoli, G.P.: Green Walls, a Critical Review: Knowledge Gaps,Design Parameters Thermal Performances and Multi-Criteria Design Approaches. *Energies*, 13, 2296, 2020.
4. Boogaard, F., Lucke, T.: Long-Term Infiltration Performance Evaluation of Dutch Permeable Pavements Using the Full-Scale Infiltration Method. *Water,* 11, 320, 2019.
5. Bressy, A., Gromaire, M.C., Lorgeoux, C, Saad, M., Leroy, F., Chebbo, G.: Efficiency of source control systems for reducing runoff pollutant loads: Feedback on experimental catchments within Paris conurbation. *Water Research,* 57, 234–246, 2014. DOI:10.1016/j.watres.2014.03.040.
6. Demuzerea, M.K., Orru, O., Heidrich, E. et al.: Mitigating and adapting to climate change: Multi-functional and multi-scale assessment of green urban infrastructure. *Journal of Environmental Management,* 146, 107e115, 2014. DOI:10.1016/j.jenvman.2014.07.025.
7. Dietz, M.: Low impact development practices: A review of current research and recommendations for future directions. *Water, Air, & Soil Pollution,* 186, 351–363, 2007.
8. Elliott, A.H., Trowsdale, S.A.: A review of models for low impact urban stormwater drainage. *Environmental Modelling & Software*, 22, 394–405, 2007.

9. Ellis, J.B., D'Arcy, B.J. Chatfield, P.R.: Sustainable urban-drainage systems and catchment planning. *Water Environtal Journal*, 16, 286–291, 2002.
10. Gaffin, S.R., Khanbilvardi, R., Rosenzweig, C.: Development of a Green Roof Environmental Monitoring and Meteorological Network in New York City. *Sensors*, 9, 2647–2660, 2009.
11. Gdela, M.,Widomski, M.K., Musz-Pomorska, A.: Hydraulic efficency of selected intensive green roof substrates. *Ecological Chemistry and Engineering A*, 26(1–2), 37–45, 2019. DOI:10.2428/ecea.2019.26(1–2)4.
12. Huong, H.T.L., Pathirana, A.: Urbanization and climate change impacts on future urban flooding in Can Tho City, Vietnam. *Hydrology and Earth System Sciences*, 17, 379–394, 2013.
13. Kaykhosravi, S., Khan, U.T., Jadidi, A.: A Comprehensive Review of Low Impact Development Models for Research, Conceptual, Preliminary and Detailed Design Applications. *Water*, 10, 1541, 2018.
14. Khan, U.T., Valeo, C., Chu, A., van Duin, B.: Bioretention cell efficacy in cold climates: Part 2-Water quality performance. *Canadian Journal of Civil Engineering*, 39, 1222–1233, 2012.
15. Pereira, B., David, L.M., Galvno, A.: Green Infrastructures in Stormwater Control and Treatment Strategies. *Proceedings*, 48, 7, 2020. DOI:0.3390/ECWS-4-06526.
16. Sabat, M., Musz-Pomorska, A., Widomski, M.K.: Wpływ rodzaju nawierzchni na wybrane parametry hydrauliczne i jakościowe kanalizacji deszczowej. *Gaz, Woda i Technika Sanitarna*, 95(7–8), 12–17, 2021 (in Polish).
17. Semadeni-Davies, A., Hernebring, C., Svensson, G., Gustafsson, L.G.: The impacts of climate change and urbanisation on drainage in Helsingborg, Sweden: Suburban stormwater. *Journal of Hydrology*, 350, 114–125, 2008.
18. Stovin, V., Vesuviano, G., Kasmin, H.: The hydrological performance of a green roof test bed under UK climatic conditions. *Journal of Hydrology*, 414–415, 148–161, 2012. DOI:10.1016/j.jhydrol.2011.10.022.
19. Šijanec Zavrl, M., Zeren, T.M.: Sustainability of Urban Infrastructures. *Sustainability*, 2, 950–2964, 2010.
20. Timm, A., Kluge, B., Wessolek, G.: Hydrological balance of pawed surfaces in moist mid-latitude climate – A review. *Landscape and Urban Planning*, 175, 80–91, 2018.

21. TU1206 COST Sub-Urban WG2. Reported. (Eds.) Mielby S., Eriksson I., Campbell D., et al. Considering access to subsurface knowledge – Evaluation of practices and techniques.

22. Varotsos, C.A., Efstathiou, M.N., Cracknell, A.P.: On the scaling effect in global surface air temperature anomalies. *Atmospheric Chemistry and Physics*, 13(10), 5243–5253, 2013. DOI:10.5194/acp-13-5243-2013.

23. Karamouz, M., Hosseinpour, A., Nazif, S.: Improvement of urban drainage system performance under climate change impact. Case study. *Journal of Hydrologic Engineering*, 16(5), 2011. DOI:10.1061/(ASCE)HE.1943-5584.0000317.

24. Dong, X., Guo, H., Zeng, S.: Enhancing future resilience in urban drainage system: green versus grey infrastructure. *Water Research*, 747, 124, 280–289, 2017. DOI:10.1016/j.watres.2017.07.038.

25. Wang, M., Zhang, D., Lou, S., Hou, Q., Liu, Y., Cheng, Y., Qi, J., Tan, S.K.: "Assessing Hydrological Effects of Bioretention Cells for Urban Stormwater Runoff in Response to Climatic Changes. *Water*, 11, 997, 2019.

26. Zhou, Q.: A Review of Sustainable Urban Drainage Systems Considering the Climate Change and Urbanization Impacts. *Water*, 6, 976–992, 2014.

27. Zhu, H., Yu, M., Zhu, J., Lu, H., Cao, R.: Simulation study on effect of permeable pavement on reducing flood risk of urban runoff. *International Journal of Transportation Science and Technology*, 8, 373–382, 2019.

Study of enzymatic processing of organic waste from fat and oil production

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Abstract

The study is devoted to the theoretical and experimental substantiation of the improvement of biotechnological reprocessing by enzymatic hydrolysis of the waste from fat and oil production i.e. a spent catalyst, in order to reduce its effect on environmental components and obtain a valuable product – a hydrolyzate of higher fatty acids, which can be used in cosmetology.

The method for processing waste from fat and oil production, namely, spent catalyst, has been improved, and the possibility of obtaining a hydrolyzate of the fat component of waste has been experimentally substantiated. The choice of microbial lipase based on enzymatic activity and substrate specificity has been substantiated. Due to the fact that lipases are substrate specific, the difference in the activities of the studied lipases relative to different substrates is significant. The lipase of Rhizopus japonicus is the most active in relation to the fatty component of waste i.e. hydrogenated oil.

The optimum pH of the medium during enzymatic hydrolysis was 7.0; thermooptimum of lipase – 40°C.

The rational conditions for the enzymatic hydrolysis of the fatty component of the hydrogenated oil waste are the pH of the medium – 7.0, temperature – 40°C, weight ratio of lipase:substrate 1:50.

The qualitative composition of the hydrolyzate is represented by monoglycerides, diglycerides, triglycerides, free fatty acids and aliphatic alcohols.

The use of activated carbon with a grain size of 2.0–2.8 for the immobilization of lipase was substantiated; the weight ratio of carrier: enzyme during lipase immobilization was 1 g of biopolymer carrier per 500 mg of lipase (1:0.5).

Keywords: enzymatic hydrolysis, lipase, biotechnology, organic waste processing

1. Introduction

Recycling waste and converting it into products suitable for further use is one of the most important components of environmental protection technologies. When disposing of waste in dumping grounds / landfills, there is a threat of pollution and fire, which will contribute to the formation of an environmental hazard. Promising for practical use is the method of biotechnological conversion of fatty waste using enzymes – lipases of microbial origin.

One of these alternative technologies is biotechnology, which provides for methods of converting raw materials, which are waste products from the food, pulp and paper industry and agriculture, using enzymes and microorganisms to obtain useful substances (Krusir et al., 2020; Khomych et al., 2020; Malovanyy et al., 2018; Krusir et al., 2019). Enzymes are increasingly used in various biotechnological processes and industries, but by the 60s of the XX century. This direction was restrained by the difficulty of obtaining them, instability, and high cost.

Enzymatic conversion of fatty waste is promising not only from the point of view of creating independent low-waste technologies, but also from the standpoint of reducing the environmental hazard of various industries that process fatty raw materials and are accompanied by the formation of a significant amount of waste (Polishchuk et al., 2020).

Lipases constitute an important group of valuable biotechnological enzymes (Filho et al., 2019; Satyanarayana, 2005). The reasons for the enormous biotechnological potential of microbial lipases are the facts that they:

– function better at low temperatures;

– can be used as a substitute for aggressive chemical compounds, which reduces environmental hazard, prevents pollution, excludes the use of corrosion-resistant equipment;

– are highly specific, therefore, the formation of undesirable by-products and the need for complex technological processes are excluded;

– are possible for modification by immobilization, contributing to their repeated use;

– can be used for the treatment and disposal of waste containing harmful compounds;

– are able to decompose naturally with the help of destructors; therefore, all chemical components of enzymes are included in the natural ecological cycle (Krusir, 2007, 2008).

The process of hydrogenation of vegetable oils is accompanied by the formation of a significant amount of waste, the main of which is the spent catalyst. In 2017, in Ukraine, the production of hydrogenated oils amounted to 16.268 tons/year, and the volume of spent catalyst formation – 56.435 kg/year.

There is a need to improve existing and develop new technological solutions for handling wastes of fat and oil production. Biotechnological methods of waste destruction are productive and are of considerable interest in solving the accumulation of organic waste. Biotechnological processes are subject to control and regulation, are implemented under normal flow conditions, are natural and do not have side negative effects on biota and the environment, do not require significant land areas, do not require the use of pesticides, herbicides and other agents alien to the environment.

In this work, the conditions of enzymatic hydrolysis were investigated to obtain a product – a hydrolyzate, which was later used in cosmetology.

Enzymatic hydrolysis of the fat fraction of fat and oil production wastes will reduce the technogenic impact on the environment and bring them to a new production cycle (Khomych et al., 2020).

2. Materials and Methods

To characterize the physical and chemical properties of lipase, the conditions of lipolysis and immobilization of lipase, standard unified and original methods of physical, physical and chemical, and biochemical research methods were used. A unit of lipase activity was taken to be the amount of enzymes that, at a temperature of 37°C and a pH of 7.0 for 60 minutes, catalyzes the hydrolysis of a 40% aqueous emulsion of olive oil to form 1 g of oleic acid (stearic acid) (Cherno, et al., 2008). A 40% emulsion of olive oil (hydrogenated oil) was prepared using a 2% solution of polyvinyl alcohol as an emulsifier and stabilizer. The preparation of the water-in-fat emulsion (inverse emulsion) was started with melting the fat mass at a temperature 5–10°C higher than the melting temperature, after which a buffer solution with the same temperature was added. The mixture was emulsified at 500 min, the emulsion was stabilized with polyvinyl alcohol. The resulting emulsion was kept on ice for 60 minutes. When the emulsion was stratified, homogenization was repeated. The content of the aqueous phase did not exceed 20%.

The sample was prepared using 1 cm^3 of water, 0.1 cm^3 of 0.1% lipase solution, 0.8 cm^3 of phosphate buffer (the pH of the medium corresponded to the pH optimum of lipase) was added to a test tube containing 8–15 mg of the sample and kept for 5 min at 37°C. Then 1.0 cm^3 40% emulsion of olive oil (hydrogenated oil) with polyvinyl alcohol was added and kept under the same conditions. After 1 h of incubation, the reaction was interrupted by the addition of 5 cm^3 of 96% ethanol.

In the control sample, an emulsion was added after adding ethanol. In the control and experimental samples, three drops of a phenolphthalein solution were added and titrated with a sodium hydroxide solution with a concentration of 0.05 mol/dm^3 to a light pink color. The level of lipase activity was assessed in arbitrary units by the difference in the amount of alkali, which was used for titration of the experimental and control samples during the hydrolysis of 40% emulsion.

Lipolytic activity was determined using an aqueous solution of sodium hydroxide with a concentration of 0.05 mol/dm^3, based on the calculation of the amount of fatty acids formed during hydrolysis of the substrate.

The pH optimum of the lipase was determined in such a way that a buffer solution with different pH values of the medium in the range of 2.5–12.0 was added to the enzyme samples of equal activity, and the enzymatic activity was determined. The determination of the pH optimum of the enzyme preparation was carried out at 37°C using the following buffer solutions: glycine – NaCl – HCl, 0.1 mol/dm^3 (pH 2–3.5); acetate buffer solution, 0.1 mol/dm^3 (pH 3.5–5.5); phosphate buffer solution 0.1 mol/dm^3.

The thermooptimum of the enzyme was determined in identical samples of the free enzyme by activity at a temperature of 20–80°C in an appropriate buffer, which corresponds to the pH optimum of this enzyme.

To determine the pH stability of lipase, enzyme samples of equal activity were incubated at different pH values of 2.5–12.0 for 0–360 min, then the pH of the solution was adjusted to the optimal value and the enzymatic activity was determined.

The thermostability of lipase was investigated in this way: samples of the enzyme equal in activity in the corresponding buffer solution corresponding to the pH optimum were incubated at 20, 37, 45 and 60°C for 0–360 min, then the temperature was brought to 37°C and the enzyme activity was determined.

The enzyme was immobilized by physical sorption as follows: a weighed portion of the carrier (1 g) was impregnated with a 10% enzyme solution in 0.1 M phosphate buffer, pH 7.0, after which it was dried and again impregnated with the enzyme solution until did not reach the desired weight ratio carrier: enzyme (Krusir, 2008).

For agar-agar and carrageenan, the hydromodule (HM - weight ratio of carrier: enzyme solution) was 3, for clays (kieselguhr, ascanite, bergmeal) HM 1, for activated carbon and chitosan – HM 1.5.

To study the conditions for productive hydrolysis of hydrogenated oil, we used: chemical methods for determining the activity and physicochemical properties of the native forms of lipase, thin-layer chromatography – to determine the composition of hydrolysates of hydrogenated oil, stabilization methods – using immobilization of lipase on carriers of different origins. The emulsification of the mixture under study was carried out on a homogenizer Nomogenzen Ture 302 (Poland). The obtained chromatograms were developed in a desiccator saturated with iodine; the chromatograms were processed using the TLC-Manager 4.0.1 software. Determination of the lipid composition of the hydrolysates was carried out according to Rf (mobility coefficient – the ratio of the distance from the center of the spot to the distance traveled by the solvent).

3. Results and discussion

The analysis of scientific and technical literature and the study of existing scientific and practical directions for the disposal of wastes of the fat and oil industry indicate the feasibility of further research aimed at enzymatic processing of hydrogenated oil waste using lipolytic enzymes. The choice of enzyme preparations was determined by the composition of the wastes of the fat-and-oil industry, containing a significant amount of mono-, di- and triglycerides.

In contrast to nonbiological catalysts, specificity is one of the properties of enzymes, which consists in the fact that the enzyme can catalyze the conversion of one specific substrate or a group of structurally similar substrates. As a result of the binding of the enzyme to the substrates, a temporary connection of the enzyme-substrate complex is formed, which decomposes with the formation of the enzyme and reaction products. Energetically, this process is more beneficial than converting a substrate into a product without the participation of an enzyme. Without it, the reaction may require high temperatures, pressure, high acidity of the environment, etc., that is, it cannot effectively take place in living cells and is not ecological from the point of view of effective environmental management (Cherno, 2009).

In order to determine the most effective lipase for the hydrolysis of fat, we determined the enzymatic activity of the most common lipases used in the food and processing industry in relation to olive oil, which is traditionally used as a substrate for determining lipolytic activity, as well as in relation to fat. The research results are presented in table. 1.

Table 1. Characteristics of substrate specificity of enzymes

Lipases	**Activity relative to olive oil, units**	**Activity relative to hydrogenated oil, units**
Lipase MM	1532	408
Lipase RJ	1356	457
Lipase RO	1752	353
Lipase AN	1311	205
Lipase G AO	1450	347
Yeast Lipase	1715	435
Lipase A	1553	226

From the results of the studies presented in Table 1, it can be seen that the Rhizopus oryzae lipase is most active in relation to olive oil. The lipase of Rhizopus japonicus, which was later used for the enzymolysis of wastes from the fat and oil industry, is distinguished by the highest activity in relation to hydrogenated oil. As you know, the activity of the enzyme depends on the substrate and its characteristics: fatty acid composition, spatial structure, as well as the composition and spatial structure of the active center of the enzyme, the conformational correspondence of the enzyme and the substrate of the «key-lock» type and the induced correspondence of the "hand-glove" type, i.e. substrate specific, which can explain the difference in the activities of the studied lipases in relation to different substrates (Nawani and Kaur, 2007).

Thin layer chromatography was used to determine the qualitative and quantitative lipid composition of hydrogenated oil hydrolyzate obtained by enzymatic hydrolysis using Rhizopus japonicus lipase.

As evidenced by the results of chromatography, manifestations using iodine and identification of chromatograms by Rf, the qualitative composition of the hydrolyzate is represented by monoglycerides, diglycerides, triglycerides, free fatty acids and aliphatic alcohols.

The content of each lipid fraction was determined gravimetrically. The results of studying the dynamics of changes in the lipid composition of hydrogenated oil are presented in Table 2.

Table 2. Dynamics of changes in the lipid composition of hydrogenated oil during enzymolysis

Duration of hydrolysis, hours	**Lipid content, %**			
	Monoglycerides	**Diglycerides**	**Triglycerides**	**Fatty acids**
0	0	9.5	88.1	0
0.3	3.3	15.1	53.4	25.7
0.5	4.2	17.5	20.3	52.5
1.0	3.4	13.8	13.5	60.1
1.5	3.2	11.9	11.2	62.1
2.0	1.5	7.2	11.2	62.1

It was found (Table 2) that the content of free fatty acids in the hydrolyzate reached the saturation level after 1 hour of hydrolysis, and the concentration of triglycerides and free fatty acids did not significantly decrease during the next hour of hydrolysis.

For the effective implementation of the enzymatic conversion process, it is necessary not only to have an active preparation, but also to know under what conditions its maximum enzymatic activity is manifested and what factors and how affect the enzyme. The most important for enzymes is the substrate and its concentration, the pH of the medium and temperature, the duration of interaction and the effect of individual chemical compounds.

Enzymes are generally active only in a certain pH range and in most cases there is a certain pH optimum for each enzyme.

The presence of such an optimum may have several reasons:

– the effect of pH on the reaction rate (under conditions of saturation with the substrate);

– the effect of pH on the affinity of the enzyme for the substrate;

– the effect of pH on the stability of the enzyme, which can be irreversibly inactivated when the pH of the medium differs from the optimal one (Krusir, 2008).

These factors usually work in combination with each other. The effect of these factors can be distinguished experimentally. Changes in the ionization state of an enzyme with a change in pH are due to the existence of a whole series of different ionic forms, and the distribution of the entire amount of the enzyme between these ionic forms depends on pH and on the ionization constants of different groups. Since usually only one of these forms is catalytically active, the form of the pH dependence has the form of a bell.

The temperature optimum for most lipases fluctuates in the range 37–43°C, the pH optimum of Rhizopus japonicus lipase was determined at 40°C (Lima et al., 2004).

For Rhizopus japonicus lipase, the optimum pH value of the medium is 7.0, a decrease in the pH of the medium from optimumto pH 6.0 is accompanied by a decrease in activity by 30%, and an increase in pH from 7.0 to 9.0 – causes a decrease by 20%, which allows us to conclude that lipase is quite sensitive to changes in pH.

The effect of temperature on the rate of enzymatic reactions may be due to the action of various factors. Temperature affects the stability of the enzyme, the rate of decomposition of the enzyme-substrate complex, and the affinity of the enzyme for the substrate.

When carrying out an enzymatic reaction, two different factors act simultaneously that determine the effect of temperature: on the one hand, an increase in the initial rate, on the other, denaturation of the enzyme under the influence of temperature, which leads to a continuous decrease in the concentration of the active enzyme. The optimum temperature depends on the relationship between the effect of temperature on the rate of the enzymatic reaction and its effect on the rate of denaturation of the enzyme. The position of the thermooptimum of the enzymatic activity of the Rhizopus japonicus preparation was determined at the optimum pH-activity (7.0) and a temperature of 10–100°C.

From the experimental data of the study, it follows that the thermooptimum of lipase is 40°C. Lipase is stable in the range of 15–85°C with 50% of the maximum activity being preserved. When the temperature rises, the activity decreases sharply. Thus, the maximum activity of the enzyme is observed at 40°C with its rapid decrease with a further increase in temperature, which is caused by thermal denaturation of the native protein molecule, as well as changes in the nature of the microenvironment of the native enzyme.

The pH stability was studied at the optimal pH value (7.0), at the acidic pH of the medium (pH 2.5) and at the alkaline pH of the medium (pH 9.0) at a temperature of 40°C for 3 hours.

The results of the study of lipase pH stability indicate that lipase is less stable at pH 2.5. When incubated at pH 2.5, lipolytic activity is lost after 30 minutes. When lipase functions at a pH of 9.0. The pH lipolytic activity is completely lost after 2.5 hours incubation of the enzyme under these conditions.

Thus, the enzyme does not change its activity during one hour of its incubation at the optimal pH value with further loss, which may be due to denaturation changes in the protein molecule.

Thermal stability was determined at the optimum pH value (7.0) and temperatures (40, 60, 80 and 100°C) correspondingly to the thermooptimal temperature and the possible drying temperatures of the enzyme (60, 80 and 100°C) for 3 hours.

Studies of the effect of temperature on the stability of lipase indicate that at 100°C the lipolytic activity of the native lipase decreased to 2% of the original already after 20 min. of incubation under these conditions. The highest lipase stability was observed at a temperature of 40°C – the lipase activity remained stable for 1.5 hours and was completely lost after 3 hours of incubation.

It is known that the inactivation of enzymes under the influence of pH and temperature is the result of previous ionization processes, deeply affecting electrostatic interactions in the enzyme molecule.

Due to the fact that the lipolysis reaction is heterogeneous, that is, it occurs at the oil-water interface, its course can be changed by acting directly on the enzyme or its sorption on the interface, as well as on the orientation of substrate molecules and diffusion of lipolysis products.

The efficiency of enzymatic hydrolysis also depends on the weight ratio of lipase:substrate. The results of determining the optimal weight ratio of lipase:substrate are presented in table 3.

As evidenced by the results of experimental studies to determine the optimal weight ratio of lipase:substrate, the maximum value of lipolytic activity corresponds to a weight ratio of 1:50.

Thus, the rational conditions for the hydrolysis of the fatty component of the hydrogenated oil waste are: the optimum pH of the medium is 7.0, thermooptimum of lipase is 40°C, rational weight ratio of lipase: substrate is 1:50.

One of the usual methods for stabilizing enzymes is their adsorption on biopolymer matrices. In order to obtain a stable lipase preparation exhibiting a lipolytic activity sufficient for the fermentolysis of hydrogenated oil, it was proposed to carry out immobilization of Rhizopus japonicus lipase on inorganic carriers.

Table 3. Determination of rational weight ratio of lipase:substrate

Weight ratio of lipase: substrate	**Lipolytic activity, LU/g carrier**
1:1	23
1:10	54
1:20	120
1:30	270
1:40	350
1:50	457
1:60	250
1:70	83
1:80	17

In the course of the research, the optimal conditions for sorption immobilization were selected: the carrier was impregnated with a 10% solution of the enzyme in 0.1 M phosphate buffer solution at pH 7.0, using HM 3 for agar-agar and carrageenan, HM 1 – clays (kieselguhr, ascanite, bergmeal) and HM 1.5 – for activated carbon and chitosan, at 23°C and dried the preparation at 40°C.

The choice of a carrier for immobilization of lipase was made in order to maximize the preservation of the initial lipolytic activity. The experimental results of determining the optimal weight ratio of the carrier:enzyme are shown in table 4.

As evidenced by the results of experimental studies, the use of activated carbon as a carrier for the immobilization of lipase leads to the maximum preservation of the initial lipolytic activity. The optimal weight ratio of carrier: enzyme in terms of maintaining lipolytic activity is 1 g of biopolymer carrier per 500 mg of lipase (1:0.5) with 36.33% of the initial activity of the native enzyme retained.

4. Summary and Conclusions

It was shown that the lipase of Rhizopus japonicus, which was later used for the enzymolysis of wastes from the fat and oil industry, is distinguished by the highest activity in relation to hydrogenated oil.

For the Rhizopus japonicus lipase, its physical and chemical properties have been determined: pH – and thermooptimum, pH – and thermostability. For Rhizopus japonicus lipase, the optimum pH value of the medium is 7.0; a decrease in the pH of the medium from optimal to pH 6.0 is accompanied by a decrease in activity by 30%, and an increase in pH from 7.0 to 9.0 causes a decrease by 20%, which allows us to conclude that lipase is quite sensitive to pH changes, the thermooptimum for lipase is 40°C, lipase is stable in the range 15–85°C, while maintaining 50% of the maximum activity; lipase is less stable at pH 2.5, under conditions of incubation at pH 2.5.

Table 4. The value of the optimal carriage performance:enzyme

Carrier	**Weight ratio of carrier: enzyme**	**Lipolytic activity**	
		LU/g carrier	**% of the native preservation**
1	2	3	4
Kieselguhr (Ukraine)	1:0.1	10.0	23.81
	1:0.3	26.1	20.71
	1:0.5	69.3	33.00
	1:0.7	91.4	31.09
	1:0.9	55.2	14.60
Activated carbon (2.0–2.8) (Ukraine)	1:0.1	14.0	33.33
	1:0.3	34.1	27.06
	1:0.5	76.3	36.33
	1:0.7	99.4	33.81
	1:0.9	88.2	23.33
Askanite (Georgia)	1:0.1	7.0	16.67
	1:0.3	28.1	22.30
	1:0.5	66.4	31.62
	1:0.7	52.3	17.79
	1:0.9	50.1	13.25
Bergmeal (diatomite) (Ukraine	1:0.1	6.2	14.76
	1:0.3	13.1	10.40
	1:0.5	62.3	29.67
	1:0.7	66.4	22.59
	1:0.9	52.1	13.78
Agar (China)	1:0.1	8.6	20.48
	1:0.3	26.2	20.79
	1:0.5	58.1	27.67
	1:0.7	62.3	21.19
	1:0.9	47.4	12.54
Carrageenan (E407) (China)	1:0.1	8.1	19.29
	1:0.3	19.3	15.32
	1:0.5	54.2	25.81
	1:0.7	62.1	21.12
	1:0.9	47.4	12.54
Chitosan (China)	1:0.1	6.2	14.76
	1:0.3	23.5	18.65
	1:0.5	69.4	33.05
	1:0.7	87.1	29.63
	1:0.9	77.3	20.45

It has been established that the rational conditions for the enzymatic hydrolysis of the fatty component of the waste of the hydrogenated oil bleaching process are: pH of the medium – 7.0, temperature – 40°C, weight ratio of lipase:substrate 1:50.

It was found that the content of free fatty acids in the hydrolyzate upon hydrolysis with native lipase reached the saturation level after 1 hour, and the concentration of triglycerides and free fatty acids did not significantly decrease during the next hour of hydrolysis.

As evidenced by the results of chromatography of hydrolysates, the manifestation of chromatograms and identification of components, the qualitative composition of the hydrolyzate is represented by monoglycerides, diglycerides, triglycerides, free fatty acids and aliphatic alcohols.

The results of determining the pH and thermal stability of lipase indicate that the lipase is unstable and requires stabilization for more efficient functioning.

The use of activated carbon as a carrier for the immobilization of lipase with a grain size of 2.0–2.8 leads to the maximum preservation of the initial lipolytic activity: the weight ratio of carrier:enzyme is 1 g of biopolymer carrier per 500 mg of lipase (1:0.5) yields preservation of 36.33% of the original activity of the native enzyme.

References

1. Krusir, G., Sagdeeva, O., Malovanyy, M., Shunko, H., Gnizdovskyi, O.: Investigation of Enzymatic Degradation of Solid Winemaking Wastes. *J. Ecol. Eng.*, 21(2), 72–79, 2020. DOI:10.12911/22998993/116345.

2. Khomych, G., Krusir, G., Horobets, O., Levchenko, Y., Gaivoronska, Z.: Development of Resource Effective and Cleaner Technologies Using the Waste of Plant Raw Materials. *Journal of Ecological Engineering*, 21, 4, 178–184, 2020.

3. Malovanyy, M., Krusir, G., Holodovska, O., Masikevych, A.: Reagent purification of the processing industry enterprises effluents. *Харчова наука і технологія*, 123, 109–116, 2018. DOI:10.15673/fst.v12i3.1046.

4. Krusir, G., Shpyrko, T., Sagdeeva, O., Zakharchuk, V.: The role of soil microbiocenosis in the composting of the organic component of the municipal solid waste. *Food science and technology*, 13, 2, 34-43, 2019. DOI:10.15673/fst.v13i2.1387.

5. Polishchuk, V.M., Shvorov, S.A., Krusir, G.V., Davidenko, T.S.: Increased Biogas Output during Fermentation of Manure of Cattle with Winemaking Waste in Biogas Plants. *Problemele Energeticii regionale*, 2, 46, 123–134, 2020. DOI:10.5281/zenodo.3898326.

6. Filho, D.G., Silva, A.G., Guidini, C.Z.: Lipases: sources, immobilization methods, and industrial applications. *Appl Microbiol Biotechnol,* 103, 7399–7423, 2019. DOI:10.1007/s00253-019-10027-6.

7. Satyanarayana, T.: Microbial Diversity: Current Perspectives and Potential Applications. I. K. International Pvt Ltd, 1133, 2005.

8. Krusir, H.V.: Nasinnia rapsu – dzherelo vysokoaktyvnoi lipazy. H.V. Krusir, O.V. Sevastianova. Zb. nauk. pr. Prohresyvni tekhnika ta tekhnolohii kharchovykh vyrobnytstv, restorannoho hospodarstva i torhivli, *KhDUKhT. Kharki*v, 1(5), 193–197, 2007.

9. Krusyr, H.V.: K voprosu ob ynhybyrovanyy pankreatycheskoi lypazы fenolnымy soedynenyiamy y fosfolypydamy rapsa. H.V. Krusyr, E.V., Sevastianova, V.V. Yashkyna. Innovats. enerho- y resursozberihaiuchi tekhnolohii ta oblad. v khlibopekar., kondyter., makaron., kharchokontsentrat. i zernopererob. haluziakh kharch. prom. sti: temat. zb. nauk. pr. NUKhT. Kyiv, 25, 2, 21–23, 2008.

10. Cherno, N.K., Sevastianova, E.V., Krusyr, H.V., Yashkina, V.V.: Kharch Doslidzhennia mekhanizmu inhibuvannia pankreatychnoi lipazy fenolnymy spolukamy ripaku. *Nauka i Tekhnolohiia,* 2, 23–25, 2008.

11. Krusir, H.V.: Bilkovi inhibitory yak rehuliatory homeostaza orhanizmu liudyny [Tekst] Kharch. *Nauka i Tekhnologia*, 2, 30–34, 2008.

12. Cherno, N.K.: Rastytelnыe kompleksы, ynhybyruiushchye deistvye pankreatycheskoi lypazы, y ykh yspolzovanye. N.K. Cherno, H.V. Krusyr, V.V.Iashkyna. *Zernovi produkty i kombikormy*, 2(34), 13–17, 2009.

13. Nawani, N., Kaur, J.: Studies on lipolytic isoenzymes from a thermophilic Bacillus sp. Production, purification and biochemical characterization. *Enzyme Microb. Technol*., 40, 881–887, 2007.

14. Lima, V., Krieger, N., Mitchell, D., Baratti, J., De Filippis, I., Fontana, J.: Evaluation of the potential for use in biocatalysis of a lipase from a wild strain of Bacillus megaterium. Journal Molecular Catal. B. *Enzyme*., 31, 5361, 2004.

Development of reagents for removal of sediments from pipelines and equipment of water circulation systems and drainage systems

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Abstract

Studies have been conducted to evaluate the effectiveness of a number of compositions that should be used as washing solutions for cleaning metal surfaces from scale deposits, as well as stabilizers of scale formation with anti-corrosion action. The proposed compositions were created on the basis of hydrochloric, sulfuric, phosphoric acids in the presence of urotropin or urotropin with thiourea.

The obtained data demonstrate that all compositions have a higher corrosion aggressiveness than tap water. The composition R-29 is characterized by the lowest corrosion aggressiveness among the studied variants. The mass metric corrosion index of this composition is 0.106881 g/($m^2 \cdot h$), the depth of corrosion, respectively 0.118907 mm/year.

Hydrochloric acid has the greatest efficiency of dissolving the precipitate on calcium sulfate among the considered acids. The solubility of gypsum in phosphonic acids is 2.0–2.5 times less than in hydrochloric acid. For their solutions in concentrations of 10%, this figure is approximately 18 g/dm^3. However, their use for equipment washing is expedient, these compounds are known to be effective scale stabilizers and metal corrosion inhibitors.

To increase the efficiency of dissolution of gypsum in acids, treatment with alkali and soda solutions was performed in two stages to convert calcium sulfate into alkaline and carbonate form.

Keywords: scale formation stabilizer, corrosion inhibitor, water circulation systems, restoration of metal equipment surfaces, corrosion aggressiveness of water environments

1. Introduction

At the existing enterprises in the process of increasing the resource efficiency of water use systems, in particular, cooling systems, quite often switch to the use of metal corrosion inhibitors and antiscalants (Driker et al., 2000; Nosachova et al., 2006). As a result of long-term use of heat exchange equipment at industrial facilities, metal surfaces of pipelines, boilers, etc. are covered with a layer of corrosion products and carbonate-sulfate scale. The inner surfaces of heat exchange equipment and pipelines, which are covered with products of scale and corrosion (Singh et al., 2018; Zhi-Hui, 2020), significantly reduce the efficiency of heat transfer and almost completely eliminate the effectiveness of corrosion inhibitors and scale stabilizers.

To ensure the proper efficiency of the reagents, it is necessary to either increase their concentrations by tens to hundreds of times, or to carry out preliminary cleaning of the inner surfaces of pipelines and heat exchangers from deposits. The first option is impractical from both environmental and economic points of view. In the case of successful selection of the composition for cleaning the surfaces of pipelines from deposits, the result of further use of inhibitors is economically feasible and long-lasting.

The simplest and most affordable way to restore the surfaces of pipelines, heat exchangers, boilers is to wash them with acidic solutions.

However, the use of pure acids for flushing pipes has a number of disadvantages. The literature emphasizes the danger of using inorganic acids as pickling solutions. In particular, the use of sulfuric acid leads to the formation of insoluble calcium sulfate, and hydrochloric acid due to the presence of chlorides – to increase the corrosive aggressiveness of the environment (Hegazy et al., 2015; Chichenin et al., 2015).

An alternative is the use of organic acids. It is known that sulfamic acid (10% solution) is an effective reagent for cleaning pipes from corrosion and scale. However, this solution is corrosive to steel 20. The average polarization resistance (Rp_{aw}) is 70 Ohms (Hegazy et al., 2015; Daminov et al., 2006).

At the present stage, phosphonic acids are the most effective stabilizers of scale formation. Their zinc salts are the most effective inhibitors of metal corrosion. However, the use of these acids as pickling solutions remains unresolved.

Despite the long use of water circulation systems in industry, the issue of restoration of metal equipment remains unresolved. In particular, there is a shortage of effective and at the same time non-corrosive etching solutions for cleaning metal surfaces from sediment.

Another important issue is the prevention of the deposit formation in pipelines for drainage of reservoir water, equipment where oil, gas and reservoir water are separated in oil and gas production technologies. The main source of sediment formation on the surfaces of pipelines and equipment is the deposition of calcium carbonate and sulfate. The content of corrosion products of metals in the sediments is relatively small. A significant part of the sediments consists of suspensions – fine sand and clay minerals. They are poorly soluble in acids, and in alkalis they are not easy to dissolve. But the main binders that contribute to the strength of deposits are calcium carbonate and mainly gypsum (calcium sulfate).

The subject of the work are water-efficient circulating heat exchange systems in energy, industry and utilities.

The aim of the study was to determine the composition and effectiveness of compositions based on inorganic acids as corrosion-neutral washing solutions for the restoration of metal pipe surfaces, as well as compositions for periodic use in industrial air conditioning processes.

2. Material and Methods

Compositions of pickling solutions on the basis of hydrochloric, sulfuric, phosphoric acids in the presence of urotropin or urotropin with thiourea were used in the work.

Evaluation of the corrosion properties of the proposed compositions was performed in two ways: by the method of polarization resistance and by the method of massometry.

Determination of the polarization resistance was performed using the polarization resistance indicator P5126 and a two-electrode sensor from the corrosion indicator unit UK-2 with electrodes made of steel 20, pre-treated and weighed. The sensor was installed in a beaker with a volume of 150 cm^3. Measurements of polarization resistance Rp (Ohm) were performed every two hours using the indicator P5126. The value of the polarization resistance is inversely proportional to the corrosion rate of the metal.

Massmetric determination of the corrosion rate was determined by the difference between the masses of the corroding sample, in grams before and after corrosion. The duration of the experiments was 18–23 hours.

The experiments were performed in stationary media at a temperature of 15–20°C in free contact of water with air.

3. Results and Discussion

Dissolution of calcium carbonate in acidic environments is quite effective. The problem of dissolving gypsum is more complicated. Therefore, in further studies, the processes of dissolution of carbonate and calcium sulfate in different media were studied (Tables 1, 2).

Phosphoric acid is a fairly common reagent used in the removal of deposits from metal surfaces. It is able to form water-insoluble phosphates with iron and aluminum, and therefore often the corrosion of these metals in an acidic environment is inhibited by the formation of water-insoluble corrosion products. Although in concentrated solutions this effect is offset by the separation of the cathode and anode zone in the galvanic pairs formed during corrosion. In addition, in an acidic environment, aluminum and iron are easily soluble.

Table 1. Solubility of calcium carbonate and sulfate in orthophosphoric acid of different concentrations

Concentration H_3PO_4, %	**Solubility, g/dm^3**	
	$CaCO_3$	**$CaSO_4$**
1.0	10.3–10.9	5.9–6.4
2.0	20.4–20.8	6.5–6.9
3.0	31.4–32	7.2–7.7
5.0	43.1–43.6	10.4–10.9
10.0	49.8–50.3	11.4–11.9

On the example of phosphoric acid, the solubility of carbonate and calcium sulfate is compared (Table 1). As expected, calcium carbonate dissolves better than calcium sulfate.

Thus, in the range of orthophosphoric acid concentrations of 10–100 g/dm^3, the solubility of calcium carbonate was 4.5 times higher than the solubility of calcium sulfate.

It should be noted that orthophosphoric acid has a much lower ability to dissolve calcium sulfate compared to other inorganic and organic acids and is 11.4–11.9 g/dm^3 for 10 % solution (Table 2).

Calcium sulfate has the highest solubility in hydrochloric acid. Thus, for hydrochloric acid with a concentration of 30 g/dm^3, this figure was 24.5–24.9 g/dm^3. In a more concentrated solution (10%) the solubility increased to 36.2–36.7 g/dm^3.

The solubility of calcium sulfate in phosphonic acids was 2.0–2.5 times lower than in hydrochloric acid. For their solutions in concentrations of 10%, this figure was approximately 18 g/dm^3. However, their use for equipment washing is expedient, as these compounds are effective scale stabilizers and metal corrosion inhibitors.

The creation of compositions based on the considered acids, for example, H_3PO_4+NH_4OH+ATMP, does not always increase the effect of dissolution, as is observed in the case of the composition R-29. The composition of the composition R-29 (TU U 20.1-05761293-001: 2016) are given in table 3.

To increase the efficiency of dissolving gypsum in acids, a two-stage treatment was performed. In the first stage, it was treated with 5% alkali solution (Table 4) or 10% soda solution (Table 5). It is possible to partially transfer gypsum to lime or calcium carbonate by reactions 1 and 2.

$$2NaOH + CaSO_4 = Ca(OH)_2 + Na_2SO_4, \tag{1}$$

$$Na_2CO_3 + CaSO_4 = CaCO_3 + Na_2SO_4. \tag{2}$$

The latter compounds are easily soluble by interaction with acids. For hydrochloric acid by reactions 3 and 4.

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O, \tag{3}$$

$$CaCO_3 + 2HCl = CaCl_2 + H_2CO_3. \tag{4}$$

Lime and gypsum interact similarly with other acids.

In the case of hydrochloric acid, the dissolution of gypsum was worse when treated with basic reagents, as without their use in the entire range of concentrations used (Tables 2, 3 and 5). A similar trend was observed for orthophosphoric acid. The solubility of gypsum in sulfuric acid was low. This is due to the fact that with increasing concentration of sulfates, the solubility of gypsum should decrease. Its insignificant dissolution is explained by change of pH, formation of lyophobic colloidal particles which pass into solvent, forming colloidal solution.

Table 2. Solubility of calcium sulfate in different media

Reagent	**Concentration, %**	**Solubility $CaSO_4$, g/dm^3**
Tap water	–	1.76
H_3PO_4	3.0	7.2–7.7
	5.0	10.4–10.9
	10.0	11.4–11.9
HCl	3.0	24.5–24.9
	5.0	30.3–30.8
	10.0	36.2–36.7
Etidronic acid	3.0	12.1–12.6
	5.0	13.4–13.9
	10.0	18.0–18.5
Methylenephosphonic acid (ATMP)	3.0	9.3–9.8
	5.0	11.7–12.2
	10.0	17.7–18.2
Sulfamic acid	3.0	7.5–8.0
	5.0	10.2–10.7
	10.0	17.6–18.1
H_3PO_4 NH_4OH ATMP	5.0 0.5 0.5	7.0–7.5
R-29	5.0	12.5–13.7

Table 3. Organoleptic and physicochemical parameters of the reagent R-29

Indicator	**The norm for reagent R-29**	**The method of control according to**
1. Appearance, color, odor	Colorless clear liquid, odorless	6.1
2. Density for temperatures (20±1)°C, g/cm^3	1020–1030	State standard of Ukraine (ДСТУ) 7261
3. Hydrogen index, units pH	3.0–6.5	6.2.1
4. Boiling point, °C, not less	95	State standard of Ukraine (ДСТУ ГОСТ) 18995.6
5. Mass fraction of inorganic salts, %, not less	5.0	6.2.10
6. Mass fraction of orthophosphoric acid, %, not less	5.0	6.2.2
7. Mass fraction of ammonium, %, not less	0.1	6.2.6
8. Mass fraction of urotropin, %, not less	1.0	6.2.8
9. Destruction of chemically precipitated gypsum, %, not less	90	6.2.9

Table 4. The effect of treatment with 5% solution of NaOH gypsum on its solubility in acids (100cm^3)

Acid	**Acid concentration, %**	**m_{init}, g**	**m_{res}, g**	**Δm, g**	**Solubility, g/dm^3**
HCl	2	12.44	11.12	1.32	13.2
	5	11.12	8.44	2.68	26.8
	10	8.44	5.64	2.8	29.0
H_2SO_4	2	6.16	5.90	0.26	2.6
	5	7.65	7.38	0.27	2.7
	10	6.44	6.17	0.27	2.7
H_3PO_4	2	3.95	3.22	0.73	7.9
	5	4.37	3.56	0.81	9.0
	10	5.73	4.62	1.11	11.1

Table 5. The effect of treatment with 10% solution of Na_2CO_3 gypsum on its solubility in acids (100 cm^3)

Acid	**Acid concentration, %**	**m_{init}, g**	**m_{res}, g**	**Δm, g**	**Solubility, g/dm^3**
HCl	2	7.21	5.6	1.61	16.1
	5	7.54	4.96	2.58	25.8
	10	6.15	3.33	2.82	28.2
H_2SO_4	2	6.87	6.64	0.23	2.3
	5	8.73	8.49	0.24	2.4
	10	6.45	6.16	0.29	2.9
H_3PO_4	2	5.37	4.74	0.63	6.3
	5	4.88	4.04	0.84	8.4
	10	4.10	3.01	1.09	10.9

Kinetic factors are important in the processes of acid dissolution of sediments on the surface of pipes and equipment. Therefore, we investigated the dissolution rate of the selected gypsum mass in different volumes of pickling solutions (5% H_3PO_4 + 0.5% NH_4OH). The results are presented in Figure 1.

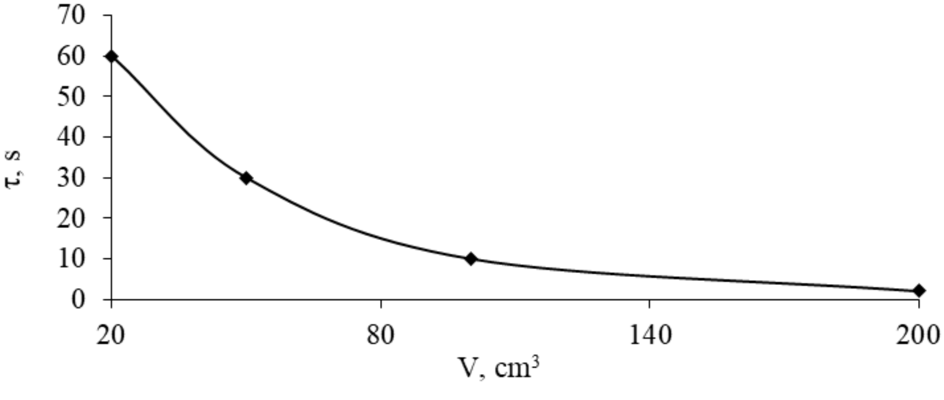

Fig. 1. Dependence of the time of dissolution of calcium sulfate (100 mg) on the volume of the pickling solution (5% H_3PO_4 + 0.5% NH_4OH)

As can be seen from Figure 1, the dissolution rate depends on the reagent/gypsum ratio. With increasing this ratio 10 times, the dissolution rate increased 30 times.

The main factor limiting the use of acidic solutions is the corrosion of metals from which the pipelines or elements of heat exchange, mass transfer and other equipment are made. Therefore, to determine alternative compositions for the removal of sediment from the surface of pipes and other equipment, studies were conducted to determine the corrosion rate of metals in various acid solutions and their compositions with acid corrosion inhibitors.

A fairly common alloy, which is used in the engineering industry for a long time, is steel 20. In particular, its mechanical properties determine the widespread use of this brand in boiler construction, manufacture of pipes and heating elements for various purposes. Therefore, all studies in the work were conducted with steel 20.

From the above results (Figs. 2–4) it is seen that in static conditions the polarization resistance of tap water in Kyiv is insignificant and is 305–316 Ohms. Solutions of hydrochloric, sulfuric, phosphoric acids, in concentrations of 10%, cause significant corrosion of steel 20. The polarization resistance of these solutions is 5.3; 8.4 and 15.1 Ohms. Adsorbed on the metal surface, these anions form compounds that have good solubility. This leads to an increase in the rate of corrosion of steel. The most aggressive are chloride anions, which are able to easily penetrate through the protective surface films of the metal (Shabliy, et al., 2017; Cervova, 2014).

The presence of urotropin in the solution at a concentration of 5 g/dm^3 causes an increase in polarization resistance, ie an increase in the protective effect. The maximum protective effect after two hours was observed:

– for a mixture of hydrochloric acid and urotropin in a ratio of 100:5, the polarization resistance increased to 164.5 Ohms;

– for sulfuric acid with urotropin (100:5) these figures increased to 75.3 Ohms;

– for a mixture of phosphoric acid and urotropin (50:5) it reached 94.5 Ohms.

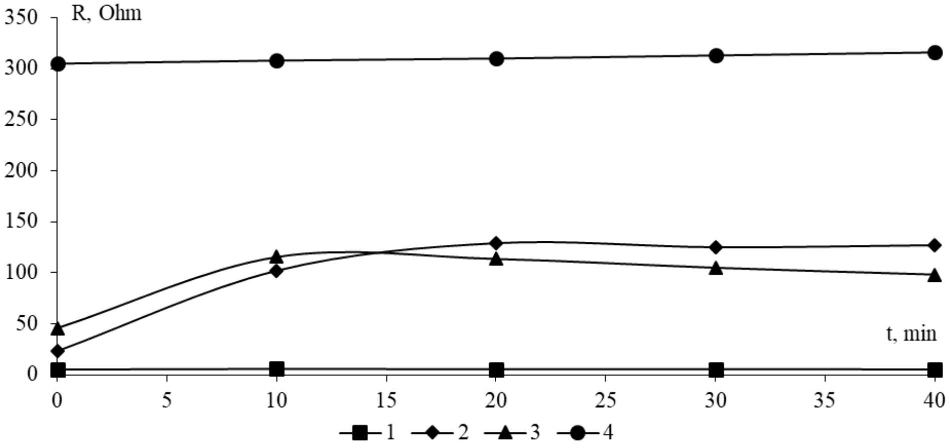

Fig. 2. Dependence of polarization resistance on the composition of the initial solution under static conditions: 1 – HCl (100 g/dm^3); 2 – HCl: urotropin (100:5); 3 – HCl: urotropin: thiourea (100:5:1); 4 – tap water (Kyiv)

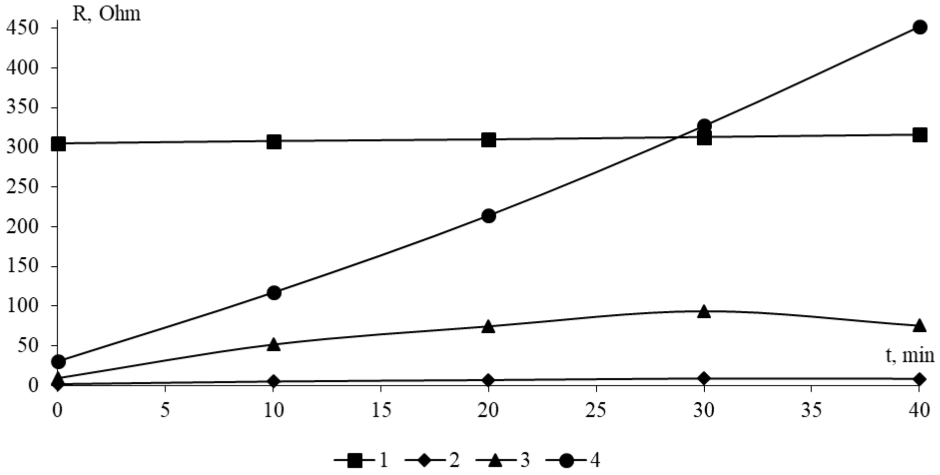

Fig. 3. Dependence of polarization resistance on the composition of the initial solution in static conditions: 1 – tap water (Kyiv); 2 – H_2SO_4 (100 g/dm^3); 3 – H_2SO_4: urotropin (100:5); 4 – H_2SO_4: urotropin: thiourea (100:5:1)

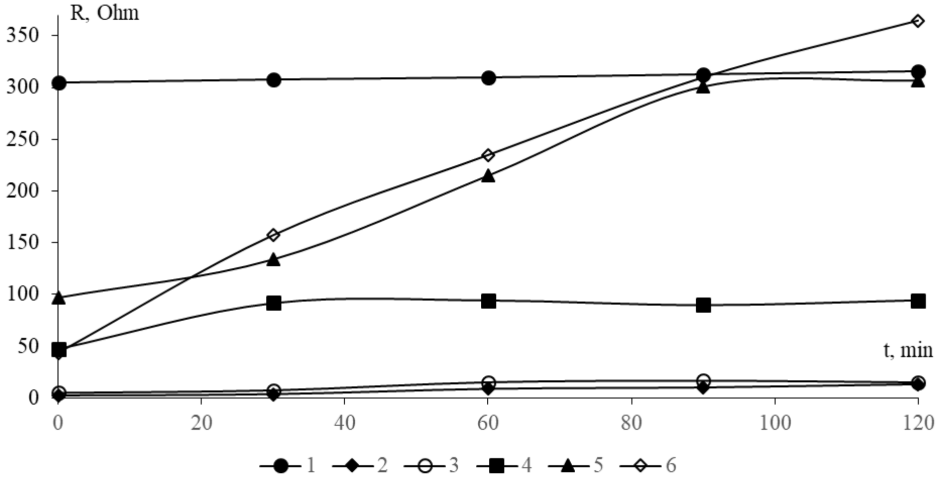

Fig. 4. Dependence of polarization resistance on the composition of the initial solution in static conditions: 1 – tap water (Kyiv); 2 – H_3PO_4 (50 g/dm^3); 3 – H_3PO_4 (100 g/dm^3); 4 – H_3PO_4: urotropin (50:5); 5 – H_3PO_4: urotropin: thiourea (50:5:1); 6 – H_3PO_4: urotropin: thiourea (100:5:1)

However, the corrosion rate in these media is higher compared to tap water. The result of the addition of thiourea is not unambiguous. Thus, its use in a mixture with hydrochloric acid and urotropin (100:5:1) had a negative effect – the polarization resistance is reduced to 49.8 ohms. In the presence of phosphoric acid under the same conditions, this figure reaches the values of tap water and is 365 ohms. An impressive effect is observed when used in a mixture of sulfuric acid: the polarization resistance increased to 1136 Ohms.

The reliability of the obtained results is confirmed by experiments conducted by the massometric method (Table 6).

Table 6. Corrosion of steel in acid solutions and acid compositions

№	**Solution**	**Concentration, g/dm^3**	**Corrosion rate**	
			massometric, g/(m^2·h)	**deep, mm/year, (massometric method/method of polarization resistance)**
1	Tap water	–	0.014012	0.015618
2	HCl	50	2.903103	3.229766
3	HCl	100	5.192697	5.776991/10.63869
4	HCl urotropin	50 5	0.203566	0.226472
5	HCl urotropin	50 10	0.247372	0.275206
6	HCl urotropin	100 5	0.324675	0.361209/0.392655
7	HCl urotropin	100 10	0.373634	0.415676
8	H_3PO_4	50	2.591353	2.882938/2.734004
9	H_3PO_4	100	3.865855	4.300849/2.898746
10	H_3PO_4 ammonia	100 5	0.302843	0.336919
11	H_3PO_4 ammonia thiourea	100 5 1	0.131168	0.145927
12	H_3PO_4 ammonia thiourea	50 5 1	0.183512	0.204161
13	R-29	(pH=1.66)	0.106881	0.118907

From the results shown in table 6 it is seen that all the compositions have a higher corrosion aggressiveness than tap water, the depth of corrosion was 0.015618 mm/year.

The composition R-29 is characterized by the least corrosive aggressiveness among the considered variants. The massometric corrosion index of this composition was 0.106881 g/($m^2 \cdot h$), the depth of corrosion, respectively – 0.118907 mm/year. The mixture R-29, which was created on the basis of orthophosphoric acid, is used as a reagent for the removal of scale products – carbonates and calcium sulfates. Its destruction rate of chemically precipitated gypsum is not less than 90%. Therefore, it can be considered that the composition R-29 is an effective non-corrosive reagent for cleaning the equipment of water supply systems from salt deposition and corrosion.

4. Conclusion

Developed compositions for cleaning pipelines, surfaces of heat exchange equipment based on available inexpensive reagents that outperform analogues in efficiency, are characterized by low corrosion activity and provide removal from the metal surface of even insoluble chemically stable substances, including gypsum deposits. In neutral media, the main components of the reagent R-29 are inhibitors of salt deposits and corrosion.

The integrated use of reagents for pipeline cleaning and the use of scale stabilizers will increase the efficiency and reliability of equipment operation in heating systems, water and cooling systems in the protection of pipelines in the gas and oil industry.

In the case of effective cleaning of metal surfaces of heat exchange equipment with the subsequent use of corrosion inhibitors and sediments in water circulation systems, it is possible to increase the service life of heat exchange units by 5–10 times. In addition, in cooling systems it is possible to switch to drain-free mode and refuse to discharge circulating water to purge the systems.

In the case of acid cleaning of surfaces from deposits, there is a risk of their insufficiently effective washing from the remains of acidic reagents, which can affect the corrosion processes of the equipment when the reaction of the environment in the operating systems will be acidic. Under normal operating conditions, this threat is unrealistic. When using antiscalants, the level of water hardness in water circulation systems can increase several times. This helps to reduce the corrosive activity of water, but in the case of improper control of the dosage of the sediment inhibitor may be intense deposition of sediment on the heat exchange surfaces. There is also a risk of exceeding the permissible concentrations of reagents when discharging water during purging of the system.

References

1. Daminov, A., Ragulin, V., Voloshin, A.: Mechanism of Corrosion Damage Formation in Downhole Equipment in Wells protected by Continuous Scale Inhibitor dosing using Surface Dosing Systems. Testing of Scale and Corrosion Inhibitors. SPE International Oilfield Corrosion Symposium, Aberdeen, UK, 2006.
2. Cervova, J.: Corrosive protection of metal materials in cooling water. *American Journal of Materials Science and Application*, 1, 6–10, 2014.
3. Chichenin, V.V.: Investigation of the rate of corrosion and accumulation of sediments during evaporation of circulating water in laboratory studies. *Eastern-European Journal of Enterprise Technologies*, 5/8(77), 14–20, 2015 (in Russia).
4. Driker, B.N., Vankov, A.L.: Comparative evaluation of the effectiveness of domestic and imported salt inhibitors. *Energysaving and Watertreatment*, 1, 55–59, 2020.
5. Hegazy, M.A., Rashwan, S.M., Kamel, M.M., El, Kotb, M.S.: Synthesis, surface properties and inhibition behavior of novel cationic gemini surfactant for corrosion of carbon steel tubes in acidic solution. *Journal of Molecular Liquids*, 211, 126–134, 2015.
6. Nosachova, Yu.V.: Creation of new means and technologies for maintenance of resource saving in industrial water consumption: the dissertation ... Cand. tech. Science: 21.06.01. Kyiv: National Technical University of Ukraine "*Kyiv Polytechnic Institute*", 166, 2006 (in Ukraine).
7. Shabliy, T., Nosachova, J., Radovenchik, Y., Vember, V.: Study of effectiveness of heavy metals ions as the inhibitors of steel corrosion. *Eastern-European Journal of Enterprise Technologiesthis redundant*, 4(12–88), 10–17, 2017.
8. Singh, A., Sharma, V., Mittal, S., Pandey, G., Mudgal, D., Gupta, P.: An overview of problems and solutions for components subjected to fireside of boilers (Review). *International Journal of Industrial Chemistry*, 9, 1, 2018.
9. Zhi-Hui, X., Liang, Wu.: Corrosion inhibition of layered double hydroxide coating for Mg alloy in acidic corrosive environments. *Materials and Corrosion*, 71, 1, 118–124, 2020.

Efficient treatment of industrial wastewater using immobilized microorganisms

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Abstract

Highly concentrated wastewater from industrial enterprises, in particular the food industry, is a complex multicomponent heterogeneous system. The results of researches and a number of developed technologies of wastewater treatment of food enterprises are given. Among them, wastewater treatment with a high content of organic matter on the example of a dairy plant; removal of nitrogen compounds on the example of wastewater from a confectionery factory; phosphate treatment of meat processing plant wastewater. The method of biological treatment with immobilized microorganisms is characterized by simplicity, reliability, low energy costs, which determine its viability and cost-effectiveness.

Keywords: wastewater, immobilized microorganisms, food industry

1. Introduction

Increasing pollution of natural waterbodies by compounds of nutrients that come from insufficiently treated wastewater as a communal, as well as industrial origin, leads to an increase of eutrophication processes in water sources. The results are: the rapid development of aquatic plants and algae, water pollution, reduction of oxygen concentration in water, deterioration of the waterbodies state, strengthening of saprogenic processes, reduction of the hydrobionts species diversity, etc.

Biological and physico-chemical purification technologies are used for wastewater treatment from nitrogen and phosphorus compounds (Malovanyy et al., 2014; Tulaydan et al., 2017). Recently, biological methods based on processes of denitrification for the removal of nitrate from wastewater and dephosphotation for the removal of phosphorus compounds are becoming more widespread (Akpor and Muchie, 2010; Wei et al., 2014; Kim et al., 2011; Zhukova et al., 2011; Dytczak et al., 2008; Othman et al., 2013). In such methods, activated sludge is used and certain conditions for wastewater treatment are created. Thus, for dephosphotation it is necessary to create sequentially anaerobic and aerobic conditions (Wang et al., 2009; Yang et al., 2010). Then, in anaerobic conditions, activated sludge is stressed, and, consequently, it accumulates granules of polyphosphate in the bacterial cells, decomposition of which generate energy for bacteria (Lemaire et al., 2009; Nielsen et al., 2012). In aerobic conditions, bacteria accumulate phosphate in excess amounts, which is removed from water. They receive energy as a result of the decomposition of polyhydroxyalcanoates or polyhydroxybutyrate, which are synthesized by the cells under anaerobic conditions. For the growth and development of bacteria in the processes of dephosphotation of wastewater, they need the presence of carbon sources easily digested by cells, for example, volatile fatty acids: acetic, propionic, etc (Yuan et al., 2012).

According to recent studies of the dephosphotation processes in wastewaters, the degree of phosphorus compounds removal affected by the nitrate concentration, because in anaerobic conditions denitrification is possible in parallel with dephosphotation (Brown et al., 2011; Zubrowska-Sudol et al., 2005; Podedworna et al., 2012; Rahimi et al., 2011). Bacteria that remove nitrate from water – denitrifiers, as well as bacteria that remove phosphate, require carbonaceous compounds that are easily digestible by them in anaerobic conditions (Blackburne et al., 2008; Kapagiannidis et al., 2012). Thus, the question arises whether the process of denitrification will inhibit the activity of bacteria that remove phosphorus from the water and, if so, at what degree (Beuckels et al., 2015).

Highly concentrated wastewater from industrial enterprises, in particular the food industry, is a complex multicomponent heterogeneous system that contains coarse impurities, suspended solids, emulsified fat particles, organic colloidal and solutes, surfactants, nutrients nitrogen and phosphorus compounds, etc. (Table 1).

Table 1. Indicators of highly concentrated wastewater from the food industry, mg/dm^3

Indicator	**Dairy**	**Confectionery factor**	**Meatfactory**	**MPC at assignment**	
				For biological treatment	**In a water body**
Suspended substances	600	900	725–1150	500	+0.25
COD	3000	5160–12000	2060–3040	500	15.0
BOD	2400	–	–	350	3.0
BOD5	–	3200-6800	1620–1760	–	–
Ammonium nitrogen	15-50	39–41	–	–	2
Phosphates	16	25	45–50	–	2
Fats	60-100	–	–	–	0
Synthetic surfactants	–	–	35	20	0,5
pH	5.1–8.4	5.5–5.7	6.5–7.5	6.5–8.5	6.5–8.5

Traditional technologies of biological treatment of such wastewater have a number of disadvantages:

– non-compliance of the quality of treated water with sanitary requirements due to changes in the composition of wastewater – new technologies are needed;
– long duration of aeration and low rate of oxidation of organic pollutants;
– incorrect treatment of nitrogen and phosphorus compounds leads to flowering and overgrowing of water bodies;
– swelling of activated sludge as a result of mass development of filamentous bacteria; difficulties associated with the need to maintain high doses of activated sludge;
– large amounts of sludge and the cost of their disposal; the possibility of "poisoning" of activated sludge and the death of microorganisms upon receipt of toxic substances (surfactants, etc.);
– significant costs of electricity for air supply, recirculation of activated sludge;
– instability during periodic and seasonal work;
– large areas of treatment facilities.

2. Materials and Methods

The assessment of COD in the effluent was carried out on the basis of standard procedure using dichromate method. The potentiometric method involving the use of ion selective electrodes was used to assess the nitrogen concentration found in the effluent. The concentration of suspended solids was determined by gravimetric method.

Wastewater was supplied to the first anaerobic bioreactor and then passed through the following anaerobic and aerobic bioreactors. The pumps located at the bottom of the anaerobic bioreactors as well as the perforated recirculation pipe with holes enabling to sprinkle water, were employed in order to carry out mixing of the reacting masses. The required quantity of air was provided to the anoxic chambers by means of a micro-compressor, in order to keep the concentrations of dissolved oxygen at the level of 0.1–0.2 mg/dm^3 and in the case of the aerobic chamber – within 1.6–2.5 g/m^3. The biomass immobilization was performed by installing the carriers made of VIYA (Eyelash) type artificial fibers in the bioreactors. The specific surface carriers gradually reduced from approximately 3800–3700 m^2/m^3 in the anaerobic bioreactors to 380 m^2/m^3 in aerobic ones.

The reliability of the obtained data is $P < 0.05$, i.e. statistically significant differences are found. To assess the significance of the difference between the averages of the two groups, t–test (Student's test) was used.

3. Results and Discussion

To treat wastewater with a high content of organic matter in the first stage, it was proposed to use an anaerobic method in a bioreactor with microorganisms immobilized on fibrous carriers. Verification of the method on the wastewater of the dairy on experimental model of a two-stage anaerobic bioreactor with immobilized microorganisms (Fig. 1) allowed to establish rational parameters of its operation. At the initial COD of wastewater 4400 mg/dm^3: hydraulic load – 2 m^3/(m^3·day) (Fig. 2), which provides a degree of treatment by COD up to 70% (Fig. 2); duration – 12 hours (in sludge digester it takes 10–20 days); concentration of immobilized biomass – up to 20 g/dm^3.

The influence of the initial concentration of organic substances in wastewater (according to the COD) on the effect of their removal is shown in Fig. 3 – in an anaerobic bioreactor of the I degree, and Fig. 4 – in anaerobic II degree. In stage I, a significant effect of the initial COD on the removal effect was observed with a change in effect from 45% to 85% with a decrease in COD 4400 mg/dm^3 to 500 mg/dm^3. In the second stage, where the wastewater contained products formed by the destruction of organic matter by biofouling microorganisms on the carriers of the first stage bioreactor, a slower growth of the effect from 60 to 80% with a change in COD 2390 mg/dm^3 to 100 mg/dm^3.

Fig. 1. Photo of an experimental model of a two-stage anaerobic bioreactor with microorganisms immobilized on carriers

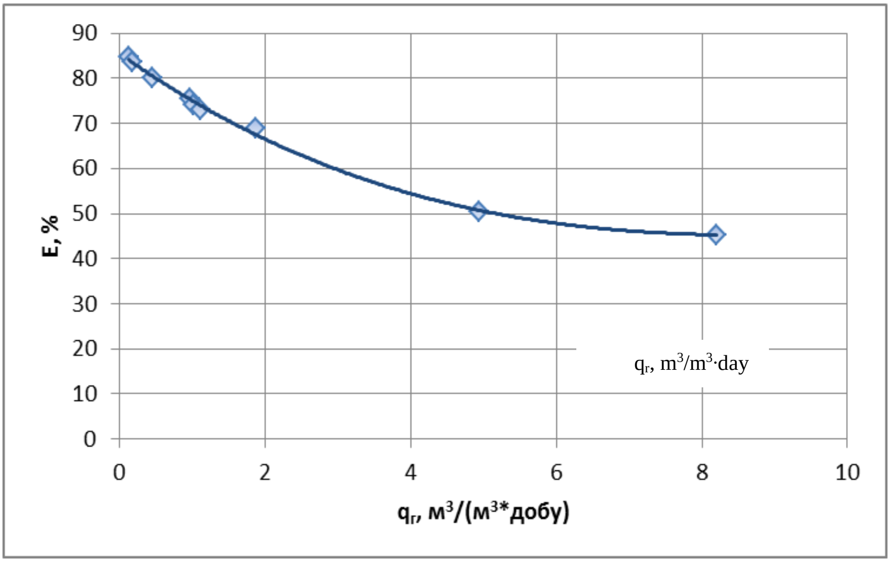

Fig. 2. Dependence of the effect of wastewater treatment on COD (E) in anaerobic sections from hydraulic loading (q_r)

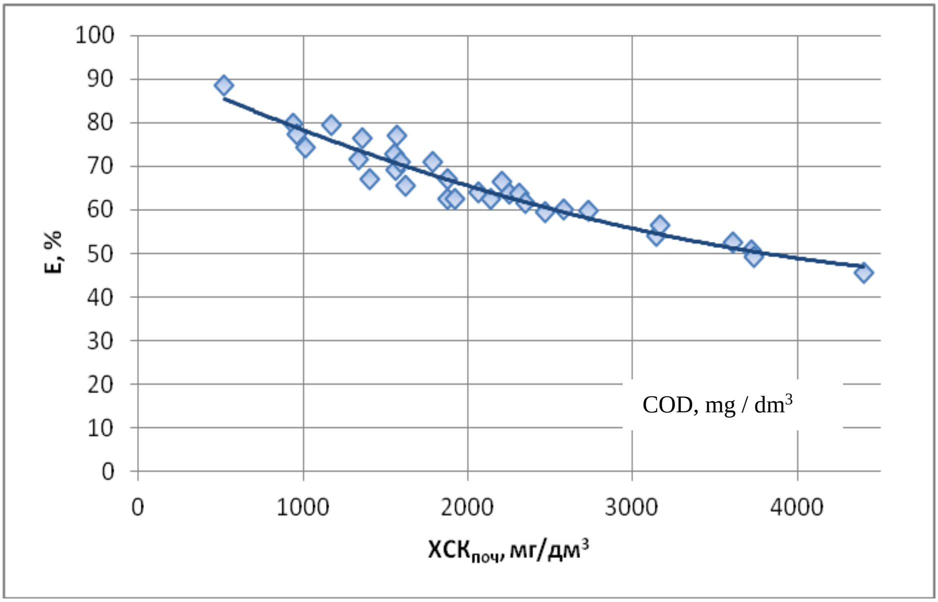

Fig. 3. Dependence of the COD (E) effect of treatment on the initial value of COD in anaerobic bioreactor of the I degree

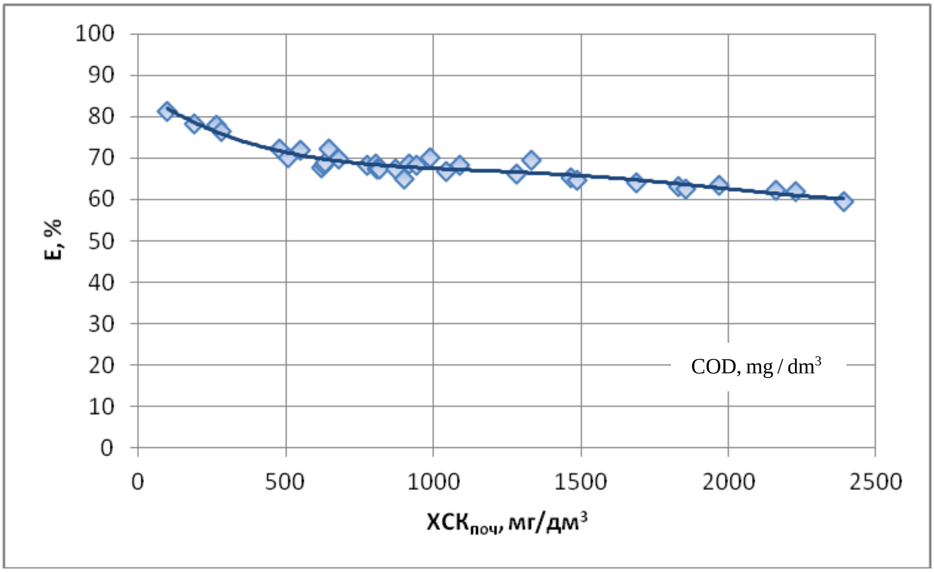

Fig. 4. Dependence of the COD (E) effect of treatment from organic substances on the initial value of COD in anaerobic bioreactor of the II degree

To oxidize the organic matter remaining after the second stage of the anaerobic process, the aerobic method of wastewater treatment in bioreactors with immobilized microorganisms was used. Experimental verification of the aerobic stage was performed in the model shown in Fig. 5.

In aerobic bioreactors there is not only the oxidation of organic matter, but also the processes of nitrification and dephosphotation. Ammonium nitrogen is oxidized to nitrites and nitrates, the change in the concentration of nitrogen compounds in anaerobic and aerobic conditions is shown in Fig. 6. After wastewater treatment at the outlet of the aerobic bioreactor, the highest concentration of nitrates was 30 mg/dm^3 – within normal limits when discharged into natural reservoirs of Ukraine.

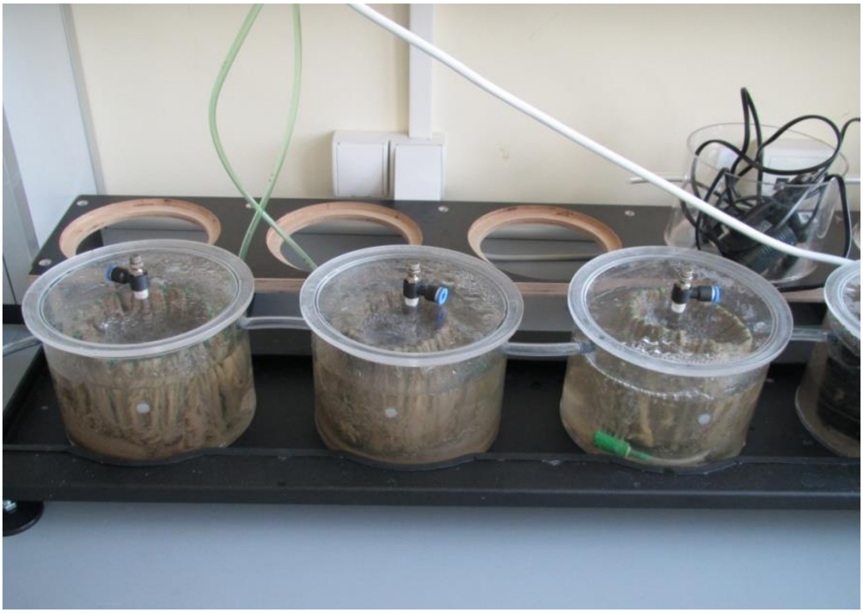

Fig. 5. Photo of an experimental model of three-stage aerobic bioreactor with immobilized on carriers microorganisms

As a result of the research, the technology of anaerobic-aerobic biological treatment of highly concentrated wastewater was developed (Fig. 7), which can be recommended for food industry enterprises: dairies, cheese factories, meat plants, breweries, malt plants, confectioneries, etc.).

The technology was tested on five-stage bioreactors with immobilized microorganisms (Fig. 8) in the wastewater of the dairy plant.

According to the proposed technology, in the first two stages wastewater is treated in anaerobic bioreactors, which allowed to treat them from organic matter by 60–70% in conditions of high concentrations of biomass immobilized on carriers of microorganisms – up to 40 g/dm^3.

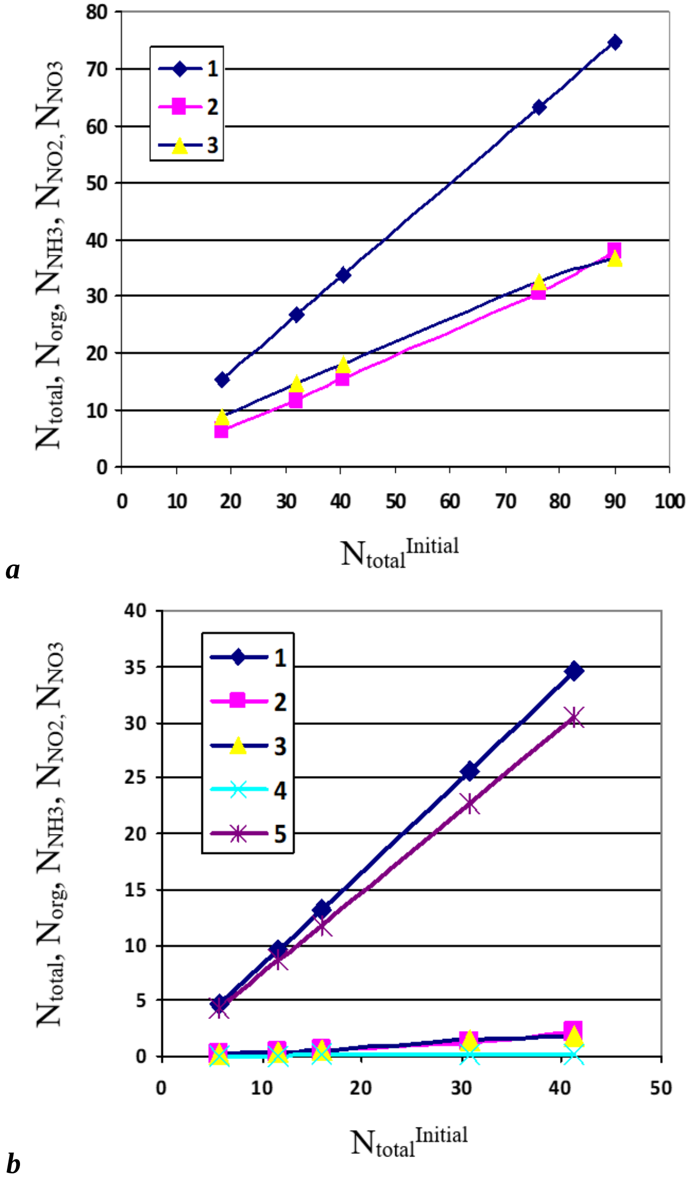

Fig. 6. Change in the concentration of nitrogen compounds (mg / dm^3) in bioreactors: a – in anaerobic; b – in aerobic: 1 – concentration of total nitrogen compounds at the exit of the bioreactor N; 2 – the same, organic nitrogen N_{org}; 3 – the same, ammonium nitrogen N_{NH3}; 4 – the same, nitrite N_{NO2}; 5 – the same, nitrates N_{NO3}

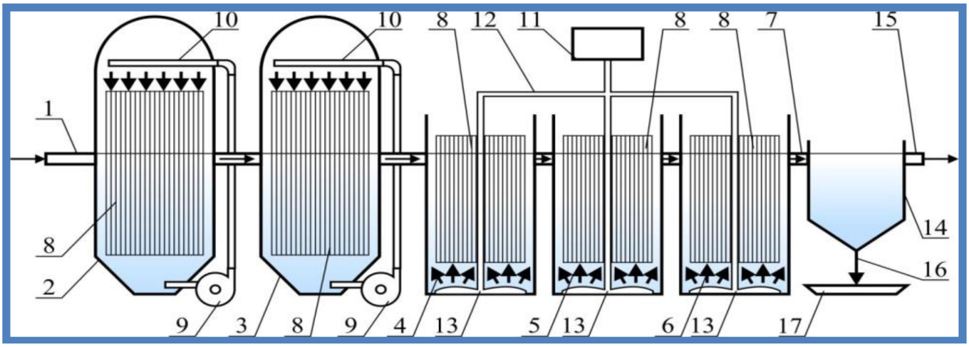

Fig. 7. Scheme of technology of anaerobic-aerobic treatment of highly concentrated wastewater: 1 – wastewater after mechanical treatment and averaging; 2,3 – anaerobic bioreactors; 4,5 – anoxide bioreactors; 6 – aerobic bioreactor; 7 – removal of a mixture of wastewater and activated sludge; 8 – fibrous carrier; 9 – circulating pump; 10 – pipe with holes for recirculating water; 11 – blower station; 12 – air ducts; 13 – aerators; 14 – secondary settling tank; 15 – drainage pipeline for treatment water; 16 – sludge removal; 17 – sludge sites

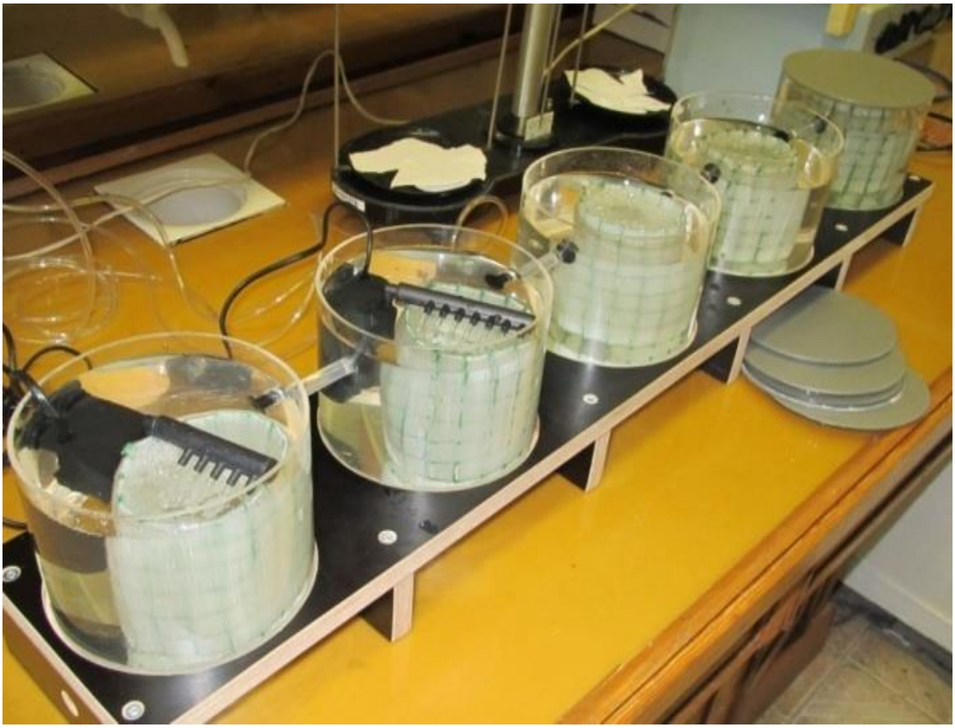

Fig. 8. Photo of experimental model of five-stage bioreactors with immobilized on carriers microorganisms

Next, wastewater is treated under anoxide conditions in the next two bioreactors, also equipped with carriers with a biomass concentration of up to 25 g/dm^3. Under these conditions, the destruction of organic compounds continues, the formation of simple inorganic ones, and the process of denitrification takes place, as a result of which the content of nitrogen compounds decreases. The final stage is an aerobic process in a bioreactor with immobilized microorganisms, in which the removal of organic pollutants reaches more than 95%. There is a process of nitrification and purification of water from phosphorus compounds. In terms of pollution, treated wastewater meets the requirements for discharge into natural reservoirs.

The advantages of the developed technology include:

– increase in oxidative capacity of buildings (2–3.5 times compared to traditional buildings) and the rate of destruction due to increased biomass of microorganisms when using fibrous media;
– increasing the degree of wastewater treatment and bringing their quality to current sanitary standards;
– reduction of sediment volumes by 25–35% due to the anaerobic process and in aerobic - in the trophic chains of the biocenosis;
– reduction of energy costs up to 40% due to the anaerobic process;
– obtaining energy;
– reduction of capital and operating costs by 30–45%.

As carriers of immobilized microorganisms, the use of nylon textured thread with a specific surface area of 4000–5000 m^2/m^3, fiber diameter of 1.5–2.5 mm, microfiber diameter of 100 μm (Fig. 9). In anaerobic bioreactors, the formation of biofouling on carriers (Figs. 10, 1), granular sludge (Figs. 10, 3) was observed. In aerobic there was free-floating activated sludge (Fig. 10, 2).

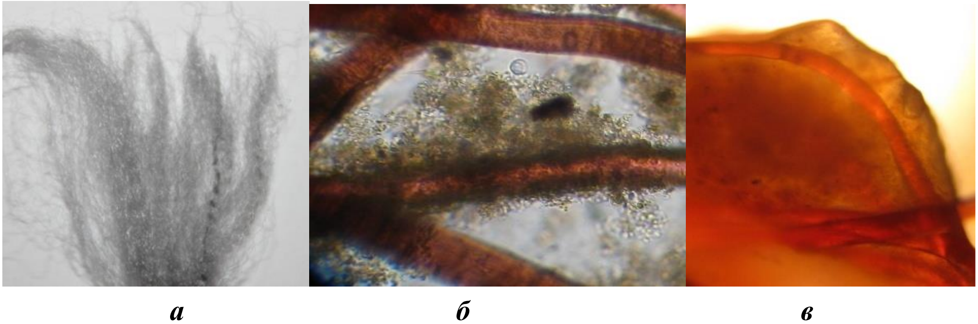

Fig. 9. Media: a – photo; b, c – microphotograph of fiber with immobilized biomass at magnification x200 (a) and microfibers at magnification x100 (b)

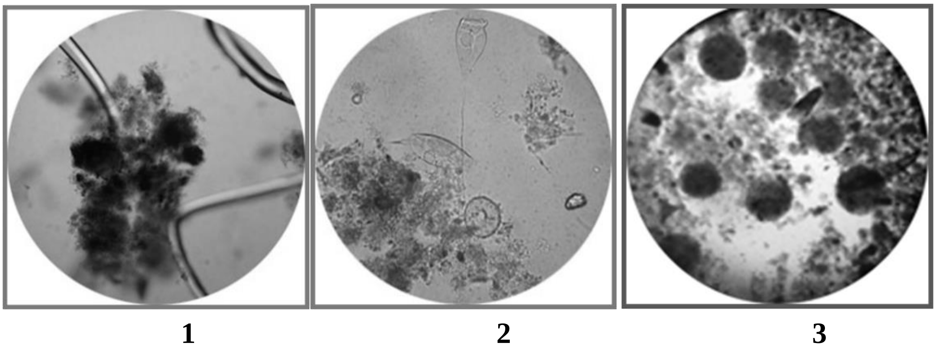

Fig. 10. Microphotographs (x200): 1 – biofouling of carriers in bioreactors; 2 – free-floating activated sludge in aerobic bioreactor; 3 – granular activated sludge in anaerobic bioreactor

The developed anaerobic-aerobic technology (Fig. 11) was implemented in the project of treatment facilities of a confectionery factory in Rivne region. In order to remove phosphorus compounds, the technology of anaerobic-aerobic treatment of industrial wastewater was developed, shown in Fig. 12, which can be used for wastewater from meat processing plants, dairy plants, malting plants, etc.

The technology for deep treatment of wastewater from phosphates offers a two-stage biological treatment with phosphoaccumulating activated sludge (PAM) sequentially in anaerobic and aerobic bioreactors. Verification of the work of technology in the production of wastewater treatment of malt plant with indicators, in particular, COD 1700–2100 mg/dm^3; phosphate concentration – 29–35 mg/dm^3, showed that the use of the proposed technology provides a degree of purification of 93–95% and 82–85%, respectively, and the quality of purified water, according to current requirements.

The technology was used in the project of treatment facilities of a meat plant (with a cattle slaughterhouse) in Rivne region (Fig. 13) with a wastewater capacity of 500 m^3/day and for which a treatment plant was built and put into operation.

The wastewater of the meat plant is characterized by uneven flow and consumption of contaminants during the day, the ability to foam, contains sand, fat, blood, particles of kaniga, bristles, etc. Indicators of untreated wastewater were, m/dm^3: for COD – 2060–3040; for BOD$_5$ – 1220–1760; for suspended solids – 730–1150; for phosphates – 46–200; for nitrites – 23–38; for nitrates – 52–60; for surfactant – 35.

After the biocoagulator-flotator, an averager is arranged, from which the wastewater is fed for biological treatment into anoxide and aerobic bioreactors for purification from organic matter, removal of nitrogen and phosphorus compounds. The use of nitrite in wastewater up to 38 mg/dm^3 and nitrate up to 60 mg/dm^3 in the first stage of biological treatment of anoxide conditions for denitrification is promoted. After biological treatment, disinfection with sodium hypochlorite is provided. Indicators of treated wastewater do not exceed sanitary norms before discharge into the Goryn River.

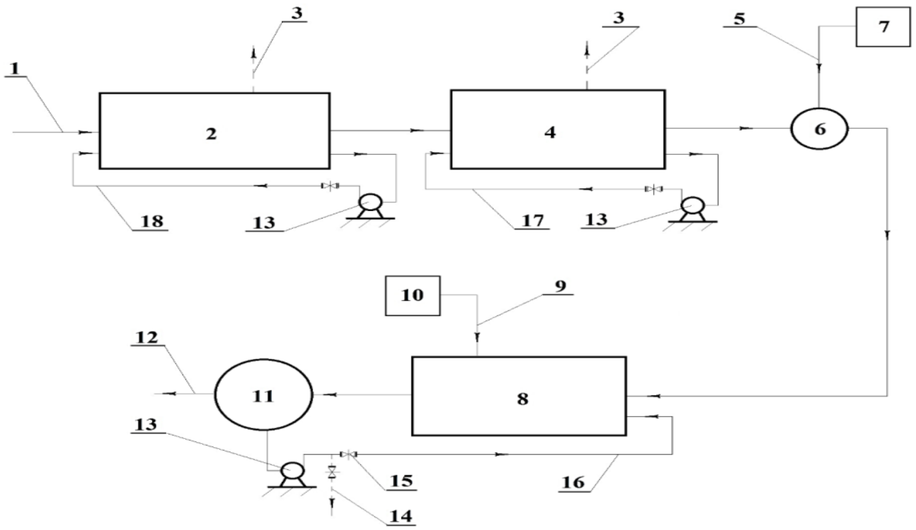

Fig. 11. Scheme of technology of biological sewage treatment of confectionery factory: 1 – sewage supply pipeline for treatment; 2 – averaging; 3 – exhaust; 4 – anaerobic bioreactor; 5 – alkali pipeline; 6 – mixer; 8 – aeration tank; 9 – air duct; 10 – compressor; 11 – secondary settling tank; 12 – pipeline for discharge of treated wastewater into the city sewer; 13 – pump; 14 – pipeline removal of excess activated sludge; 15 – latch; 16 – pipeline recirculating activated sludge; 17 – pipeline recirculation of sludge mixture; 18 – wastewater recirculation pipeline

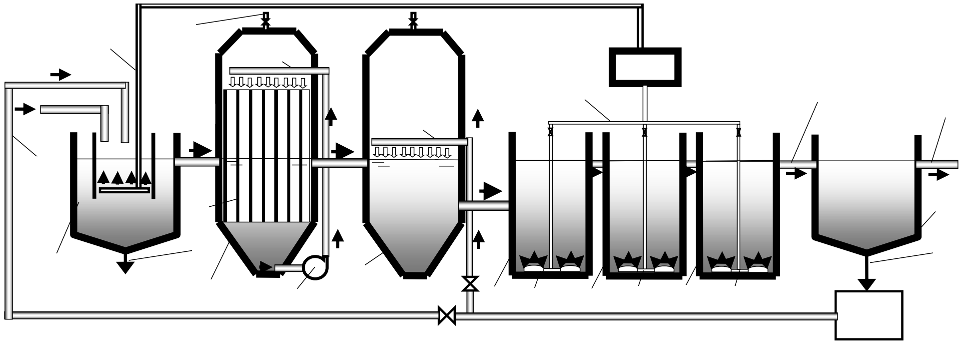

Fig. 12. Scheme of technology of anaerobic-aerobic treatment of industrial wastewater with phosphate removal: 1 – primary settling tank with biocoagulation chamber; 2 – anaerobic bioreactor; 3 – anaerobic bioreactor with FAM; 4, 5, 6 – aerobic bioreactors with FAM; 7 – drainage of a mixture of wastewater and FAM; 8 – fibrous carrier; 9 – circulating pump; 10 – pipe with holes for recirculation water; 11 – blower station; 12 – air ducts; 13 – aerators; 14 – secondary settling tank; 15 – purified water pipeline; 16 – removal of activated sludge (AM); 17 – sludge pumping station; 18 – reverse AM pipeline; 19 – pipeline of excess AM; 20 – sludge for disposal; 21 – removal of gas in the gasholder [Sewage enters after mechanical treatment (on grates, in sand traps) and averaging].

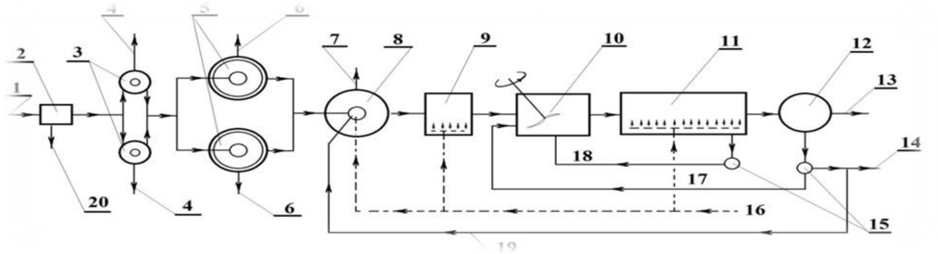

Fig. 13. Recommended technology of wastewater treatment plant: 1 - supply of wastewater to treatment facilities; 2 – receiving chamber with grilles; 3 – sand traps with circular motion of water; 4 – sand pulp on sandy sites; 5 – fat traps; 6 – removal of retained fat; 7 – removal of flotation sludge; 8 – biocoagulator-floater; 9 – averaging with air bubbling; 10 – anoxide bioreactor; 11–aerobic ioreactor; 12 – secondary settling tank; 13 – supply of wastewater for treatment and disinfection; 14 –excess activated sludge on silt sites; 15 – pump; 16 – air supply from the blower station; 17 – reverse activated sludge from the secondary settling tank; 18 – nitrate recycling pipeline; 19 – supply of excess activated sludge in the biocoagulator-floater; 20 – removal of coarse impurities

4. Summary and Conclusions

The recommended and implemented wastewater treatment technology of the meat plant provides high treatment efficiency: up to 98% for COD, up to 99% for ammonium nitrogen, up to 96% for nitrates, and up to 98% for phosphates. Concentrations of pollutants in treated water after the introduction of technologies at treatment plants do not exceed the maximum allowable discharge into a natural reservoir.

Therefore, the use of immobilized microorganisms for biological treatment of industrial wastewater can significantly increase the efficiency of treatment of organic compounds, nutrients – nitrogen and phosphorus compounds. This is due to the growth on the surface of carriers – nylon fibers, biomass of destructive microorganisms in both anaerobic and aerobic conditions for the gradual breakdown of complex organic compounds to form minerals and gases. The method of biological treatment with immobilized microorganisms is characterized by simplicity, reliability, low energy costs, which determine its viability and cost-effectiveness.

References

1. Malovanyy, A., Plaza, E., Trela, J., Malovanyy, M.: Combination of ion exchange and partial nitritation/Anammox process for ammonium removal from mainstream municipal wastewater. *Water Science and Technology,* 70, 1, 144–151, 2014.

2. Tulaydan, Y., Malovanyy, M., Kochubei, V., Sakalova, H.: Treatment of high-strength wastewater from ammonium and phosphate ions with the obtaining of struvite. 463–468 2017.
3. Akpor, O.B., Muchie, M.: Bioremediation of polluted wastewater influent: Phosphorus and nitrogen removal. *Scientific Research and Essays*, 5, 21. 3222–3230, 2010.
4. Wei, D., Shi, L., Yan, T., Zhang, G., Wang, Y., Du, B.: Aerobic granules formation and simultaneous nitrogen and phosphorus removal treating high strength ammonia wastewater in sequencing batch reactor. *Bioresource Technology*, 171, 211–216, 2014.
5. Kim, Y.M., Cho, H.U., Lee, D.S., Park, D., Park, J.M.: Influence of operational parameters on nitrogen removal efficiency and microbial communities in a full-scale activated sludge process. *Water Research*, 45, 17. 5785–5795, 2011.
6. Zhukova, V., Sabliy, L., Lagod, G.: Biotechnology of the food industry wastewater treatment from nitrogen compounds. *Proceedings of ECOpole*, 5(1), 133–138, 2011.
7. Dytczak, M.A., Londry, K.L., Oleszkiewicz, J.A.: Activated sludge operational regime has significant impact on the type of nitrifying community and its nitrification rates. *Water Research*, 42, 8–9, 2320–2328, 2008.
8. Othman, I., Anuar, A.N., Ujang, Z., Rosman, N.H., Harun, H., Chelliapan, S.: Livestock wastewater treatment using aerobic granular sludge. *Bioresource Technology*, 133, 630–634, 2013.
9. Wang, Y., Peng, Y., Stephenson, T.: Effect of influent nutrient ratios and hydraulic retention time (HRT) on simultaneous phosphorus and nitrogen removal in a two-sludge sequencing batch reactor process. *Bioresource Technology*, 100, 14, 3506–3512, 2009.
10. Yang, S., Yang, F., Fu, Z., Wang, T., Lei, R.: Simultaneous nitrogen and phosphorus removal by a novel sequencing batch moving bed membrane bioreactor for wastewater treatment. *Journal of Hazardous Materials*, 175, 1–3, 551–557, 2010.
11. Lemaire, R., Yuan, Z., Bernet, N., Marcos, M., Yilmaz, G., Keller, J.: A sequencing batch reactor system for high-level biological nitrogen and phosphorus removal from abattoir wastewater. *Biodegradation*, 20(3), 339–350, 2009.

12. Nielsen, P.H., Saunders, A.M., Hansen, A.A., Larsen, P., Nielsen, J.L.: Microbial communities involved in enhanced biological phosphorus removal from wastewater — a model system in environmental biotechnology. *Current Opinion in Biotechnology*, 23, 3, 452–459, 2012.

13. Yuan, Z., Pratt, S., Batstone, D.J.: Phosphorus recovery from wastewater through microbial processes. *Current Opinion in Biotechnology*, 23, 6, 878–883, 2012.

14. Brown, P., Ong, S.K., Lee, Y. W.: Influence of anoxic and anaerobic hydraulic retention time on biological nitrogen and phosphorus removal in a membrane bioreactor. *Desalination*, 270, 1–3, 227–232, 2011.

15. Zubrowska-Sudol, M., Walczak, J.: Enhancing combined biological nitrogen and phosphorus removal from wastewater by applying mechanically disintegrated excess sludge. *Water Research*, 76, 10–18, 2015.

16. Podedworna, J., Żubrowska-Sudoł, M.: Nitrogen and phosphorus removal in a denitrifying phosphorus removal process in a sequencing batch reactor with a forced anoxic phase. *Environmental Technology*, 33, 2, 237–245, 2012.

17. Rahimi, Y., Torabian, A., Mehrdadi, N., Shahmoradi, B.: Simultaneous nitrification–denitrification and phosphorus removal in a fixed bed sequencing batch reactor (FBSBR). *Journal of Hazardous Materials*, 185, 2–3, 852–857, 2011.

18. Blackburne, R., Yuan, Z., Keller, J.: Demonstration of nitrogen removal via nitrite in a sequencing batch reactor treating domestic wastewater. *Water Research*, 42, 8–9, 2166–2176, 2008.

19. Kapagiannidis, A.G., Zafiriadis, I., Aivasidis, A.: Effect of basic operating parameters on biological phosphorus removal in a continuous-flow anaerobic–anoxic activated sludge system. *Bioprocess and Biosystems Engineering*, 35, 3, 371–382, 2012.

20. Beuckels, A., Smolders, E., Muylaert, K.: Nitrogen availability influences phosphorus removal in microalgae-based wastewater treatment. *Water Research*, 77, 98–106, 2015.

The impact of electrolytic pretreatment of aqueous media from an anthropogenic polluted resource on anaerobic activated sludge from wastewater treatment systems – a case study

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Abstract

This paper focused on the impact of electrolysis pretreatment to intensify bioprocesses in wastewater treatment systems and additional energy production through biogas. Pretreatment methods aim to increase the rate of biodegradability of organic matter and to utilize by-products. Electrolysis decomposition deforms the cell walls of substrates, making their contents easily accessible to bacteria for anaerobic digestion. The effect of electrolysis pretreatment was investigated, particularly through a comparison of the impact of treatment with anode-activated effluent and cathode-activated effluent together with the excessive activated sludge. The effects on the dominance of ecological-trophic groups of bacteria were observed, as well as positive impacts of cathodic treatment, in particular stabilization of acid-base balance of the system and increase of biogas during anaerobic digestion, at the same time the inhibiting effect of anode-activated effluent on the growth of anaerobic activated sludge. The combination of electrolysis cells with bioreactors is considered promising.

Keywords: electrolytic pretreatment, anaerobic digestion, activated sludge, cathode-activated effluent, anode-activated effluent

1. Introduction

Nowadays, many water bodies are suffering from anthropogenic impact, pollutants of organic and anthropogenic origin. Overall, in Ukraine, the anthropogenic pressure on water bodies increases every year; in particular, the volume of discharged reclaimed water rises. The capacity of the wastewater treatment plant exceeds the volume of wastewater flowing to it and is not used to its total capacity, but the technical condition of almost all wastewater treatment plants requires modernization or reconstruction. According to the assessment of the regions, the east of Ukraine has the highest rates of discharges of polluted and normative-treated reclaimed water into water bodies for 2019, and the volumes of discharges of normative-treated and polluted reclaimed water are quite close. Almost one-third of the wastewater is treated using biological wastewater treatment methods, leading to the next challenging issue of disposal and recycling of excess activated sludge because the volume of sewage sludge accumulation is sufficient (Ministry of Environmental Protection and Natural Resources of Ukraine, 2018).

The sewage sludge treatment is managed by different methods, such as dumping into water bodies, burning, landfilling, drying, and used as organic fertilizer. Furthermore, the utilization of excess sewage sludge in anaerobic digestion processes is considered promising, providing additional energy in the utilization process and improving the quality of the fertilizer after the process. The review paper (Wacławek et al., 2019) describes advances in the anaerobic digestion of activated sludge that has led to increased biogas production, with different variations of the pre-disintegration treatment: biological, physical, and chemical. The paper revealed that ultrasonic and microwave digestion provides the highest biogas yield but are also the most energy demanding. Optimization of pretreatment methods is an important task in the development of new approaches and techniques to intensify the process of methanogenesis. Bioelectrochemical reactions can shorten the anaerobic digestion reactor stabilization period and increase the amount of released methane. The treatment of liquid medium with electrical pulses enables the inactivation of microorganisms at lower temperatures and a shorter time.

This study aims to investigate the effect of electrolytic pretreatment of aqueous media from an anthropogenic polluted resource on anaerobic activated sludge from wastewater treatment systems.

2. Materials and Methods

2.1. Features of the liquid phase from the reservoir

The water used as a substrate for anaerobic digestion was taken from the Kosivshchynske water reservoir, one of the largest reservoirs in the Sumy region. The water reservoir was created in the 1960s with an area of 132 ha on the Sumka river to fulfill the technical needs of the enterprise.

Kosivshchynske reservoir occasionally experiences ecological problems: the discharge of untreated reclaimed water from the surrounding territories and cases of mass fish mortality. It happens because there is no water flow circulation in the reservoir; besides, the source of pollution is the sewage waste of the nearby village, which flows through the river into the reservoir (https://debaty.sumy.ua).

The reservoir condition continues to improve with the introduction of an artificial culture of green algae called chlorella, but additional water treatment and improvement methods are needed, especially in summer, when there are active algal blooms (http://everyday.sumy.ua/u-kosivshhinske-vodosxovishhe-vneseno-zhivu-suspenziyu).

Reservoir water was sampled from the dam near the point where the reservoir became a river (Fig. 1,2). The parameters obtained for the liquid phase from the reservoir: hydrogen ion exponent (pH) 9.14; redox potential (ORP) 21 mV; total dissolved solids (TDS) 297 ppm.

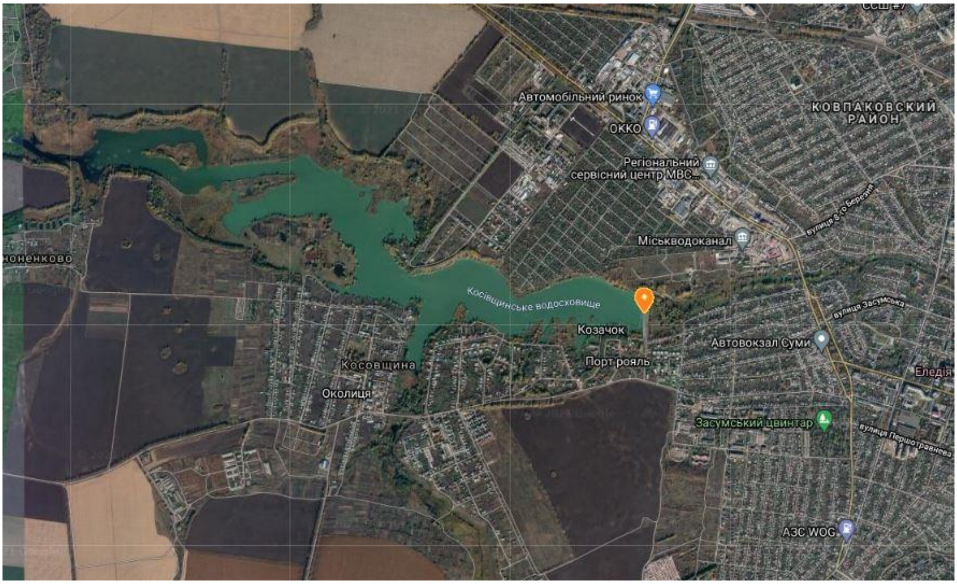


Fig. 1. Map of the sampling location

Fig. 2. Liquid phase from the reservoir, Sumy region, Ukraine

The situation of mass fish mortality in Kosivshchynske reservoir was observed every year in July-August. The environmental inspectorate in the Sumy region initiated a commission inspection of the reservoir after complaints from residents of Kosovschina about fish mortality in the reservoir in the summer of 2021. As a result of laboratory research of water samples on specific hydrochemical indicators, significant exceedances of some indicators, in particular, the content of ammonium nitrogen – 2.93 mg/L (standard – 0.5–1 mg/L), biological oxygen demand (BOD_5) – 12.6 mg/L (standard – 3 mg/L) were identified.

The analysis results showed indicators of impaired biochemical processes: swampy smell increased colored and high ammonia content. Moreover, microbiological contamination of the water body with excrements was detected.

2.2. Characteristics of excess activated sludge

Excess activated sludge from anaerobic transformation systems of the MHP "Orel Lider" was used as an inoculum. One of the enterprise's areas of operation is the process of producing biogas and digestate via anaerobic digestion of poultry manure mixed with sweet sorghum or maize silage. The plant is located in the Dnipropetrovsk region in the south of Ukraine.

Pre-treatment of the sludge required temperature incubation at 35°C for 48 hours. The parameters obtained for the sludge: pH 6.73; ORP – 409 mV; TDS 112 ppm.

2.3. Experimental set-up

2.1.1. Laboratory anaerobic digester

The experimental setup for studies of the anaerobic digestion process and biogas synthesis without pre-treatment was shown in Fig. 3.

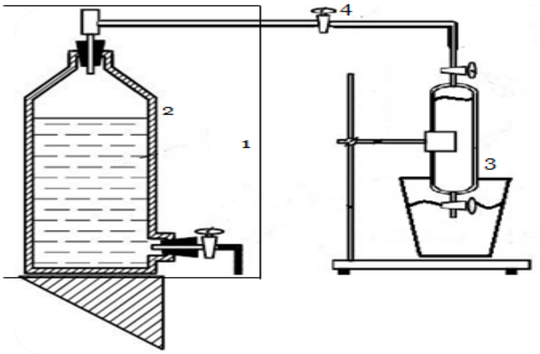


Fig. 3. A scheme of the laboratory installation: 1 — thermal chambers; 2 — bioreactor; 3 — water displacement system for collecting biogas; 4 — tube

For the experiments, the bioreactor (2) was loaded with eutrophic water from a polluted source mixed with activated sludge from a sewage treatment plant, which contains a significant amount of anaerobic bacteria. To support the productivity of the anaerobic digestion process, the bioreactor was placed in a heat chamber to maintain a constant temperature of approximately 35°C (mesophilic conditions) and wrapped in a light-proof material. The bottom part of the bioreactor was equipped with a digestate sampling point during the anaerobic digestion process.

A leak-tight plug seals the reactor with a gas collection tube (4). The biogas produced was collected in calibrated flasks (3) with acidic pH water to avoid dissolving carbon dioxide/acetate solution to precipitate the sulfide biogas fraction. The contents of the reactor were stirred mechanically by hand for 1 min every day.

2.1.2. Electrolytic pretreatment

The laboratory setup for electrolytic pretreatment of the anaerobic digestion substrate includes a generator, a tank, and two graphite electrodes – a negative cathode and a positive anode – separated by a thin membrane that allows the electrolysis products to pass through and divides the electrodes from each other. The operating principle of the unit was illustrated in Fig. 4.

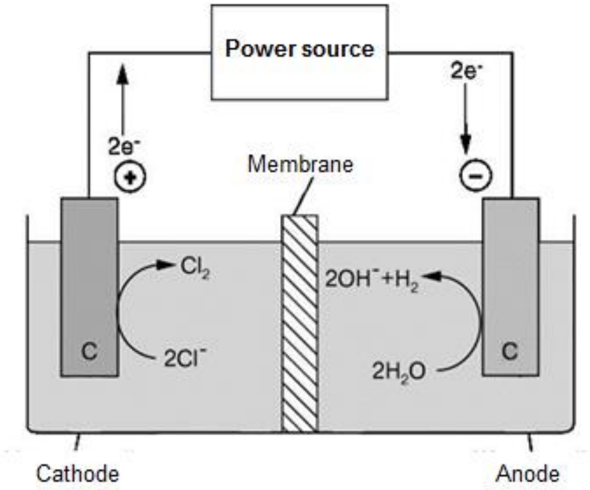


Fig. 4. Scheme of the electrolysis cells

A constant voltage source was connected to the electrodes immersed in the solution. A voltage of 10 A was supplied, and a current begins to flow from the power supply to the electrodes of all the cells in the unit. The electrolysis process leads to the attraction of anions (positively charged ions) of the substance dissolved in the water to the negatively charged cathode. The positively charged anode breaks down the water molecules, producing two hydrogen atoms and one oxygen atom. The unit has two drains for positively and negatively charged water that collects the water in different vessels. The range of treatment time is 60–90 minutes for 10 l of water. 75 minutes was taken in the experiment. Once the unit starts up, the first batch of treated water is flushed out, and after 20–30 minutes, the treated water begins to be collected for loading the bioreactor.

2.4. Cultivation Set-Up – case study

A total volume of mixture equal to 3000 ml was used for cultivation. The volumetric ratio of eutrophic water to activated sludge was 2:1.

Cultivation was performed under anaerobic conditions at 35°C (mesophilic conditions), with mechanical shaking of the water bath (once a day).

A water column displacement system (250 ml) was used to collect and determine the biogas volume. In addition, H_2S deposition occurred in an acetate trap (0.1 M $Zn(CH_3COO)_2$-$2H_2O$) as zinc sulfide (white flakes).

The main parameters measured during anaerobic digestion were pH, ORP, TDS. The experiments were conducted in the summertime and the eutrophic water was withdrawn just before the start of the experiments in July.

3. Results

After the electrolysis treatment, the activated effluent is obtained as anode and cathode liquid with the following parameters shown in Table 1.

Table 3. Liquid phase activation characteristics after passage through the electrolysis cell

Parameters	***ORP, mV***	***pH***	***TDS, ppm***
Anode activated liquid phase	1187	2.57	134
Cathode water eutrophic liquid phase	-360	10.86	865

The liquid differs visually in color, as shown in Fig. 5, and in smell, cathode water has a characteristic smell of chlorine, which is released during the process.

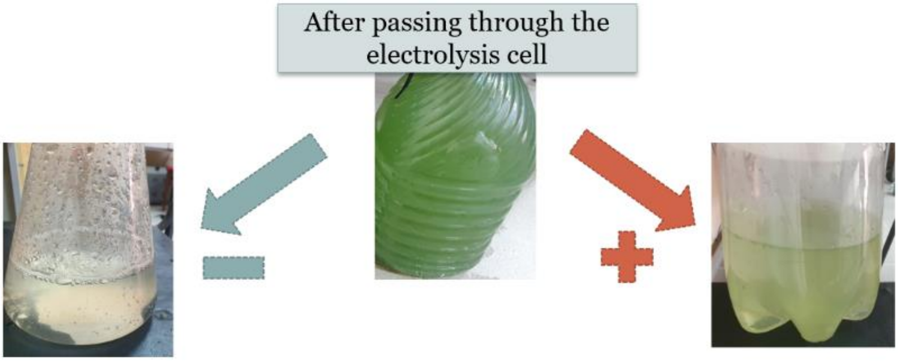


Fig. 5. Liquid phase from the reservoir after electrolysis pretreatment

Anaerobic digestion experiments were subsequently carried out in the following variations: 1. control experiment – without electrolysis treatment of the effluent; 2. experiment with anode-activated effluent together with inoculum; 3. experiment with cathode-activated effluent together with inoculum.

Comparing the results obtained from the series of experiments is shown in the graphs in Figs. 6–8. It is necessary to point out that the process of self-regulation of pH values was observed with the decrease of pH value from the initial 9.10 to 7.13 on the 3rd day in experiment 3 (Fig. 6), which could be presumably connected with the yield of volatile fatty acids in the process of acetogenesis, because for two days beforehand the hydrolysis phase was already going on during inoculum pretreatment and its thermostatted. The biogas volume was the highest with cathode-activated sludge (experiment 3) and the lowest with anode-activated sludge (experiment 2). Thus, in the control experiment (experiment 1), the biogas increase was 14 ml/: by the 15th day, in anaerobic digestion of activated sludge with anode-activated sludge – 11 ml/L, and with cathode-activated sludge – 20 ml/L (Fig. 7). It is worth noting that the system was initially designed with a low proportion of activated sludge. Consequently, the gas yield was generally lower than in experiments with a bigger portion of the inoculum (Wang et al., 2013;Thorin et al., 2017). As is known, ORP represents the degree of electron acceptance. For the growth of anaerobic microorganisms, ORP values need to be at a low level. Several previous studies outline the range of possible optimum values of this potential during methanogenesis Vongvichiankul et al., 2017). Since oxygen has a high ORP (+1.78), this is unfavorable for the development of anaerobes. In the process of sealing the system, the concentration of oxygen gradually decreases due to its absorption by the initially present aerobes. Due to natural processes, there is replacement and appearance of facultative anaerobes and subsequently of obligate ones. The lowest ORP values were in the control experiment (–330... –335) mV, when using activated effluent, the ORP values varied and stabilized at (–35... –40) mV, which is shown in Fig. 8.

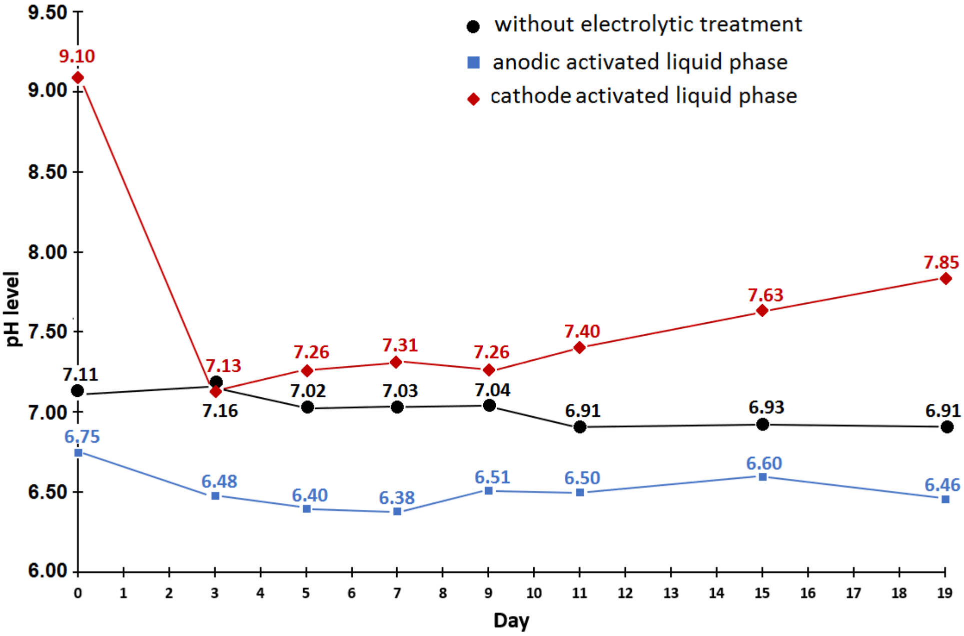


Fig.6. Changing pH values during experiments

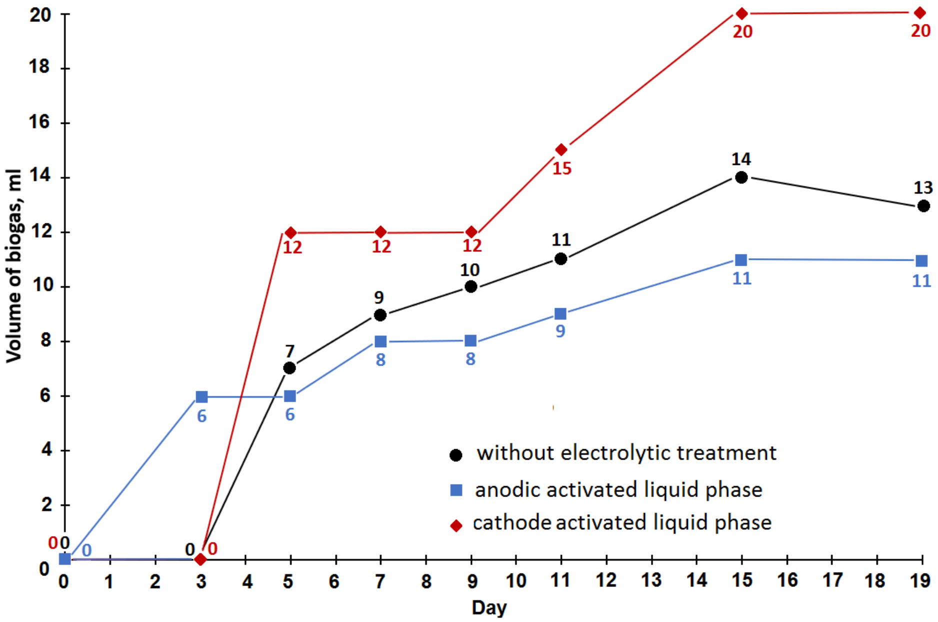


Fig.7. Changing biogas volume during experiments

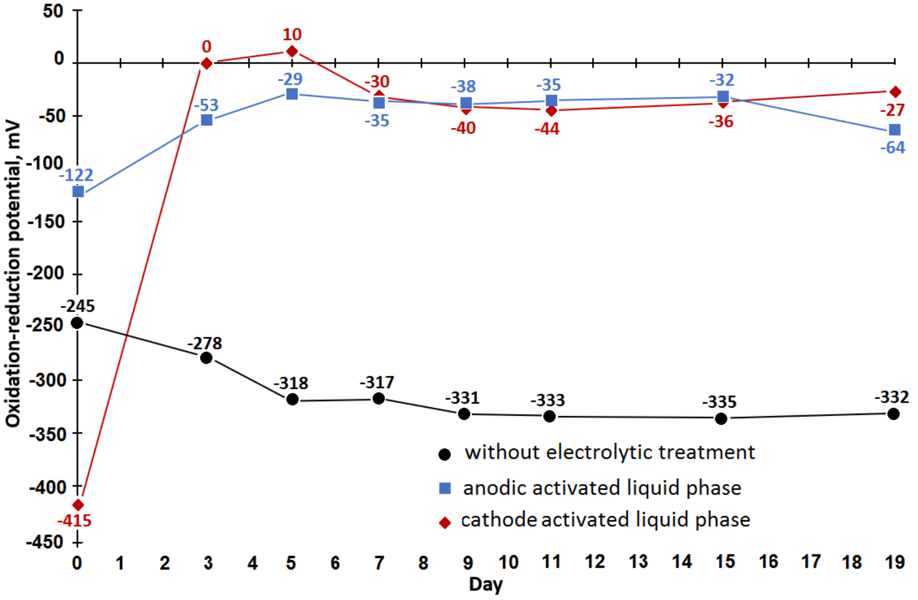
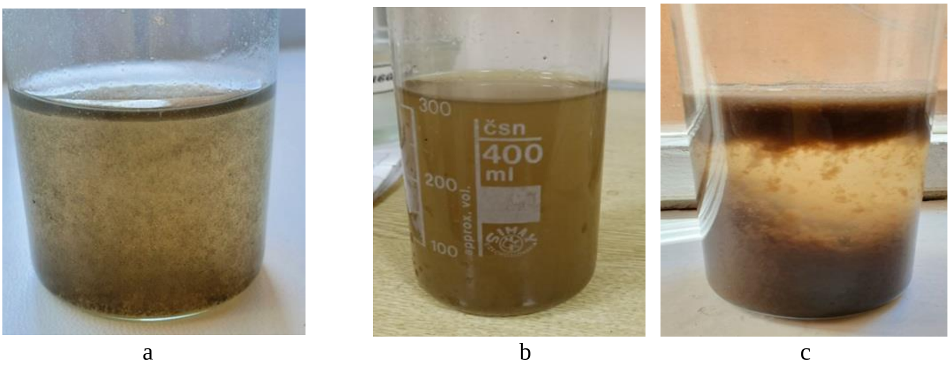


Fig. 8. Changing ORP during experiments

The condition of activated sludge after anaerobic digestion together with activated effluent in a series of experiments was visually assessed. It was found that during digestion with anode-activated effluent, sludge flocs were not formed, there was a process of settling and de-aggregation with cellular debris. Generally, this result confirms the inhibition effect of anode-activated liquids, which was also confirmed in papers (Liu et al., 2016; Jung, and Regan, 2011). Fig. 9 shows samples of activated sludge from experiments 1, 2, and 3.



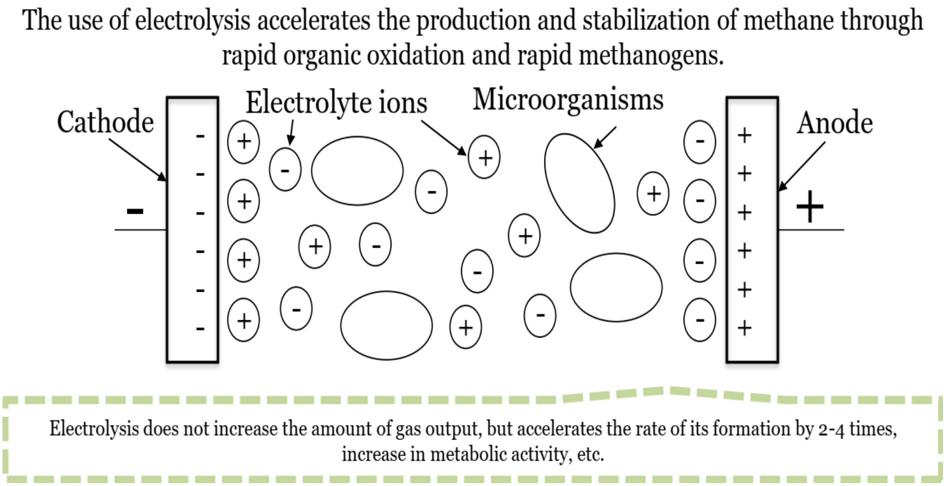
a b c

Fig. 9: Samples of anaerobic activated sludge: (a) control experiment – without electrolysis treatment of liquid effluent; (b) experiment with anode-activated liquid effluent together with inoculum; (c) experiment with cathode-activated liquid effluent together with inoculum

There was a biomass increase in experiment 3 with cathode-activated effluent digestion.

3. Discussion

Based on the obtained experimental results, several types of effects of activated effluent on anaerobic activated sludge can be observed: (i) an effect on the dominance of ecological-trophic groups in the anaerobic digestion process, which is also confirmed by several previous studies (Wang et al., 2019; Park et al., 2021); (ii) the effect of cathodic treatment of the effluent revealed the auto stabilization of the acid-base balance of the system, which requires further study and may be useful for industrial regulation of pH values (iii) the increase of biogas in anaerobic digestion of activated sludge with cathode-activated effluent during bioelectrochemical reactions, which also requires further confirmation; (iv) the inhibiting effect of anode-activated effluent on anaerobic activated sludge development. Furthermore, the design combination of electrolysis cells with bioreactors is promising, so in Fig. 10, we have formalized the occurring processes based on the results of previous studies and our conclusions.


The use of electrolysis accelerates the production and stabilization of methane through rapid organic oxidation and rapid methanogens.

Electrolysis does not increase the amount of gas output, but accelerates the rate of its formation by 2-4 times, increase in metabolic activity, etc.

Fig. 10. Stimulation of anaerobic digestion by electrolytic processes

Further research is required to combine the electrolysis cell with the bioreactor internals to intensify the process during fermentation.

4. Conclusion

The laboratory experiment confirmed the effects of electrolytic pretreatment on the dominance of groups of bacteria under anaerobic conditions, such as positive impacts of cathodic treatment, in particular stabilization of acid-base balance of the system and increase of biogas during anaerobic digestion, at the same time the inhibiting effect of anode-activated effluent on the growth of anaerobic activated sludge. Thus, in the control experiment (without pretreatment), the biogas increase was 14 ml/L by the 15th day, in anaerobic digestion of activated sludge with anode-activated sludge – 11 ml/L, and with cathode-activated sludge – 20 ml/L. In further research, variation of volumetric ratios of eutrophic water and activated sludge, as well as other parameters will be carried out to optimize the pretreatment process.

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References

1. Ministry of Environmental Protection and Natural Resources of Ukraine: Official portal. National report on the state of the environment environment in Ukraine in 2018, https://mepr.gov.ua/news/37844.html. Last accessed 2 Aug 2021.
2. Wacławek. S., Grübel. K., Silvestri. D., Padil. V.V.T., Wacławek. M., Černík. M., Varma, R.S.: Disintegration of Wastewater Activated Sludge (WAS) for Improved Biogas Production. *Energies*, 12(21), 2019. DOI:10.3390/en12010021.
3. Debaty. Sumy. Kosivshchyna Reservoir wants to save from environmental disaster, https://debaty.sumy.ua/news/politics/kosivshhynske-odoshovyshhe-hochut-vryatuvaty-vid-ekologichnogo-lyha. Last accessed 30 Aug 2017.
4. Information portal "Everyday.Sumy". Live suspension introduced into Kosivshchyna reservoir, http://everyday.sumy.ua/u-kosivshhinske-vodosxovishhe-vneseno-zhivu-suspenziyu/. Last accessed 30 Sept 2021.
5. Wang, M., Sahu, A.K, Rusten, B., Park, C.: Anaerobic co-digestion of microalgae Chlorella sp. and waste activated sludge. *Bioresour Technol.*, 142, 585–90, 2013. DOI:10.1016/j.biortech.2013.05.096.
6. Thorin, E., Olsson, J., Schwede, S., Nehrenheim, E.: Biogas from Co-digestion of Sewage Sludge and Microalgae. *Energy Procedia,* 105, 1037–1042, 2017. DOI:10.1016/j.egypro.2017.03.449.
7. Vongvichiankul, C., Deebao, J., Khongnakorn, W.: Relationship between pH, oxidation reduction potential (ORP) and biogas production in mesophilic screw anaerobic digester. *Energy Procedia*, 138, 877–882, 2017.
8. Liu, Q., Ren, Z.J., Huang, C. et al.: Multiple syntrophic interactions drive biohythane production from waste sludge in microbial electrolysis cells. *Biotechnol Biofuels,* 9, 162, 2016. DOI:10.1186/s13068-016-0579-x.
9. Jung, S., Regan, J.M.: Influence of external resistance on electrogenesis, methanogenesis and anode prokaryotic communities in microbial fuel cells. *Applied and Environmental Microbiology*, 77, 564–571, 2011.
10. Wang, H., Xu, J., Sheng, L., et al.: Anaerobic digestion technology for methane production using deer manure under different experimental conditions. *Energies*. 12(9), 1819, 2019.
11. Park, J.G., Lee, B., Lee, U.J., Jun, H.B.: An anaerobic digester with microbial electrolysis cell enhances relative abundance of methylotrophic methanogens in bulk solution. *Environmental Engineering Research*, 27(4), 210666, 2021.

Synergy of ultrasound and advanced oxidation process "Peroxate" in decolorization of aqueous solution of thiazine dye methylene blue

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Abstract

Periodate oxidants are selective action on compounds which contain carbonyl or hydroxyl groups. During the activation of periodates in the aquatic environment under the action of ultrasonic vibrations, ultraviolet, visible, microwave radiation, high or low temperatures, the formation of a wide range of powerful oxidants – both radicals (hydroxyl, iodine, periodic) and non-radical species, iodate ions, hydrogen peroxide, atomic oxygen, singlet oxygen), etc., which actively oxidize persistent toxic organic compounds. A combination of ultrasonic radiation and the Peroxate process (H_2O_2/KIO_4), the so-called Sonoperoxate process ($US/H_2O_2/KIO_4$), has been proposed for highly efficient and intensive oxidative decolorization of an aqueous solution of thiazine methylene blue dye (MB). The synergetic coefficient of the “Sonoperoxate” process was calculated, which at the molar ratio $MB:H_2O_2:KIO_4$ = 1:100:25 was equal to 3.25, and at the molar ratio $MB:H_2O_2:KIO_4$ = 1: 200: 50 – 1.62. The influence of molar ratio of dye: oxidant, presence/absence of ultrasonic radiation, its power, pH value of initial solution, initial concentration of MB in solution on the degree of its discoloration is analyzed. It was found that due to the use of the process "Sonoperoxate" for 5 minutes. at the pH of the initial solution 4.0, the molar ratio $MB:H_2O_2:KIO_4$ = 1:100:25, the initial concentration of MB in its aqueous solution 62.6 μM, power US 60 W, temperature 17°C managed to achieve a degree of discoloration MB 95.6%.

Keywords: stable organic compounds, aqueous solutions, dyes, methylene blue, aromatic compounds, oxidants, periodates, discoloration, ultrasound, cavitation

1. Introduction

Periodates (IO_4^-) have the highest, among all forms of iodine, redox potential, and therefore can play the role of oxidizing agents in advanced oxidation processes of toxic organic compounds: aromatic compounds, their halogenated derivatives, dyes and the like. Periodates are oxidants of selective action against compounds that contain carbonyl or hydroxyl groups (Seid-Mohammadi et al., 2016). During the activation of periodates in an aqueous medium under the action of ultrasonic vibrations (Hamdaoui and Merouani, 2017), ultraviolet (Lee and Yoon, 2004; Niehues et al., 2010; Li et al., 2015; Ghodbane and Hamdaoui, 2016; Bendjama et al. ., 2018), visible radiation (Yun et al., 2017), high (Kayan et al., 2010) or low (Choi et al., 2018) temperatures are the formation of a wide range of powerful oxidants – as radicals (hydroxyl $^{\bullet}OH$, iodine $IO_3^{\bullet}$, periodic $IO_4^{\bullet}$) and non-radical species (ozone O_3, periodate ions IO_4^-, iodate ions IO_3^-, hydrogen peroxide H_2O_2, atomic oxygen $O(^3P)$, singlet oxygen $^1O_2$), etc., which actively oxidize persistent toxic organic compounds. The generation of such a complex of oxidizing agents leads to a significant increase in the rate of oxidation of biodegradation-resistant organic compounds.

Hamdaoui and Merouani (2017) for the first time proposed the mechanism of sonolysis reactions of periodate ions in the range of pH values of the medium 2.0… 8.0:

$$IO_4^- + {}^{\bullet}OH \rightarrow IO_4^{\bullet} + OH^-, \tag{1}$$

$$IO_4^- + H^{\bullet} \rightarrow IO_3^- + {}^{\bullet}OH, \tag{2}$$

$$IO_4^- + H_2O_2 \rightarrow IO_3^- + O_2 + H_2O, \tag{3}$$

$$IO_3^- + {}^{\bullet}OH \rightarrow HIO_4^-, \tag{4}$$

$$IO_3^- + {}^{\bullet}OH \rightarrow IO_3^{\bullet} + OH^-, \tag{5}$$

$$IO_3^- + H^{\bullet} \rightarrow IO_2^- + {}^{\bullet}OH, \tag{6}$$

$$IO_4^- + IO_3^{\bullet} \rightarrow IO_4^{\bullet} + IO_3^-, \tag{7}$$

$$IO_3^{\bullet} + IO_3^{\bullet} \rightarrow I_2O_6, \tag{8}$$

$$I_2O_6 + H_2O \rightarrow IO_4^- + IO_3^- + 2H^+, \tag{9}$$

$$IO_4^{\bullet} + IO_4^{\bullet} \rightarrow I_2O_8, \tag{10}$$

$$I_2O_8 + H_2O \rightarrow IO_4^- + IO_3^- + 2H^+ + O_2. \tag{11}$$

Hydrogen and hydroxyl radicals are formed by sonolysis of water, and hydrogen peroxide is a product of recombination of hydroxyl radicals. These compounds are involved in the conversion of periodate ions.

Hydrogen radicals generated by the ultrasonic cavitation treatment of water, which are not known to be effective for the degradation of organic matter, are key precursors of hydroxyl radicals as a result of interaction with IO_4^- and IO_3^- (eq. (2) and eq. (6), respectively). These reactions are an important additional source for the generation of hydroxyl radicals, which opens up more opportunities for the degradation of organic compounds.

Equations (1)–(3) indicate a decrease in the concentration of periodate ions over time. Therefore, the reactions described by equations (8)–(11) play a crucial role in regeneration IO_4^-.

High concentrations of periodate ions cause quenching of hydroxyl (eq. (1)) and iodyl (eq. (7)) radicals. Therefore, the optimization of the molar ratio of periodate ions and organic compounds (water pollutants) is an important parameter in such reaction systems.

Wagner and Strehlow (Chia et al., 2004; Ghodbane and Hamdaoui, 2016) proposed a simple mechanism for photolysis of periodates under the action of ultraviolet radiation, according to which the periodate can be decomposed by two photoinitiated pathways:

Way I

$$IO_4^- + h\nu \rightarrow IO_3^\bullet + O^{\bullet -}, \tag{12}$$

$$O^{\bullet -} + H^+ \leftrightarrow {}^\bullet OH, \tag{13}$$

$${}^\bullet OH + IO_4^- \rightarrow OH^- + IO_4^\bullet, \tag{14}$$

$$2{}^\bullet OH \rightarrow H_2O_2, \tag{15}$$

$$2IO_4^\bullet \leftrightarrow I_2O_8, \tag{16}$$

$$I_2O_8 + H_2O \rightarrow IO_4^- + IO_3^- + 2H^+ + O_2, \tag{17}$$

$$2IO_3^\bullet \leftrightarrow I_2O_6, \tag{18}$$

$$I_2O_6 + H_2O \rightarrow IO_4^- + IO_3^- + 2H^+. \tag{19}$$

Way II

$$IO_4^- + h\nu \rightarrow IO_3^- + O(^3P), \tag{20}$$

$$O_2 + O(^3P) \rightarrow O_3, \tag{21}$$

$$O_3 + IO_3^{\bullet} \rightarrow IO_4^{\bullet} + O_2. \qquad (22)$$

According to the mechanism of UV photolysis of periodate ions described above, a number of radicals ($IO_3^{\bullet}, IO_4^{\bullet}, {}^{\bullet}OH$) and intermediate non-radical compounds (IO_3^-, $O(^3P)$, H_2O_2 and O_3) are formed. However, analysis of hydrogen peroxide and ozone yield measurements (Chia et al., 2004) during saturation of the reaction medium with air showed the formation of small amounts of hydrogen peroxide and a very low rate of ozone generation (8 μg/(min·dm^3)). This indicates that hydrogen peroxide, ozone and hydroxyl radicals (eq. (15)) do not play a significant role in the oxidation system UV/IO_4^-. It is also known that hydrogen peroxide, iodate ions and periodate ions are inefficient in the processes of direct oxidation of organic pollutants (Hamdaoui and Merouani, 2017). Therefore, it is believed that Iodine intermediates ($IO_3^{\bullet}, IO_4^{\bullet}$) play a key role in the degradation of organic pollutants by photoactivated periodates.

The use of microwave radiation to extract organic compounds is effective in combination with oxidants (particularly periodates) or catalysts (Seid-Mohammadi et al., 2016). The mechanism of activation of periodates by microwave radiation is similar to the mechanism of photoactivation of periodates by UV radiation.

Seid-Mohammadi et al. (2015) found that due to the combination of ultrasound radiation and reagent treatment of an aqueous medium (pH 3.0) with a phenol concentration of 50 mg/dm^3 of sodium periodate (concentration – 3 mmol/dm^3) for 90 min. the degree of phenol degradation was 87.8%. The introduction of iron nanoparticles into the reaction medium caused the generation of additional hydroxyl radicals (by the Fenton process), which led to an increase in the degree of phenol degradation to 96.6% and a decrease in the duration of the process by 30 minutes. (Seid-Mohammadi et al., 2019). Use of microwave radiation with a power of 600 W to activate sodium periodate (concentration – 0.2 mol/dm^3) for 30 minutes made it possible to achieve a degree of degradation of phenol (concentration – 100 mg/dm^3) in synthetic wastewater (pH 11.0), which was equal to 98.8% (Seid-Mohammadi et al., 2016). It was found that the greatest role in the oxidation of 4-chlorophenol is played by atomic oxygen and iodine radicals (Chia et al., 2004), which were formed during the photoactivation of periodates.

Chadi et al. (2019) reported a new advanced oxidation process for the degradation of persistent organic pollutants, called "Peroxate". It is based on the use of a system H_2O_2/IO_4^- to generate oxidants. The mechanism of the Peroxate process is described by the following reaction equations:

$$IO_4^- + H_2O_2 \rightarrow IO_3^{\bullet} + O_2^{\bullet -} + H_2O, \qquad (23)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow {}^{\bullet}OH + OH^- + {}^1O_2, \tag{24}$$

$$IO_4^- + 2O_2^{\bullet -} + H_2O \rightarrow 2\,{}^1O_2 + IO_3^- + 2OH^-, \tag{25}$$

$$2O_2^{\bullet -} + 2H_2O \rightarrow {}^1O_2 + H_2O_2 + 2OH^-, \tag{26}$$

$$O_2^{\bullet -} + {}^{\bullet}OH \rightarrow {}^1O_2 + OH^-, \tag{27}$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2, \tag{28}$$

$$O_2^{\bullet -} + H^+ \leftrightarrow HO_2^{\bullet}, \tag{29}$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O, \tag{30}$$

$$IO_4^- + IO_3^{\bullet} \rightarrow IO_4^{\bullet} + IO_3^-, \tag{31}$$

$$IO_3^{\bullet} + IO_3^{\bullet} \rightarrow I_2O_6, \tag{32}$$

$$I_2O_6 + H_2O \rightarrow IO_4^- + IO_3^- + 2H^+, \tag{33}$$

$$IO_4^{\bullet} + IO_4^{\bullet} \rightarrow I_2O_8, \tag{34}$$

$$I_2O_8 + H_2O \rightarrow IO_4^- + IO_3^- + 2H^+ + O_2, \tag{35}$$

$$IO_4^- + {}^{\bullet}OH \rightarrow IO_4^{\bullet} + OH^-. \tag{36}$$

Ascorbic acid, tert-butanol, 2-propanol, sodium azide and phenol were used as radical traps in the identification of free radicals. According to the above mechanism, the superoxide anion radical ($O_2^{\bullet -}$) is a precursor of free radicals.

Chadi et al. (2019) found that the use of the system H_2O_2 / IO_4^- for 1 min. at a molar ratio $H_2O_2 : IO_4^- = 10:1$, pH of 5.4 and temperature of 25°C for the degradation of the dye Toluidine blue (TB) (concentration of TB in aqueous solution – 10 mg/dm^3) allowed to achieve a high degree of degradation (98%) of this dye. The researchers observed a decrease in the content of total organic carbon by 73%. The authors noted that a key role in the degradation of Toluidine blue is played by ${}^{\bullet}OH$, ${}^1O_2$ and $IO_3^{\bullet}$.

In view of the above, it can be argued that the synergistic effect of combinations of periodates with other known oxidants, in particular hydrogen peroxide, is the basis of new highly efficient alternative advanced processes for the oxidation of wastewater pollutants.

2. Materials and Methods

2.1. Reagents

For studies of oxidative decolorization of an aqueous solution of thiazine dye methylene blue used the following reagents: methylene blue (abbreviation: MB; molecular formula: $C_{16}H_{18}ClN_3S$; molar mass: 319.85 $g \cdot mol^{-1}$); hydrogen peroxide (60% w/v); potassium periodate. Reagents were obtained from Merck (Germany).

2.1.1. Experimental set up

The installation for experimental studies of methylene blue discoloration using the "Sonoperoxate" process consisted of an ultrasonic magnetostrictive emitter Bandelin Sonopuls HD 2200.2 (Germany) with variable power (60, 120 and 180 W), a chemical beaker with a capacity of 2 liters, a magnetic stirrer and a thermometer. The frequency of ultrasonic radiation is 20 kHz. The working element of the ultrasound generator is a titanium horn (diameter – 12 mm). The coefficient of filling the glass with an aqueous solution of dye MB – 50%.

2.2. Laboratory studies of oxidative decolorization of aqueous solution of dye MB

The working volume (1L) of an aqueous solution of MB dye with a concentration of 20 mg/L (62.6 μM), 10 mg/L (31.3 μM) and 5 mg/L (15.65 μM) was prepared using distilled water and with constant stirring. During studies using the combinations of ultrasonic radiation + oxidant, the molar ratio MB: oxidant was changed within: 1) for the combination of US radiation + H_2O_2 – the molar ratio MB:H_2O_2 from 1: 100 to 1: 200; 2) for the combination of US radiation +KIO_4 – molar ratio MB:KIO_4 from 1:25 to 1:50; 3) for the combination of US radiation +H_2O_2+KIO_4 – molar ratio MB:H_2O_2:KIO_4 from 1: 100: 25 to 1: 200: 50. The duration of treatment of the aqueous solution of MB using ultrasonic radiation and/or oxidants under adiabatic conditions was 60 minutes The initial temperature of the aqueous solution MB 17 ± 1°C. The pH of the medium after mixing with reagents (H_2O_2, KIO_4 or H_2O_2+KIO_4) was equal to 7.0. 0.1 M H_2SO_4 or 0.1 M KOH was used to adjust the pH of the solution (ranging from 4.0 to 10.0). The pH of the solution was measured with a pH meter brand pH-301 by Kelilong (China).

2.3. Analytical procedure

A modern UV-Vis spectrophotometer UV-3100PC by Shanghai Mapada Instruments Co., Ltd. was used to analyze the sample solutions. (China). The thickness of quartz ditches is 1 cm. The working wavelength range is 200… 1100 nm. The concentration of MB (corresponding to the maximum absorption at a wavelength of 664 nm) was calculated using a pre-constructed calibration graph.

3. Results and Discussion

Methylene blue (MB) is a typical thiazine dye with a variety of applications – textile industry (dyeing silk, wool, and cotton), medicine, chemistry, biology and more. The developed aromatic structure of MB, which is characterized by the presence of heteroatoms N, S, Cl, its hydrophilicity, resistance to chemical and physical factors significantly, limits the choice of methods for cleaning water systems from this pollutant. The most effective methods today for the degradation and mineralization of stable organic compounds in general and, methylene blue in particular, are methods based on the use of advanced oxidation processes.

The aim of this work was to study the oxidative decolorization of aqueous MB solution under adiabatic conditions using a combination of ultrasonic radiation + process "Peroxate" ($US/H_2O_2/IO_4^-$).

Under the conditions closest to natural (ie at neutral pH), the power of US radiation is 180 W and the duration of the process is 1 hour the degree of discoloration of the aqueous solution MB (concentration MB – 62.6 μM) increased from 3.6 to 6.7% with increasing molar ratio of dye: H_2O_2 from 1:100 to 1:200. This is due to the formation of hydroxyl radicals due to the sonolysis of hydrogen peroxide. The main reason for such a low degree of discoloration is a neutral environment (Kumar et al., 2017). However, under such conditions, the intensity of corrosion processes is minimal, which allows to increase the service life of ultrasonic cavitation generators.

Apply the US/KIO_4 process for 1 hour for decolorization of aqueous MB solution was also ineffective. The degree of discoloration of the aqueous solution MB was 1.3% at a molar ratio of dye: KIO_4 1:25 and 2.9% at a molar ratio of 1:50. The low efficiency of the US/KIO_4 process is due to the quenching of hydroxyl and iodine radicals (hydroxyl and iodine) formed by ultrasonic cavitation with an excess of periodate (Hamdaoui and Merouani, 2017) (eq. (41), eq. (42)):

$$H_2O \xrightarrow{US})))H^{\bullet} + {}^{\bullet}OH, \quad (37)$$

$$H_2O \leftrightarrow H^+ + OH^-, \quad (38)$$

$$IO_4^- \xrightarrow{US})))IO_3^{\bullet} + O^{\bullet -}, \quad (39)$$

$$O^{\bullet -} + H^+ \rightarrow {}^{\bullet}OH, \quad (40)$$

$$IO_4^- + {}^{\bullet}OH \rightarrow IO_4^{\bullet} + OH^-, \quad (41)$$

$$IO_4^- + IO_3^{\bullet} \rightarrow IO_4^{\bullet} + IO_3^-. \quad (42)$$

Another factor-inhibitor is a much higher rate of competitive reactions of recombination of hydroxyl, iodine and periodic radicals (eq. (28), eq. (32), eq. (34)), compared with the rate of their interaction with MB molecules. Ghodbane and Hamdaoui (2016) reported a negative effect of elevated concentrations of UV-activated periodate on the decolorization efficiency of an aqueous solution of Acid blue 25.

With an increase in the consumption of oxidizing agents (H_2O_2 and KIO_4) in 2 times (equivalent to increasing the molar ratio of MB:H_2O_2:KIO_4 from 1:100:25 to 1:200:50) the degree of discoloration of the aqueous solution MB using the process "Peroxate" (H_2O_2/KIO_4) for 1 hour increased from 55.6 to 94.8% (by 39.2%), and using the “Sonoperoxate” process (US / H_2O_2 /KIO_4) – from 74.1 to 98.9 (by 24.8%) (Fig. 1).

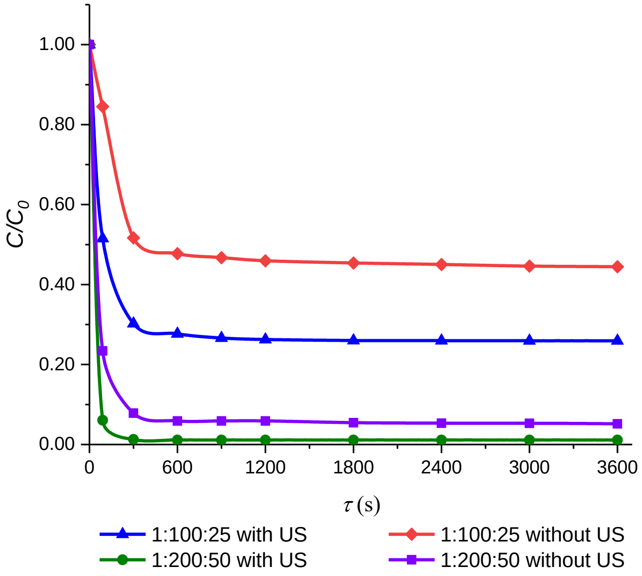

Fig. 1. The effect of MB:H_2O_2:KIO_4 molar ratio on the decolorization kinetics of the MB aqueous solution using the H_2O_2/KIO_4 process as independent and in combination with US (conditions: V = 1 L, C_0 = 62.6 µM, pH 7.0, initial temperature – 17°C, US power – 180 W)

The effect of ultrasound on MB discoloration is more noticeable at a lower molar ratio of MB: H_2O_2: KIO_4. In particular, at a molar ratio of MB:H_2O_2: KIO_4 1:100:25, the use of the Sonoperoxate process increased the degree of discoloration of the aqueous MB solution by 18.5% (up to 74.1%) compared to the Peroxate process (discoloration rate – 55.6%). At a higher molar ratio of MB:H_2O_2:KIO_4 (1:200:50), only a slight increase in the degree of discoloration (by 4.1% – from 94.8 to 98.9%) was recorded using similar processes (Fig. 1). Therefore, the cost of decolorization can be significantly reduced by optimizing the technological conditions of the processes "Peroxate" and "Sonoperoxate" (in particular, the cost of oxidants, the molar ratio between them, the pH of the medium, and the power of US radiation).

The discoloration rate constant of the aqueous MB solution was calculated by the formula inherent in first-order reactions (Kumar et al., 2018). The calculated rate constants of the aqueous solution MB (at a power of the ultrasonic generator of 180 W) were equal to:

– for the process US/H_2O_2 – at a molar ratio of MB: H_2O_2 = 1:100 – $3.064 \cdot 10^{-5}$ s^{-1}; at a molar ratio of MB: H_2O = 1:200 – $1.682 \cdot 10^{-4}$ s^{-1};

– for the process US/KIO_4 – for the molar ratio MB:KIO_4 = 1:25 – $3.781 \cdot 10^{-5}$ s^{-1}; at a molar ratio of MB:KIO_4 = 1:50 – $3.971 \cdot 10^{-5}$ s^{-1};

– for the process H_2O_2/KIO_4 – for the molar ratio MB:H_2O_2:KIO_4 = 1:100:25 – $2.201 \cdot 10^{-3}$ c^{-1}; at a molar ratio of MB:H_2O_2:KIO_4 = 1:200:50 – $1.901 \cdot 10^{-2}$ c^{-1};

– for the process US/H_2O_2/KIO_4 – for the molar ratio MB:H_2O_2:KIO_4 = 1:100:25 – $7.369 \cdot 10^{-3}$ c^{-1}; at a molar ratio of MB: H_2O_2:KIO_4 = 1:200:50 – $3.112 \cdot 10^{-2}$ c^{-1}.

The synergistic effect of the combined process US/H_2O_2/KIO_4 (process "Sonoperoxate") was evaluated based on the above rate constants. At the molar ratio MB:H_2O_2:KIO_4 = 1:100:25, the synergetic coefficient of the "Sonoperoxate" process was 3.25, and at the molar ratio MB:H_2O_2:KIO_4 = 1:200:50 – 1.62. Synergy is achieved due to the formation in the reaction system, in addition to hydroxyl, iodine and periodic radicals, another powerful oxidant of singlet oxygen ($^1O_2$) (eqs. (23)–(27)).

The decrease in the initial concentration of MB dye in its aqueous solution from 62.6 μM to 15.65 μM causes a decrease in the degree of discoloration from 98.9 to 73.4%, ie by 25.5%. Reducing the concentration of the dye in the solution leads to a decrease in the probability of meeting and, accordingly, the interaction of radicals, primarily hydroxyl, with two electrophilic centers of the dye molecule - chromophore = $N^+(CH_3)_2$ and functional C – S^+ = C groups (Mouele et al., 2020).

To reduce the cost of the process "Sonoperoxate" further studies were performed at low cost of oxidants (molar ratio MB:H_2O_2:KIO_4 = 1:100:25). It was found that the increase in US power from 60 to 180 W had almost no effect on the degree of discoloration of the aqueous solution MB: it increased by only 0.6% (from 73.5 to 74.1%). This indicates that the US performs only the function of activator of oxidizing agents (potassium periodate, hydrogen peroxide) in an aqueous medium. Further, the process of decolorization of an aqueous solution of MB develops as a chain by a radical mechanism. The revealed regularity of the independence of the degree of discoloration of the aqueous solution of MB using the process "Sonoperoxate" from the power of the US was confirmed by the higher consumption of oxidants (at a molar ratio of MB:H_2O_2:KIO_4 = 1:200:50). In this case, the degree of discoloration of MB remained constant and was equal to 98.9%.

The use of US leads to heating of the reaction medium due to acoustic cavitation (Fig. 2).

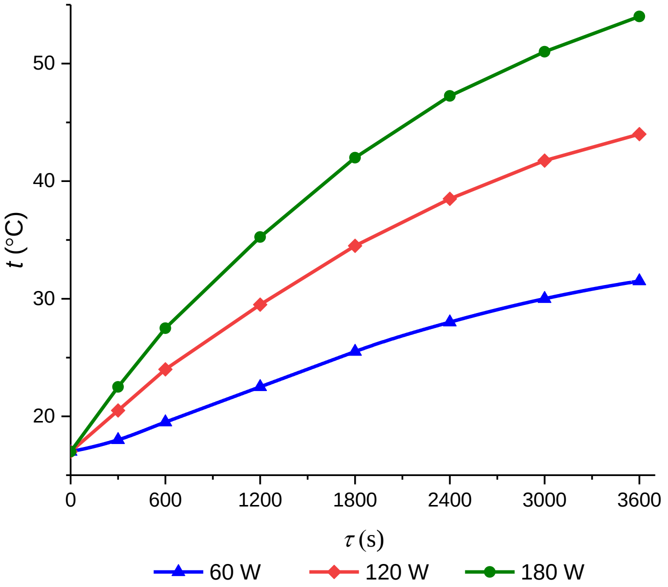

Fig. 2. The effect of ultrasound power on the temperature of the MB aqueous solution using the US/H_2O_2/KIO_4 process (conditions: V = 1L, C_0 = 62.6 μM, the molar ratio of MB:H_2O_2:KIO_4 = 1:100:25, pH 7.0, initial temperature – 17°C)

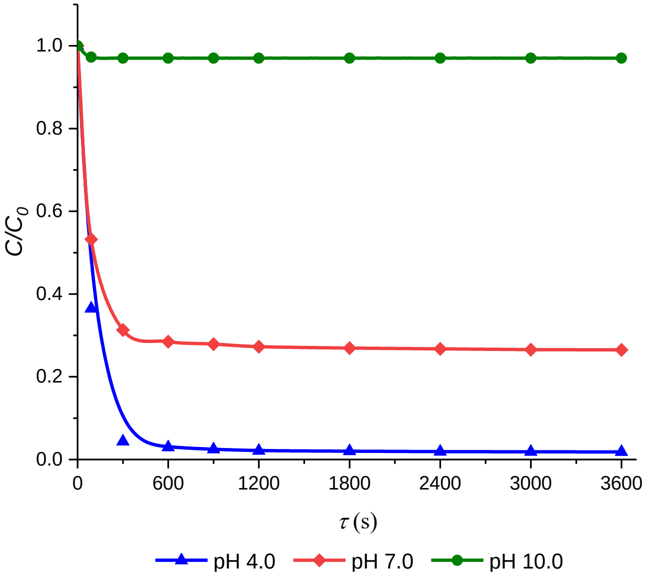

Fig. 3. The effect of initial pH on the decolorization kinetics of the MB aqueous solution using

the US/H_2O_2/KIO_4 process (conditions: V = 1L, C_0 = 62.6 μM, the molar ratio of MB:H_2O_2:KIO_4 = 1:100:25, initial temperature – 17°C, US power – 60 W)

The increase in US power from 60 to 180 W is accompanied by an increase in the heating rate of the aqueous solution MB (Fig. 2). However, at higher power US cavitation bubbles are formed and flattened too quickly (Bi et al., 2019), and the formed radical species do not have time to interact with the dye molecules. Therefore, the increase in US power has little effect on the degree of discoloration MB. Therefore, it is economically feasible to use the US with the lowest power tested, ie 60 watts.

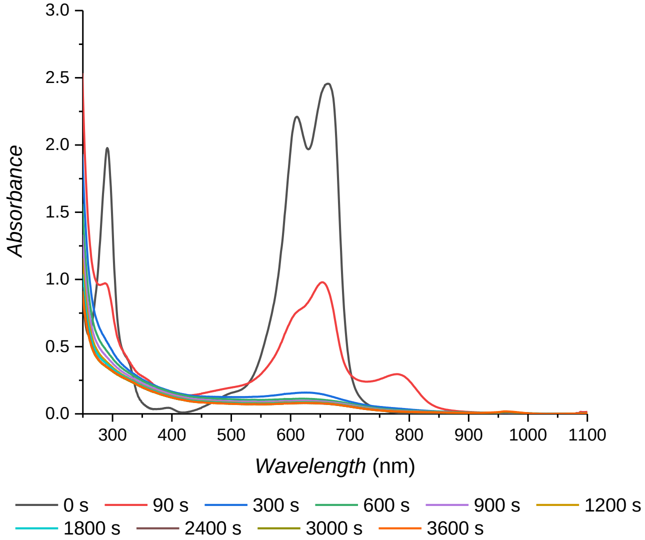

Fig. 4. UV-Vis-spectra of aqueous MB solution during its decolorization using the US/H_2O_2/KIO_4 process (conditions: V = 1L, C_0 = 62.6 μM, the molar ratio of MB:H_2O_2:KIO_4 = 1:100:25, initial temperature – 17°C, US power – 60 W) at the initial pH 4.0

A colossal decrease (by 95.2% – from 98.2 to 3.0%) in the degree of discoloration of the aqueous MB solution was revealed due to the increase in the initial pH of the solution from 4.0 to 10.0 (Fig. 3). Under alkaline conditions, ions (HCO_3^- or CO_3^{2-}) that can be formed from CO_2 (Chadi et al., 2019), as a product of MB mineralization, perform the functions of free radical scavengers (${}^\bullet OH$ and $O_2^{\bullet -}$):

$$HCO_3^- + {}^\bullet OH \rightarrow CO_3^{\bullet -} + H_2O, \tag{43}$$

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow CO_3^{\bullet -} + OH^{-}, \qquad (44)$$

$$HCO_3^{-} + O_2^{\bullet -} \rightarrow CO_3^{\bullet -} + HO_2^{-}, \qquad (45)$$

$$CO_3^{2-} + O_2^{\bullet -} \rightarrow CO_3^{\bullet -} + O_2^{2-}. \qquad (46)$$

Since $CO_3^{\bullet -}$ is formed (eqs. (43)–(46)), which is a weaker oxidant than ${}^{\bullet}OH$ and $O_2^{\bullet -}$ (precursor of singlet oxygen ${}^1O_2$), the degree of discoloration of the aqueous solution MB in alkaline conditions decreases sharply.

The progressive degradation of the two groups (chromophore = $N^+(CH_3)_2$ and functional $C–S^+=C$) during the use of the process "Sonoperoxate" is evidenced by the presence of a hypochromic effect (reduction of the intensity of absorption bands) at wavelengths of 664 and 291 nm on UV–Vis- spectra of aqueous solution MB (Fig. 4). The use of the US/H_2O_2/KIO_4 process for 300 s at a pH of the initial solution 4.0, molar ratio MB:H_2O_2:KIO_4, power US 60 W, temperature 17°C allowed to achieve a degree of discoloration MB 95.6%. The initial concentration of MB in its aqueous solution was 62.6 μM.

4. Summary and Conclusions

Periodates are oxidants of selective action against compounds that contain carbonyl or hydroxyl groups. During the activation of periodates in the aquatic environment under the action of ultrasonic vibrations, ultraviolet, visible, microwave radiation, high or low temperatures, the formation of a wide range of powerful oxidants – both radicals (hydroxyl, iodine, periodic) and non-radical species, iodate ions, hydrogen peroxide, atomic oxygen, singlet oxygen), etc., which actively oxidize persistent toxic organic compounds. The Sonoperoxate process (US/H_2O_2/KIO_4) has been proposed for highly efficient and intensive oxidative decolorization of an aqueous solution of thiazine methylene blue dye. It was found that due to the use of this process for 5 minutes. at the pH of the initial solution 4.0, the molar ratio MB:H_2O_2:KIO_4 = 1:100:25, the initial concentration of MB in its aqueous solution 62.6 μM, power US 60 W, temperature 17°C managed to achieve a degree of discoloration MB 95.6%.

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References

1. Bendjama, H., Merouani, S., Hamdaoui, O., Bouhelassa, M.: Efficient degradation method of emerging organic pollutants in marine environment

using UV/periodate process: case of chlorazol black. *Marine Pollution Bulletin*, 126, 557–564, 2018.

2. Bi, Y.G., Zhang, X.T., Zhou, S.Q.: Experimental study on single factor effect of divergent ultrasonic degradation of methylene blue in water. *E3S Web of Conferences*, 118, 03051, 2019.
3. Chadi, N.E., Merouani, S., Hamdaoui, O., Bouhelassa, M., Ashokkumar, M.: H_2O_2/periodate (IO_4^-): a novel advanced oxidation technology for the degradation of refractory organic pollutants. *Environmental Science: Water Research & Technology*, 5(6), 1113–1123, 2019.
4. Chia, L.H., Tang, X., Weavers, L.K.: Kinetics and mechanism of photoactivated periodate reaction with 4-chlorophenol in acidic solution. *Environmental Science and Technology*, 38, 6875–6880, 2004.
5. Choi, Y., Yoon, H.I., Lee, C., Vetráková, L., Heger, D., et al.: Activation of periodate by freezing for the degradation of aqueous organic pollutants. *Environmental Science and Technology*, 52(9), 5378–5385, 2018.
6. Ghodbane, H., Hamdaoui, O.: Degradation of anthraquinonic dye in water by photoactivated periodate. *Desalination and Water Treatment*, 57(9), 4100–4109, 2016.
7. Hamdaoui, O., Merouani, S.: Improvement of sonochemical degradation of Brilliant blue R in water using periodate ions: implication of iodine radicals in the oxidation process. *Ultrasonics Sonochemistry*, 37, 344–350, 2017.
8. Kayan, B., Gözmen, B., Demirel, M., Gizir, A.M.: Degradation of acid red 97 dye in aqueous medium using wet oxidation and electro-Fenton techniques. *Journal of Hazardous Materials*, 177(1–3), 95–102, 2010.
9. Kumar, M.S., Sonawane, S.H., Pandit, A.B.: Degradation of methylene blue dye in aqueous solution using hydrodynamic cavitation based hybrid advanced oxidation processes. *Chemical Engineering and Processing: Process Intensification*, 122, 288–295, 2017.
10. Kumar, M.S., Sonawane, S.H., Bhanvase, B.A., Bethi, B.: Treatment of ternary dye wastewater by hydrodynamic cavitation combined with other advanced oxidation processes (AOP's). *Journal of Water Process Engineering*, 23, 250–256, 2018.
11. Lee, C., Yoon, J.: Application of photoactivated periodate to the decolorization of reactive dye: reaction parameters and mechanism. *Journal of Photochemistry and Photobiology A: Chemistry*, 165(1–3), 35–41, 2004.

12. Li, J., Zhong, J., Wang, T., Zeng, J., He, J., Li, M.: Photocatalytic decolorization of methyl orange solution with KIO_3. *Desalination and Water Treatment*, 54(8), 2252–2258, 2015.

13. Mouele, E.S.M., Tijani, J.O., Masikini, M., Fatoba, O.O., Eze, C.P., Onwordi, et al.: Spectroscopic measurements of dissolved O_3, H_2O_2 and OH radicals in double cylindrical dielectric barrier discharge technology: treatment of methylene blue dye simulated wastewater. *Plasma*, 3, 59–91, 2020.

14. Niehues, E., Scarminio, I.S., Takashima, K.: Optimization of photocatalytic decolorization of the azo dye direct Orange 34 by statistical experimental design. *Journal of the Chilean Chemical Society*, 55(3), 320–324, 2010.

15. Seid-Mohammadi, A., Asgari, G., Shokoohi, R., Adabi, S.: Phenol disgrace via periodate in integrating by using supersonic radiation. *Journal of Medicine and Life*, 8(3), 233–237, 2015.

16. Seid-Mohammadi, A.M., Asgari, G., Poormohammadi, A., Ahmadian, M.: Oxidation of phenol from synthetic wastewater by a novel advance oxidation process: microwave-assisted periodate. *Journal of Scientific and Industrial Research*, 75, 267–272, 2016.

17. Seid-Mohammadi, A., Asgari, G., Shokoohi, R., Baziar, M., Mirzaei, N., et al.: Degradation of phenol using US/periodate/nZVI system from aqueous solutions. *Global NEST Journal*, 21(3), 360–367, 2019.

18. Yun, E.T., Yoo, H.Y., Kim, W., Kim, H.E., Kang, G., Lee, H., et al.: Visible-light-induced activation of periodate that mimics dye-sensitization of TiO_2: Simultaneous decolorization of dyes and production of oxidizing radicals. *Applied Catalysis B: Environmental*, 203, 475–484, 2017.

Use of the glycerin fraction from biodiesel production in the process of sewage sludge fermentation

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Abstract

Production of fuel based on fatty acid methyl esters (FAME), commonly called biodiesel, is one of the ways to increase the share of renewable fuels. In theory, the products of transesterification are FAME and free glycerol though, in fact, it results in the obtaining of byproduct composed of free glycerol, soaps, small amounts of FAME, methyl alcohol and many other compounds called glycerin phase. The crude glycerin phase may constitute a major threat to the environment because of its high BOD, basicity and content of toxic methanol.

Further development of biodiesel production and increasing the production and use of fatty acid methyl esters will also increase the total amount of the obtained glycerin phase to the point where we have a surplus of glycerol in relation to demand.

One of the methods to utilize the crude glycerin phase may be to use crude glycerol as an additive to sewage sludge and anaerobic fermentation of the obtained mixture. The method has two important advantages: firstly, utilization of the waste byproduct and, secondly, possibility to use the methane obtained during the fermentation process as an environmentally-friendly and renewable energy source.

The anaerobic fermentation of sewage sludge with addition of raw glycerin fraction has been studied, as well as kinetics of free glycerol and FAME decomposition during examined process. The influence of pH of the initial mixture on the course of the fermentation process was investigated.

Studies have shown that both glycerol and FAME are completely decomposed within approx. 5 days, while for glycerol this time is faster.

Adding the glycerin fraction obtained during biodiesel production to the sewage sludge fermentation process may be one of methods of utilization of the biofuel process byproduct, especially when the demand for alternative uses of glycerol is insufficient in the region where biodiesel is produced.

Keywords: Sewage sludge, glycerin layer, fermentation, biofuel, waste removal

1. Introduction

The production of fatty acid methyl esters (FAME) commonly called biodiesel is one of the ways of increasing the share of renewable fuels.

Biodiesel is most often obtained from vegetable oils such as sunflower, cotton, soybean, corn, rapeseed. Potential raw materials for the production of fatty acid methyl esters are also animal fats or even waste material containing acylglycerols (Lim and Tong, 2010; Lu et al. 2010).

The biodiesel production process called transesterification is a chemical reaction between a fat and methyl alcohol in the presence of a specific catalyst. As a result of the reaction, new alcohol and a new ester are formed. Generally, the process of transesterification of oil can be represented by the equation (Fig. 1).

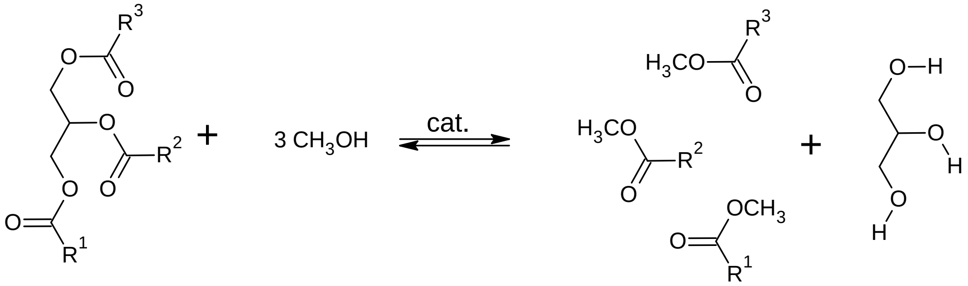

Fig. 1. Transesterification process scheme

Thus, it can be concluded that biofuel and glycerol are obtained after phase separation. This is just a simplification while, in reality, the process dealt with is one with a three-step equilibrium. It results in the obtaining of two liquids after completing the reaction: one containing mainly FAME (biodiesel), the other composed of free glycerol, soaps, small amounts of FAME, methyl alcohol, and many other compounds. This lower layer containing by-products is called a glycerin layer or glycerin phase.

The crude glycerin phase may constitute a major threat to the environment especially because of its high BOD, content of toxic methanol, or corrosive alkaline (in some cases acidic) catalysts. Besides, it is highly hygroscopic, so adding water to glycerol will decrease the mixture’s freezing temperature (Kijeński and Krawczyk, 2007).

It is generally assumed that glycerine (1,2,3-propanotriol) is a valuable raw product used in industry and that glycerin, which is obtained as a side product in the process of biofuel production, will be fully used. However, analysis of the uses of glycerine in various industries reveals that glycerine must satisfy certain qualitative requirements to be attractive for industry while the glycerin fraction obtained in the biodiesel production process does not meet such requirements.

Free glycerol is widely used in many industries. Glycerol is an ideal ingredient in many personal care products and pharmaceuticals. It mostly helps prevent moisture loss and provides lubrication and smoothness to many cough syrups and elixirs. Glycerol is also commonly used in toothpaste, mouthwash, and sugar-free chewing gums giving it a sweet taste without contributing to tooth decay, as well as in cosmetics to hold moisture against the skin to prevent it from drying (Neumann, 1991).

Glycerol demand is still increasing in the food industry. Total use of glycerol in the food industry, especially as a sweetener or humectant, has reached about 11% of overall glycerol production. Glycerol is a source of carbohydrates and provides a sweet taste without causing insulin secretion during digestion. Glycerol is also used in foodstuffs: it helps preserve food products and keep them fresh (Pagliaro and Rossi, 2008).

Glycerol is used in process of formulation of alkyd resins. The consumption of glycerol in the alkyd resins industry is about 8% and was still increasing during last decade. Alkyd resins are used as coatings, especially in paints and components of composites (Ayoub and Abdullah, 2012).

The application of glycerol in the explosives industry is also emerging. It is used for the production of nitroglycerine which is a powerful explosive. Therefore, glycerol is now used as a component during the explosives production process and its consumption in the explosives industry was about 2% in the year 2020 (Kaur et al., 2020).

The use of glycerol in the chemical industry as a polyether or alcoholic hydroxyl group polyol was raising during last years. It provides one of the basic chemical building blocks for the construction of polyurethane foams.

Another common use of crude glycerine is to burn the substance with a temperature of 290–300◦C for heating of industrial boilers (Nda-Umar et al., 2019). However, the chemical composition and physicochemical properties of this type of waste differs significantly from the requirements posed to fuel oils. The chemical composition and physicochemical properties determine the feasibility and the proper running of the combustion process.

Glycerol can be used for the synthesis of many products or as a raw material in the chemical industry. One of the concepts of using glycerol is to transform it into ketals. Ketals can be used as a biodiesel anti-freeze additive (De Torres et al., 2012).

There are several concepts of the chemical transformation of glycerine (Jerzykiewicz et al., 2007):
– oxidation to carboxylic acids or dihydroxyacetone;
– etherification;
– dehydration – obtaining acrolein (Lehr, 2009);
– hydrochlorination – obtaining epichlorohydrin;
– hydrogenolysis – obtaining propane-diols or ethylene glycol;

– pyrolysis – mixture of alkanes, olefins and alcohols;
– production of hydrogen or synthesis gas by glycerol pyrolysis, gasification and steam reforming (Valliyappan et al., 2008);
– production of 1,3 propanediol (Numpilai et al., 2021).

There are also biochemical methods, in which the glycerol is processed in a variety of organic substances on the road enzymatic, such as:
– succinic acid (biological conversion), using Actinobacillus succinogenes (Anestis Vlysidis et al., 2011);
– ethyl alcohol, using Escherichia coli (Dharmadi et al., 2006; Suhaimi et al., 2012);
– rhamnolipids production, using Pseudomonas aeruginosa (Baskaran et al., 2021);
– propionic acid, using Propionibacterium acidipropionici, Propionibacterium acnes and Clostridium propionicum (Barbirato et al., 1997);
– citric acid (Papanikolaou et al., 2008);
– poly(3-hydroxybutyrate), using Cupriavidus necator (Cavalheiro et al., 2009; Kumar et al., 2021);
– phytase, using Pichia pastoris (Tang et al., 2009);
– 1,3 propanediol (Pan et al., 2019).

Development of the production of methyl esters results in the formation of large amounts of the glycerol fraction. With such large-scale production, the problem of development of several thousand tonnes of a glycerol fraction containing primarily glycerine, methanol, and soap is very important (Ang et al., 2014).

Further development of biodiesel production and increasing the production and use of fatty acid methyl esters will also increase the total amount of the obtained glycerin phase to the point where we have a surplus of glycerol in relation to demand.

One of the methods to utilize the crude glycerin phase may be to use crude glycerol as an additive to sewage sludge and anaerobic fermentation of the obtained mixture. The method has two important advantages: firstly, utilization of the waste byproduct and, secondly, the possibility to use the methane obtained during the fermentation process as a renewable and environmentally friendly energy source.

Methane fermentation is the anaerobic decomposition of organic matter into methane and carbon dioxide with the use of bacteria. It occurs in four stages, with three groups of microorganisms, each of which requires appropriate environmental conditions (Jędrczak, 2007).

First stage of fermentation is called hydrolysis. In this stage polarized compounds, which are insoluble in most organic compounds (carbohydrates, proteins, lipids), are processed by enzymes hydrolyzing the respective strains (amylase, protease, lipase) into soluble monomers and dimers such as monosaccharides, amino acids and acids.

The second stage is commonly called the "acidification phase". During this phase which the dominant acidogenic bacteria hydrolyse products, short-chain organic acids (C1–C6) (formic, acetic, propionic, butyric, valeric, hexanoic), alcohols (methanol, ethanol), aldehydes, and carbon dioxide and hydrogen. At this stage hydrogen sulfide and ammonia are formed, which are responsible for giving off an unpleasant odour. There is a significant reduction in pH (pH = 5.5) related to the production of volatile fatty acids, however, it is buffered simultaneous transformation resulting compounds into final products. It will maintain pH in the range of 6.8–7.4.

The third stage is acetategenesis. In this process, the respective bacterial species convert higher organic acids (mainly C3–C6) to acetic acid, carbon dioxide and hydrogen, that is, the substrates that can be converted into methane. The distribution of fatty acids, alcohols and organic acids causes the release of hydrogen, which has an unfavourable impact on the bacteria of this phase. It is, therefore, a necessary symbiosis with autotrophic methane bacteria consuming hydrogen. This phase determines the efficiency of biogas production. The transformation of organic acids is the source of approximately 25% of acetate and 11% hydrogen.

During fourth stage, called methanogenesis, methanogenic bacteria convert the products of the previous phase: acetic acid, carbon dioxide and hydrogen into methane. A vast majority of methane (approximately 70%) are formed by decomposition of acetic acid in heterogeneous reactions:

$$CH_3COOH \longrightarrow CO_2 + CH_4. \tag{1}$$

The remaining part (about 30%) is a product of degradation by autotrophic bacteria:

$$CO_2 + 4\,H_2 \longrightarrow CH_4 + 2\,H_2O. \tag{2}$$

The main parameters that determine the proper course of the methane fermentation process are (Buraczewski and Bartoszek, 1990):

– temperature;
– pH of the environment;
– fermentation time;
– content of volatile acids and alkalinity;
– scope of oxidation-reduction.

Stages in chemical and biochemical processes depend on temperature: with an increasing temperature, the rate of the chemical reactions also increases. Moreover, enzymatic reactions are subject to the laws of thermodynamics, thus, elevating temperature in the system increases the reaction rate. The increase, however, is limited. Since a typical temperature for the microorganism, the reaction rate decreases as a result of the denaturation of the enzyme protein.

It can be inferred that temperature directly affects the processing time and the activity of methanogenic bacteria.

Table 1. Basic parameters of methane fermentation in mesophilic digestion (Buraczewski and Bartoszek, 1990)

Parameter	**Optimal**	**Extreme values**
pH	6.8–7.4	6.4–7.8
Temperature [ºC]	30–35	20–40
oxidation potential [mV]	(–520)–(–530)	(–490)–(–550)
Alkalinity [mg $CaCO_3/dm^3$]	1500–3000	1000–5000
Volatile org. acids [mg CH_3COOH/dm^3]	50–500	>2000
Time of fermentation, days	10–15	7–30
Consists of biogas:		
Methane (CH4), [%vol.]	65–70	60–75
Carbon dioxide, [% vol.]	30–35	25–40

Another important factor affecting the stability of the methane fermentation process is the pH. The pH is determined by the presence in the sludge of weak acids and weak bases. These compounds are buffering the capacity of the reaction, so the pH value can be maintained in the range of 6.8–7.4, which is optimum for most anaerobic bacteria. Adjusting the pH is also connected with the alkalinity and the presence of carbon dioxide in the gas.

2. Materials and Methods

The glycerin layer used in the fermentation process came from a local agro-refinery and was characterized by the following properties:
– pH: 11.2;
– free glycerol content: 65.2% m/m;
– total FAME content: 15.2% m/m;
– methanol content: 11.1% m/m.

The fermentation process was carried out by placing parallel samples of active sludge with and without the addition of glycerin fraction in conical flasks closed with a fermentation tube. The flasks were placed in a water bath at 38°C on a laboratory shaker. The addition of glycerin fraction was 1, 2, and 3% by weight. Samples were taken at specified intervals up to 21 days of fermentation. A volume of 250 cm^3 was taken in each flask and was subjected to a detailed analysis.

At the same time, fermentation was carried out in two thermostatic bioreactors (Fig. 2) equipped with mechanical stirrers. Both contained 10.5 kg of inoculated activated sludge (one of them contained a 3% addition of glycerin fraction). The process was carried out at the temperature of 38°C for 21 days.

Fig. 2. 2 bioreactors thermostatic in water bath

The samples for chromatography were prepared by weighing 5 g of the sludge. The sample was then extracted with 25 cm^3 of methanol for 24 hours After that time, the precipitate was filtered and washed with an additional 4 cm^3 volume of methanol. The filtrate was evaporated under a stream of inert gas. The evaporation residue was quantitatively transferred to a 5 cm^3 volumetric flask and made up with isopropanol. Then 2µl of the obtained sample was then taken and injected into the injection port.

Chromatographic analysis was carried out using a gas chromatograph from Hewlett-Packard 6890, equipped with a flame ionization detector and an HP-FFAP column (length = 30 m, internal diameter = 0.53 mm).

The analysis used a oven temperature program starting from 120°C to 240°C for 20 minutes. In the initial phase of the study, the sample was kept at a temperature of 120°C for 0.5 minutes, then heated to 160°C at the rate of 20°C per minute. At 160°C sample was kept for 1 minute. Then the temperature was increased at the rate of 6°C per minute to a temperature of 240°C, at which the sample was kept for 10 minutes. These conditions of chromatographic analysis enable both glycerol and FAME to be determined in a single pass analysis.

The results of the chromatographic analysis are the mean of 3 independent samples.

A thermogravimetric analysis was performed on Derivatograph Q 1500 D. A 1000 mg sample was used for the analysis. TG, DTG and DTA curves were performed.

3. Results and Discussion

The maximum addition of 3% by weight of the glycerin layer resulted from the need to maintain the pH required for the proper course of the methane fermentation process. The pH values for the initial samples are presented in Table 2.

Table 2. Initial pH values of obtained samples

Sample	**Content of glycerin layer [%] m/m**	**pH**
1	0.0	6.12
2	1.0	6.43
3	2.0	7.05
4	3.0	7.72

As we can see, adding more glycerin layer to the sewage sludge will cause the pH to rise above 8, which can effectively disrupt the methane fermentation process (see Table 1.).

Chromatographic analyses were performed to detect any changes in the concentrations of free glycerol and FAME during the fermentation process. No free glycerol or fatty acid methyl esters were found in the initial samples of raw sewage sludge (without the addition of a glycerol layer).

Studies on the kinetics of free glycerol decomposition has clearly shown that it decomposes very quickly. Already in the first day of the fermentation process, up to 85% of the initial glycerol content was decomposed in sample containing 3% of glycerin layer. In the samples containing 1% and 2% of the glycerol layer, the percentage loss of glycerol content in the first day was lower. In all samples analysed after 7 days of the fermentation process, glycerol was practically undetectable, regardless of the initial content of the glycerin layer. Detailed data showing the kinetics of free glycerol degradation are presented in Figure 3.

In the glycerin layer used for performing the fermentation process, also were present fatty acid methyl esters. The kinetics of degradation of esters during fermentation was analysed. The content of methyl esters was determined as the sum of the percentages of the following fatty acid esters: oleic, linoleic, linolenic, palmitic and stearic. As the glycerin layer used in the process came from the transesterification of rapeseed oil, esters of the above-mentioned acids constituted approx. 93% of all esters were contained in the glycerin layer.

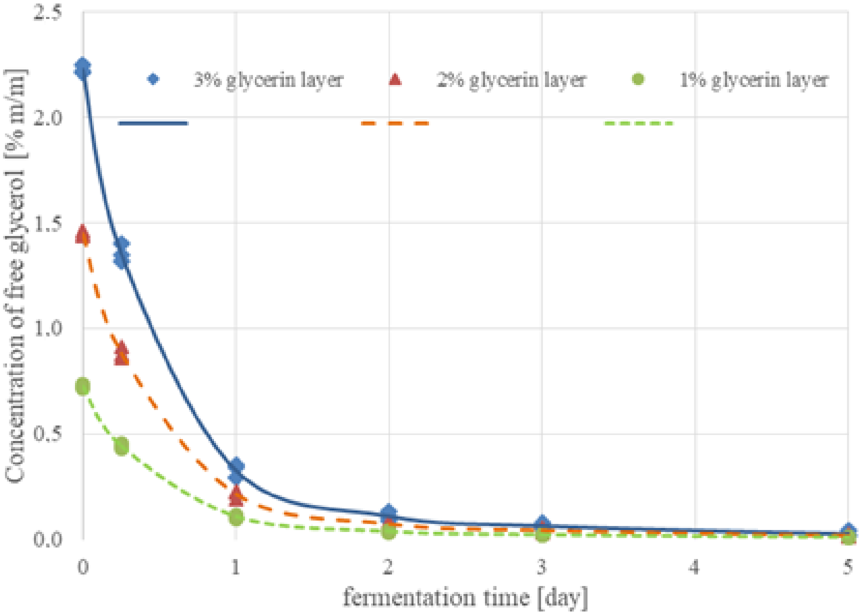

Fig. 3. Decomposition of free glycerol during fermentation process

Methyl esters, similarly to glycerol, were decomposed during the fermentation process, but the rate of decreasing of the ester content in the reaction mixture was lower than for glycerol. After five days of fermentation, nearly 80% of the initial content of esters was decomposed in the case of the sample containing 3% of the glycerin layer. In the case of samples with a lower content of the glycerin layer, this value was relatively lower. A further decrease in the content of methyl esters was observed in the samples taken after 14 days of fermentation. In samples taken after 21 days, the presence of esters was not detected, regardless of their initial content. The lack of the content of esters after 21 days of fermentation was also confirmed by the analyzes of samples taken from the bioreactors.

Detailed data showing the kinetics of fatty acid methyl esters decomposition are presented in Figure 4.

A rapid decrease in the concentration of fatty acids methyl esters during the first days of the fermentation process, combined with a decrease in the pH of the mixture, is probably due to hydrolysis of the esters occurring in free fatty acids.

The addition of a glycerin fraction (containing alkaline catalyst) can have an impact on the pH of the sludge during the fermentation process. The pH of the obtained samples was determined and the results are presented in Fig. 5. Although the initial pH in the case of the samples containing glycerol is much higher (especially for a sample containing 3% of glycerin layer), during the decomposition of esters and glycerol the pH value was significantly decreased. This effect was the most pronounced in the first 3 days of the process, when pH value decreased to about 7, which is the optimum for the process being conducted. Then after 8 days the pH value decreased slowly until the fermentation process stopped, achieving a value of 6.5 after 21 days of the process. In the case of the sample containing only 1% of the glycerin layer, it was observed that the pH of the sample increased slightly from the beginning, as in the case of raw sewage sludge.

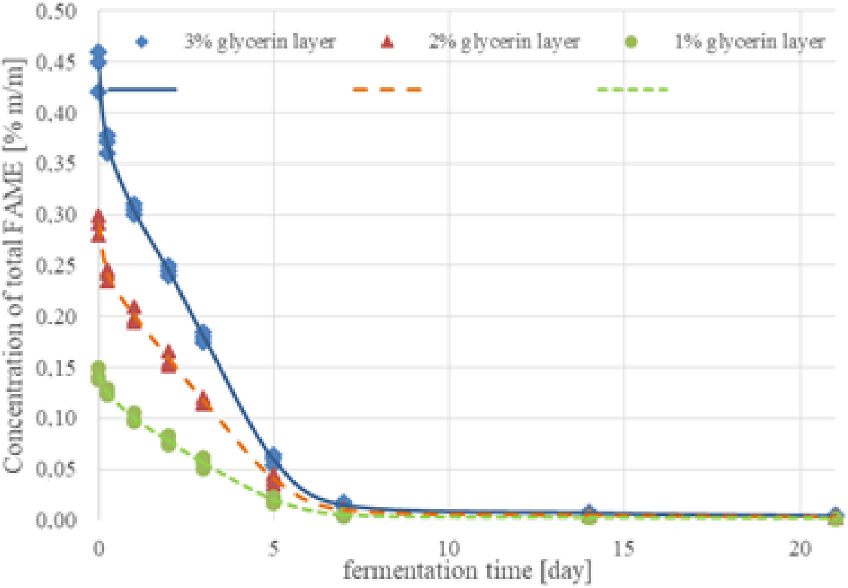

Fig. 4. Decomposition of fatty acid methyl esters (FAME) during fermentation process

In contrast to the sample containing the glycerin fraction, in the case of raw sewage sludge, where the glycerin fraction was not added, the initial pH value was about 6.2 and slowly raising during the 21 days of the fermentation process. The maximum pH value noted after 21 days was about 7.0.

The rapid decrease of the pH value for the sample containing the glycerin fraction was probably caused by hydrolysis of esters and soaps, occurring in the first stage of the fermentation process, which increases the concentration of free organic acids.

The dry matter content in the sludge subjected to fermentation was determined. A comparison of changes in dry matter of samples of the fermented sludge containing glycerin fraction and raw sludge is presented in Figure 6.

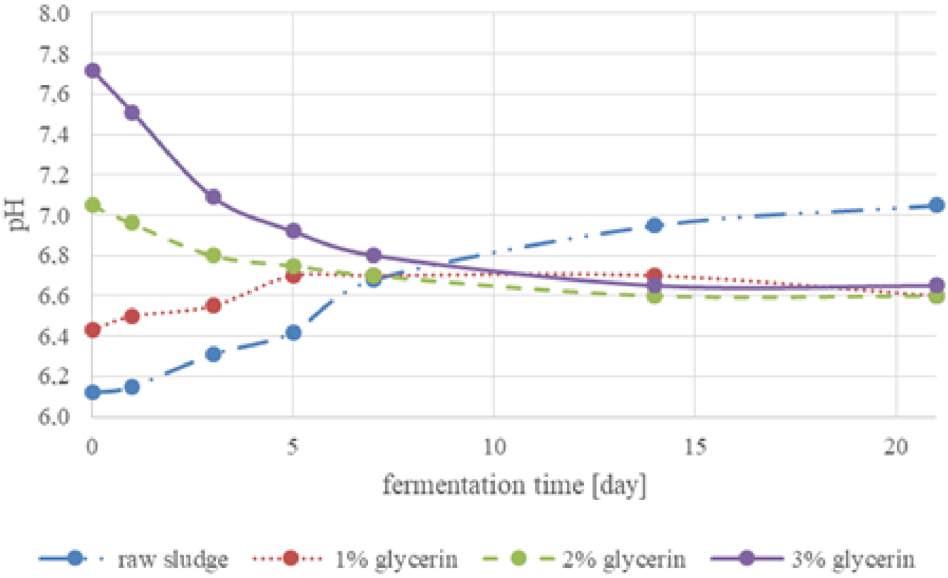

Fig. 5 Changes of pH of the sewage sludge during fermentation

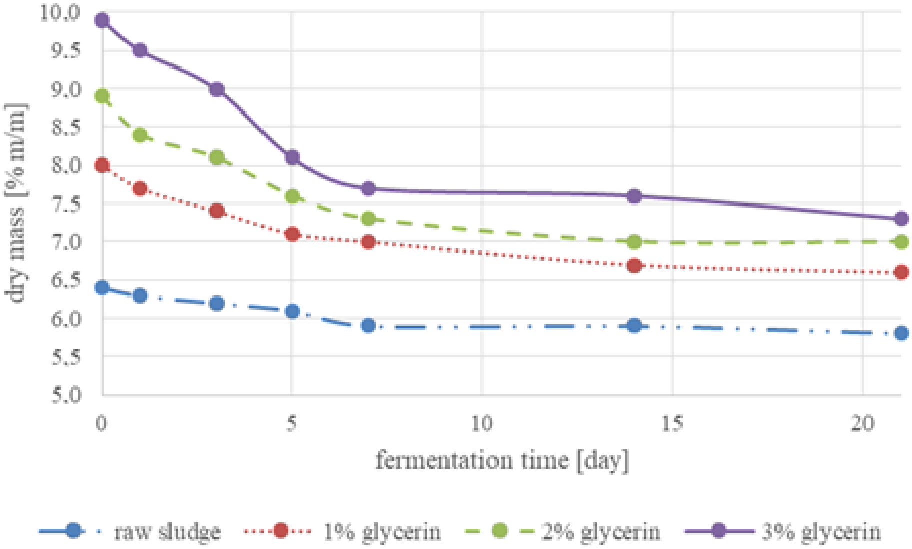

Fig. 6. Changes of dry mass of the sewage sludge during fermentation

The figure shows that the loss of dry matter is higher in the case of addition of the glycerin fraction to the fermented sludge.

More accurate thermogravimetric comparison of final products of the fermentation process were performed for raw sewage sludge and sample with addition of 3% glycerin layer obtained in bioreactors.

The comparison of the sample results is presented in Fig. 8 (sludge with glycerin fraction) and Fig. 7 (raw sewage sludge). After analyzing the thermograms, it can be concluded that the thermal decomposition of the samples takes place in two main stages. The first one is carried out in the range of approx. 50–120ºC and causes a weight loss of approx. 2–22%, depending on the sample, and may be the result of water evaporation.

The second stage takes place in the range of approximately 160–310ºC, as seen in the graphs in the form of the peak on the DTA curve, is the result of decomposition of unspecified compounds. Also notable is the temperature of completion of thermal decomposition, which is around 550ºC for both samples (raw sludge and containing glycerin layer). Both the samples reached about 80% weight loss at that temperature.

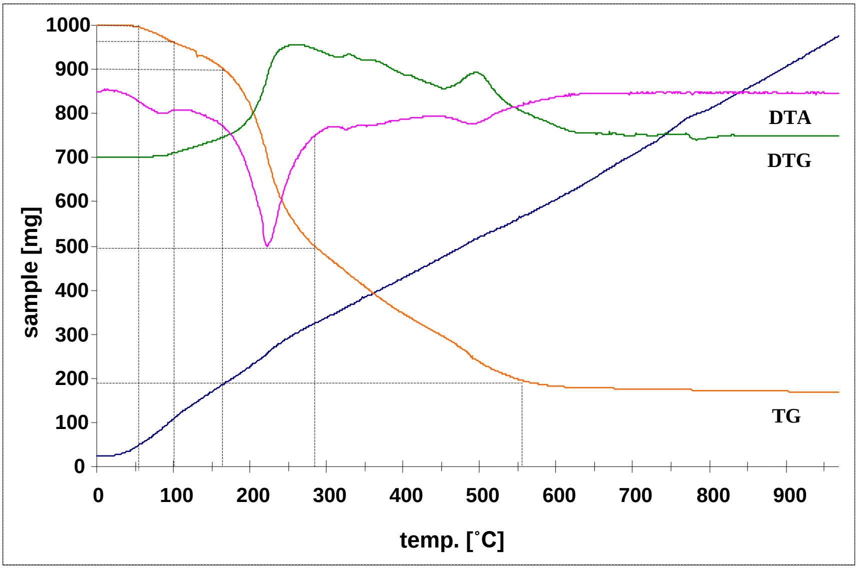

Fig. 7. Thermogravimetric analysis of sewage sludge sample without glycerine addition

A DTA curve analysis indicates that, for the sample with the glycerin fraction added, the process of thermal decomposition in the range of 50ºC–160ºC is more endothermic than for the raw sewage sludge.

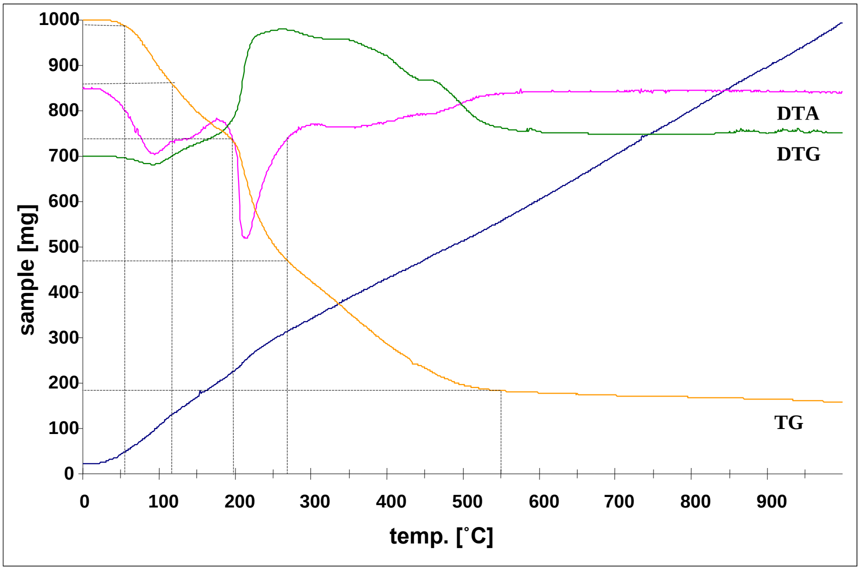

Fig. 8. Thermogravimetric analysis of sewage sludge sample with glycerine addition

In the case of the sample containing the glycerin fraction, the process of thermal decomposition between 60°C and 200°C was completed more quickly than for the sample without any glycerin fraction added to it.

4. Summary and Conclusions

In the course of the study, it was confirmed that the addition of the glycerin fraction obtained in the biodiesel production to the sewage sludge fermentation process degrades the products contained in the glycerin fraction (free glycerol and fatty acid methyl esters) as the result of the fermentation process. The parameters of the mixture constituting the residue from the fermentation process do not differ significantly for the samples with or without the glycerin fraction.

The addition of an alkaline glycerin fraction to the sludge does not interfere with the fermentation process, provided the pH does not exceed the limits suggested for the process (usually in range 6.5–8). The value of the pH parameter should be under control all the time during the fermentation process due to the fact that the pH of the reaction mixture containing the glycerin fraction tends to drop during the process.

Adding the glycerin fraction obtained during biodiesel production to the sewage sludge fermentation process may be one of methods of utilization of the biofuel process byproduct. However, there are many ways to convert glycerine into other compounds that may find application in various industries, especially when the demand for alternative uses of glycerol is insufficient in the region where biodiesel is produced, this method can be considered. This method of utilization of the glycerin fraction is environmentally friendly and is potentially cost-effective because of the use of biogas energy.

Although our studies have shown that the components of the glycerin layer are decomposed in the process of anaerobic fermentation of sewage sludge, the effect of glycerin addition on the composition and amount of biogas generated in the process should be investigated. This can be important for the energy and economic aspects of the fermentation of sewage sludge.

References

1. Ang, G., Tan, K., Lee, K.: Recent development and economic analysis of glycerol-free processes via supercritical fluid transesterification for biodiesel production. *Renewable and Sustainable Energy Reviews,* 31, 61–70, 2014.

2. Ayoub, M., Abdullah, A.: Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry. *Renewable and Sustainable Energy Reviews,* 16(5), 2671–2686, 2012.

3. Barbirato, F., Chedaille, D., Bories, A.: Propionic acid fermentation from glycerol: comparison with conventional substrates. *Applied Microbiology and Biotechnology,* 47, 441–446, 1997.

4. Baskaran, S., Zakaria, M., Sabri, A., Mohamed, M., Wasoh, H., Toshinari, M., Hassan, M., Banatt, I.: Valorization of biodiesel side stream waste glycerol for rhamnolipids production by Pseudomonas aeruginosa RS6. *Environmental Pollution,* 276, 116742, 2021.

5. Buraczewski, B., Bartoszek, B.: Biogaz wytwarzanie i wykorzystanie (Biogas production and use). PWN Warszawa, 1990 (in Polish).

6. Cavalheiro, J., de Almeida, M., Grandfils, C., da Fonseca, M.: Poly(3-hydroxybutyrate) production by Cupriavidus necator using waste glycerol. *Process Biochemistry,* 44(5), 509–515, 2009.

7. Dharmadi, Y., Murarka, A., Gonzalez, R.: Anaerobic fermentation of glycerol by Escherichia coli: a new platform for metabolic engineering. *Biotechnology and Bioengineering,* 94, 821–829, 2006.

8. Jędrczak, A.: Biologiczne przetwarzanie odpadów (Biological waste treatment). Wydawnictwo Naukowe PWN Warszawa, 2007 (in Polish).

9. Jerzykiewicz, W., Naraniecki, B., Terelak, K., Trybula, S., Kosno, J., Lukosek, M.: Zagospodarowanie frakcji glicerynowych z instalacji biodiesla (Utilization of glycerol fractions from biodiesel plants). *Przemysl Chemiczny*, 86(5), 397–402, 2007 (in Polish).

10. Kaur, J., Sarma, A., Jha, M., Gera, P.: Valorisation of crude glycerol to value-added products: Perspectives of process technology, economics and environmental issues. *Biotechnology Reports*, 27, e00487, 2020.

11. Kijeński, J., Krawczyk, Z.: Perspektywy rynku gliceryny (Perspectives of the glycerol market). *Przemysl chemiczny,* 86(4), 273–277, 2007 (in Polish).

12. Kumar, L., Kaur, R., Tyagi, R., Drogui, P.: Identifying economical route for crude glycerol valorization: Biodiesel versus polyhydroxy-butyrate (PHB). *Bioresource Technology,* 323, 124565, 2021.

13. Lehr, V.: Dehydratisierung von Glycerol zu Acrolein in alternativen Lösemitteln unter Druck und hohen Temperaturen. Ph.D. Thesis, Technische Universität Darmstadt, 2009 (in German).

14. Lim S., Teong L.: Recent trends, opportunities and challenges of biodiesel in Malaysia: An overview. *Renewable and Sustainable Energy Reviews,* 14(3), 938–954, 2010.

15. Lu, P., Yuan, Z., Li, L., Wang, Z., Luo, W.: Biodiesel from different oil using fixed-bed and plug-flow reactors. *Renewable Energy,* 35, 283–287, 2010.

16. Nda-Umar, U., Ramli, I., Taufiq-Yap, Y., Muhamad, E.: An Overview of Recent Research in the Conversion of Glycerol into Biofuels, Fuel Additives and other Bio-Based Chemicals. *Catalysts,* 9(1), 15, 2019.

17. Neumann, W.: Glycerin and its history. In: Jungermann E, Sonntag N., (eds.): *Cosmetic Science and Technology Series*, 11, 7–14, 1991.

18. Numpilai, T., Cheng, C., Seubsai, A., Faungnawakij, K., Limtrakul, J., Witoon, T.: Sustainable utilization of waste glycerol for 1,3-propanediol production over Pt/WOx/Al2O3 catalysts: Effects of catalyst pore sizes and optimization of synthesis conditions. *Environmental Pollution*, 272, 116029, 2021.

19. Pagliaro, M., Rossi, M.: The Future of Glycerol: New Uses of a Versatile Raw Material. Green Chemistry Book Series, RSC Publishing, Cambridge 2008.

20. Pan, C., Tan, G., Ge, L., Chen, C., Wang, J.: Two-stage microbial conversion of crude glycerol to 1,3-propanediol and polyhydroxyalkanoates after pretreatment. *Journal of Environmental Management*, 232, 615–624, 2019.

21. Papanikolaou, S., Fakas, S., Fick, M., Chevalot, I., Galiotou-Panayotou, M., Komaitis, M., et al.: Biotechnological valorisation of raw glycerol discharged after bio-diesel (fatty acid methyl esters) manufacturing process: production of 1,3-propanediol, citric acid and single cell oil. *Biomass Bioenergy*, 32(1), 60–71, 2008.
22. Suhaimi, S., Phang, L., Toshinari, M., Abd-Aziz, S., Wakisaka, M., Shirai, Y., Hassan, M.: Bioconversion of glycerol for bioethanol production using isolated escherichia coli SS1. *Brazilian Journal of Microbiology*, 43(2), 506–516, 2012.
23. Tang, S., Boehme, L., Lam, H., Zhang, Z.: Pichia pastoris fermentation for phytase production using crude glycerol from biodiesel production as the sole carbon source. *Biochemical Engineering Journal*, 43(2), 157–162, 2009.
24. Torres, M., Jiménez-Osés, G., Mayoral, J., Pires, E., de Los Santos, M.: Glycerol Ketals: synthesis and profits in biodiesel blends. *Fuel,* 94, 614–616, 2012.
25. Valliyappan, T., Bakhshi, N., Dalai, A.: Pyrolysis of glycerol for the production of hydrogen or syn gas. *Bioresource Technology*, 99(10), 4476–4483, 2008.
26. Vlysidis, A., Binns, M.,Webb, C., Theodoropoulos, C.: Glycerol utilisation for the production of chemicals: Conversion to succinic acid, a combined experimental and computational study. *Biochemical Engineering Journal*, 58–59, 1–11, 2011.

Technological aspects of landfill reclamation using industrial waste

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Abstract

Our study was conducted to optimize the waste management system. Ways of rational use of waste generated in the region as a secondary raw material in technological processes in the operation and reclamation of landfills were proposed. The analysis of the impact on the environment of jointly buried household and industrial waste at the landfill of solid household waste is carried out.

Studies of the quality of atmospheric air, soils and groundwater in the area of probable impact of the landfill were considered separately:
– during the period of delivery of foundry waste to the landfill;
– during the period of delivery of drilling mud waste to the landfill.

According to the research results, it is established that the cleaned molding waste, crushed construction waste, dry drilling mud residue obtained by the "Filter Basin" technology should be used as an insulating layer on solid waste landfills, as well as in reprofiling the landfill body during the process. stage of reclamation. The implementation of this solution will provide an opportunity to reuse waste, as well as reduce the number of sludge barns and waste heaps of foundry production.

Keywords: household waste, recycling, industrial waste, landfill reclamation, ecological safety

1. Introduction

An important aspect of sustainable development is environmentally sound waste management and landfill reclamation. By signing the Association Agreement with the European Union, Ukraine has made its choice in favor of European legislation. The first priority of EU legislation is to prevent the generation of waste, and last but not least, landfilling. Ukraine sends about 94% of household waste to landfills (National Forum, 2019).

Disposal of waste in unequipped landfills leads to environmental pollution. The formed filtrate, flowing through the thickness of the waste, is able to contaminate soils and groundwater with hazardous liquids of multicomponent chemical composition. One of the main problems of the soil cover is its contamination with heavy metals, the content of which exceeds the maximum allowable concentration. Soil toxicity is caused by compounds of such heavy metals as lead, cadmium, zinc and copper. Excessive amounts of heavy metals in soils are a very dangerous environmental factor, the effect of which is exacerbated by the penetration of heavy metal compounds into groundwater.

Another significant problem of landfills is the impact on atmospheric air. During the decomposition of the organic component of waste, carbon dioxide and methane are released into the air. Emissions of biogas into the atmosphere have an adverse effect on the environment, because the components of biogas are greenhouse gases that have toxic and explosive properties (Shmandiy, 2021). Methane should be attributed to gases that damage the ozone layer in the upper atmosphere. Under such circumstances, it is obvious that landfills are a source of environmental pollution (Kornienko and Godovska, 2012).

Recently, there has been a rapid increase in the amount of waste generated both in the home and in the manufacturing sector. At the same time, the urgency of landfill reclamation is growing. There are 562 landfills for solid waste in Ukraine. Therefore, the current problem is the introduction of measures to reduce the negative impact of landfills on the environment, as well as reduce the number of existing landfills (Law "On Waste", Voloshyn, 2012). In the case when it is not possible to use waste-free technologies, it is necessary to look for ways to reuse waste as a secondary raw material, energy resources. The ability of waste to replace high-value materials in construction work cannot be ignored. It is necessary to consider the possibility of efficient use of waste in all possible areas of activity.

The main problem that requires special attention in the field of household and industrial waste management is the lack of a comprehensive infrastructure for the collection, sorting and processing of waste. As a result – the loss of a significant amount of resource-intensive materials that could potentially be put into economic circulation. As a result, there are threats of sanitary and environmental nature associated with an increase in the number of waste disposal sites and the alienation of large amounts of land and their clogging, deterioration of the sanitary and epidemiological situation in the areas of these facilities (Malovany, 2011; Shmandiy, 2003; Kharlamova, 2014; Titova, 2021). No less important are the threats and socio-economic nature associated with the loss of a significant amount of resource-intensive materials for their further processing or use in production or technological processes.

Given the fact that a significant number of landfills in Ukraine need reclamation, and in modern management conditions with insufficient funding, such work is almost not performed, the possibility of replacing the necessary materials for reclamation with waste.

Landfill reclamation should include two stages, namely: technical (leveling of the landfill, arrangement of protective structures) and biological (creation of reclamation cover on the surface of the landfill and vegetation layer on the whole plane). Biological reclamation of the landfill should be based on an ecosystem approach.

It was for the technical stage that the possibility of replacing the clay needed to insulate and level the dome of the landfill was considered (DBN B.2.4-2-2005).

Studies of types of waste that can be used as raw materials for technological needs in the operation of landfills were conducted on the example of the landfill for solid waste in Kremenchuk, Poltava region, which has been in operation since 1965. The landfill area is about 28 ha, of which almost 14 ha are filled with household waste and industrial waste (Fig. 1). The height of waste storage is approximately 30 m. The nearest residential area is located 1000 m from the landfill. The level of groundwater varies from 25 to 62 m from the earth's surface.

Every year the landfill receives up to 80 thousand tons of solid household waste and not less than 20 thousand tons of industrial waste of the 4th class of danger. The technology of waste disposal provides for their storage and compaction by a bulldozer. As the work card is filled in, the waste is isolated. Industrial inert waste is used as an intermediate insulating layer (DBN B.2.4-2-2005).

In order to extract biogas (hydrocarbons) at the landfill in Kremenchuk provided 45 wells. From each well there is a loop pipeline, which goes to the collection chamber, from where the biogas is sent to the collector pipeline, through which the biogas is transferred to the process site. Every year, about 4.000 tons of biogas are extracted from the landfill body, which is converted into electricity and supplied to the grid.

To convert biogas energy into electricity, a JMS 412 GS-BL power generating unit with a capacity of 850 kW has been installed at the landfill, which is a set of technological equipment (gas compressor, four-stroke gas internal combustion engine with turbocharging and coolant cooler). electronic control system for the preparation of the gas mixture, etc.). The installation is based on a gas car engine, electric generator and auxiliary process equipment. The torque of the piston from the internal combustion engine is transmitted to the generator, which is a source of electrical energy. The cogeneration unit is located in a special container. Management, control and protection of EHU is completely carried out by means of automation system. Biogas is used as fuel.

Fig. 1. Landfill of solid household waste of Kremenchuk

To date, the resource of most of the landfill is almost exhausted (Shmandiy, 2020). The slopes of the landfill have reached the normative value. There is a need to rehabilitate existing waste disposal maps and open new maps. Reclamation measures will minimize the formation of infiltrates and facilitate the collection and disposal of methane, while preventing contamination of surrounding areas and the spread of infections.

To solve the problem of reclamation of the existing part of the landfill in Kremenchuk, taking into account the existing system of collection and utilization of biogas (as for many landfills in Ukraine), we consider it appropriate to identify the following technological stages:

– reduction of the slope angle of the landfill, which can be achieved by filling the surrounding area with inert waste or clay;
– strengthening of slopes;
– planning the entire area of the landfill with inert materials that have a dense structure, while maximally filling the cracks and leveling the entire surface;
– installation of a filtrate treatment plant and a protective screen on top of the planned waste layer.

After completion of the technical stage, biological is carried out, which includes soil preparation, selection of planting material, sowing of plants.

One of the tasks of reclamation is to strengthen the slopes and plan the surface of the landfill. Soil or inert waste can be used for this purpose.

It is for the first two operations on technical reclamation that the possibility of replacing the soil with production waste is considered. The importance of solving this problem is due to the lack of soil for leveling the landfill, because the landfill is a fairly high structure, which occupies a large area of more than 10 hectares and has an irregular geometric shape. The high cost of materials that can be used in construction works is also important. Therefore, an alternative such as the use of waste will reduce the need for minerals, will allow the reuse of industrial waste, disposing of it in an environmentally friendly way. This will allow you to effectively plan areas for waste disposal.

We conducted a study of the impact of waste molding mixture and dry drilling mud residue on the components of the environment when placing them at the landfill in Kremenchuk.

As Poltava region belongs to the regions of Ukraine with a developed oil and gas industry, on the territory of which there are significant fields, a special group of industrial waste is waste from oil and gas production. The largest amount of such waste is generated during the drilling of wells, in particular drilling mud and oil sludge. Most of the drilling waste is disposed of in barns, which occupy large areas. The rapid and continuous development of the mining industry leads to an increase in waste volumes and, as a result, there is a problem with their management.

At the same time, the Poltava region has for the first time introduced a (Regional Plan to 2030) modern technological cycle for the reception, treatment and disposal of drilling waste, which included drilling mud waste. Due to the used technology of cleaning, neutralization and dehydration of drilling muds "Filter Basin" it is advisable to reuse the liquid phase (technical water) and the extracted rock. Treatment of drilling waste was carried out using a flocculation station, using flocculants and coagulants that have been certified in Ukraine (Regional plan, 2021) (Fig. 2,3).

Fig. 2. Filtration of water through the wall of the installation, after treatment of drilling waste with flocculants

Fig. 3. Dry residue of drilling mud

According to the results of the research it is established that the formed dry residue according to the indicators of sanitary-chemical researches and hygienic analysis is a low-toxic waste (provided dust formation is prevented at all stages of waste management), according to the content of toxic component: heavy metals: Pb, Ni, Cr, Cd, Zn) does not belong to hazardous waste. According to the results of the analysis of the composition of the water extract, the level of acid-base balance and the content of heavy metals was established, laboratory-model studies of the influence of different concentrations of drilling mud on the growth of barley plants were carried out. On the basis of the conducted researches it is established that the rational way of waste utilization is use:

– when creating landfills for storage of solid household and industrial;
– waste, as well as their further operation - dumping and layering of waste;
– as a filler in the manufacture of concrete mixtures, cinder blocks;
– construction of auxiliary and storage facilities;
– for filling the foundations in the planning of territories during the construction of industrial facilities and roads;
– for the purpose of arrangement of bypass and blocking shafts and dams.

In addition to mining waste, foundry waste is generated in the region.

In particular, in the city of Kremenchuk there are enterprises in the process of which waste of the spent molding mix is formed (Ecological passport of the city of Kremenchuk).Spent molding mixtures belong to large-capacity waste. Quite large areas are required for their placement.

These wastes pose a certain danger to the environment, as they contain a significant range of toxic substances.

The composition of any spent molding mixture in contact with hot metal includes its inclusion.

Therefore, the first stage of disposal is their purification from metal residues. The molding mixture is fed to a conveyor, over the belt of which a magnetic trap is installed.

Passing on a tape, the mix is cleared of metal inclusions.

At the next stage, the waste material is crushed and divided into fractions of about 5 mm.

Next, mechanical cleaning of dust.

As a result of processing the regenerated sand which can be used as a building material is safe.

Also, considerable attention needs to be paid to construction and demolition waste, which is typical for all regions of Ukraine. In general, they consist of such products as concrete and reinforced concrete, brick, metal, soil, sand contaminated with clay, plumbing ceramics, wood, glass, plasterboard, plastic, asphalt concrete. Recently, there has been a trend of gradual increase in the volume of waste from construction and repair work. In order to create a management system for this waste, a number of solutions and measures for their reuse in the Poltava region (Regional Plan to 2030):

– in the future the creation of facilities for processing construction waste and demolition with stationary or mobile crushing plants;
– use of inert materials (shredded construction waste) for layered;
– storage of mixed household waste at landfills and dumps;
– use of crushed construction waste in the road industry;
– reuse of certain types of construction waste, etc.

Thus, the results of previous studies have shown that the use of waste dry drilling mud residue and spent molding mixture, provided it is regenerated, it is advisable to use in the technological reclamation of landfills. Shredded construction waste should be used for access roads, as well as in combination with the above waste for landfill reclamation.

The environmental effect is to reduce the negative impact of waste on the environment by ensuring their rational use, increasing the percentage of recycled and reused waste. The need to dump waste into dumps and sludge amber will be reduced.

2. Materials and Methods

The Kremenchuk landfill accepts for disposal household and some types of industrial waste of the 4th class of danger. Since 2009 in Kremenchuk the program of separate collecting of MSW on such components as polymers, glass, plastic, residual garbage is introduced. Waste is collected in special containers, then they are transported to the manual sorting shop, pressed and sent for disposal to specialized organizations. There is no mechanized sorting complex at the landfill. Therefore, the landfill often gets not only reusable waste, but also hazardous. The results of the analysis of the morphological composition of the waste are given in Table 1.

An analysis of the morphological composition revealed that the bulk of mixed solid waste is organic waste. These wastes are confirmed by organic decomposition, as a result of which biogas is released. To prevent uncontrolled leakage of biogas from the landfill body, the waste is compacted and isolated.

The study of the possibilities of waste use in landfill reclamation was carried out for waste typical in the Poltava region. Their characteristics were determined, the impact on the environment during their storage at the existing landfill was analyzed. The possibility of their perspective use in the process of technical reclamation is considered, namely:

– as a leveling layer of the landfill (Fig. 4);
– as a side outer insulating layer, an intermediate insulating layer (Fig. 5).

Table 1. Morphological composition of solid household waste

№	Type of waste	Mass fraction, %
1	Biodegradable waste (garden and kitchen waste)	44.26
2	Cardboard/ paper /tetrapack	14
3	PET / PE film (plastic bags)/other plastic (PS, PP, PVC, HDPE)	14.76
4	Metals	3.16
5	Glass	8.37
6	Textile	6.76
7	Skin	1.69
8	Wood	1.36
9	Hygiene products	4.80
10	Inert waste	0.84
	Total:	100

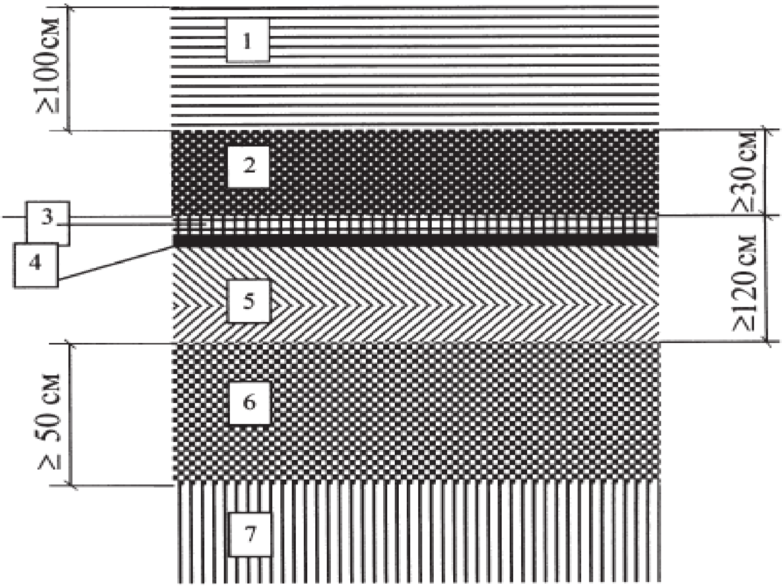

Fig. 4. Scheme of construction of the protective screen of the surface of the landfill. 1– reclamation layer; 2 – drainage layer; 3 – protective layer; 4 – synthetic waterproofing; 5 – mineral waterproofing layer; 6 – leveled layer, gas drainage; 7 – landfills

To do this, an analysis of the results of laboratory studies of waste, air, soil and groundwater. A comparative analysis of the impact of waste on the environment during their use at the landfill. The analysis of air and soil was performed at 5 points of the landfill: №1 – on the landfill, № 2–5 – within the sanitary protection zone of the landfill. From 5 samples the average value of indicators of pollutants was received. Indicators studied in the analysis of air: nitrogen dioxide, sulfur dioxide, carbon monoxide, phenol, formaldehyde, hydrogen sulfide, methane. Among the chemical contaminants of soils to persistent toxicants include nitrates and heavy metals (analysis was performed only on lead), which enter the soil as a result of infiltration through the body of the landfill. Hydrogen index indicates soil salinity.

Indicators studied in the analysis of soil: pH, nitrates, lead, cadmium, zinc.

Groundwater analysis was performed from 2 wells located near the landfill downstream of groundwater. From 2 samples received the average value of pollutants. Indicators studied: pH, nitrites, nitrates, dry residue, chlorides, sulfates, heavy metals (Fe, Cu, Pb, Ni, Cd). The study was conducted according to current methods in Ukraine.

The obtained results were compared with background samples and maximum permissible concentrations set for pollutants in Ukraine. The background test was taken as the results of research in the period when the waste of the molding mixture and dry residue was not used at the landfill.

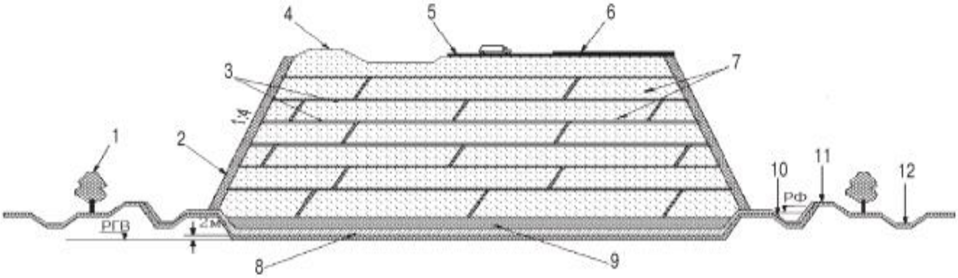

Fig. 5. Scheme of the landfill with an insulating layer: 1 – forest strip; 2 – lateral outer insulating layer; 3 – intermediate insulating layer; 4 – MSW, which are placed on the work card; 5 – temporary dead-end road; 6 – temporary travel with a hard surface; 7 – MSW; 8 – natural or artificial waterproof base; 9 – waste saturated with filtrate; 10 – tray for collecting and discharging the filtrate; 11 – embankment; 12 – upland ditch for collecting rain and melt water

3. Results and discussion

According to the technological process, household waste, which is imported to the landfill, is dumped on work cards. After compaction by the bulldozer the unloading zone is leveled on the covered layer of inert waste. Waste of the spent molding mixture is used as an insulating material. Such waste was imported to the landfill for several years and accumulated on a specially designated site.

Then, as needed, they were transported on work cards to insulate household waste. In addition to the insulation of working maps, the waste was used to isolate the slopes of the landfill. The most effective is the use of waste to extinguish the fire that periodically occurred at the landfill. Such fires are among the most complex and long-lasting, extinguishing which requires significant resources, effort, resources and time.

In addition to foundry waste, waste from drilling mud residue was accepted at the landfill. They were also used during the operation of the landfill for layering and insulation of household waste. To determine the physicochemical properties of drilling mud, laboratory studies of drilling mud waste before cleaning and dry residue after the filter basin were performed. According to the results of research, it is established that the dry residue consists of mineral components (silicates and aluminosilicates of parent rocks) and belong to the waste of hazard class 4. In accordance with table 1 of Annex W DBN B.2.4-2-2005 aluminosilicate sludge is included in the list of industrial wastes that are accepted at the landfill without restriction and used as insulating material.

Waste from construction works is typical for all landfills and landfills. They are formed both in the production sphere and in everyday life. Studies have shown that construction waste consists of mineral components (silicon, granite, gypsum, etc.). When shredding waste, they can be used not only for road construction at the landfill, but also as an insulating material.

When using the waste of the molding mixture at the landfill, the state of the environment was monitored (Table 2–3).

Water samples taken from well №1 do not meet the sanitary requirements set for drinking water for nitrates and dry residue both during the period of use of waste molding mixture, and before this period (State sanitary norms and rules, 2010).

Water samples taken from well №2 do not meet the sanitary requirements for drinking water for nitrates.

The results of the analysis indicate that the water is contaminated with filtrate, which is formed as a result of infiltration of precipitation into the body of the landfill. The main pollutants are nitrates and dry matter. Contamination occurs both during the use of molding waste and during the period when the waste was not imported, or imported in small quantities. The concentration of heavy metals, which are characteristic of the waste molding mixture, does not exceed the normative values. Indicators of pollutants in the studied period of delivery and use of waste molding mixture at the landfill do not exceed the background values adopted in the study. That is, the deterioration of the environment due to the placement of waste in the molding mixture waste is not observed.

Table 2. The results of research of water with a well №1 when using waste molding mixture

Indicator	**Norm mg/dm^3**	**Actual values, mg/dm^3**						
		2013	**2014 I stage**	**2014 II stage**	**2015 I stage**	**2015 II stage**	**2016**	**Back-ground indicators**
pH	6.5–8.5	7.41	7.6	7.38	7.57	7.57	7.96	7.01
Nitrites	≤3.3	< 0.03	0.03	0.064	0.006	0.005	0.003	0.21
Nitrates	≤50	308.6	211.7	213.5	216.7	201.8	174.8	207
Dry residue	≤1500	1614	1745	1571	1631	938.5	1623.5	1513
Chlorides	≤350	151	150	144	132	130	136	116
Sulfates	≤500	175	259.4	202.5	192	112.6	204.3	142
Fe	≤0.2	2.14	0.18	0.13	0.17	0.1	0.1	0.1
Cu	≤1	0.01	0.012	0.012	0.01	0.009	0.008	0.001
Pb	≤0,01	0.001	0.001	0.001	0.001	0.001	0.004	0.001
Ni	≤0,02	0.009	0.004	0.01	0.008	0.011	0.006	0.0012
Cd	≤0,001	0.0001	0.0001	0.0002	0.0001	0.0002	0.001	0.0001

Table 3. The results of studies of water with a well № 2 using waste molding mixture

Indicator	**Norm mg/dm^3**	**Actual values, mg/dm^3**						
		2013	**2014 I stage**	**2014 II stage**	**2015 I stage**	**2015 II stage**	**2016**	**Back-ground indicators**
pH	6.5–8.5	8.46	6.8	7.64	7.5	7.19	8.06	7.01
Nitrites	≤3.3	0.084	0.003	0.02	0.003	0.069	0.003	0.21
Nitrates	≤50	196.6	215.6	30.5	33.65	216.7	28.9	207
Dry residue	≤1500	1485	356	831	446	1012	345	1513
Chlorides	≤350	130	28	40	36	96	28	116
Sulfates	≤500	286.7	5.8	281.9	270.2	120.1	38.4	142
Fe	≤0.2	–	0.1	0.02	0.13	0.12	0.1	0.1
Cu	≤1	0.005	0.004	0.009	0.005	0.006	0.011	0.001
Pb	≤0.01	0.001	0.002	0.002	0.002	0.001	0.002	0.001
Ni	≤0.02	0.010	0.007	0.011	0.012	0.009	0.006	0.0012
Cd	≤0.001	0.0002	0.0001	0.0001	0.0001	0.0003	0.001	0.0001

Another object of study was the possible impact of waste on environmental components (Table 4).

Table 4. The results of soil research using waste molding mixture

Indicator	**Norm mg/l**	**Actual values, mg/l**						
		2013	**2014 I stage**	**2014 II stage**	**2015 I stage**	**2015 II stage**	**2016**	**Back-ground indicators**
pH	–	6.0	6.8	6.1	6.4	6.5	6.9	6.8
Nitrates	130	80	16.6	20	19	–	–	20.0
Lead	≤32.0	5.1	4.5	6.0	5.0	4.1	3.1	6.0

Thus, as a result of a comparative analysis of the quality of soils, it was found that the concentrations of pollutants do not exceed the permissible norms.

The next step in the study was to analyze the impact of waste on ambient air (Table 5).

According to the results of the analysis it is seen that the exceedances of the normative indicators in the atmospheric air during the use of waste in the technological process of operation of the landfill are not established.

Table 5. The results of studies of the state of atmospheric air using waste molding mixture

Indicator	**Norm, mg/m^3**	**Actual values, mg/m^3**				
		2013	**2014**	**2015**	**2016**	**Background indicators**
Nitrogen dioxide	0.2	0.07	0.1	0.055	0.123	0.08
sulfur dioxide	0.5	0.18	0.32	0.055	0.02	0.3
carbon monoxide	5.0	1.2	2.5	0.014	0.9	2.4
phenol	0.01	0.008	0.004	–	0.004	0.008
formaldehyde	0.035	0.02	0.025	–	0.02	0.028
hydrogen sulfide	0.008	–	0.004	–	–	0.005

The negative impact of the use of foundry waste was recorded during the operation of the biogas collection and extraction system. Due to their excessive use during fires at the landfill or when laying waste in a layer larger than 0.5 m, the degassing process of the landfill was slowed down, which led to a decrease in the extraction and utilization of biogas.

Thus, the analysis of the results of the research indicates that the use of waste from foundry production (spent molding mixture, after cleaning) should be carried out at the landfill as an insulating material, provided that the proportions of household waste with industrial waste.

The next waste, the environmental impact of which was considered in the research, is the dry residue of drilling mud. Waste began to be used at the landfill as an insulating layer as an alternative to waste molding mixture. One of the advantages of such substitution was the better physical properties that characterized the waste, because drilling mud has a clay consistency, which is less loose than burnt earth and more plastic and dense. Having such characteristics, the waste was used not only to insulate the layers of household waste, but also to strengthen the slopes.

During the use of waste at the landfill, the state of the environment was monitored on the same principle as before (Table 6–7). To assess the release of biogas from the landfill, a study of the presence of methane at the landfill and within its sanitary protection zone. The research results are given below.

Table 6. The results of studies of water with a well № 1 when using drilling mud

Indicator	**Norm mg/m^3**	**Actual values, mg/dm^3**				
		2019 I stage	**2019 II stage**	**2020 I stage**	**2020 II stage**	**Background indicators**
pH	6.5–8.5	7.55	7.27	7.55	7.18	7.01
Nitrites	≤3.3	<0.003	0.005	0.008	0.004	0.21
Nitrates	≤50	11.4	11.1	4.30	156.1	207
Dry residue	≤1500	404	442.0	481.0	1512.5	1513
Chlorides	≤350	15.3	14.2	14.8	90.76	116
Sulfates	≤500	172	175.3	128.08	217.6	142
Fe	≤0.2	0.10	0.10	0.16	0.08	0.1
Cu	≤1	0.002	0.003	0.003	0.004	0.001
Pb	≤0.01	0.001	0.002	0.003	0.002	0.001
Ni	≤0.02	0.007	0.014	0.01	0.009	0.0012
Cd	≤0.001	0.0002	0.0001	0.007	0.001	0.0001

Background indicators for comparative analysis are taken based on the results of monitoring the state of the environment in the period when drilling mud was not imported to the landfill.

The water quality in the well № 1 for several periods of research met sanitary standards. In the second stage of 2020, water indicators deteriorated due to the presence of nitrates and dry matter. Nevertheless, the indicators of pollutants do not exceed the background concentration accepted in the study.

Table 7. The results of studies of water with a well № 2 when using drilling mud

Indicator	**Norm mg/dm^3**	**Actual values, mg/dm^3**				
		2019 I stage	**2019 II stage**	**2020 I stage**	**2020 II stage**	**Background indicators**
pH	6.5–8.5	7.81	7.44	7.36	7.81	7.01
Nitrites	≤3.3	0.006	0.096	0.004	0.003	0.21
Nitrates	≤50	15.4	21.9	35.1	8.6	207
Dry residue	≤1500	315.0	310.0	705	391.5	1513
Chlorides	≤350	23.0	21.3	18.44	24.11	116
Sulfates	≤500	44.6	77.3	148.43	63.6	142
Fe	≤0.2	0.10	0.10	0.12	0.1	0.1
Cu	≤1	0.002	0.003	0.003	0.003	0.001
Pb	≤0.01	0.002	0.002	0.003	0.003	0.001
Ni	≤0.02	0.006	0.014	0.008	0.005	0.0012
Cd	≤0.001	0.0001	0.0001	0.000	0.001	0.0001

The water quality in the well № 2 during the conducted researches corresponded to sanitary norms.

Thus, according to the results of research, there is a decrease in groundwater pollution.

The analysis of the impact of the landfill during the use of drilling mud waste on soils and atmospheric air (Table 8–9). As in previous studies, the background indicators are the results of monitoring in the period when drilling mud waste was not imported to the landfill.

Table 8. The results of soil research using drilling mud

Indicator	**Norm mg/l**	**Actual values, mg/L**				
		2019 I stage	**2019 II stage**	**2020 I stage**	**2020 II stage**	**Background indicators**
pH	not normalized	8.0	7.38	7.48	7.48	6.8
Lead	≤32.0	4.09	3.42	4.32	4.58	6.0
Cadmium	1.5	0.21	0.18	1.4	1.4	0.23
Zinc	23	19.7	18.37	16.73	13.8	18.0

In general, at all points the concentrations of pollutants do not exceed the maximum allowable norms. In general, there is a tendency to reduce the degree of soil contamination with the distance from the contours of the landfill. Compared to background samples, there is an increase in cadmium concentration, but the concentration is within acceptable limits.

Table 9. The results of studies of atmospheric air using drilling mud

Indicator	**Norm, mg/m^3**	**Actual values, mg/m^3**		
		2019	**2020**	**Background indicators**
Nitrogen dioxide	0.2	0.14	0.17	0.08
Sulfur dioxide	0.5	0.04	0.06	0.3
Carbon monoxide	5.0	0.48	0.66	2.4
Methane	50.0	0.008	6.55	6.5
Formaldehyde	0.035	0.00001	0.00001	0.028
Hydrogen sulfide	0.008	0.0001	0.0001	0.005

Analysis of the state of atmospheric air indicates the normative concentrations of pollutants in the area of impact of the landfill. The concentration of methane is quite insignificant, which indicates the absence of uncontrolled release of landfill gas from the landfill.

The concentration of methane is close to the maximum allowable single dose (50.0 mg/m^3) recorded on an open map, which was operated at the time of the study. However, at a distance, the methane rate decreased rapidly and at a distance of 50 meters from the working map was less than 7 mg/m^3. The concentration of methane within the sanitary protection zone of the landfill is about 7.0 mg/m^3.

The concentration of methane within the sanitary protection zone of the landfill is about 7.0 mg/m^3.

The obtained results indicate that on the open working map of the landfill biogas is freely released. With high-quality compaction of the household waste layer with inert stabilizing waste, biogas remains in the body of the landfill, which is safe, because the landfill is equipped with a system of collection, disposal and utilization of biogas.

Therefore, when placing the dry residue of drilling mud on the landfill as an insulating material and technical soil for strengthening the slopes, there was no negative impact on the environment. The quality of groundwater has not deteriorated, at certain intervals there has been a tendency to improve water quality. No negative impact on soils and groundwater has been recorded.

Compaction of household waste with waste dry drilling mud residue did not worsen the landfill degassing process. Extraction and utilization of biogas took place in the usual way.

4. Summary and Conclusions

For the purpose of rational use of waste and their utilization the research of influence of waste of the fulfilled molding mix and dry residue of drilling mud on components of environment at their placement on the landfill of household waste of Kremenchuk as isolating material is carried out.

The influence of foundry waste was considered. According to the results of research conducted during the use of waste as an insulating layer and material for firefighting, shelter of landfills, deterioration of the environment in the area of probable impact of the landfill is not recorded. There was a tendency to reduce biogas production, which may be due to an increase in the height of the arrangement of insulating layers.

The impact of waste solid residues of drilling mud was observed for the same components of the environment. Deterioration of the environment due to the use of waste was not observed. The quality of groundwater during certain periods of research has improved, which indicates the safety of using such waste as an insulating material.

Factors that negatively affect the environment, namely: odor, leachate, fire risk, are minimized by covering the working maps of the landfill with inert waste and elimination (strengthening) of emergency slopes.

Therefore, based on the results of the research, we came to the conclusion that crushed construction waste, cleaned waste of molding mixture (in moderation), dry residue of drilling mud using the technology "Filter Pool" should be used not only for layering and strengthening the slopes of landfills, but also in the technological process of their reclamation. This will have both economic and environmental positive effects, namely:

– the number of industrial waste dumps will decrease;
– the number of barns for removing drilling mud will decrease;
– the issue of waste disposal will be resolved;
– the estimated cost of works on reclamation of landfills and dumps will decrease;
– will reduce the cost of disposal of drilling waste, waste molding mixture, because they must change the status of "waste" to "secondary raw materials".

It should be noted that the choice of waste method should be determined separately.

For each landfill according to its specific operating conditions, adopted reclamation technologies, as well as under the condition of analysis of the chemical composition of waste planned for use as technological material.

References

1. Ecological passport of the city of Kremenchuk (Electronic resource). Access mode:https://kremen.gov.ua/assets/uploads/files/2f333de4c2140bfa1e487bbc64a1a5420901aad0ekologichnyj_pasport_mista_kremenchuka.pdf.
2. Hodovsʹka, T.B., Hurelya, V.V.: Ecological analysis and modeling of pollutant scattering from the landfill for solid waste. *Transactions of Kremenchuk Mykhailo Ostrohradskyi National University*, 5/(76), 115–118, 2012.
3. Kharlamova, O.V.: Anthropocentric approach in environmental safety management at the regional level. *Ecological Safety and Balanced Use of Resources*, 2, 142–149, 2014.
4. Korniyenko, I.V., Koshma, A.I.: Status and directions of solving the problem of disposal of ecological dander household waste. *Technical sciences and technologie. Chernihiv Polytechnic National University*, 1(3), 122–127, 2012.
5. Law of Ukraine on Waste 187/98-VR, version 6.10.2020, grounds – 124–IX.
6. Malʹovanyy, M.S., Holodovsʹka, O.Y.A., Pasternak, M.I.: Municipal solid waste of Lviv and their impact on the environment. *Scientific journal of the National University "Lviv Polytechnic Chemistry, technology and application of substances,* 700, 250–252, 2011.
7. National Waste Management Plan (Electronic resource). Access mode: https://zakon.rada.gov.ua/laws/show/117-2019-%D1%80#Text.
8. Proceedings of the National Forum "Waste Management in Ukraine: Legislation, Economy, Technology" (Electronic resource), 2019. https://www.ecoleague.net/images/Збірник_Форум-2019.pdf.

9. Regional waste management plan in Poltava region until 2030, 2021 (Electronic resource). https://www.adm-pl.gov.ua/advert/oprilyudnennya-dlya-obgovorennya-proektu-regionalniy-plan-upravlinnya-vidhodami-u-poltavskiy.
10. Shmandiy, V.M.: Ecological safety management at the regional level (theoretical and practical aspects), Thesis abstract for Doc. Sc. (Engineering.), Kharkiv, Ukraine, 2003.
11. Shmandiy, V.M., Soloshych, I.O., Kolyesnik, D.V.: Ecological danger management of solid waste in the region. *Transactions of Kremenchuk Mykhailo Ostrohradskyi National University*, 2, 60–65, 2021.
12. State building codes of Ukraine. Designing. Landfills for solid waste. Basic design provisions. DBN B.2.4-2-2005.
13. State sanitary norms and rules "Hygienic requirements for drinking water, intended for human consumption ", approved by the order of the Ministry of Health of Ukraine, 2010, 400.
14. Titova, A.O., Kharlamova, O.V., Bezdyenyezhnykh, L.A., Bihdan, S.A.: Optimization of the solid waste management system in the Kremenchug territorial community. *Transactions of Kremenchuk Mykhailo Ostrohradskyi National University*, 3(128), 51–56, 2021.
15. Voloshyn, P.: Analysis of the impact of Lviv waste on the natural environment. Visnyk of the Lviv University. *Geology Series,* 26, 139–147, 2012.
16. Shmandiy, V., Bezdeneznych, L., Kharlamova, O., Rigas, T.: Improving the Method for Producing Adsorbents from Agro-Industrial Wastes. *Journal of Ecological Engineering*, 21(6), 147–154, 2020.

Effect of stabilization treatment of water on the quality of its reverse osmotic desalination

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Abstract

Nowadays, the problem of a sharp increase in water mineralization in surface water is quite acute. An important and urgent task is to provide high-quality drinking water to the population and industry, especially in areas with limited water resources. Therefore, softening and reducing salt content is important in preparing water. To create low-waste processes of water desalination, the selectivity of the reverse osmosis membrane towards chlorides, sulfates, hardness ions depending on the degree of permiate selection was determined. When purifying water using membrane technologies, there is a problem of formation of deposits and fouling on the membranes, which reduces the flow of filtrate and increases the transmembrane pressure. Therefore, the influence of pre-treatment of water on the ultrafiltration membrane and stabilization treatment of water on weakly acid cation exchange resin in acid form on the quality of reverse osmosis desalination of mineralized waters is studied.

Keywords: desalination, membrane, pollutant, productivity, selectivity

1. Introduction

In this study, the optimum parameters of membrane desalination of model solutions were determined and the required efficiency was achieved. Methods for stabilizing treatment of water before barometric desalination were developed to improve the efficiency of membranes.

Nowadays, the problem of salinization of water is very common in Ukraine due to natural and anthropogenic factors, and industrial regions suffer the most. The high level of mineralization is occurred due to the presence of coal, iron ore and uranium mines. Great contribution to the salinity of water objects is made by the discharge of mine water, saline wastewater, water from cooling systems and brine infiltration of many slime storages (Buzylo et al., 2018; Liu et al., 2019).

Wastewater from Ukrainian mines is characterized by a high content of suspended solids (up to 0.1 g/dm^3), increased mineralization (salt content up to 3 g/dm^3), increased alkalinity (4–16 mmol/dm^3) and total hardness (7–16 mval/dm^3), due to which more than 3 million tons of mineral salts and substances are discharged into water reservoirs and rivers annually. This leads to a deterioration in the quality of surface and groundwater due to increasing salinity up to 2–2.9 g/dm^3, increasing the content of heavy metals and siltation of water reservoir and lake.

Unfortunately, modern methods of saline water treatment do not solve the problem, but only aggravate the situation in densely populated areas with well-developed industries (Gomelya et al., 2016).

The solution to this problem is the introduction of innovative complex water desalination technologies at the utilities and industrial enterprises (Kinnunen et al., 2018). It will helps to use water that has an increased mineralization, which will ensure a significant reduction of discharges of mineralized sewage and will lead to improvement of the quality of groundwater.

In water treatment systems, the use of membrane technologies is gradually expanding, which leads to replacement of traditional filtration methods: with the application of sand, of rotary drum and mesh filters, etc. For microfiltration, ultrafiltration and nanofiltration are distinguished according to classification of membrane filters, three groups of filters. For the mentioned filters order the transmembrane pressure increases from 0.5–3 to 15–50 bar, at the same time the pore size decreases.

The main advantages of baromembrane methods of water purification are high reliability of barrier filtration, compactness of equipment, possibility of full process automation, minimal use of reagents, low energy consumption. The disadvantages include: high cost of equipment, formation of deposits on the membranes, certain requirements for the quality of source water.

Membrane technologies have high efficiency and can be used at different stages of water treatment (Amaya-Vías et al., 2019), as well as together with other methods of purification (Kim et al., 2018).

In regions with a lack of fresh water, membrane technologies are widely used to desalinate highly mineralized waters (Haan et al., 2018).

Depending on the quality of the water and the requirements for the treated water, membrane separation methods are regarded as quite promising and most appropriate that can be used for water treatment and wastewater treatment in a technologically grounded combination (Ambiado et al., 2017; Gomelya et al., 2014).

The aim of this paper was to study the processes of desalination of mineralized waters by the membrane method for the creation of innovative technologies of water treatment for ecologically safe water supply systems.

2. Materials and Methods

In this work, water desalination was studied using cartridges with low-pressure reverse osmosis membrane Filmtec TW30-1812-50 and the properties of the membrane is described in Table 1.

Table 1. Properties of the reverse osmosis membrane Filmtec TW30−1812−50

Parameter	**Value**
Productivity, dm^3/day at a pressure of 4–7 bar and temperature 25°C	225−395
Stable salt removal, %	98
Minimal salt removal, %	96
Maximum water supply, dm^3/min	7.6
Maximum operating pressure, bar	21
Maximum operating temperature, °C	45
Maximum colloidal index	5
Ph range (long-term work)	2−11
Ph range (flushing up to 30 min)	1−13
Maximum concentration of free chlorine, mg/dm^3	<0.1
Size, mm	295 × 55

The model solution was used through experiments: hardness – 9.0 $mval/dm^3$, alkalinity – 5.0 $mmol/dm^3$, SO_4^{2-} – 620.0 mg/dm^3, Cl^- – 100. mg/dm^3, pH = 8.9.

After filtering the solution through the weakly acid cationite Dowex MAC-3 in acid form, it had the following characteristics: hardness – 3.9 mval / dm^3, acidity – 0.6 $mmol/dm^3$, Cl^- – 100.0 mg/dm^3, SO_4^{2-} – 620.0 mg/dm^3, pH = 3.9.

Filtration through an ultrafiltration membrane was used to reduce turbidity of the water, which reduced the turbidity and color of the water.

Filtration through weakly acid cation exchange resin in H^+ form was used for stabilization water treatment.

For desalination of water, samples of 10 dm^3 were used. The degree of selection of permeate was changed from 10 to 90%.

The concentrations of chlorides, sulfates, hardness and alkalinity were determined in initial solutions and in permeates. The selectivity (%) and productivity (dm^3/m^2 h) of the membrane were calculated:

$$R = \frac{C_0 - C_n}{C_0} \cdot 100, \tag{1}$$

$$J = \frac{\Delta V}{S \cdot \Delta t}. \tag{2}$$

where: C_0, $C_{n.}$ (mg/dm^3; $mval/dm^3$) – concentration of pollutant in initial solution and in treated solution, respectively, ΔV – volume of treated solution (dm^3), that passed through the membrane S (m^2) for the time of selection Δt (h).

3. Results and Discussion

In order to prevent the sediment deposition on membranes in barometric methods, it is necessary to provide an effective stabilizing treatment of water. It is believed that water with a turbidity of 0.5 mg/dm^3 and a color of up to 20 degrees meets the requirements for water supplied to reverse osmosis systems. An effective lighting and discoloration of water is important at baromembrane water purification. Therefore, to reduce the load on the reverse osmosis membrane, increase the process productivity, increase the period of operation of reverse osmosis membranes, we proposed to conduct pre-treatment with the application of ultrafiltration membranes to purify water from suspended solids.

In the work, the effect of the mechanical water purification on the productivity and selectivity of the reverse osmosis membrane of low pressure Filmtec TW30−1812−50 was determined.

The membrane Filmtec TW-30-1812-50 provides an effective water desalting at pressures up to 1 MPa (in this case, P = 0.3 MPa) with high process efficiency. Despite the fact that through a cassette with a reverse osmosis membrane only 10 dm^3 of model solution was passed, its pre-lighting significantly influenced the productivity of the membrane. When passing water through the ultrafiltration membrane, the turbidity and color of the water is reduced to ~ 0–0.1. The operation of the ultrafiltration device is at a dead end. The duration of the filter cycle is 2 hours, the duration of washing is 40–60 seconds, while the amount of washing water is 1–2%. During filtering an increase in membrane productivity on 12–20% is observed.

As shown in Fig. 2–4, the efficiency of removal of sulfates and chlorides as well as ions of hardness from water depends on the pre-purification stage of water treatment. During the desalination of the model solution, the highest final concentrations were fixed in the permeate for chlorides. The sulfates and hardness ions residual concentrations were rather low. The residual content of ions in concentrates depend on the initial concentration of ions in solution as well as on the membrane effectiveness of detention.

In concentrates, the increase in concentrations of all cations and anions that were controlled in this process were observed. The highest concentrations correspond to hardness ions and to sulfates (hardness – 34–75 mval/dm^3, SO_4^{2-} – 490–550 mg/dm^3, Cl^- – 75–83 mg/dm^3).

Since the efficiency of water purification from any ions depends not only on the residual concentrations of ions, but also on their initial concentration, then the efficiency of the water purification process from any ions is better to evaluate by the values of the membrane selectivity (Fig. 1).

During filtering, the Filmtec TW30-1812-50 membrane was characterized by the lowest selectivity of 89–95% in relation to chlorides; the selectivity towards sulfates and ions of hardness reached the values 98.8–99.7% (Fig. 2–4).

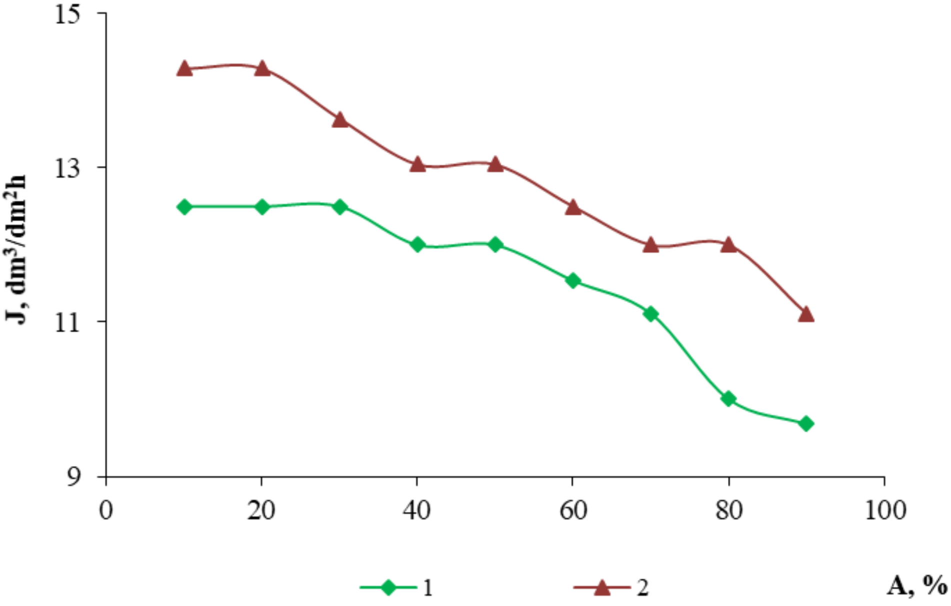

Fig. 1. Dependence of the productivity of the reverse osmosis membrane Filmtec TW-30-1812-50 on the degree of selection of permeate during desalination of unfiltered (1) and filtered model solution (2)

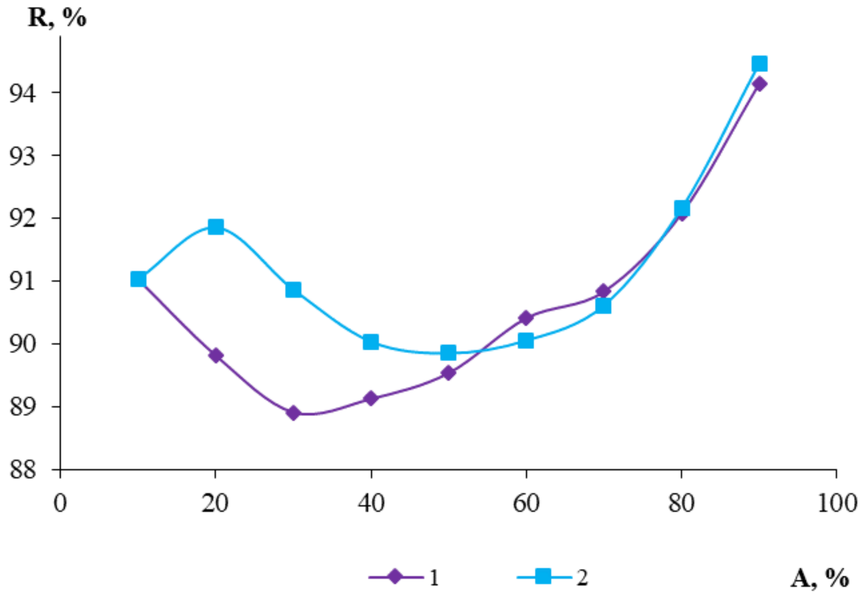

Fig. 2. Dependence of the selectivity of the reverse osmosis membrane on chlorides (pH = 8.6 (1), pH = 3.9 (2))

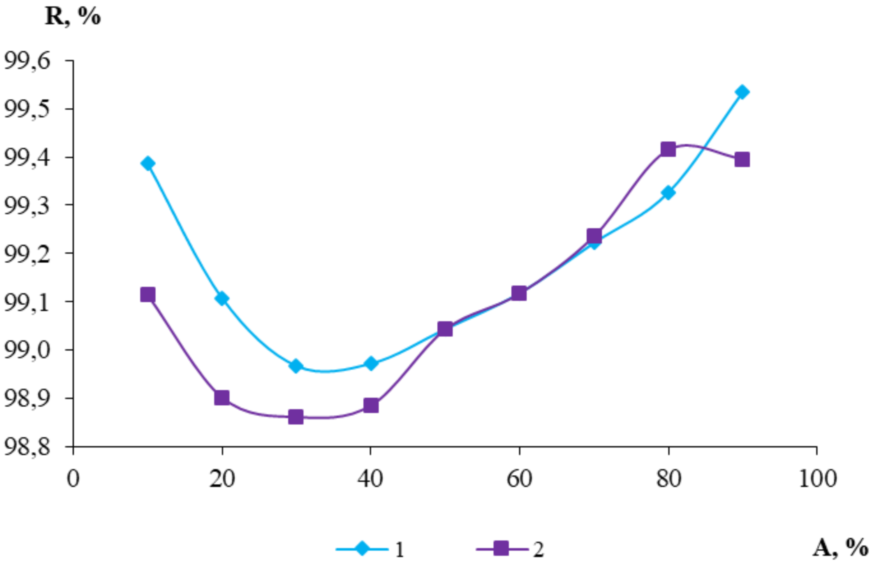

Fig. 3. Dependence of the selectivity of the reverse osmosis membrane on sulfates (pH = 8.6 (1), pH = 3.9 (2))

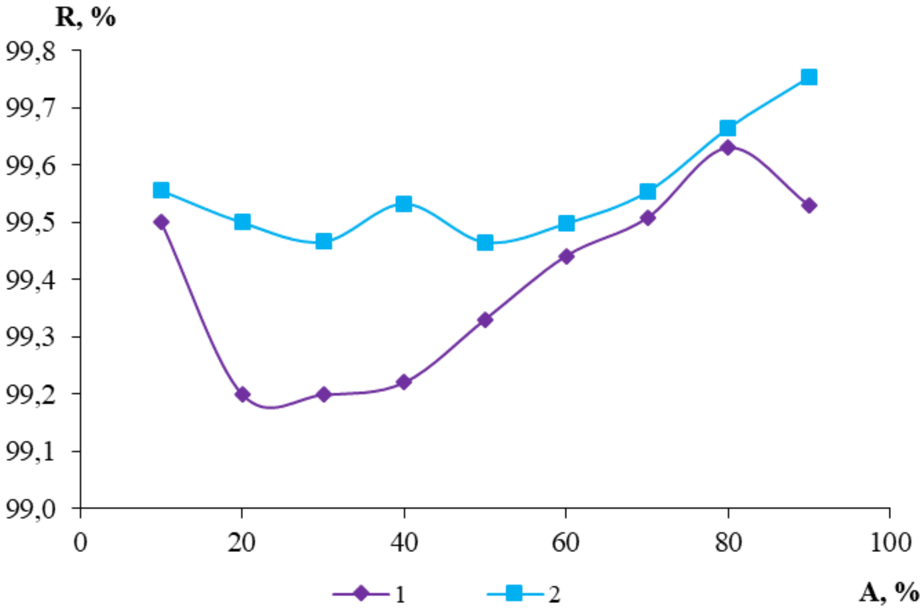

Fig. 4. Dependence of the selectivity of the reverse osmosis membrane on ions of hardness (pH = 8.6 (1), pH = 3.9 (2))

Thus, initial lighting of water leads to a decrease in water turbidity from 0.5 mg/dm^3 to 0.1 mg/dm^3 and to increase in membrane productivity up to 1.2–2.0 times.

Another complicated problem of reverse-osmosis water purification is its preparation before membrane treatments. During treatment of water with membrane technologies, there is a problem of formation of deposits on the membranes, resulting in a decrease in the flow of filtrate and increased transmembrane pressure (Gryta, 2018). Therefore, along with effective lighting and discoloration, the problem of its stabilization to prevent sediment deposition on membranes is acute. The main reason for deposition of sediments is the deposition of calcium carbonate on the surface of the membrane. The main methods of preventing sedimentation of poorly water-soluble salts on membranes are based on the dosing of inhibitors into the row water and chemical washing (Gomelya et al., 2017). By accurately dosing the inhibitor, regulation of the pH, water flow and transverse flow rate, membrane contamination can be significantly reduced. Sodium hydroxide, ethylenediaminetetraacetic acid complexing agent (EDTA), sodium dodecyl sulfate, hydrogen peroxide, sodium chloride, etc. are used as reagents for chemical cleaning of membranes. The efficiency can be increased by sequential use of two reagents or a mixture of reagents.

For water pretreatment with a high content of non-carbonate hardness it is rational to use antiscalants. In the preliminary preparation of water with high hardness, the use of the method of ion-exchange water softening at the stage of preliminary preparation is expedient when the content of hardness ions in the water is less than 20 mval/dm^3 (Trus et al., 2019).

In the application of weakly acid cationite Dowex MAC-3 in the H$^+$ form there is a decrease in the alkalinity of water is observed (Trus et al., 2020; Trokhymenko and Gomelya, 2017). In this case, the alkalinity of water decreased to zero values, and the pH reached 3.9; and such water can not lead to the formation of carbonate deposits on the membrane.

During the application of Dowex MAC-3 cation exchange resin in acid form, partial softening of water and its almost complete decarbonization due to partial acidification are taken place. The processes follow the reactions:

$$2Kt^-H^+ + Ca(HCO_3)_2 = (Kt^-)_2Ca^{2+} + 2H_2CO_3,$$

$$2Kt^-H^+ + Mg(HCO_3)_2 = (Kt^-)_2Mg^{2+} + 2H_2CO_3,$$

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O,$$

where: Kt$^-$ – fragment of cation exchange resin.

In the work, the effect of stabilizing treatment of water on weakly acidic cake Dowex MAC-3 in the H$^+$ form on the efficiency of water desalination in a reverse osmosis membrane Filmtec TW 30-1812-50 was determined. The model solution after filtration through weakly acidic cake Dowex MAC-3 in acid form had the following characteristics: hardness – 3.5 mval/dm^3, acidity – 0.6 mmol/dm^3, Cl$^-$ – 100.0 mg/dm^3, SO_4^{2-} – 620.0 mg/dm^3, pH = 3.9.

The results of the evaluation of the productivity of the reverse osmosis membrane are shown in Fig. 5.

As can be seen from Fig. 3, the productivity of the membrane at a working pressure of 0.30 MPa a little depends on the pH of the solution. Acidification of the solution with partial softening improves the productivity of the reverse osmosis membrane. It happens primarily due to the partial demineralization of the solution on the ion exchange filter and due to the absence of carbonate deposits on the membrane. During filtering of 10 dm^3 of water, there is no significant deposition of sediments on the membrane, so the effect of the pH of the medium on the performance is insignificant. At longer tests and larger volumes of water, the membrane's productivity after stabilization treatment of water will stay high during the time of use.

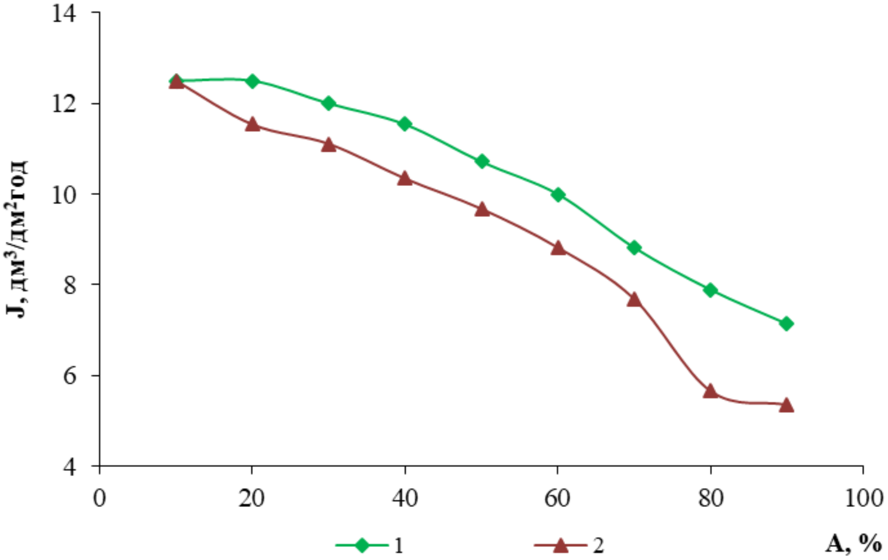

Fig. 5. Dependence of the productivity of the reverse osmosis membrane on the degree of selection of permeate during desalting the filtrate after the cation filter Dowex MAC-3 in acid form pH = 3.9 (1) and model solution pH = 8.6 (2)

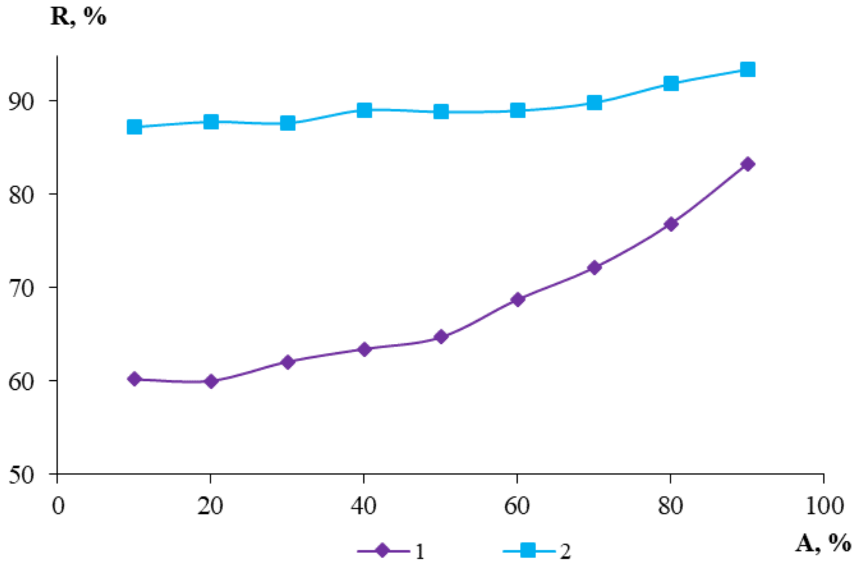

Fig. 6. Dependence of the selectivity of the reverse osmosis membrane towards chlorides on the degree of selection of permeate during desalination of solutions (pH = 3.9 (1), pH = 8.6 (2))

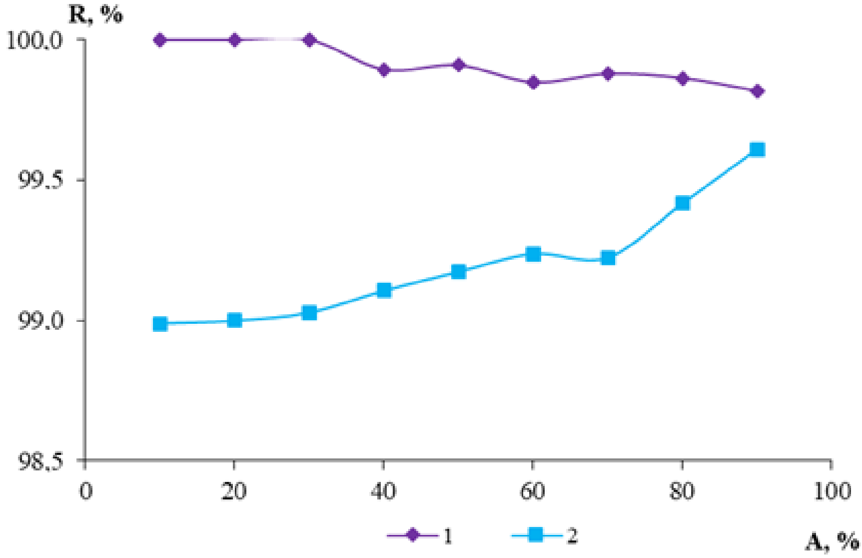

Fig. 7. Dependence of the selectivity of the reverse osmosis membrane towards sulfates on the degree of selection of permeate during desalination of solutions (pH = 3.9 (1), pH = 8.6 (2))

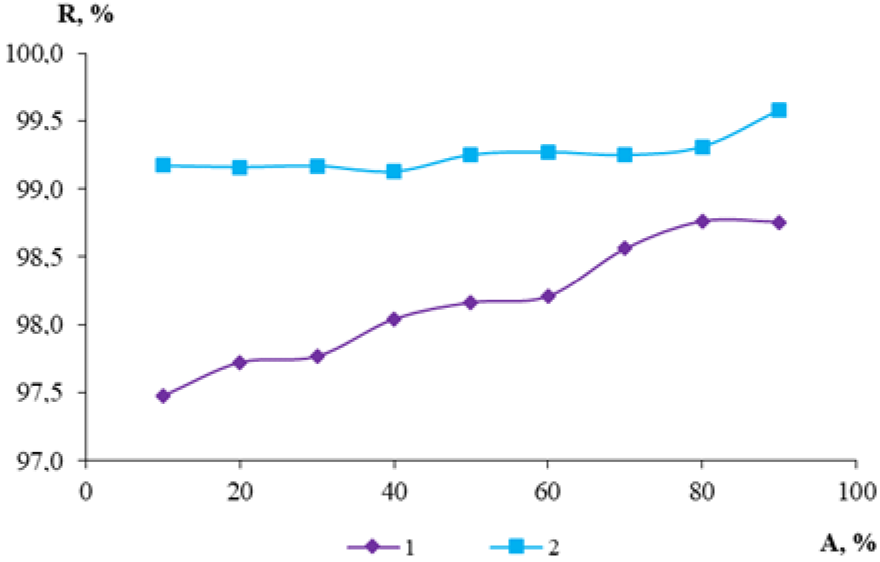

Fig. 8. Dependence of the selectivity of the reverse osmosis membrane towards ions of hardness on the degree of selection of permeate during desalination of solutions (pH = 3.9 (1), pH = 8.6 (2))

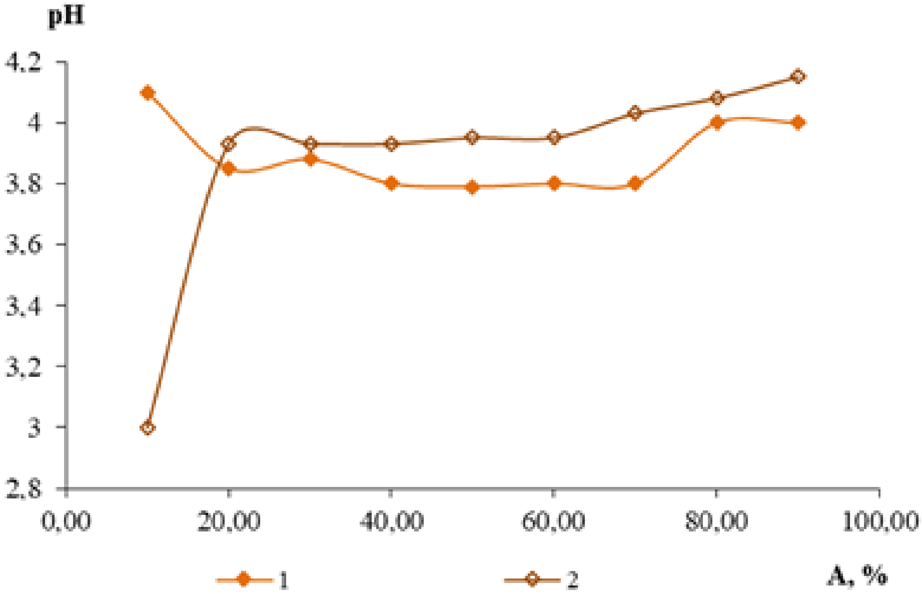

Fig. 9. Dependence of pH on the degree of selection of permiate during desalinating of solution with pH = 3.9 (1 – pH of permiate, 2 – pH of concentrate)

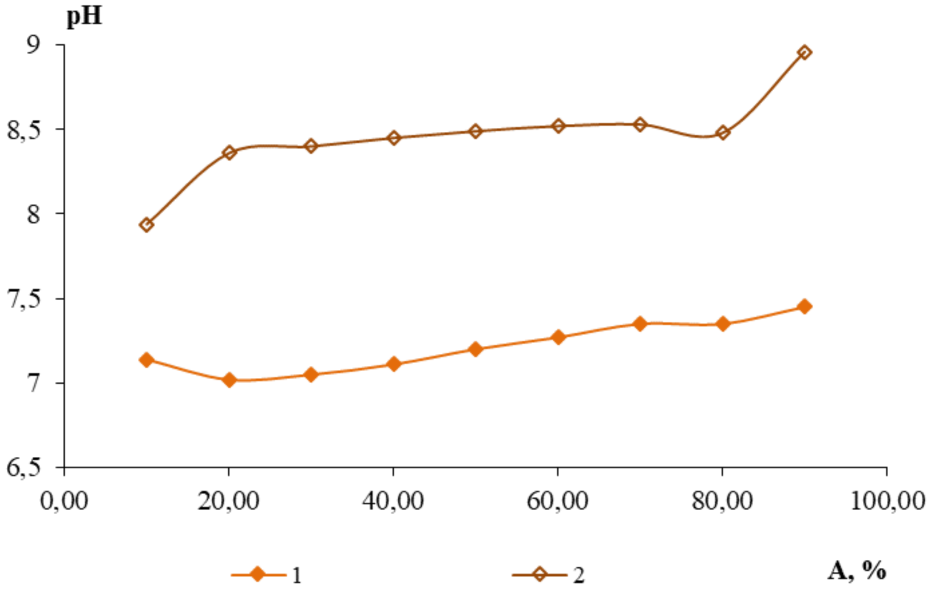

Fig. 10. Dependence of pH on the degree of selection of permiate during desalination of the model solution with pH = 8.6 (1 – pH of permiate, 2 – pH of concentrate)

However, the selectivity of the membrane depends on the pre-treatment of water on cation exchanges. As can be seen from Fig. 6–8, as the pH of the medium was decreased, a slight increase in the selectivity of the membrane by sulfates and a significant decrease in its selectivity by chlorides was observed. Acidification of water leads to a decrease in the selectivity of the reverse osmosis membrane by chlorides by 10–30%. The selectivity of the membrane practically does not depend on working pressure and stays high towards sulfates and ions of hardness (98–99%), regardless of the pH and degree of selection of permeate.

It should be noted that during filtering of solutions, which were pre-treated on the cation exchange resin in acid form, the pH of treated water and of concentrate were close in values (Fig. 9). During filtration of the original model solution, a decrease in the pH of the solution in the permiate to 7.02–7.45 was observed (Fig. 10). The pH of the concentrate reached values of 8.36–8.96. This is due to the difference in membrane selectivity for hardness ions and hydrocarbonates.

As a result of reverse osmosis desalination, highly mineralized concentrates are formed, which are characterized by a high content of chlorides, sulfates and hardness ions. The process of processing such concentrates was developed in (Trus et al., 2017; Gomelya et al., 2014).

4. Conclusions

The optimal parameters of membrane desalinization of solutions providing high water quality were determined in the work.

The methods of stabilization treatment of water before barometric desalination was developed to increase the efficiency of the productivity and the operation time of the membranes.

Proposed method of integrated treatment of mineralized waters allows to create low-waste technologies of waters desalting.

References

1. Buzylo, V., Pavlychenko, A., Savelieva, T., Borysovska, O.: Ecological aspects of managing the stressed-deformed state of the mountain massif during the development of multiple coal layers. *E3S Web of Conferences*, 60, 2018.
2. Liu, D., Edraki, M., Malekizadeh, A., Schenk, P.M., Berry, L.: Introducing the hydrate gel membrane technology for filtration of mine tailings. *Minerals Engineering*, 135, 1–8, 2019.

3. Gomelya, M., Hrabitchenko, V., Trohymennko, A., Shablij, T.: Research into ion exchange softening of highly mineralized waters. *Eastern-European Journal of Enterprise Technologies,* 4(10–82), 4–9, 2016.
4. Kinnunen, P., Kyllönen, H., Kaartinen, T., Mäkinen, J., Heikkinen, J., Miettinen, V.: Sulphate removal from mine water with chemical, biological and membrane technologies. *Water Science and Technology*, 1, 194–205, 2018.
5. Amaya-Vías, D., Tataru, L., Herce-Sesa, B., López-López, J.A., López-Ramírez, J.A.: Metals removal from acid mine drainage (tinto river, SW spain) by water gap and air gap membrane distillation. *Journal of Membrane Science*, 20–29, 2019.
6. Kim, J.E., Phuntsho, S., Chekli, L., Choi, J.Y., Shon, H.K.: Environmental and economic assessment of hybrid FO-RO/NF system with selected inorganic draw solutes for the treatment of mine impaired water. *Desalination*, 429, 96–104, 2018.
7. Haan, T.Y., Shah, M., Chun, H.K., Mohammad, A.W.: A study on membrane technology for surface water treatment: Synthesis, characterization and performance test. *Membrane Water Treatment*, 9(2), 69–77, 2018.
8. Ambiado, K., Bustos, C., Schwarz, A., Bórquez, R.: Membrane technology applied to acid mine drainage from copper mining. *Water Science and Technology*, 75(3), 705–715, 2017.
9. Gomelya, M.D., Trus, I.M., Radovenchyk, I.V.: Influence of stabilizing water treatment on weak acid cation exchange resin in acidic form on quality of mine water nanofiltration desalination. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu*, 5, 100–105, 2014.
10. Gryta, M.: Chemical pretreatment of feed water for membrane distillation. *Chemical Papers*, 62(6), 100–105,2008.
11. Gomelya, N.D., Shabliy, T.A., Trohymenko, A.G., Shuryberko, M.M.: New inhibitors of corrosion and depositions of sediments for water circulation systems. *Journal of Water Chemistry and Technology*, 39(2), 92–96, 2017.
12. Trus, I., Radovenchyk, I., Halysh, V., Skiba, M., Vasylenko, I., Vorobyov, V., et al.: Innovative Approach in Creation of Integrated Technology of Desalination of Mineralized Water. *Journal of Ecological Engineering*, 20(8), 107–113, 2019.
13. Trus, I., Gomelya, N., Halysh, V., Radovenchyk, I., Stepova, O., Levytska, O.: Technology of the comprehensive desalination of wastewater from mines. *Eastern-European Journal of Enterprise Technologies*, 3/6 (105), 21–27, 2020.

14. Trokhymenko, G., Gomelya, M.: Development of low waste technology of water purification from copper ions. *Chemistry and Chemical Technology*, 11(3), 372–377, 2017.

15. Gomelya, N.D., Trus, I.N., Nosacheva, Y.V.: Water purification of sulfates by liming when adding reagents containing aluminum. *Journal of Water Chemistry and Technology*, 36(2), 70–74, 2014.

16. Gomelya, M., Trus, I., Shabliy, T.: Application of aluminium coagulants for the removal of sulphate from mine water. *Chemistry and Chemical Technology*, 8(2), 197–203, 2014.

17. Trus, I.M., Fleisher, H.Y., Tokarchuk, V.V., Gomelya, M.D., Vorobyova, V.I.: Utilization of the residues obtained during the process of purification of mineral mine water as a component of binding materials. *Voprosy Khimii i Khimicheskoi Tekhnologii*, (6), 104–109, 2017.

Review of the latest methods of reducing heavy metals from water and soil

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Abstract

Heavy metals are found in the earth's crust. Natural processes such as the decomposition of parent rocks or volcanic eruptions lead to the spread of metals into water and soil. The concentration of those heavy metals represents a natural level of contamination (so-called water or soil background) and does not pose any threat to the environment. However, when the amount of heavy metals in water or soil is atypical, i.e. much higher than the background, pollution occurs. That phenomenon is unfortunately closely related to human activity, especially progressive urbanization, rapid industrial development, smelting, and metal mining processes.

The removal of heavy metals contamination (remediation, recultivation processes) has nowadays become a key issue in the protection of the aquatic and the terrestrial environment. A large number of methods are designed for that application. Water solutions can be treated using physical, chemical, and biological methods. Well-known conventional techniques such as chemical precipitation, reverse osmosis, evaporation, and ion exchange, can be used for the removal of heavy metal ions from water and wastewater. Recultivation or remediation, which can be performed in case of heavy metals in contaminated soil, can be in-situ or ex-situ methods. In-situ remediation is related to carrying out cleaning processes at the site of contamination, whereas ex-situ remediation consists of extracting contaminated soil and transporting it to the place in which it will be cleansed.

The presented paper describes the latest methods of removing toxic heavy metals from water and soil. Some of the methods have the potential to be applied on a large scale.

Keywords: water, wastewater, soil, heavy metal, removal, pollution, recultivation, remediation

1. Introduction

Recent years have seen a significant increase in the care for the natural environment. This is due to the fact that more stringent legal regulations have been introduced. There are designed to minimize the number of possible threats that may directly affect the life and health of humans and animals.

Heavy metals are one of the major threats to the environment, especially when their concentration in water or in the soil is atypical, i.e. much higher than the natural background, which represents a natural level of contamination caused by, among others, decomposition of parent rocks or volcanic eruptions leading to the spread of metals.

It is well known that waste from various industries, such as metallurgy, galvanizing, tanning, dyeing, textiles, paper, energy, communication or agriculture, has a negative impact on the natural environment. Dust, sludge and sewage produced as a result of complicated industrial processes often contain toxic heavy metals.

Permeable reactive barriers (PRBs) are commonly used into grounds for in-situ (on-site) groundwater remediation. PRBs are among the technologies that are recognized as being cost-effective. PRBs are ground zones filled with reactive materials that are permeable to some (but not all) substances and passively capture a plume of contaminants, then remove it or break it down, and finally release uncontaminated water. PRBs can work via sorption and precipitation processes, chemical reactions, or using biological mechanisms. Substances that are neutralized on barriers can enter into two main processes: immobilization and transformation. Metal ions are usually subject to sorption by electrostatic attraction or undergo complexation reactions, while the organic compounds are transformed into a less harmful or non-toxic form. Various materials can be used to create PRBs. Commonly used materials for removing metal ions from the environment include: zerovalent iron, activated carbons, peat, lignite, magnetite, zeolites, lime, fly ash, etc.

Bearing in mind the most importance of the problem of heavy metals for the biosphere, more effective and eco-friendly solutions that differ from traditional methods of removing metallic elements are currently sought.

The presented paper describes the latest propositions of the different Authors for removing toxic heavy metals from water and soil.

2. Water and wastewater treatment

Most often, heavy metals are removed from water and wastewater with the use of conventional techniques: chemical precipitation, reverse osmosis, evaporation, and ion exchange. The above-mentioned techniques have many advantages, but either are quite often ineffective at low concentrations, or require substantial funds, and, most importantly, generate toxic waste (Kumar et al., 2020). For these reasons new methods are nowadays used for water and wastewater treatment, including microorganisms and plants, biochar, natural materials (e.g. rocks), zeolites, nanomaterials, membrane techniques, photocatalysts and plasma technologies.

2.1. Microorganisms and plants

Bioengineering enables the construction of genetically modified microorganisms to reduce the level of pollutants in water. The discovery of a large number of genes responsible for the degradation of pollutants allows the construction of various strains of microorganisms specialized in removing, among others, heavy metals and other impurities that are difficult to decompose. The challenge remains to predict the long-term environmental impact of improved bacterial strains (Rogowska et al., 2021).

El Awady et al. (El Awady et al., 2021) studied the process of phytoremediation with three aquatic plant powders obtained from Lemna minor L., Azollafiliculoides Lam. and Pistia stratiotes L. and modified with interfacial layer synthesized silver nanoparticles. The obtained results reveal that Lemna minor and Pistia stratiotes show selective absorption against Pb(II) ions, while Azollafiliculoides show higher absorption against chromium. Moreover, the absorption of all heavy metal ions increased after interfacial modification with green synthesized silver nanoparticles.

The water hyacinth (Eichhorniacrassipes) is as well an aquatic floating macrophyte, which has known phytoremediation potential. The Eichhorniacrassipes was used to build pilot floating treatment wetlands (FTWs) for the removal of nutrients and heavy metals from the polluted Marriott Lake in Egypt (Gaballah et al., 2021). Various water depths (15, 25, and 35 cm; D15, D25, and D35, respectively) and plant coverage (90%, 70%, 50%, and 0%; P90, P70, P50, and P0, respectively) were used. The pilot FTWs worked over a 7-day operation cycle. The optimum conditions for remediation of the lake water were with a coverage of 70%, 25 cm water depth, and hydraulic retention time of 3–5 days. The metals were removed in the following order: Fe > Pb > Cu > Ni (62.5%, 88.9%, 81.7%, and 80.4% for D25P50, D25P70, D25P50, and D25P90, respectively) through bioaccumulation in plant tissues.

Agricultural wastes including organic products, e.g. vegetables, fruits meat, and dairy items, nowadays have also been used as economic and environment-friendly adsorbents. Wastes which contain cellulose have a high biosorption capacity (Dan et al., 2021; Sabir et al., 2021).

2.2. Biochars

There are lots of biomass materials that can be used to produce biochar through pyrolysis processes, for example bamboo, sugarcane and neem (Singh E. et al., 2021), pinecone (Lan et al., 2021), rice straw waste (Medha et al., 2021). Biochar reduces the levels of heavy metal ion pollutants in water. Conducted studies show that raw materials and pyrolysis temperature have a significant influence on the adsorption properties of the obtained biochar because the capacity of unmodified biochar is limited. Physical and chemical modifications increase the number and type of functional groups and surface area, which leads to an increased adsorption capacity for heavy metals (Qiu et al., 2021). Studies conducted by Peter et al. (Peter et al., 2021) show that ultrasound treatment and alkali activations of biochar have a positive impact on the adsorption behavior of the material. The adsorption experiments revealed that ultrasound biochars have better adsorption capacity as compared to untreated biochar samples after activation.

Metal ions react with biochar by a combination of physical adsorption, ion exchange, electrostatic interaction, precipitation, complexation, and redox mechanisms.

Furthermore, the adsorption process is related to, among others, the initial biochar dosage and its aging, pH and temperature of the polluted water, initial concentrations, and types of heavy metal ions in water. Biochar is a good and inexpensive adsorbent with some benefits over other adsorbents, but successful application of biochar for large scale must be improved (Qiu et al., 2021).

2.3. Natural materials

Human activity uses a wide spectrum of materials, from minerals and rocks to modern nanostructures (Oulguidoum et al., 2021). Both natural and anthropogenic materials are utilized. Natural materials include zeolites derived from hard coal, moreover lignite, calcite, quartz, pyrite, hydroxyapatite, and silica gel, while synthetic materials include metal-organic framework MOF (Esrafili et al., 2021), active carbon (Mariana et al., 2021), and carbon nanotubes (Odrobina and Pajdak, 2020).

In lignite mining, a significant amount of by-product clayey materials – the so-called Pliocene clays is obtained. Jabłońska (Jabłońska, 2021) considers using these materials as inexpensive adsorbents to remove Pb(II), Ni(II), and Zn(II) ions from wastewaters. She examined their mineralogical composition, physicochemical, granulometric, structural, and surface properties. The optimal values of the adsorbent mass and the pH solution for all metals were determined. To avoid the possible precipitation of metal ions in the form of hydroxides, neutral pH was applied (in the range of 6 to 7) and the adsorbent dose used was

18–24 g/dm^3. It was found that the sorption process took place for several minutes and the temperature had a considerable impact on the process. Moreover, the study proved that Pb(II) and Zn(II) ions were strongly bound in the adsorbent, whereas Ni(II) ions were characterized by greater mobility. The author indicated that the tested clays can be used as adsorption agents for the removal of metal ions in water and wastewater treatment, or as permeable barriers in groundwater remediation.

2.4. Zeolites

Li et al. (Li et al., 2021) reviewed the application of an inexpensive, water-stable metal-organic framework, which was zeolitic imidazolate framework (ZIF-8). The authors proposed an easy synthesis to the obtained zeolite and studied its suitability for heavy metal removal from aqueous solutions. They discussed removal efficiency in terms of adsorption capacity and the underlying mechanism of ZIF-8. Also, Tanihara et al. (Tanihara et al., 2021) used monodisperse ZIF-8 fine particles synthesized in an aqueous solution with a nonionic surfactant as a purifying agent for water treatment. In their paper, physicochemical properties of zeolite were described and the mechanism of the adsorption of metal ions was discussed in comparison with other papers. The authors suggested the adsorption mechanism for Pb^{2+} removal, whereas Cu^{2+} removal occurs through an ion-exchange process.

2.5. Nanomaterials

The application of nanomaterials (Mikulski et al., 2021) as potential adsorbents for heavy metal removal from water and soil guarantees high adsorption capacities, high chemical reactivity, active atomicity, and environmentally friendly performance. In their paper, Yu et al. (Yu et al., 2021) show also the disadvantages of using nanoparticles: the toxicity of nanomaterials against plants, animals, and microbial community; the regeneration of nanomaterials; the recovery of heavy metal ions from saturated nanomaterials; methods to decrease the aging of nanomaterials; and the long-term stability of heavy metal remediation by nanomaterials.

2.6. Membrane technics

A membrane is defined as a semi-permeable mass transport barrier which is placed between two phases (liquid or gas). This barrier can be biological or synthetic. It is crucial that the individual components of the mixture to be separated on the membrane should move at different speeds. At least one of the components of the mixture must pass unhindered through the membrane while others are retained on it. A membrane is a barrier that restricts the transport of various chemicals in a selective manner. During separation, the feed solution stream is divided into a concentrate (retentate) stream and a filtrate (permeate) stream. The components separated during the process do not undergo any thermal, chemical, or biological changes, and can therefore be reused.

Membranes can be classified according to many criteria. The most commonly used classification is based on membrane structure and, therefore, the driving force of the process causing particle transport. Membrane processes are distinguished according to the following driving forces:

– difference of pressure values (processes: microfiltration, ultrafiltration, nanofiltration, reverse osmosis and pezidialysis);
– difference of concentrations/activities (processes: pervaporation, gas separation, dialysis, liquid membranes and catalytic membranes);
– difference of temperatures (processes: thermoosmosis and membrane distillation);
– potential differences (processes: electrodialysis, bipolar membranes and electroosmosis).

Membrane techniques enable the recovery of waters difficult to treat. Membrane processes allow for effective purification of water from organic and inorganic compounds (e.g. heavy metals).

Most of the described membrane processes are commonly used in industries, but their application is not cheap. For this reason, adsorption is currently one of the most commonly used methods (Pei et al., 2021). During adsorption, physical and chemical interactions between heavy metal ions and adsorbents take place. Vo et al. (Vo et al., 2020) examined both advantages and disadvantages of the applications of adsorptive membranes: polymeric membranes (PMs), polymer-ceramic membranes (PCMs), electrospinning nanofiber membranes (ENMs), and nano-enhanced membranes (NEMs). The investigated membranes have demonstrated high effectiveness in the removal of heavy metals from wastewater, as well as their further recycling (regeneration) in the desorption of heavy ions from the surface of the membrane. The influence of the morphological and chemical structures of adsorptive membranes (AMs) was also shown. Despite the presented advantages, the abovementioned authors pointed to the necessity of further improvements, including advanced research on the recycling of AMs for a large number of cycles without using any expensive desorbing chemicals, fabrication process development, and also utilization of multiligand or multifunctional materials. Moreover, although the incorporation of nanoparticles in the membrane was supported by surface area, porosity, and high adsorption capacity, the expansion and improvement in the fabrication of AMs will be required to create promising eco-friendly and affordable AMs.

In the case of obtaining polymeric membrane (Fig.1), commercial substances are typically used.

Fig. 1. Polymeric membrane (PM) (Witt et al., 2021)

For example, the ionic liquid Cyphos IL 101 was applied to obtain a polymer film for the simultaneous recovery of precious and heavy metal ions (Ni(II), Zn(II), Co(II), Cu(II), Sn(II), Pb(II), Ag(I), Pd(II), and Au(III)) from waste electrical and electronic equipment (WEEE) (Witt et al., 2021). The experiments were performed for solutions containing metal ions released from computer e-waste (Fig. 2) due to leaching carried out with concentrated nitric(V) acid and aqua regia. It was found that the applied polymer film allows for the efficient recovery of precious metals (98.9% of Au(III), 79.3% of Ag(I), and 63.6% of Pd(II)). The results of the performed sorption/desorption processes show that the polymer film with Cyphos IL 101 can be successfully used after regeneration to recover metal ions several times.

Commercial compounds have some limitations. One of them is their high price, which is why new compounds insoluble in water, which are able to bind metal ions from solutions, are constantly sought. The application of new substituted 2,6-bis((benzoyl-R)amino)pyridine (R = H,4-Me, and 4-NMe_2) derivatives for the recovery of Cu(II), Ni(II), Co(II), and Zn(II) ions was described (Bożejewicz et al., 2021). Three different derivatives of 2,6-bis((benzoyl-R)amino)pyridine were used as carriers in membrane processes. The experiments of complexation properties confirmed that the series of new compounds exhibited high complex-forming properties and can be used as very efficient, relatively easy to synthase and inexpensive carriers in the membrane processes for removing metal ions from aqueous solutions. However, the effectiveness of the synthesized compounds depends on both the structure of compounds and properties of metals, as well as on their concentration.

Fig. 2. The computer e-waste (Witt et al., 2021)

2.7. Photocatalysis

Bodzek and Konieczny (Bodzek and Konieczny, 2021) propose the use of photocatalysis for the neutralization of hazardous substances such as pesticides, phenols, pharmaceuticals, dyes, microorganisms and, finally, heavy metals. The authors reviewed recent photo-catalyst methods using, for example, ZnO, ZnS, semiconductor-graphene composites, titanium dioxide etc., but they focused on the application of nano-catalysts.

2.8. Plasma

Plasma technologies are an important supplement to traditional techniques of industrial and municipal waste management. The utilization of difficult industrial waste is a serious alternative to other conventional methods (especially landfilling). Those methods have an advantage over others because of their parameters which cannot be reached for other technologies, e.g. extremely high temperatures and UV radiation causing complete decomposition of the waste material into simple compounds. Plasma is considered a state of matter – the fourth state of aggregation. Under normal earth conditions, plasma is rarely found – it is observed after electrical discharges. Plasma is an ionized gas in which matter decays into positively charged ions and free electrons without or with the participation of neutral particles. At very high temperatures, above 30.000 K, complete ionization takes place, and plasma becomes a mixture of positive ions and electrons without the participation of neutral particles. A few examples of applications of plasma technologies are listed below:

– recycling of precious metals from spent catalysts with the use of thermal treatment in plasma arc melting furnaces;

– management of post-production waste in the metallurgical industry, in particular dusts, skimmings, scale containing chromium and nickel;

– management of waste such as asbestos, electronic scrap, petrochemical waste, steel dust, waste generated in primary aluminum smelting industry (toxic compounds of fluorine and cyanide), the so-called SPL Spent Potliner, catalysts, nuclear and other waste commonly considered as hazardous (Lewandowski et al., 2021).

3. Soil treatment

Remediation is a method of removing or reducing the amount of contamination of the earth's surface that has been introduced into it as a result of human activity. Removal of heavy metals from contaminated soil can be done by in-situ or ex-situ methods. The in-situ remediation consists in carrying out cleaning processes at the site of contamination, while ex-situ remediation relies on extracting contaminated soil, transporting it to the place where it will be cleansed.

Some of the methods described in the previous paragraph may also be useful for soil treatment, e.g. the application of microorganisms and plants (Verma et al., 2021), biochar, natural materials (Fijałkowska et al., 2021), zeolites (Głąb et al., 2021), nanomaterials, or photocatalysts.

3.1. Microorganisms and plants

Thakare et al. (Thakare et al., 2021) describe the combination of a unique plant-microbe system to eliminate heavy metals and radionuclides via the soil bioremediation process. Microorganisms are able to biosorb and biomineralise metals through their inherent catabolic process. The microbe overexpresses a gene encoding a metal carrier that helps in the transformation of metals. The authors predicted that microbes in the future will be used to create novel biomaterials with special properties for the reuse of metal waste.

Halecki et al. (Halecki et al., 2021) deposited the material from industrial waste and municipal sewage sludge in the post-mining area. The obtained results suggest that the applied method limits the accumulation of heavy metals. Moreover, the spontaneous emergence of Taraxacum officinale was observedon the recultivated areas. The authors proved that industrial and municipal waste can be used for the circular economy and land reclamation.

3.2. Biochar

As it was mentioned earlier, biochars could not be applied on a large scale for environmental samples with high heavy metal content, due to poor physicochemical characteristics. Therefore, ultrasound-treated modified functionalized biochar (UFB), sludge-derived biochar (SDB) and sewage sludge (SS) were evaluated by Hazrati et al. (Hazrati et al., 2021). The effects of these additives on the soil were investigated during a 2-month stabilization process. The results showed that ultrasound treatment and functionalization increased the surface area and the number of functional groups of the biochars, which significantly decreased the total heavy metals concentration in the soil and the ecological risk index for heavy metals.

Novel biochar-supported nano-scale zero-valent iron (nZVI-BC) was also used for the remediation of contaminated soil consisting arsenic, cadmium and lead. The nZVI-BC significantly decreased the content of As, Cd and Pb by 97.94–98.45%, 42.86–81.12%, and 82.14–92.49%, respectively (Yang et al., 2021).

3.3. Nanoparticles

Nowadays, the use of nanoparticles is common due to their easy application and eco-friendly nature. For example, magnetic iron oxide (Fe_3O_4) nanoparticles can be used for the removal of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb and Zn) from water and soil samples. The highest efficiency of removing metal ions from the soil were achieved in remediation time of less than 20 minutes, at pH of 0.7 and ranged from 69.6 to 99.6%. Lead was separated the most effectively. The advantage of nanoparticles is the easy and efficient removal of the nanoparticles from the treated solutions by using an ordinary magnet (Singh A. et al., 2021).

3.4. Composite adsorbents

The waste textile coated with double layers of Mg-Al hydroxides (MgAl-LDH@WT) was prepared for the separation of As(V) and Cr(VI) ions from soil samples. The adsorption behavior of the co-existing As(V) and Cr(VI) ions in the soil indicated that As(V) rather than Cr(VI) possesses preferential adsorption. The results indicated by XRD, SEM and XPS methods showed that the removal mechanism of metal ions was mainly based on ion-exchange (Zhao, 2021).

A thiol-functionalized nano-silica (SiO_2-SH) was investigated by the uptake of the heavy metals into growing lettuce and pakchoi. It was found that the SiO_2-SH can significantly reduce the amount of Cd, Pb, Cu in pakchoi by 92.02%, 68.03%, 76.34% and in lettuce by 89.81%, 43.41%, 5.76%, respectively. The results indicate that SiO_2-SH can transform the heavy metal into a reducible and oxidizable fraction, thereby inhibiting the extraction of heavy metals into the soil solution (Lian et al., 2021).

3.5. Soil washing

All methods described above belong to in-situ technics. On the other hand, soil washing is a method of ex-situ remediation that causes rapid reuse of contaminated areas, but finding eco-friendly and low-cost washing reagents (Imteaz and Arulrajah, 2021; Sumalatha et al., 2021) is of the greatest importance. For example Peng et al. (Peng et al., 2021) selected polyamino polyether methylene phosphonate (PPMP) and bis (hexamethylene triamine penta (methylenephosphonic acid)) (BHMT) for cadmium and lead removal from soil. Optimal removal coefficients using PPMP reagent reached 83.98% and 41.29% for Cd and Pb, respectively; whereas in case of BHMT leaching the coefficients reached 69.31 and 28.11%. The results show that PPMP and BHMT are two feasible reagents for washing the industrial soils contaminated by heavy metals.

4. Summary

Summarizing all presented methods of removing heavy metals from the environment (water and soil), it is clearly visible that the ways proposed by the various authors are mainly based on improving of already existed techniques by modification. The trend is moving directly towards the solutions that are cheap, eco-friendly and low-cost. The uses of microorganisms, plants, biochars and natural materials is economical, but efficiency is not very high. On the other hand, the application of zeolites, nanomaterials, plasma or photocatalysts guarantees high heavy metals removal coefficients, but the final total cost of the processes will be much higher (Tab. 1).

Table 1. The comparison of methods of removing heavy metals from the environment (water and soil) in terms of costs and efficiency

biochar, natural materials, microorganisms and plants	**zeolites, nanomaterials, photocatalysts, plasma technologies**
+ low cost	+ high efficiency
– low efficiency	– high cost

In this situation, the use of adsorptive polymeric membranes seems to be a balanced method (Tab. 2). Membranes can be manufactured from cheap, stable materials that provide a high number of purification and recovery cycles, high metal removal factors and are easily recyclable.

Table 2. The advantages of adsorptive polymeric membranes

adsorptive polymeric membranes
+ low cost + high efficiency + high stability + possibility of recycling

The commercial, as well as the newly synthesized compounds can be used to prepare the membranes. The selection of each component can be arbitrary, i.e. tailored to the individual requirements of the metal removal process. Adsorption membranes are already used to remove metals from aqueous solutions, e.g. industrial wastewater, but it is also possible to use them in situ as a barrier against contaminants that threaten soil and groundwater. This direction deserves greater attention from scientists and requires further extended research.

References

1. Bodzek, M., Konieczny, K.: Możliwości wykorzystania nanotechnologii i nanomateriałów w procesach uzdatniania wody i oczyszczania ścieków, cz. 3, Fotokataliza (Possibility of nanotechnology and nanomaterials application in water and wastewater treatment processes, Part. 3, Photocatalysis). *Technologia Wody*, 1(75), 4–18, 2021 (in Polish).

2. Bożejewicz, D., Ośmiałowski, B., Kaczorowska, M.A., Witt, K.: 2,6-bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe_2) derivatives for the removal of Cu(II), Ni(II), Co(II), and Zn(II) ions from aqueous solutions in classic solvent extraction and a membrane extraction. *Membranes*, 11, 233, 1–19, 2021.

3. Dan, Y., Xu, L., Qiang, Z., Dong, H., Shi, H.: Preparation of green biosorbent using rice hull to preconcentrate, remove and recover heavy metal and other metal elements from water. *Chemosphere*, 262, 127940, 2021.

4. El Awady, F.R., Abbas, M.A., Abdelghany, A.M., El-Amir, Y.A.: Silver Modified Hydrophytes for Heavy Metal Removal from Different Water Resources. *Biointerface Research in Applied Chemistry*, 11(6), 14555–14563, 2021.

5. Esrafili, L., Firuzabadi, F.D., Morsali, A., Hu, M. L.: Reuse of Predesigned Dual-Functional Metal Organic Frameworks (DF-MOFs) after Heavy Metal Removal. *Journal of Hazardous Materials*, 403, 123696, 2021.

6. Fijałkowska, G., Szewczuk-Karpisz, K., Wiśniewska, M.: Polyacrylamide Soil Conditioners: The Impact on Nanostructured Clay Minerals' Aggregation and Heavy Metals' Circulation in the Soil Environment. In: Fesenko O., Yatsenko L. (eds) *Nanomaterials and Nanocomposites, Nanostructure Surfaces, and Their Applications. Springer Proceedings in Physics*, 246. Springer, Cham, 2021.
7. Imteaz, M.A., Arulrajah, A.: Removal of heavy metals from contaminated foundry sand through repeated soil-washing. *International Journal of Sustainable Engineering* 14, 39–45, 2021.
8. Gaballah, M.S., Ismail, K., Aboagye, D., Ismail, M.M., Sobhi, M., Stefanakis, A.I. Effect of design and operational parameters on nutrients and heavy metal removal in pilot floating treatment wetlands with Eichhornia Crassipes treating polluted lake water. *Environmental Science and Pollution Research*, 28, 25664–25678, 2021.
9. Głąb, T., Gondek, K., Mierzwa–Hersztek, M.: Biological effects of biochar and zeolite used for remediation of soil contaminated with toxic heavy metals. *Scientific Reports*, 11, 6998, 2021.
10. Halecki, W., Bedla, D., Koźmińska, A., Dacewicz, E., Chmielowski, K., Baran, A., Klatka, S.: Gospodarka o obiegu zamkniętym odpadami komunalnymi i przemysłowymi w rekultywacji terenów zdegradowanych (Municipal and industrial waste management towards a circular economy for reclamation of degraded areas), *Przemysł Chemiczny*, 100(2), 182–184, 2021 (in Polish).
11. Hazrati, S., Farahbakhsh, M., Cerdà, A., Heydarpoor, G.: Functionalization of ultrasound enhanced sewage sludge-derived biochar: Physicochemical improvement and its effects on soil enzyme activities and heavy metals availability. *Chemosphere*, 269, 128767, 2021.
12. Jabłońska, B.: Optimization of Ni(II), Pb(II), and Zn(II) Ion Adsorption Conditions on Pliocene Clays from Post-Mining Waste. *Minerals*, 11(568), 1–19, 2021.
13. Kumar, V., Sharma, A., Cerdà, A.: *Heavy Metals in the Environment. Impact, Assessment, and Remediation*. Elsevier Science Publishing Co Inc 2020.
14. Lan, J., Zhang, S., Dong, Y., Li, J., Li, S., Feng, L., Hou, H.: Stabilization and passivation of multiple heavy metals in soil facilitating by pinecone-based biochar: Mechanisms and microbial community evolution. *Journal of Hazardous Materials*, 420, 126588, 2021.

15. Lewandowski, D., Szałatkiewicz, J., Bogacka, M.: Plazmowe technologie w zagospodarowaniu odpadów przemysłowych i komunalnych. In Bogacka M., Pikonia K.: *Współczesne Problemy Ochrony Środowiska i Energetyki 2020*, 89–98, Politechnika Śląska, Gliwice 2021.

16. Li, K., Miwornunyuie, N., Chen, L., Jingyu, H., Amaniampong, P.S., Koomson, D.A., Ewusi-Mensah, D., Xue, W., Li, G., Lu, H.: Sustainable Application of ZIF-8 for Heavy-Metal Removal in Aqueous Solutions. *Sustainability*, 13, 984, 1–11, 2021.

17. Lian, M., Wang, L., Feng, Q., Niu, L., Zhao, Z., Wang, P., Song, Ch., Li, X., Zhan, Z.: Thiol-functionalized nano-silica for in-situ remediation of Pb, Cd, Cu contaminated soils and improving soil environment. *Environmental Pollution*, 280, 116879, 2021.

18. Mariana, M., Khali, H.P.S.A., Mistar, E.M., Yahya, E.B., Alfatah, T., Danish, M., Amayreh, M.: Recent advances in activated carbon modification techniques for enhanced heavy metal adsorption. *Journal of Water Process Engineering*, 43, 102221, 2021.

19. Medha, I., Chandra, S., Vanapalli, K.R., Samal, B., Bhattacharya, J., Das, B.K.: (3-Aminopropyl)triethoxysilane and iron rice straw biochar composites for the sorption of Cr (VI) and Zn (II) using the extract of heavy metals contaminated soil. *Science of The Total Environment,* 771, 144764, 2021.

20. Mikulski, P., Krzywonos, M., Borowiak, D.: Usuwanie metali ciężkich ze ścieków za pomocą nanomateriałów węglowych (Removal of heavy metals from wastewater using carbon nanomaterials), *Przemysł Chemiczny*, 100/7, 685–688, 2021 (in Polish).

21. Odrobina, A., Pajdak, A.: Wybrane zastosowania skał, minerałów oraz nowoczesnych nanomateriałów w biotechnologii (Selected applications of rocks, minerals and modern nanomaterials in biotechnology), *Prace Instytutu Mechaniki Górotworu PAN*, 22 (1-4), 93–101, 2020 (in Polish).

22. Oulguidoum, A., Bouiahya, K., Bouyarmane, H., Talbaoui, A., Nunzi J.M., Laghzizil, A.: Mesoporous nanocrystalline sulfonated hydroxyapatites enhance heavy metal removal and antimicrobial activity. *Separation and Purification Technology*, 255, 117777, 2021.

23. Pei, X., Gan, L., Tong, Z., Gao, H., Meng, S., Zhang, W., Wang, P., Chen, Y.: Robust cellulose-based composite adsorption membrane for heavy metal removal. *Journal of Hazardous Materials*, 406, 124746, 2021.

24. Peng, Y., Zhang, S., Zhong, Q., Wang, G., Feng, C., Xu, X., Pu, Y., Guo, X.: Removal of heavy metals from abandoned smelter contaminated soil with poly-phosphonic acid: Two-objective optimization based on washing efficiency and risk assessment. *Chemical Engineering Journal,* 421(1), 129882, 2021.
25. Peter, A., Chabot, B., Loranger, E.: Enhanced activation of ultrasonic pre-treated softwood biochar for efficient heavy metal removal from water. *Journal of Environmental Management*, 290, 112569, 2–9, 2021.
26. Qiu, B., Tao, X., Wang, H., Li, W., Ding, X., Chu, H.: Biochar as a low-cost adsorbent for aqueous heavy metal removal: A review. *Journal of Analytical and Applied Pyrolysis*, 155, 105081, 1–14, 2021.
27. Rogowska, A., Szypulska, D., Janiak, K.: Bioinżynieria w technologii wody i ścieków (Bioengineering in water and wastewater technology). *Technologia Wody,* 6(74), 80–83, 2020 (in Polish).
28. Sabir, A., Altaf, F., Batool, R., Shafiq, M., Khan, R.U., Jacob, K.I.: Agricultural Waste Absorbents for Heavy Metal Removal. In: Inamuddin, Ahamed M., Lichtfouse E., Asiri A. (eds) *Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water. Environmental Chemistry for a Sustainable World*, 49. Springer, Cham. 2020.
29. Singh, A., Chaudhary, S., Dehiya, B.S.: Fast removal of heavy metals from water and soil samples using magnetic Fe_3O_4 nanoparticles. *Environmental Science and Pollution Research*, 28, 3942–3952, 2021.
30. Singh, E., Kumar, A., Mishra, R., You, S., Singh, L., Kumar, S., Kumar, R.: Pyrolysis of waste biomass and plastics for production of biochar and its use for removal of heavy metals from aqueous solution. *Bioresource Technology,* 320, Part A, 124278, 1–9, 2021.
31. Sumalatha, J., Prabhakara, R., Sivapullaiah, P.V.: Removal Efficiency of Heavy Metals by Washing the Contaminated Soil Using Effective Leaching Agents. In: Pathak K.K., Bandara J.M.S.J., Agrawal R. (eds) *Recent Trends in Civil Engineering. Lecture Notes in Civil Engineering*. Springer, Singapore, 77, 1041–1051, 2021.
32. Tanihara, A., Kikuchi, K., Konno, H.: Insight into the mechanism of heavy metal removal from water by monodisperse ZIF-8 fine particles. *Inorganic Chemistry Communications*, 131, 108782, 1–6, 2021.
33. Thakare, M., Sarma, H., Datar, S., Roy, A., Pawar, P., Gupta, K., Pandit, S., Prasad, R.: Understanding the holistic approach to plant-microbe remediation technologies for removing heavy metals and radionuclides from soil. *Current Research in Biotechnology*, 3, 84–98, 2021.

34. Verma, A., Roy, A., Bharadvaja, N.: 13 – Remediation of heavy metals using nanophytoremediation. *Advanced Oxidation Processes for Effluent Treatment Plants*, 273–296, 2021.

35. Vo, T.S., Hossain, M.M., Jeong, H.M., Kim, K.: Heavy metal removal applications using adsorptive membranes. *Nano Convergence*, 7(36), 1–26, 2020.

36. Witt, K., Urbaniak, W., Kaczorowska, M.A., Bożejewicz, D.: Simultaneous recovery of precious and heavy metals ions from waste electrical and electronic equipment (WEEE) using polymer films containing Cyphos IL 101. *Polymers*, 13, 1454, 1–18, 2021.

37. Yang, D., Yang, S., Yuan, H., Wang, F., Wang, H., Xu, J., Liu, X.: Co-benefits of biochar-supported nanoscale zero-valent iron in simultaneously stabilizing soil heavy metals and reducing their bioaccessibility. *Journal of Hazardous Materials*, 418, 126292, 2021.

38. Yu, G., Wang, X., Liu, J., Jiang, P., You, S., Ding, N., et al.: Applications of Nanomaterials for Heavy Metal Removal from Water and Soil: A Review. *Sustainability*, 13(2), 713, 2021.

39. Zhao, S., Li, Z., Wang, H., Huang, H., Xia, C., Liang, D., et al.: Effective removal and expedient recovery of As(V) and Cr(VI) from soil by layered double hydroxides coated waste textile. *Separation and Purification Technology*, 263, 118419, 2021.

Monitoring and assessment of migration of toxic and radioactive wastewater pollution in ecosystems

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Abstract

The paper provides the approach to assessment of migration of toxic and radioactive wastewater pollution in ecosystems, which include monitoring of contaminants migration into environment in case of natural or technogenic accidents which may influence on soil, subsoil waters and landfills or repository installations structures. The aim of the research is the development of the system of estimation of toxic or radioactive state of the environment in the area of waste landfills or radioactive repository, based on the cumulative data, the knowledge base, set of rules of production, logical deduction gear and conclusion building gear by means of uncertain and incomplete input data. It is proposed the use of several models for the spectral characteristics of toxic and radioactive pollutants migration. The evaluation of possible damages of repository containment is made. The heuristics for the radioactive waste repository expert system are developed. The proposed procedure of quality definition of decision making for the ecosystem monitoring should take into account the reliability of information about the state of the radioactive repository.

Keywords: toxic or radioactive wastewater, monitoring, spectral characteristics, fuzzy set, heuristics

1. Introduction

In case of necessity, carrying out operational control over the development of the state of the ecosystem in abnormal and emergency situations in order to assess the extent of emissions or discharges of toxic or radioactive pollution and predict their consequences for the environment (taking into account hydrometeorological and other factors that influence the processes of distribution and metabolism of pollution), as well to work out recommendations for the further functioning of certain objects and development of protective structures and the use of other means of environmental protection, is used as standard monitoring procedures, the frequency of which significantly increases depending on the dynamics of situation, and special procedures, designed for a wide range of changes in both quantitative and qualitative composition of pollution. In the post-accident period, control with the aim of clarifying the patterns of pollution distribution, identifying the effectiveness of measures for the protection of the area or minimizing the impact of pollution on the reservoir and forecasting the boundaries and terms of normalization of the water body is performed as standard staffing through standard procedures and special means (including mobile and equipment with high sensitivity and precision, which determines trace amounts of pollution of any nature), which allow to detect unexpected components under clarify the limits and dynamic reallocation of pollution in the region and so on.

For information provision of monitoring and assessment procedures it is necessary to provide appropriate formatting of monitoring data. It is a matter of ensuring that all data are unified in terms of the dimension and degree of presentation of the data, as well as the order in which they are provided to the monitoring system. In order to simplify the template, all data should be presented in an exponential form, where the mantises of the number represented as an integer or as the correct decimal fraction is followed by symbols of the exponential representation of the number, the sign and the degree indicator. In order that all the information could be successfully searched, stored, corrected and displayed, it is necessary to adopt an appropriate format, that is, the order of their placement in the message from the source of information.

Environmental safety ensuring is the actual problem as for the radioactive waste repositories at the nuclear power plants so and for tailings and mine dams at mining enterprises (Melnychuk and Barabash, 2001). Moreover, monitoring of radioactive pollutants migration is the essential part of such wastes storages management and should include understanding the role of diffusion, filtration and real conditions of environment in the affected of repositories of radioactive waste areas (Yeremeyev et al., 2019).

The going systems of monitoring for the radioactive waste repositories include the simulation with the only model of pollutants migration (Dudar, 2019) and do not take into account the possibility of natural or man-made impacts on the facilities stability (Duro et al., 2020; Mallants et al., 2020).

As any monitoring system that deals with fuzzy data and uncertainty conditions, waste landfills and radioactive repositories operate with the limited retrievals of data and the laws of their distributing are unknown a priori. So here, the methods with the use of the Bayes theorem, fuzzy set theory and linguistic estimations of researched data are used widely (Hoeting et al., 1999; Karadimos et al., 2006; Dychko et al., 2020, 2021).

2. The assessment system for the toxic or radioactive pollution of ecosystem

2.1. Real status of the ecosystem definition

The aim of the research is the development of the system of estimation of toxic or radioactive state of the environment in the area of waste landfills or radioactive repository.

The expert system of ecosystem monitoring that suggestible by toxic wastewater includes the rules of production or heuristics (IF (precondition), THEN (action) [index of distinctness – ID]), the quintets conjunctions and action which includes the quintet's parameters value definition. For the action's quintet ID computation there are used the rule's ID together with the ID of related to the rule quintets. ID statements define ID precondition. If the quintet is not formed the ID are calculated as:

$$ID = OI + RI(1 - OI), RI, OI > 0, \tag{1}$$

$$ID = -(|RI|(1 - |OI|)), RI, OI < 0,$$

$$ID = \frac{|OI| + |RI|}{1 - \min\{|OI|, |RI|\}}, RI, OI < 0.$$

Let's consider several heuristics for the ecosystem influenced with toxic or radioactive wastewater (RAW):

IF ([the RAW spot dynamics is within the 2σ limits (SPOTSTAB)] *AND* [natural and/or man-made accidents during the previous measurements' cycles are absent (NMMA = 0)]), *THEN* [monitoring procedure is routine (MONROUT)].

IF [SPOTSTAB] *AND* [NMMA = 1], *THEN* [together with MONROUT the causal monitoring MONCAUS for the points which are laid on the direction from accident epicenter (AEC) should be provided, i.e. MONROUT + MONCAUS AEC].

IF [SPOTSTAB] *AND* [it is a tendency to increase of average monotonous displacement of RAW spot in the same direction within 2σ limits (TMD2σ), *THEN* [MONROUT + MONCAUS MD] (MONCAUS MD – extra causal monitoring in monotonous RAW spot displacement's direction).

IF [SPOTSTAB] *AND* [NMMA = 0] *AND* [NONSTABSPOTNOCR], *THEN* [check the RAW expansion model conformity CHECKEXPMODCONF] (NONSTABSPOTNOCR – RAW spot dynamics is not critical).

Checking the model may be realized by definition of its sensitivity to parameters' deviations and adjustment of certain parameters for the purpose of accordance the predicted on the time of extrapolation and real measured at that time values of RAW. After this adjustment the RAW spot dynamics modeling is implemented along the all period of functioning of landfill or repository. There is also another permissible step (if there are several models of RAW spot dynamics): implementation of concurrent modeling by several models and using the model that has the minimal metrics of predicted distribution of RAW spot relative to the real distribution.

IF ([SPOTNSTAB$_{n-1}$] *AND* [SPOTNSTAB$_n$] *AND* [NMMA = 0] *AND* [NONSTABSPOTNOCR] *AND* [the vectors of RAW spot shifts are situated in different quadrants – VECTSPOTSHIFTDIFQUAD]), *THEN* [CHECKEXPMODCONF]. The [SPOTNSTAB$_{n-1}$] and [SPOTNSTAB$_n$] correspond to the RAW spot dynamics detection in (n-1)-th and n-th measurement cycles.

IF ([SPOTNSTABn-1] *AND* [SPOTNSTABn] *AND* [NONSTABSPOTNOCR] *AND* [NMMA = 0] *AND* [the vectors of RAW spot shifts are situated in the same quadrant – VECTSPOTSHIFTSAMQUAD]), *THEN* [CHECKEXPMODCONF] *AND* [check the density of separate blocks or containment as a whole – CHECKCONTDENS].

IF ([NONSTABSPOTCRIT] *AND* [NMMA = 1] *AND* [VECTSPOTSHIFTDIFQUAD], *THEN* ([it is necessary to change MONROUT at the critical procedures of monitoring MONCRITIC] *AND* [use the RAW expansion critical models RAWEXPCRITMOD]. MONCRITIC assumes the changing of range – instead of 0.5 *Bk/l* the threshold of several *Bk/l*, changing of parameters' measuring frequency in the all points around repository with the selective measurements in the points in which the parameters have the largest values. RAWEXPCRITMOD – the models concerned with formation of the channels along which the RAW expansion is realized more strongly (for example along the subterranean waters-bed or along the joint fissure and so on).

IF ([NONSTABSPOTCRIT] *AND* [NMMA = 1] *AND* [VECTSPOTSHIFTSAMQUAD], *THEN* [MONCRITIC] *AND* [RAWEXPCRITMOD] *AND* [man-made protective barrier establishing across the RAW spot movement path PROTBAR if the movement is directed to the settlements, the water supply points and so on].

One of the main problem of repository's impermeability is the seismic resistance which is realized by adequate repository's design and by means of installations and design monitoring (with the help of direct and mediate methods) for the exposure and elimination the danger of their destruction, the great landslides data collection, knowledge level increasing about deviations in the main direction of subterranean waters redistribution, drawing up the seismic dangerous maps connected with the repository's influence zone. Mentioned monitoring in routine process periodically analyzes the repository conditions but in the cases of natural or man-made accidents which may influent on the repository conditions the code of causal monitoring is activated.

For simplifying of the mentioned types of monitoring procedures there are recommended the accelerometers setting in separate assemblies of repository's structure for the recording of vibrations caused by possible landslide sources. Similar action promotes the analysis and interpretation of appeared situation. Seismic landslides and landslips, which challenge the soil vibration, generate the destructive waves in the reservoirs and rivers, dangerous for the installations and soil structure. On the maps characterized the prospective surface movements (for example, natural frequency and intensity of earthquakes) repositories in-situ it is necessary to insert the instructions related to possible damages, local geological structure, probability of steady landslides, landslips and soil rarefactions inside of every seismic zone and immediately in zone of repository location.

Analysis and interpretation of information about hypothetic results of each landslide or earthquake are very difficult because of lack the precise and single meaning data. Therefore these facts should be taken into account in process of acceptance of decision. After the significant earthquake the installations may be damaged but as a rule the results of these injuries are difficultly observed – there may be microcracks, changes in internal repository's bearing structures and so on. The results may be observed later, for example by increasing of RAW components concentration in subsoil waters in wells drilling around of repository. Index of RAW components leakage may be represented as "summary area of microcracks – to summary area of repository walls and bottom" relation (or "summary area of microcracks – to area of repository bottom" relation). As a repository damage scale it may be used the following categories of status: A – damages are absent or immaterial; B – the slight or medium damages; C – the significant damages; D – entire damage of repository when its functioning is not possible.

The monolithic constructions as repositories theoretically may be checked by their reaction on the external vibrations. Their natural frequency and external source vibration's absorption factor may be used for evaluation. As it is known, the more damages – the less (droningly) natural frequency but external source vibration's absorption factor from the beginning arises and then – decreases. Hence, the alternations in constructions' inflexibility and especially vibrations may be used as indexes of structural damages. Such research should be carry out after each earthquake that is fixed in-situ of repository. It is necessary also to fulfill some analytical inspection, which supposes the careful study of initial constructive calculations, designed specifications, and implementation of extra structural analysis combined with field observations and test data.

The first step in containment's evaluation procedure consists of status scale definition (for example – four):

"0" – the absence of whatever problem (during the several previous years there were no natural or man-made accidents which may influence on soil, subsoil waters and repository' installations structures; the monitoring results witness that level of RAW components pollution in the points being periodically controlled is not characterized by monotonous changes and registered deviations out of natural background in limits of doubled error of measuring methods or measuring instruments.

"1" – presence of negligible problems (during the previous routine monitoring cycle it was a certain accident epicenter of which was remote from repository but in controlled zone the some small shocks were observed; during the previous and current routine monitoring cycles the monotonous changes of RAW components pollution distribution were not revealed but the marginal coming out of 2σ limits in one or several controlled points were observed).

"2" – presence of increased filtration of RAW components (during the previous and current routine monitoring cycles and causal parameter measurement in points which are positioned along over direction to the meaningful accident epicenter – although this epicenter is substantial remote from the repository's influence zone – the monotonous movement of RAW components spot is found out and it oversteps the limits 2σ in every direction).

"3" – presence of essentially damaging of repository (during the previous and especially current routine monitoring cycles and causal parameter measurements the important parameter changes ($>> 2\sigma$) are found out first of all in the points joined along the considerable accident's epicenter direction and this epicenter is relatively close to repository).

The repository containment status scale definition may be presented as in the Table 1.

The containment status scale evaluation has some uncertainty and that fact may have influence upon the decision-making procedure. If the repository containment status is represented in digital form as a belonging function μ_d then for the above-mentioned stated cases the next table may be arranged (Table 2). Here [0] – absolute non true, [0.1–0.3] – the poor level of truth, [0.4–0.5] – essentially level of truth, [0.6–0.7] – the high level of verity, [0.8–0.9] – almost the verity, [1.0] – well-defined truth.

The real repository status may be defined out by taking into account the accumulated effect of seismic stresses (landslides, fractures, shocks) influence. For that, it is necessary to:

– determine the frequency and strength of shocks in-situ of repository over the all observations period and on the base of these data formulate the forecast in advance;

– simulate the influence of accumulated landslides, fractures and shocks on the repository's constructions from point of view the probability of structure changes in repository walls and bottom that may stipulate the formation of microcracks net, summary area of which promote the RAW components departure (migration);
– determine the threshold (THR) exceeding of which guarantees the more than 50% probability of microcracks net rise.

Table 1. The repositories status evaluation

Class	**Filtra-tion RAW (max)**	**Repository conditions evaluation**	**Overall technical conditions**
0	<2σ	Good	Damages are absent. The all processes are flow under license
1	≤2σ	Satisfactory	Damages are absent or immaterial
2	>2σ	Non satisfactory	Approximately uniform expansion of RAW spot evidence of overall marginal damage of compaction which may be compensated by drainage
3	>>2σ	Breakdown	Monotonous growth of RAW spot along the direction on the accident's epicenter evidence of essential damage of repository. It is necessary to build the artificial barrier between repository and important zones near the repository, which are on the way of RAW spot movement. If the RAW spot movement stopping is impossible it should be considered the question of these zones evacuation or alternation of their activity

The belonging to status, which corresponds to classes "0", "1", "2" or "3", is derived from the equation:

$$\mu = max\ \{\mu_0, \mu_1, \mu_2, \mu_3\}. \quad (2)$$

Table 2. The repository containment status in digital form

Class	**Membership function**	***d*** **= 0**	***d*** **= 1**	***d*** **= 2**	***d*** **= 3**
"0"	μ_d	0.9	0.8	0.4	0.1
"1"		0.8	0.9	0.6	0.2
"2"		0.2	0.9	0.9	0.8
"3"		0	0.5	0.8	0.9

After listed steps, it is necessary to equip the stations for repository status monitoring by accelerometers connected with automated monitoring system. The accelerometers data should be accumulated in the next format: [date, shocks amount, integrated value of shocks strain, the maximal acceleration in succession, series duration].

It is necessary to bring in heuristics the data listed in the format and at the same time transmit them to the base, where possible – with the comments (if it is connected with subsequent RAW spot dynamics detection, which is correlate with the fact).

At the same time the heuristics, presented above, may be formulated as following:

1–a. *IF* ([SPOTSTAB] *AND* [NMMA = 0] *AND* [TLS = 0]), *THEN* [MONROUT] (here TLS = 0 means that tectonic landslides [TLS] are absent or ATLS ≤ THR1 where ATLS – the accumulated TLS, THR1 – threshold for the case when the maximal shock value is within limits of average minimal shock during the all-time of observations).

2–a. *IF* ([SPOTSTAB] *AND* [NMMA = 1] *AND* [TLS = 1], *THEN* ([MONROUT + MONCAUS AEC]) (here TLS = 1 means that tectonic landslides occurs but their values are small, although exceed the TRH1).

3–a. *IF* ([SPOTSTAB] *AND* [TMD2σ] AND [TLS = 2]), *THEN* ([MONROUT] *AND* [MONCAUS MD]) (here TLS = 2 means that tectonic landslides are noticeable and accumulated landslides ALS are within limits THR1 < ALS < 0.2 THR).

4–a. *IF* ([SPOTSTAB] *AND* [NMMA = 0] *AND* [NONSTABSPOTNOCR] *AND* [TLS = 2]), *THEN* [CHECKEXPMODCONF].

5–a. *IF* ([SPOTNSTABn–1] *AND* [SPOTNSTABn] *AND* [NMMA = 0] *AND* [NONSTABSPOTNOCR] *AND* [VECTSPOTSHIFTDIFQUAD] *AND* [TLS = 2]), *THEN* [CHECKEXPMODCONF].

6–a. *IF* ([SPOTNSTABn-1] *AND* [SPOTNSTABn] AND [NMMA = 0] *AND* [NONSTABSPOTNOCR] *AND* [VECTSPOTSHIFTSAMQUAD] *AND* [TLS = 3]), THEN [CHECKCONTDENS]. (Here TLS = 3 means that tectonic landslides are noticeable and accumulated landslides ALS are within limits 0.2 THR < ALS ≤ 0.4 THR).

7–a. *IF* ([NONSTABSPOTCRIT] *AND* [NMMA = 1] *AND* [TLS = 3] *AND* [VECTSPOTSHIFTDIFQUAD], *THEN* [MONCRITIC].

8-a. *IF* ([NONSTABSPOTCRIT] *AND* [NMMA = 1] *AND* [TLS = 4] *AND* [VECTSPOTSHIFTSAMQUAD], *THEN* ([MONCRITIC] *AND* [RAWEXPCRITMOD] *AND* [PROTBAR]. (Here TLS = 4 – tectonic landslides within ALS limits 0.4 THR ≤ ALS ≤ 0.7 THR).

The approach proposed for the decision making is sufficiently general and effective way of optimal alternative (or alternatives' subset which are acceptable in principle for the decision making at specific conditions) search when there is general set of possible alternatives in circumstances, characterized by slipshod, depend on several factors and hence are not sufficiently "transparent" as to the decision making persons as well as to independent experts invited especially for optimal alternative selection. In case of definition by means of proposed approach the subset of principally accepted alternatives for the specific problem decision the following step may be as adoption the alternative characterized by the least (min min) metrics either determination of optimal alternative by experts according to majority principle or Byzantine agreement.

2.2. Decision making quality definition procedure for the toxic landfills and radioactive waste repositories management

The functional scheme of the ecosystem monitoring system consists of subsystem of environmental information collection and subsystem of information and analytical analysis. This system is proposed to be integrated to united state system of environmental monitoring, which will monitor the air, water, soil, geological changes, waste etc. and control the risks of emergencies. The highest level of this system is a territorial information and analytical center, which must perform the following functions: obtaining information from information-analytical centers of the middle level and from the part of automated (stationary and mobile) environmental control systems; continuous analysis of environmental information, trends and ecologically hazardous areas and zones; modelling and forecasting the development of emergencies and their consequences; making recommendations for the adoption of operational decision-making in emergencies; formation of a bank of statistical data on the ecological status of individual cities and districts and the entire region in whole; simulation and long-term forecasting the environmental state of ecosystems. Moreover, information and analytical centers solve the problems of identifying the risks of emergency environmental situations and forecast their development in a particular area, taking into account the specifics of toxic landfills, radioactive repositories, local industrial and agricultural production, geographical, climatic and meteorological features etc.

The principles and stages of constructing expert systems for decision making for environmental monitoring and assessment of ecosystem include the stages of conceptualization, concretization, formalization and implementation of tests. As the main criteria for checking the developed expert system, the quality of decisions is selected, which is evaluated by checking the quality and correctness of judgments while solving real problems, establishing the acceptability of the character of dialogue with the user, defining functional technical and software tools, etc.

At the same time, each situation, regardless of whether it relates to the assessment of the degree of pollution of the environment or management of technical objects in a difficult situation under conditions of indistinct and incomplete information or decision-making, is characterized by the presence of risks that need to be taken into account.

When establishing the apparatus and means of control and analysis of reliability of information about the state of the ecosystem, it is very important to justify the choice of specific control methods that take into account the specifics of the object of control, the conditions under which the system operates and the requirements for the object and system.

If there are known:

– coefficient of output uncertainty K_{ouc};

– coefficient of control of the process.

$$K_C = \{\sum_{i=1}^{l} \lambda_i D_i\} / \{\sum_{i=1}^{l} D_i\}, \tag{3}$$

where: λ_i - efficiency coefficient of the *i*-th control method, which is defined as the ratio of the number of detected errors A to the total number of errors (both detected and those that are not detected) $A + B = \delta$, and D_i – *i*-th operation of information control;

– total amount of information Q;

– number of system errors, that are not detected, B;

– estimated total coefficient of uncertainty.

$$K_{uc} = [\sum_{i=1}^{l} \frac{\delta_i}{Q}(1-\lambda_i)D_i]/(\sum_{i=1}^{l} D_i), \tag{4}$$

or

$$K_{uc} = [\sum_{i=1}^{l} B/Q)D_i]/(\sum_{i=1}^{k} D_i), \tag{5}$$

it is possible to determine the coefficient of rationality of the control system

$$K_{r.c.} = K_{ouc}(1-K_{л})/K_{uc}, \tag{6}$$

which for values $K_{rc} < 1$, that is, $K_{ouc}(1 - K_c) < K_{uc}$ indicates that the control system is built irrationally or the technology of data processing in the system is not rational.

Equally important is the choice of conceptual, informational and behavioral models of the control system and verification of their reliability by using "reverse" operations. This verification may include the following steps (procedures):

– consideration of the design of the model and the feasibility of its development;
– establishing connection of the idea and the feasibility of developing a model with determined, randomized and average values of the characteristics of the model;
– research of accepted approximations of real processes;
– consideration of criteria of the effectiveness of parameters and variables;
– research of accepted propositions and hypotheses;
– detecting the connection of the results of the two previous stages with real processes;
– analysis of the system of disturbing factors and characteristics of the operator;
– research of the interconnections of all these factors;
– verification of the information and its sources used for model development;
– consideration of the whole control procedure in connection with the definition of the task of the system;
–consideration of the task.

When selecting controlled parameters, their informational value should be considered (separately for the case of operational control of normal modes and separately for emergency control). For operational control, the informational value of a parameter can be determined as:

$$Z_{on} = (\sigma_x / C_x)\ln(\sigma_x / \lambda_x)\rho, \tag{7}$$

and for emergency – according to the following:

$$Z_a = \frac{C_x}{x_a - m_x} \ln \frac{\sigma_x}{\lambda_x} \rho \ \text{(for } \xi \geq x_a\text{)}, \tag{8}$$

where σ_x - average square deviation of the parameter ξ; C_x – the maximum rate of change of the parameter ξ in transitional modes; λ_x – an error of the measuring device; ρ – coefficient that takes into account the distribution of probabilities of values $x \in \xi$; x_a – the minimum value of the parameter ξ, which corresponds to the emergency situation; m_x – mathematical expectation ξ.

In this case, the generalized characteristic of the informational value of the parameter can be represented as:

$$Z_n = Z_{on} \cdot Z_a. \tag{9}$$

In addition, the value of information can be expressed through increasing the probability of achieving the goal:

$$I = log\ (p_1/p_0), \tag{10}$$

where: p_0 – probability of achieving the goal before receiving information, and p_1 – the same after receiving the information. If after receiving additional information the probability of achieving the goal is reduced, this indicates the need to move to an alternative strategy. And in this sense, additional received information has a real value, since it saves resources and time by refusing from no perspective strategy.

As for the choice of a particular set of control methods, it is necessary to consider a number of factors that determine not only the possibilities of certain technical means, requirements to the control system, the conditions under which the processes of collection, transmission, processing and storage of information take place, but also economic indicators.

3. Reliability of the monitoring data

Methods for assessing the state of the ecosystem are realized selectively and unsystematically, which does not allow obtaining a sufficiently high guarantee of conformity of the received data with the requirements of existing standards (Yakunina, 2009; Diduk, 2012). This, in turn, leads to an inadequate response to changes in indicators in the functioning of the ecosystem, as well as to an unreliable forecast of their further development.

Process control and analysis involve managing processes based on the compilation of heuristics with the definition of strata, the set of states, the calculation of possible states, the degree of their feasibility and the likely consequences of this implementation; the definition of the growth of the Euclidean distance between the pairs of real states that are observed and are adjacent to each other at a certain time interval, as well as the probability and possibility of such a transition and the driving forces that cause it (Zadeh et al., 2014; Beleulmi et al., 2014; Batyrbek et al., 2018; Dychko et al., 2019).

As it is asserted in (Diduk, 2012), it is impossible to consider information without considering any situation of uncertainty. Validation of reliability is based on the information obtained during the identification. Its task is to work out quantitative indicators of data reliability.

Changing the structure of the engineering system and technology of data collection and processing based on the results of identification and evaluation aims to optimize the operating modes of the information system in the specific circumstances that have developed and maximize the reliability of the results of its functioning.

Inadequacy in systems is due mainly to the incompleteness of the original data, the nebulosity (fuzzy) of the information and the limitations of the class of implemented algorithms (Zadeh et al., 2014; Radionovs et al., 2014; Yeremeyev et al., 2019).

The incompleteness of the source data, which is the result of limited observation of objects of control and insufficiency of information about the factors that affect the processes in the ecosystem, means that if there is:

$$V(N, f) = (\tilde{f} \in F : N(\tilde{f})) = N(f)\,, \tag{11}$$

the set of all elements $\tilde{f}$ that do not differ from the element f using the information N, then the value of $N(f)$ does not allow determining which of the sets $S(\tilde{f}\xi)$, where $\tilde{f} \in V(N, f)$, leads to the desired ξ – approximation (Dychko et al., 2019).

The nebulosity (fuzziness) of information resulting from the limited accuracy of measurements and estimates, as well as the presentation and processing of data, failures of equipment, interference in communication channels, drift of equipment parameters and measured parameters, etc., means that if there is

$$V(N_\rho, f) = \{\tilde{f} \in F : N_\rho(f) \in E[N(\tilde{f}), \rho]\}\,, \tag{12}$$

the set of elements f for which $N\rho(f)$ can serve as fuzzy (approximate) information and the requirement is fulfilled

$$N_\rho(f) \in E[N(f), \rho] \forall f \in F\,, \tag{13}$$

where: E – the operator of information fuzziness, ρ – a measure of fuzzy information, $E[N(f), \rho]$ – set that represents fuzzy information about f, $\forall$ – universal quantifier that confirms the validity of the equation for any values of the predicate f, then one only the value of $N\rho(f)$ does not allow stating which of the sets leads to ξ – approximation.

Limits of the class of admissible algorithms or those algorithms that are implemented to solve a particular task in specific conditions and which, of course, are associated with the duration of the implementation process, stability (perseverance) or correctness of the solution, means that if

$$Q(h) = \{\varphi(h) : \varphi \in R\}\,, \tag{14}$$

there is a plurality of results of application to $h = N\rho(f)$ of all algorithms φ from class R of those realizable algorithms, then the knowledge of only $N\rho(f)$ does not allow stating which specific (or which) of the algorithms of the set R will provide a solution to the problem under acceptable conditions (such that there are real) restrictions. At the same time, the general approach to increasing the reliability of information, if the solution space is not secured either by a norm nor by a metric, can be based on the general mathematical theory of optimal reduction of uncertainty.

In case of incompleteness or approximation of the output data, when additional information is required, the required ξ – approximation can be found only under the condition of a non-empty intersection of the ξ sets, that is,

$$A(N, f, \xi) = \bigcap_{\tilde{f} \in V(N, f)} S(\tilde{f}_i, \xi) \neq 0 , \tag{15}$$

or

$$A(N, f, \xi) = \min_{\tilde{f} \in V(N, f)} S(\tilde{f}_i, \xi) \neq 0 . \tag{16}$$

As an example a procedure (15) to increase the reliability of the differentiation of information in the case of incomplete data is given in Fig. 1.

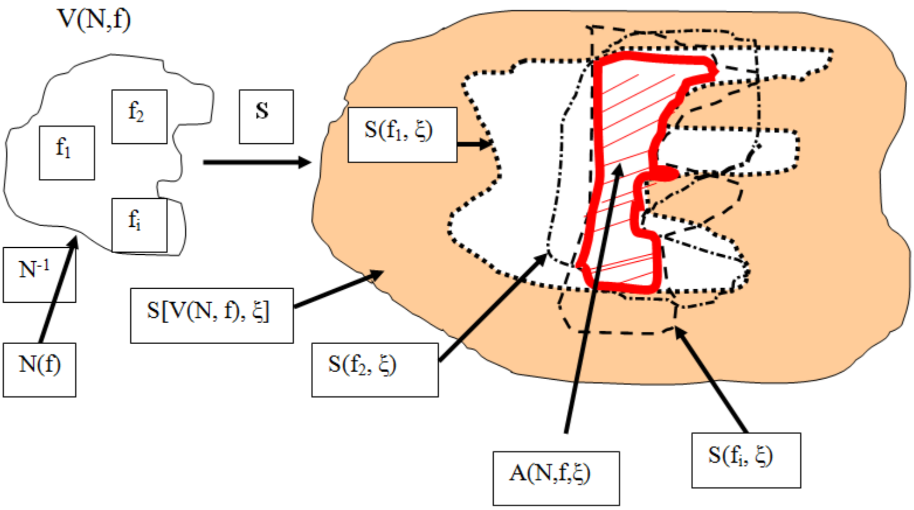

Fig. 1. The scheme of the choice of the set *A (N, f, ξ)* of all elements that do not differ from the element *f* using information *N* (counteraction principle)

The minimum amount of required information to solve a specific task with the specified degree of reliability (global radius of information) can be defined as follows. If we accept that

$$\xi_1 \leq \xi_2 \Rightarrow A(N, f, \xi_1) \subset A(N, f, \xi_2) , \tag{17}$$

and note

$$r(N,f)=\inf\{\xi : A(N, f,\xi) \neq S, \qquad (18)$$

as a local radius of information, that is, the least ξ, for which there still exists an element belonging to sets for all that do not differ from f using information N, then the global radius of information may be defined

$$r(N)=\sup_{f\in F} r(N, f)=\inf\{\xi : A(N, f,\xi), S\forall f \in F\}, \qquad (19)$$

Then for the exact solution of the problem, that is, for the case of an unambiguous definition

$$S(\tilde{f})=S(f)\forall\tilde{f} \in V(N, f), \qquad (20)$$

when $S[V(N,f)]$ is uniquely (one and only one),

$$\mathrm{r(N)}=\begin{cases} \mathrm{0, if \ \ S[V(N, f) \ \ is \ unambiguou \ s \ for \ all \ f} \in \mathrm{F} \\ +\infty \ \ \mathrm{in \ opposite \ \ case} \end{cases}, \qquad (21)$$

Thus, the search for an exact solution to a problem reduces to the definition of the minimum amount of information the presence of which $r(N)$ is converted to zero. However, since the procedures for such a search are often limited to system resources, or too high for additional information, the decision is sought with an error

$$e(\phi, N)=\sup_{f\in F} e(\phi, N, f)(=\inf\{\xi : \phi[N(f)\in S(f,\xi)\forall f \in F\}), \qquad (22)$$

where: $e(\phi, N, f)=\inf\{\xi : \phi[N(f)]\in A(N, f,\xi)\}$ – the local error in the algorithm (procedures) φ from the class of algorithms (procedures) $\varphi(N)$ that use the information N, that is, the least ξ, in which the element $\varphi[N(f)]$ belongs to $S^{(\tilde{f},\xi)}$ for all $\tilde{f}$ that can not be distinguished from f by using information N.

If the variation of the information operator N (that is, the addition of any information that is relevant to the solvable problem) is created, the conditions for choosing the "optimal" information are created. If the information operator N can be decomposed into a number of simpler information operators, then the term cardinal N is intriduced:

$$n = card(N), \qquad (23)$$

and the information is non-adaptive if the selection of simpler operators occurs independently (with the help of independent processors) and, accordingly, adaptive if this choice is made consistently, taking into account the results already obtained.

Then the minimum radii of non-adaptive and adaptive information (for the class of algorithms *R* used in solving the problem) can be represented respectively in the form

$$r^{(\text{íà})}(R,n) = \inf_{N\in\varphi^{(\text{íà})}(n)} r[R(N),N], \tag{24}$$
$$r^{(\text{àä})}(R,n) = \inf_{N\in^{(\text{àä})}(n)} r[R(N),N],$$

where

$$\varphi^{(\text{íà})}(n) = \{N^{(\text{íà})} : card(N^{(\text{íà})}) \le n\}, \tag{25}$$
$$\varphi^{(\text{àä})}(n) = \{N^{(\text{àä})} : card(N^{(\text{àä})}) \le n$$

represent classes of correspondingly non-adaptive and adaptive informational operators of cardinality not higher than n. In this case, the information operator *N* only then will become the *n*-th optimal non-adaptive (or adaptive) information (for *R*) when $N\in\varphi^{(\text{на})}(n)$ either $N\in\varphi^{(\text{ад})}(n)$, $r[R(N),N = r^{(\text{на})}(R,n)$ or $r[R(N),N] = r^{(\text{ад})}(R,n)$.

If approximate information is used

$$N\rho(f) \in E[N(f),\rho]\forall f \in F, \tag{26}$$

where: *E* – the information error operator, *ρ* – the measure of error information, then the operator *N* will be the *n*-th optimal non-adaptive (adaptive) approximate information (for *ρ, R*) if

$$N\in\varphi^{(n-a)}(n) \text{ or } N\in\varphi^{(ad)}(n), \tag{27}$$

$$r[R(N_\rho\text{,E),Nρ,E]} = r^{(n-a)}(R,n,\rho) \text{ or } r[R(N_\rho\text{,E), Nρ,E]} = r^{(ad)}(R,n,\rho). \tag{28}$$

Here

$$r^{(n-a)}(R,n,\rho) = \inf_{N\in\varphi^{(n-a)}(n)} r[R(N_\rho\text{, E), Nρ, E]}, \tag{29}$$

$$r^{(ad)}(R,n,\rho) = \inf_{N\in\varphi^{(ad)}(m)} r[R(N_\rho,E),N_\rho,E], \tag{30}$$

there are *n*-th minimum radii of non-adaptive and adaptive approximate information (for *ρ, R*).

Information systems often have to deal with fuzzy (nebulosity) data. The phenomenon of fuzziness (nebulosity) is due, in particular, to the largely incomplete information about objects (processes), when the unknown exact (complex) dependencies are replaced by approximate (simplified) or for the evaluation of the state of the engineering system (partial or complete) mediating parameters, connections, dependencies are applied. Therefore, methods and means of increasing the reliability of information in the conditions of fuzzy (nebulosity) data can be largely distributed to the area of problem solving with incomplete data. If we consider (12) and take into account that $f \in V(N\rho, f)$, and on the basis of the definition (11)

$$V(N, f) = V(N_\rho, f) \subset V(N_\rho, f) \forall f \in F, \tag{31}$$

then we can assert that the required ξ-approximation will be found only if the intersection of the set $S(fi, \xi)$ is not empty, that is,

$$A(N_\rho, f, \xi) \bigcap_{\tilde{f} \in V(N_\rho, f)} S(\tilde{f}, \xi) \neq 0 \, . \tag{32}$$

In this case, the global radius of information

$$r(N_\rho) = \sup_{f \in F} r(N_\rho, f) \; (= \inf\{\xi : A(N_\rho, f, \xi) \neq 0 \; \forall f \in F\}), \tag{33}$$

where: $r(N\rho, f) \geq r(N0, f) = r(N, f) \; \forall f \in F$ – the local radius of the approximate (nebulosity) information and *N0* characterizes *N* under condition $\rho = 0$, that is, in fact $N0(f) = N(f)$.

The traditional way of increasing the reliability in this case is to minimize $r(N\rho)$ or, that is the same, to minimize ρ.

4. Algorithms for the information about the state of ecosystem assessment

While solving any problem, there are always two questions: can this problem be solved with the necessary accuracy, and if possible, how much will this solution cost, that is, what resources will need it.

An algorithm compiled from a finite number of simple operations may be acceptable for use when achieving the goal set before the system. However, the resources required for its implementation may be such that the decision will lose all meaning: it will be late, will be unstable or incorrect, or costs may be inadequate to the results that will be achieved. Therefore, from the whole set of admissible algorithms $\psi(N\rho)$, that uses information $N\rho$, a subset of implemented algorithms is selected, so that any of the algorithms used in the system $\varphi : X = \varphi[N\rho(f)]$ is included to this subset.

Under the conditions of limited class of implemented algorithms, if we consider (14) and take into account that the element x obtained as a result of the application of the algorithm $\varphi \in R$, belongs to the set $A(N_\rho, f, \xi) \cap Q(h)$, the ξ-approximation can be found under the conditions of a nonempty intersection of the set

$$A(N_\rho, f, \xi) \cap Q(h) \neq 0, \tag{34}$$

In this case, the global radius of the approximate information (for R) will be the minimum value of ξ, for which the set $\psi(\xi)$ has at least one algorithm with n, or more precisely the value

$$r(R, N_\rho) = \inf\{\xi : \psi(\xi) \cap R \neq 0\}, \tag{35}$$

or

$$r(R, N\rho) \geq \sup_{f \in F} r(R, N_\rho, f), \tag{36}$$

or

$$r(R, N_\rho, f) = \inf\ \xi : A(N_\rho, f, \xi) \cap Q[N_\rho(f)] \neq 0, \tag{37}$$

and is the local radius of the approximate information (for *R*).

If there is a set of algorithms

$$R = \phi \in \varphi(N_\rho) : \phi[N_\rho(f)] \in Q[N_\rho(f)] \forall f \in F, \tag{38}$$

and $R \subset \overline{R}$, then if $R = \overline{R}$,

$$r(R, N_\rho) = \sup_{f \in F} r(R, N_\rho, f), \tag{39}$$

and the algorithm for calculating the ξ-approximation (realizable) for an arbitrary $f = F$ according to the information of $N\rho$ exists only in the case where $r(R, N\rho) < \xi$ or for $r(R, N\rho) = \xi$, if the error

$$\inf_{\phi \in R} e(\phi, N_\rho) = r(R, N_\rho), \tag{40}$$

is achieved by applying a certain algorithm φ for which the following value can be achieved

$$\inf\{\xi : \phi[N_\rho(f)] \in A(N_\rho, f, \xi) \forall f \in F\}. \tag{41}$$

To evaluate one or another algorithm a criterion such as complexity can be used. Any algorithm can be represented as a set of primes of simple operations, each of which is characterized by the complexity *comp(pi)*. The information complexity of the operator *Nρ(f)* if there is a calculation program consisting of a finite number of operations *p1,. . . , pk* can be represented in the form

$$comp[N_\rho(f)] = \sum_{i=1}^{k} comp(p_i). \tag{42}$$

If there is a calculation program *φ(y)* which consists of a finite number of simple operations *q1,. . . , qi*, then the combinatorial complexity of the algorithm φ(y) can be expressed as follows:

$$comp[\phi(y)] = \sum_{i=1}^{l} comp(q_i). \tag{43}$$

The complexity of the algorithm φ can be represented as

$$comp(\phi) = \sup_{f \in F}\{comp[N_\rho(f)] + comp[\phi(N_\rho(f))]\}, \tag{44}$$

and the algorithm φoc which is optimal in complexity with *R(Nρ, ξ)* for *R(Nρ)* if

$$comp(\phi^{oc}) = comp[R(N_\rho), N_\rho, \xi], \tag{45}$$

where: $comp[R(N_\rho), N_\rho, \xi] = \inf\{comp(\phi) : \phi \in R(N_\rho, \xi)\}$ – the ξ – complexity [for *R(Nρ)*] provided that $inf\psi = +\infty$.

If we accept the φ-class of admissible approximate information operators and present the complexity of the problem as ξ – complexity in the class ψ (for *R*) in the form

$$comp(R, \varphi, \xi) = \inf_{N_\rho \in \varphi} comp[R(N_\rho), N_\rho, \xi], \tag{46}$$

then the algorithm φ^{oc} will be optimal for complexity in the class ψ (for *R*) if

$$comp(\phi^{oc}) = comp(R, \varphi, \xi), \tag{47}$$

and φ^{oc} uses the approximate information *Nρ* with ψ and belongs to *R(Nρ)*.

The above considerations allow selecting (or constructing) algorithms to be implemented (or rather, the set of such algorithms), at the stage of the technical and operational design of the system. Such algorithms will correspond to specific conditions of its functioning, including for the case of decomposition of the system in case of ensuring the problems of resistance to failures, as well as when changing the dynamics of the engineering system, its overloads, etc.

Algorithms (4)–(7), which actually implement the multiplicative theorem operation, state that increasing the reliability of information is possible only through the use of redundancy (structural, procedural, informational). Indeed, in this case, the result can be achieved either under the conditions of simultaneous operation of all sets that are formed by parallel structures on the basis of a standard set of output data (structural redundancy), or during the successive execution of the same procedure over each pair of sets that are formed by one structure on the basis of a standard set of output data (procedural redundancy), or, finally, by combining the first two approaches and using additional structures or procedures that provide the formation of new sets based on all available relevant information (or adjustments already existing), as well as the results of its structuring and other types of processing (information redundancy).

In practice, this means the following:

– the use of a set of devices of the same type, communication channels and (or) data processing means instead of one in the case of structural redundancy;

– the use of multiple identical measurement procedures, data transmission and / or processing instead of one-time procedures, as well as the use of various diagnostic procedures in case of procedural redundancy;

–simultaneous use of several measurement methods (several different types of devices) for measuring the same value, entering test digits during data transmission, using multiple models or data processing algorithms that differ from each other at the conceptual level, taking into account a priori, indirect and concomitant information, as well as background information in the case of adoption of the method of informational redundancy.

It should be noted that in practice there is a combination of the above mentioned, mutually complementary approaches, improving the quality and efficiency of information system about the real state of ecosystem and toxic pollutants migration.

5. Summary and Conclusions

The developed expert system for the ecosystem monitoring and assessment includes the cumulative data, the knowledge base, and set of rules of production, logical deduction gear and conclusion building gear by means of uncertain and incomplete input data.

To avoid the errors in toxic or radioactive components migration forecast it is necessary to use several alternative models with the same input data. Such simulation allows getting the spectral characteristic in points of checking at the predetermined time of forecast.

The proposed procedure of quality definition of decision making for the radioactive waste repositories management provides a reconsideration of the task from a slightly different point of view, which contributes to a deeper and more comprehensive assessment of the system and allows creating an optimal conceptual model that is, adequate to a mathematical model and, as a result, creates conditions for effective control of reliability.

References

1. Batyrbek, A., Suleimenov, A., Sugurova, L.A., Suleimenov, A.B., Zhirnova, O.V.: Synthesis of the equipment health management system of the turbine units' of thermal power stations, *Mechanics & Industry*, 19, 209, 2018.
2. Beleulmi, S., Bellaouar, A., Lachi, M.: Cost optimization of reliability testing by a bayesian approach. *Mechanics & Industry*, 15, 449–454, 2014.
3. Diduk, N.N.: The measures of internal and external information (on example of probabilistic situations of uncertainty). *System research and information technologies*, 4, 94–110, 2012.
4. Dudar, T.V.: Uranium mining and milling facilities legacy sites: Ukraine case study. *Environmental Problems*, 4(4), 212–218, 2019.
5. Duro, L., Altmaier, M., Holt, E., Mäder, U., Claret, F., et al.: Contribution of the results of the CEBAMA project to decrease uncertainties in the Safety Case and Performance Assessment of radioactive waste repositories. *Applied Geochemistry*, 112, 104479, 2020.
6. Dychko, A., Yeremeyev, I., Kyselov, V., Remez, N., Kniazevych, A.: Ensuring Reliability of Control Data in Engineering Systems. *Latvian Journal of Physics and Technical Sciences*, 56(6), 57–69, 2019.
7. Dychko, A., Yeremeyev, I., Remez, N., Kraychuk, S., Ostapchuk, N.: Structural redundancy as robustness assurance of complex geoengineering systems. *E3SWC*, 166, 11003, 2020.
8. Hoeting, J., Madigan, D., Raftery, A., Volinsky, C.: Bayesian Model Averaging: A Tutorial. *Statistical Science*, 14(4), 382–401, 1999.
9. Karadimos, N.V., Orsoni, A.: The role of modelling and simulation in design-build projects. *Proceedings of the 20th European Conference on Modelling and Simulation*, 2006.
10. Mallants, D., Travis, K., Chapman, N., Brady, P., Griffiths H.: The State of the Science and Technology in Deep Borehole Disposal of Nuclear Waste. *Energies*, 13, 833, 2020.

11. Melnychukm, P.P., Barabashm, O.M.: Radiation-safe use of decorative granites of Zhytomyr region in the production of facing and architectural and construction products. *Proceedings of the int. sc.-pr. conf. Environmental problems, sustainable development and technogenic safety (Dnipropetrovsk, Ukraine),* 175–178, 2001.
12. Radionovs, A. Uzhga-Rebrov, O.: Application of fuzzy logic for risk assessment/ Izplūdušās loģikas pielietojums risku analīzē. *Information Technology and Management Science*. 17, 2014.
13. Yeremeyev, I., Dychko, A., Kyselov, V., Remez, N., Kraychuk, S., Ostapchuk, N.: Evaluation of Radioactive Contamination. *Latvian Journal of Physics and Technical Sciences,* 56(4), 57–67, 2019.
14. Yeremeyev, I., Dychko, A.: Monitoring and management of geoengineering repositories of radioactive waste. *Architecture, Civil Engineering, Environment,* 14(3), 103–109, 2021.
15. Yakunina, I.V.: Methods and devices of environmental control. Environmental monitoring. Tambov, TSTU: Russia, 2009.
16. Zadeh, L.A., Fu, K.S., Tanaka, K.: Fuzzy sets and their applications to cognitive and decision processes. In: *Proceedings of the US–Japan seminar on fuzzy sets and their applications, held at the University of California,* Berkeley, California, 2014.

Diversification of water intakes as an element of risk management in the water supply system

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Abstract

The aim of the study is to analyze the degree of diversification of water resources in the collective water supply system of the city Głubczyce. The analyses used the method based on the Shannon-Weaver index and the Pielou dispersion index. In the Głubczyce municipal water supply system, there are two water production subsystems: Kołłątaja and Powstańców, which pump water to the water supply network, comprising the water distribution subsystem. The operation of the water production subsystem in the city is based on the operation of 4 independent water intakes. The CWSS of the city of Głubczyce is characterized by an average annual daily water consumption of 3610 m^3/d. The greatest demand of water occurs in the spring and summer months, when there are local water shortages.

The paper presents the construction of the water supply infrastructure in the city of Głubczyce, its structure and the possibilities of diversifying and securing water supplies in terms of the operational safety of the critical infrastructure. Possible emergencies are presented and analysed, taking into account the protection of the critical infrastructure, so as to ensure the continuous supply of water in the required quantity and under the appropriate pressure.

Keywords: water supply system, risk, safety, diversification, critical infrastructure

1. Introduction

The main goal of the operation of the collective water supply system (CWSS) is supplying the population with water intended for human consumption. This system is a complex technical system comprising the water production subsystem (WPSs) and the water distribution subsystem (WDSs). The water production subsystem consists of four independent water supply resources areas covering the operation of individual intakes and water treatment stations. The water distribution subsystem consists of a water supply network with water pumping stations and network storage tanks. CWSS is a system that functions in diverse, dynamically changing operating conditions, determined by internal and external factors. The variability of conditions and a large number of elements that make up the water supply infrastructure contribute to random malfunctions appearing in various areas of the CWSS, which in extreme cases of failure lead to a complete cessation of water supply to the population. A prerequisite for maintaining water supply to consumers is maintaining the efficiency and proper operation of the water supply infrastructure, which allows to achieve a high level of reliability and safety of CWSS operation.

The approach to water safety recommended for more than 20 years by the World Health Organization, based on risk management throughout the water supply chain from the intake to the consumer's tap, resulted first in the revision of Directive 98/83/EC (Drinking Water Directive DWD) carried out in 2015 and then in the adoption of a new Directive on the quality of water intendent for human consumption by the European Parliament and the Council of the European Union in January 2021 (DWD 2020/2184, 2021). The consistent European policy relating to water management, including risk-based management of water supply to the consumer, has translated in Poland into changes introduced by the Act of 20 July 2017, Water Law, requiring water supply companies to conduct a risk analysis (Art.133) for the purposes of establishing a water intake protection zone (WLA, 2017). Consistently, as a result of the implementation of the DWD revision into Polish legislation, the 2017 Regulation of the Minister of Health on the quality of water intended for consumption (RMH, 2017) of the recommends a new approach to managing the safety of water supply based on risk assessment carried out in accordance with PN-EN 15975 standard. As of 12 January 2021, Directive 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption applies in the European Union (EU). Member States have 2 years to implement it into national law and 5–6 years to implement individual articles.

Collective water supply systems in many countries are classified as a critical infrastructure that determines the safe functioning and economic development of countries. Due to the strategic economic role of CWSS it is necessary to ensure the continuity of operation of all its components from the intake to the consumer's tap, and thus, in the event of a failure or undesirable event, quickly take rational steps to restore the proper operation of the water supply infrastructure. In Poland, in accordance with the Act of April 26, 2007 on crisis management (ACM, 2007), the collective water supply system is also included in the critical infrastructure. Consequently, water companies, in accordance with Art. 5 (1) of the Act of June 7, 2001 on collective water supply and collective sewage disposal (ACWSSCSD, 2001) are obliged, among others, to ensure that the water equipment is capable of delivering water in the required quantity and pressure, in a continuous and reliable manner. The fulfilment of this obligation depends on the maintenance of the water supply network and devices in good technical condition, ensuring the stability of the water supply system and efficient removal of possible failures. One of the significant operational problems of the CWSS for a water supply company worldwide are water supply network failures that affect the stability of water supply. Therefore, having detailed information about failures of water supply networks, including data on the frequency of failures, their place of occurrence, costs of their removal, as well as the negative effects of failure, allows for the development of both short and long-term strategies for the development of CWSS, taking into account the necessary revitalization of the water supply network. In addition, a full description of the mechanism of damage to water supply networks also allows for the development of effective protective barriers limiting the frequency and effects of damage to water supply lines. However, apart from a reliably functioning water supply network, what ensures stable water supply to consumers is also a reserve of water production capacity or the existence of emergency CWSS intakes, which guarantee the supply of water in the event of sudden deterioration of water quality in the intake or random failures of water treatment systems (Kwietniewski and Rak, 2010; Zimoch, 2011; WPF, 2021,).

One of the elements of increasing the operational safety of water supply systems is the diversification of water supply resources areas. Furthermore, diversification of the water intake system for supplying the inhabitants with water is becoming increasingly important in view of existing and worsening climate change. The effect of climate change is the observed dynamics of changes in surface and groundwater resources, which results in significant reductions in the available resources for supplying the population with water.

The aim of this article is to assess the degree of diversification of water supply to the consumer of the actual water supply system.

2. Research object

The city of Głubczyce is located in the southern part of the Opole Province. The area of the city is 12.52 km^2 and is inhabited by over 12 thousand inhabitants. The water supply system in the city of Głubczyce consists of a water production subsystem (including water intake and transport), a water storage subsystem and a water distribution subsystem. The operation of the collective water supply system of the city of Głubczyce (Tab. 1) is based on 4 water intakes and 3 reserve and equalizing tanks forming the Municipal Water Supply System (MWSS). Urban intakes additionally supply 23 villages that are included in the system (Tab. 2).

Table 1. Performance characteristics of collective water supply system in the Głubczyce city

CWSS	**Water intake (days of intake operation in a year)**	**Number of supplied towns / villages**	**Average daily water produ-ction in 2020 [m^3/d]**	**Total annual water production [m^3/year]**	**Percen-tage [%]**	**Average daily water consump-tion in Głubczyce [m^3/d]**	**Average annual water demand in rural com-munes [m ^{3}/year]**
Municipal Water Supply System	Powstańców (305)	23 including Głubczyce city	2 088.44	636 974.00	69.00	1617.01	254 924.28
	Mickiewicza (249)		220.32	54 859.00	7.00		
	Kołłątaja (366)		462.83	169 395.00	15.00		
	"Basen" (364)		258.99	94 274.00	9.00		

The municipal water supply system (Fig. 1) has two water production subsystems, WPSs Kołłątaja and WPSs Powstańców (Tab. 2), which pump water into the water supply network, comprising the municipal water distribution subsystem (MDSs). The operation of the water production subsystem in the city (Tab. 2) is based on the operation of 4 independent water intakes, from which the Kołłątaja intake takes deep water for the operational needs of the WPSs Kołłątaja. On the other hand, the intakes at Powstańców, Mickiewicza and "Basen" work in an integrated system comprising WPSs Powstańców. Although the "Basen" intake uses deep water resources mainly for the needs of the municipal swimming pool, in the event of a crisis or emergency, it also supplies the municipal network. The water captured in WPSs Powstańców is directed to two storage tanks with a total volume of 2000 m^3, from where it is pumped to the water supply network. In the event of an emergency, it is possible to turn off the water storage tanks and pump water directly to the municipal system.

Table 2. Characteristics of water intakes in the municipal water supply system

CWSS	**Water intakes**	**Max daily capacity [m^3/d]**	**Avg. daily water production [m^3/d]**	**Production capacity reserves [m^3/d]**	**Avg. daily water production for WDSs [m^3/d]**	**Storage tanks volume [m^3]**	**Supply area**
WPSs Powstańców	Mickiewicza Powstańców Basen	5 496.00	2 567.75	2 928.25	1 390.02	V1: 1000 V2: 1000	Głubczyce city - 56% of daily production
WPSs Kołłątaja	Kołłątaja	720.00	457.96	262.04	226.99	V3: 680	Głubczyce city - 49% of daily production

The WPSs Powstańców consists of two reserve equalizing tanks with a total capacity of 2000 m^3, from which water is directed to the water pumping station and then to the municipal water distribution system. The technical infrastructure of WPSs Kołłątaja, on the other hand, includes a reserve equalizing tank with a capacity of 680 m^3, from which water is directed to the water pumping room and then to the municipal water distribution system. Storage tanks secure water supplies in the event of a crisis in the water supply network.

The total length of the water pipe network in the city of Głubczyce amounts to 52.5 km, with the dominant distribution network being 33.6 km, which constitutes 64% of the total length of the water pipes in the city. A full description of the water supply infrastructure in the city of Głubczyce, taking into account the type of network, length, percentage share in the total structure, as well as the number of water supply connections is presented in Table 3.

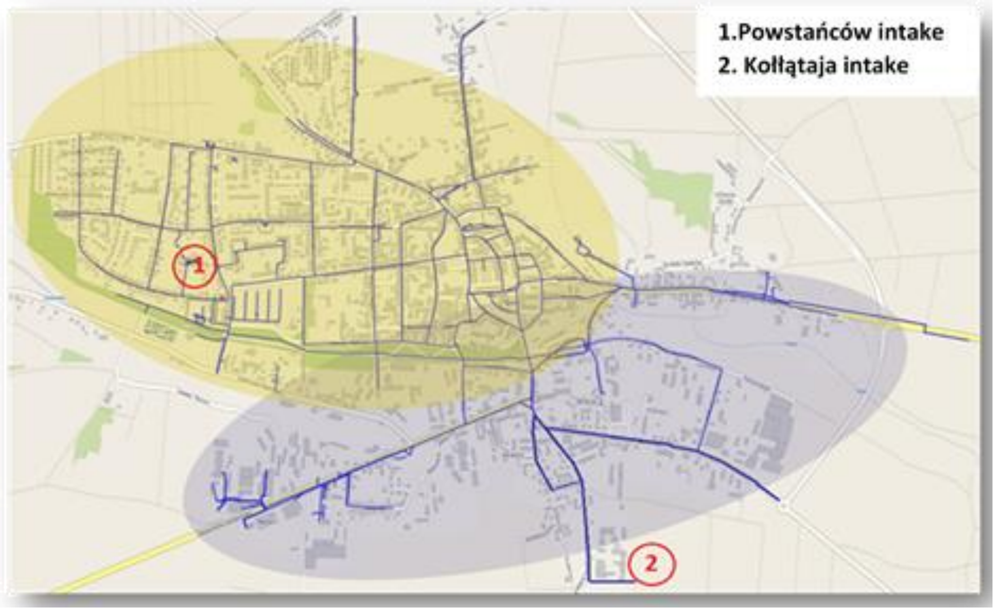

Fig. 1. Municipal Water Supply System of Głubczyce city

Table 3. Characteristic of water pipe network in Głubczyce city

Type of water pipe network	**Length [km]**	**Percentage in the total structure [%]**	**Number of water connections [pcs.]**
Main network	2.00	4%	1476
Distribution system	33.60	64%	
Water supply connections	16.90	32%	
Suma	52.50		

3. Research methods

The study analysed the emergency situations caused by the occurrence of failures in individual supply systems. In the research part, unit indicators of water demand were used for calculations, taking into account the average daily water consumption, according to the following criteria (Szpak and Tchórzewska, 2014):

- – amount of water related to human physiology: q_{ph} = 2.5 L/Inh.·day;
- – minimum amount of water for a few days: q_{min} = 7.5 L/Inh.·day;
- – necessary amount of water for a period of several weeks: q_{nec} = 15 L/Inh.·day;
- – required amount of water in an emergency: q_{req} = 30 L/Inh.·day.

The demand for water Q_{ph}, covering the physiological needs of water consumers was determined according to the formula (Szpak and Tchórzewska, 2014):

$$Q_{ph} = q_{ph} \cdot N_{Inh}, \tag{1}$$

where: q_{ph} – unit indicator of water demand for human physiological purposes [L/Inh.·day], N_{Inh} – the number of inhabitants.

Evaluating the degree of diversification of water supply in the CWSS, a two-parameter assessment using an additive model was used, in which the two-parameter diversification index was determined from the formula (Rak and Boryczko, 2016):

$$d_{CWSS}(SW) = d_{SW}(Q) + d_{SW}(V), \tag{2}$$

where: $d_{CWSS}(SW)$ – the two-parameter water supply diversification index in CWSS according to Shannon and Weaver, $d_{SW}(Q)$ – water intake diversification index, determined from Eq. 3, $d_{sw}(V)$ - index of diversification of the water volume accumulated in storage tanks, determined from Eq. 4.

The study adopted the following comparative scale for the d_{CWSS} index:

- – no diversification of $d_{CWSS} \leq 0.5$;
- – low diversification $0.5 < d_{CWSS} \leq 1.0$;
- – average diversification $1.0 < d_{CWSS} \leq 1.7$;
- – sufficient diversification $1.7 < d_{CWSS} \leq 2.3$;
- – satisfactory diversification $d_{CWSS} > 2.3$.

While evaluating the diversification, the shares of water intakes in the CWSS in the two-parameter method, the value of the intake diversification index $d_{SW}(Q)$ and the water volume in storage tanks $d_{SW}(V)$ were determined based on the Shannon and Weaver diversification model from the following formulas (Rak and Boryczko, 2016, 2018):

$$d_{SW}(Q) = -\sum_{j=1}^{m} (u_j) \cdot (\ln(u_j)), \tag{3}$$

$$d_{SW}(V) = -\sum_{k=1}^{o} (u_k) \cdot (\ln(u_k)), \tag{4}$$

where: $d_{SW}(Q)$ and $d_{SW}(V)$ are defined in Eq. 2, u_j – share of the j-th WPSs capacity in the total water demand of the CWSS, m – number of WPSs, u_k – share of the k-th storage tank's volume in the total volume of network water storage tanks, o – number of network water storage tanks.

The research method also included a safety analysis regarding the continuity of water supply to the consumer, using the Pielou dispersion index. For the interpretation of the degree of diversification, the degree of dispersion of water supply to the consumer was taken into account, which was determined using the equation 5 (Rak and Boryczko, 2018):

$$d_P = \frac{-\sum_{i=1}^{n}(ln(u_i))}{ln(n)}, \tag{5}$$

where: u_i – share of i-th elements in total the CWSS (0÷1), n – number of elements in the CWSS.

In the research process, a two-parametric evaluation of the dispersion of water supply was carried out using the Pielou index, based on the equation 6 (Rak and Boryczko, 2018):

$$d_{CWSS}(P) = d_P(Q) + \alpha \cdot d_P(V), \tag{6}$$

where: $d_{CWSS}(P)$ – two-parametric Pielou index of the dispersion of water supply in CWSS, $d_P(Q)$ – water resource dispersion index, according to equation 5, $d_p(V)$ – water volume dispersion index in storage tanks from equation 5, α – weight of the water volume allocation parameter in the CWSS.

The allocation parameter α is the ratio of the sum of the volumes of network water storage tanks to the sum of the production capacity of water intakes. The results were related to the categorisation and evaluation scale of water resources dispersion (Tab. 4).

Table 4. Categorization and assessment scale of the degree of dispersion of water resources (Rak and Boryczko, 2016)

Dispersion category	**Scale of the degree of dispersion**
No dispersion	$d_{CWSS}(P) = 0$
Low dispersion	$0 < d_{CWSS}(P) \leq 1.5$
Average dispersion	$1.5 < d_{CWSS}(P) \leq 1.8$
Sufficient dispersion	$1.8 < d_{CWSS}(P) \leq 2.1$
Satisfactory dispersion	$d_{CWSS}(P) > 2.1$

4. Results and Discussion

For the municipal system of collective water supply in the cityn of Głubczyce, a study of the degree of diversification of water supply to inhabitants was carried out using the Shannon-Weaver and Pielou two-parameter method. The individual shares were determined based on the daily production capacity of the water intakes and the volumes of the network storage water tanks.

4.1. Shannon-Weaver index for the city of Głubczyce

Q – four water intakes of MWSS of Głubczy, for which the shares in the total capacity are (according to Tab. 1):
– Powstańców: u_1 – 0.69;
– Mickiewicza: u_2 – 0.07;
– Kołłątaja: u_3 – 0.15;
– "Basen": u_4 – 0.09.

Based on the above shares of individual water intakes (from u_1 to u_4) in the total amount of daily produced water based on Eq. (3), the water intake diversification index was determined:

$$d_{SW}(\mathrm{Q}) = -(0.69\, ln(0.69) + \\ + 0.07\, ln(0.07) + 0.15\, ln(0.15) + 0.09 \mathrm{l}n(0.09)) = 0.943,$$

V – three water storage tanks, for which the shares in the total volume are:
– Powstańców: u_1 – 0.38;
– Powstańców: u_2 – 0.37;
– Kołłątaja: u_3 – 0.25.

Based on the above shares of the volume of individual storage tanks in the total amount of water accumulated in the MWSS, based on Eq. (4), the indicator of water volume diversification in network storage tanks was determined:

$$d_{SW}(V) = -(0.38 \ln(0.38) + 0.37 \ln(0.37) + 0.25 \ln(0.25)) = 1.082.$$

Consequently, the two-parameter water supply diversification Shannon and Weaver’s index in MWSS of Głubczyce city, determined from Eq. (2), achieved value:

$$d_{CWSS}(SW) = 0.943 + 1.082 = 2.025.$$

Based on the adopted scale of the two-parameter diversification Shannon and Weaver’s in the municipal water supply system of the Głubczyce city the diversification level of water resources was found to be sufficient.

4.2.Dispersion Pielou index for the city of Głubczyce

In the study process for the municipal water supply system in the city of Głubczyce, the dispersion index according to Pielou was also determined.

Q – four water intakes of MWSS of Głubczy city, of daily capacity are (according to Tab. 1):
– Powstańców: Q_1 – 2,088.44 m^3/day;
– Mickiewicza: Q_2 – 220.32 m^3/day;
– Kołłątaja: Q_3 – 462.83 m^3/day;
– "Basen": Q_4 – 258.99 m^3/day.

$$Q_P(Q) = \frac{-(0.69\,ln(0.69) + 0.07\,ln(0.07) + 0.15\,ln(0.15) + 0.09ln(0.09))}{ln\,4} = 0.680.$$

V – three water storage tanks with the individual volume are (according to Tab. 1):

– Powstańców: V1 – 1000 m^3;

– Powstańców: V2 – 1000 m^3;

– Kołłątaja: V3 – 680 m^3.

$$d_P(V) = \frac{-(0.38\,ln(0.38) + 0.37\,ln(0.37) + 0.25ln(0.25))}{ln\,3} = 0.985.$$

The calculation assumed a parameter weight of $\alpha = 0.88$ and the two-parameter diversification Pielou index of water supply in the WSS was determined according to Eq. (6):

$$d_{CWSS}(P) = 0.680 + 0.88 \cdot 0.985 = 1.547.$$

The dispersion category according to Pielou for the city of Głubczyce was defined as average dispersion. The result obtained means that upgrades or extensions to the system should be carried out in order to maintain continuity of operations in the event of an emergency. So far, the lack of events that were considered impossible, and thus apparent safety, should not dull the vigilance of the operators of municipal water supply systems, who should strive for a justifiably high diversification of water resources.

During the study, 4 scenarios of the occurrence of a crisis situation causing drinking water supply interruption in the city of Głubczyce was analysed:

– **Scenario I**: failure on the Powstańców intake;

– **Scenario II**: failure on the Kołłątaja intake;

– **Scenario III**: failure on the Mickiewicza intake;

– **Scenario IV**: failure on the "Basen" intake.

The results of the emergency analyses based on failures of individual supply systems, taking into account unit indicators of water demand, together with the average daily water consumption, are presented in Table 5.

The results of the analyses showed that in the event of an emergency at the Kołłątaja intake (scenario II), the Mickiewicza intake (scenario III) and the "Basen" intake (scenario IV), the continuity of water supply in MWSS of Głubczyce will be ensured by taking over the entire water production by the Powstańców intake.

In the event of a failure at the Powstańców water intake, due to the lack of possibility to fully cover the water supply by another active intakes, an additional analysis was carried out taking into account the required water demand, amounting to $Q_{req} = 360$ m^3/day. This scenario does not allow for the supply of water to the all inhabitants of the city, therefore, it takes into account the amount of unit water ddemand at the level of the required daily water consumption in an emergency (q_{req} = 30 L/Inh.·day). The analysis taking into account the unit indicator of the required water demand in the event of Scenario I is presented in Table 6.

Table 5. Analysis of the possibility of water supply depending on the occurrence of a given scenario of a crisis situation

Scenario	**Average daily water consumption [m^3/day]**	**Capacity of intake [m^3/day]**				**Balance [m^3/day]**	**Result**
		Powstańców	**Kołłątaja**	**Mickiewicza**	**"Basen"**		
Scenario I	1 617.01	0.00	720.00	220.00	258.00	-419.01	Need to use an alternative method of water supply
Scenario II		5.496.00	0.00	220.00	258.00	4 356.99	Water supply provided
Scenario III		5.496.00	720.00	0.00	258.00	4 856.99	Water supply provided
Scenario IV		5.496.00	720.00	220.0	0.00	4 818.99	Water supply provided

The results of the conducted analysis indicate that in the event of a failure at the Powstańców water intake, it is necessary to use water bottles, in the case of using the alternative Mickiewicza intake, in the amount of 4000 bottles per day and 4 water cisterns per day. However, if the alternative water intake "Basen" is used, it is necessary to use an additional 4 water cisterns per day. The analysis of the results showed that it is justified to purchase 4 cisterns for drinking water or sign a contract with a potential supplier of water cisterns for the duration of an emergency in the water intake.

Table 6. The results of analysis taking into account the unit indicator of the required water demand for Scenario I

	Required water demand Q_{req} [m^3/day]	**Alternative water intakes**	**Bottles [pcs]**	**Water cisterns [pcs]**
Scenario I	360	Mickiewicza intak (220 m^3/day)	4000	4
	360	"Basen" intake (258 m^3/day)	0	4

5. Conclusions

1. One of the elements of increasing the operational safety of the CWSS is the diversification of water supplies to the consumer. It ensures the continuity of water delivery to consumers in the event of emergencies on the water supply infrastructure. Diversification of the water intake system for supplying the population with water is becoming increasingly important in view of existing and worsening climate change. The effect of climate change is the observed dynamics of changes in surface and groundwater resources, which results in significant reductions in the available resources for supplying the population with water.

2. The conducted analysis of the continuity of water supply to the inhabitants of Głubczyce city showed that only in the event of a failure at the Powstańców water intake, alternative supplies of drinking water should be provided by means of water cisterns and drinking water bottles.

3. The analysis of the results showed that it is justified to purchase 4 drinking water cisterns or sign a contract with a potential supplier of cisterns for the duration of an emergency in the water intake.

4. The results of the analysis carried out according to the Pielou index ($d_{CWSS}(P)$ = 1.547) showed that it is necessary to modernize or expand the collective water supply system in order to maintain operation continuity in the event of an emergency.

References

1. ACM: Act on crisis management. Dz. U. 2007, no. 87, item 590 (in Polish).

2. ACWSSCSD: Act on collective water supply and collective sewage disposal. Dz. U. 2001, no.72, item 747 (in Polish).
3. DWD: Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption. Official Journal of the European Union L 435/1, Brussels 2021.
4. Kwietniewski, M., Rak, J.: *Niezawodność infrastruktury wodociągowej i kanalizacyjnej w Polsce (Reliability of water supply and sewage infrastructure in Polan)*, Polska Akademia Nauk, Komitet Inżynierii Lądowej i Wodnej, Instytut Podstawowych Problemów Techniki, Warszawa 2010 (in Polish).
5. Rak, J., Boryczko, K.: Dwuparametryczna metoda oceny dywersyfikacji zasobów wody w systemach zbiorowego zaopatrzenia w wodę z wykorzystaniem wskaźnika Shannon'a-Weaver'a (Two – Parameter Method for Assessing the Water Resources Diversification of Collective Water Supply Systems Using Shannon -Weaver Indicator). In Dymaczewski, Z., Jeż-Walkowiak, J. Urbaniak, A. (eds.): *Water Supply and Water Quality,* 345–369, Polskie Zrzeszenia Inżynierów i Techników Sanitarnych Oddział Wielkopolski, Poznań: 2016.
6. Rak, J., Boryczko, K.: Zmodyfikowana trójparametryczna metoda oceny dyspersji zaopatrzenia w wodę w systemach zbiorowego zaopatrzenia w wodę (Modificated three-parameter method of determining the degree of water resources dispersion in collective water supply systems). *Technologia wody,* 2 (58), 16–18, 2018 (in Polish).
7. RMH: Regulation of the Minister of Health on the quality of water intended for consumption. Dz. U. 2017, item 2294 (in Polish).
8. Szpak, D., Tchórzewska-Cieślak, B.: Analiza awaryjności sieci wodociągowej w aspekcie bezpieczeństwa funkcjonowania infrastruktury krytycznej (Assessment of the failure rate of water supply system in terms of safety of critical infrastructure). *Chemik,* 68(10), 862–864, 2014 (in Polish).
9. WLA: Water Law Act of 20 July 2017. Dz. U. 2017, item 1566 (in Polish).
10. WPF: Water pipe failure prediction and risk models: state-of-the-art review DOI:10.1139/cjce-2019-0481 (October, 2021).
11. Zimoch, I.: Zintegrowana metoda analizy niezawodności i bezpieczeństwa systemów zaopatrzenia w wodę (Integrated method of analysis of the reliability and safety of water supply systems). Monograph No. 323, Wydawnictwo Politechniki Śląskiej, Gliwice 2011 (in Polish).