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Water Supply and Wastewater Disposal

Designing, Construction, Operation and Monitoring

edited by
Henryk Sobczuk
Beata Kowalska

Lublin 2020

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Contents

The study of composition and physical and chemical properties of some natural waters of Georgia

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Abstract

The studies were carried out on the water *Gortubani* and *Naminauri* (Adigeni region), *Danisparauli*, *Dandalo, Makhinjauri* (Adjara). In the original water the following parameters were determined: the titrated acidity, the content of solids, sulfur, chlorides, hydrocarbons, nitrates, ammonium ions, pH, and electrical conductivity. It was found: the water conductivity increases in the following order: *Makhindjauri* (0.52) →*Naminauri* (0.78) → *Dandalo* (0.79) → *Gortubani* (0.98) → *Danisparauli* (3.45); increasing the amount of solids (%): *Makhinjauri* (0.1) → *Naminauri* (0.2) → *Dandalo* (0.4) = *Gurbubani* (0.4) → *Danisparauli* (0.5); increasing pH *Makhinjauri* (5.5) → *Naminauri* (6.0) → *Dandalo* (7.16) → *Gortubani* (7.18) → *Danisparauli* (7.5); the content of S^{-2} ions in the *Naminau* water is 20% higher than that in the *Makhinjauri* water; NO^{3-} and NH_4^+ ions are found in the water of *Dandalo* and *Gortubani*, and NH_4^+ ions in the water of *Dandalo* are 2.5 times as high as the norm, and in the water of *Gortubani* 5 times as low as the norm; the number of NO_3^- ions in *Dandalo* water is 25 times higher than normal, and in the *Naminauri* water is 75 times lower than normal; Cl^- ions are found in all waters, the content of SO_4^{-2} and HCO_3^- ions in the *Dandalo* and *Gortubani* waters is within the normal range; the *Dandalo* water is medium hard water (7.39 mg-equ./L), its hardness is 50% higher than normal.

It is likely that the difference in chemical and physico-chemical parameters of the studied sources is explained by the difference in their geographical location and, accordingly, the difference in soil composition.

Keywords: healing mineral water, ionic composition, solids content

1. Introduction

Sustainable development of every country determines the quality of human life and health, which depends on the state of the environment, the quality of food and drinking water (Mitryasova and Pohrebennyk, 2020; Mitryasova and Pohrebennyk, 2017; Pohrebennyk et al., 2019; Bejanidze et al., 2017; Bejanidze et al., 2018; Bejanidze et al., 2019).

Mineral waters are mineralized subterranean or surface waters which have specific physicochemical properties (temperature, radioactivity, etc.), are enriched with biologically active substances and have medicinal qualities. Water is medicinal (healing) if one liter of water contains at least 1 g of mineral substances, and treatment with such water is called balneotherapy. Water must be high-potent or have a high temperature (Pavlova et al., 2018; Pavlova et al., 2018).

The physical and chemical properties of water include: temperature, mineralization, ionic composition, dissolved gases, radioactivity, biologically active compounds, trace elements, etc.

By temperature, mineral waters are classified: very cold (up to 4°C); cold (4–20°C); warm (hypothermal) (20–37°C); hot (mesothermal) (37–42°C); very hot (hyperthermal) (> 42°C).

It was found that medicinal waters, when passing deep into the soil, dissolve its salts and get enriched with them, especially in those cases when the water is retained for some reason and becomes motionless (Lysenko, 2009).

Mineralization of water is determined by the content of the total amount of dissolved mineral substances. The following water groups are distinguished by mineralization: very low mineral content water (light mineral water) (2 g/l); low mineral content water (2–5 g/l); medium mineral content water (5–15 g/l); rich mineral content water (15–30 g/l); saturated (30–150 g/l); oversaturated (> 150 g/l).

Very low mineral content water and high-calcium water has diuretic properties, and this contributes to the removal of bacteria, mucus, sand and small stones from the body along with urine. According to the content of excess salts, mineral waters are divided into: hydrocarbonate, chloride, sulphate; combination of hydrocarbonate, chloride and sulfate waters; medicinal waters that contain biologically important ions: iron, arsenic, etc. (Raimer, 2016).

Gas containing mineral waters contain gases in a dissolved or free state. If the water contains carbon dioxide or hydrogen sulfide, it refers to a healing water for a specific purpose. Water may also contain nitrogen, methane and other gases, but currently such waters are underexplored and not fully understood. Mineral water may contain comparatively large amounts of the decay products of radioactive substances, such as radon and helium, and radioactive metals: uranium, thorium, and actinium. If the content of radon and helium is more than 1/10 of the volume of water, then the water becomes industrially significant.

On the territory of Georgia, more than two thousand springs have been discovered, including more than 730 springs of mineral waters, the daily volume of which is 130 million liters, of which a quarter is used for balneological purposes, more than half are used in heat supply and industrial bottling. Famous mineral healing waters include:

Borjomi – medicinal-table hydrocarbonate sodium mineral water of medium mineralization. The springs are in the Borjomi Gorge, in eastern Georgia. Unlike many other similar mineral waters, *Borjomi* does not have time to cool underground and comes to the surface warm (38–41°C), the water "undergoes" natural filtration and is enriched with 60 different minerals, which make its composition unique. The mineral water treats the digestive system, diseases of the gastrointestinal tract, biliary ducts, kidneys and much more.

Likani – a unique natural medicinal-table water, saturated with minerals, contains a mineral-ion complex – a combination of magnesium and calcium hydrocarbonates. *Likani* is richly saturated with natural gas, therefore it perfectly quenches thirst. Carbon dioxide helps lift mineral water from a depth of 1,500 meters and gives it a light taste. The water springs are located in the Borjomi Valley at an altitude of 810 meters above sea level.

Nabeglavi – healing-table, carbonate-hydrocarbonate, sodium-calcium sparkling water**.** The spring is located at an altitude of 475 meters above sea level**.** By its healing properties it is not inferior to the famous *Borjomi* mineral water, it is recommended both for balneology and drinking, regular use as table water helps to cleanse the body of harmful substances and enrich it with essential minerals**.** The increased content of magnesium ion has a beneficial effect on the cardiovascular and nervous systems. A small chlorine content significantly increases the therapeutic effect of water, and an increased amount of sulfates is important for the treatment of diseases of the gastrointestinal tract. Due to the unique complex of minerals that make up *Nabeglavi,* the mineral water acts as an "inside shower" and perfectly cleanses the body. In addition, it enhances immune system and is effective in the prevention and treatment of diseases of the digestive system and metabolism, also contributes to the removal of waste.

Sairme – natural table, healing-table and healing mineral waters which are formed in the deep zones of the earth's crust, where they are saturated with natural carbon dioxide and come to the surface in the form of natural ascending (nongravity) spring. They are located in the west of Georgia, at an altitude of 950 meters above sea level. The springs come from several sources and differ from each other in chemical composition and healing properties.

Bakuriani – natural very low mineral content water, saturated with mineral complexes, regulates the body's water balance. Frequent use of this water activates the physiological state of a person. The springs are in the east of Georgia. This water is characterized by a minimal concentration of calcium, potassium, sodium and magnesium, and contains a small amount of fluorine and iodine ions. It is recommended for use in baby food, and, with its unique composition, it is the best for people leading an active lifestyle.

Healing water *Lugela* is unique not only in Georgia, but throughout the world. This is calcium chloride 9% mineral water, transparent, odorless, with a slightly bitter taste, which does not freeze even at the lowest possible temperature. The springs of the *Lugela* mineral waters are located in Western Georgia. It is a healing calcium chloride water that treats diseases of the skeletal system and joints, allergies, nephritis, stomatitis and bleeding.

Mineral water *Zvare* is rich in iodine, it is used to treat the digestive system, chronic gastritis, pancreatitis, liver and biliary tract diseases, metabolic disorders and to balance acidity. The springs are located in Imereti (Western Georgia), at an altitude of 800 m above sea level.

Living water – this is the name of the thermal radon mineral waters of Tskhaltubo located at an altitude of 100 meters above sea level. Biologically active trace elements were found in the mineral springs: iodine, bromine, manganese, lithium, boron, zinc, strontium, copper which play an important role in the life of the body. The physical and chemical properties of water are unique: it is warm (35°C), light, clean and odorless. The mineral springs were mainly used for bathing and inhalation, but in recent years natural radon waters have been increasingly used for drinking treatment. Radon therapy is used for diseases of the cardiovascular system, musculoskeletal system, digestive organs, central and peripheral nervous systems, skin diseases, metabolic disorders (Romanova, 2007; Lysenko, 2009).

Mitarbi mineral water springs are located in the gorge of the river Mitarbwater. The mineral water is used to treat chronic gastritis, chronic colitis, stomach ulcer and duodenal ulcer, chronic diseases of the biliary and urinary tract, metabolic disorders, chronic pancreatitis.

Bahmaro is fresh water with a very low salinity, the chemical composition of which is dominated by magnesium and calcium hydrocarbonates, it is saturated with oxygen and has an unusually mild taste. The water is approved and recommended for use in baby food.

Sno is natural underground water which is rich in all necessary elements. This clear and tasty water is generated on the southern slopes of the central part of the Greater Caucasus Mountain Range at an altitude of 1.700 meters above sea level.

Currently, only 5 brands of mineral water are produced on an industrial scale: *Borjomi, Nabeglavi, Sairme, Likani, and Bakuriani.* However, despite the existence of such an abundance of produced and used mineral waters, the population spontaneously uses unofficial mineral springs with an unknown composition and unknown therapeutic properties to treat various types of diseases, which, naturally, poses a great threat to human health.

The objective of the work is to identify the chemical composition and physicochemical properties of natural mineral waters which are most often used by the population for drinking and for curative purposes.

2. Material and Methods

The studies were conducted on the natural waters of Georgia: *Gortubani* and *Naminauri* (Adigeni region), *Danisparauli, Dandalo* and *Makhinjauri* (Adjara), which exhibit medicinal properties: Sulfur-containing waters: *Dandalo, Makhinjauri* – treatment of fungal diseases (mycoses); *Gortubani, Naminauri, Danisparauli* – treatment of joints and diseases of the stomach.

The following water indicators were determined: titratable acidity (titrametric method), hardness (trilonometric method), solids content (refractometric method), sulfates (HACH-Method 8051), chlorides (argentometric method), hydrocarbonates (titrametric method), nitrates (HACH-Method LCK 339), ammonium salts (HACH-Method LCK 304) pH (ISO 10523: 2008) and electrical conductivity (conductometric method).

3. Results and Discussion

In the medicinal waters, the solids content and electrical conductivity were determined. The obtained data are presented in Fig. 1–4. *It was found* that the *Danisparauli* water has the highest electrical conductivity, while the lowest electrical conductivity was recorded for the *Makhinjauri* water (Fig. 1), which indicates a high salt content in the *Danisparauli* water*:* indeed, its salt content is 7 times higher than in the water *Makhinjauri,* 3.5 times higher – than in the water *Gortubani,* and 3 times higher than in the waters *Dandalo* and *Naminauri.*

By increasing the electrical conductivity (sm/cm), the medicinal waters are arranged in the following order (Fig.1):

Makhinjauri (0.52) → Naminauri (0.78) → Dandalo (0.79) → Gortubani (0.98) → Danisparauli (3.45).

The amount of solids, as well as electrical conductivity, is the most in the *Danisparauli* water - the least in the *Makhinjauri* water (Fig. 1). According to the increase in the amount of solids (%), the medicinal waters are arranged in the following order:

Makhinjauri (0.1) →Naminauri (0.2) → Dandalo (0.4) =Gortubani (0.4) → Danisparauli (0.5).

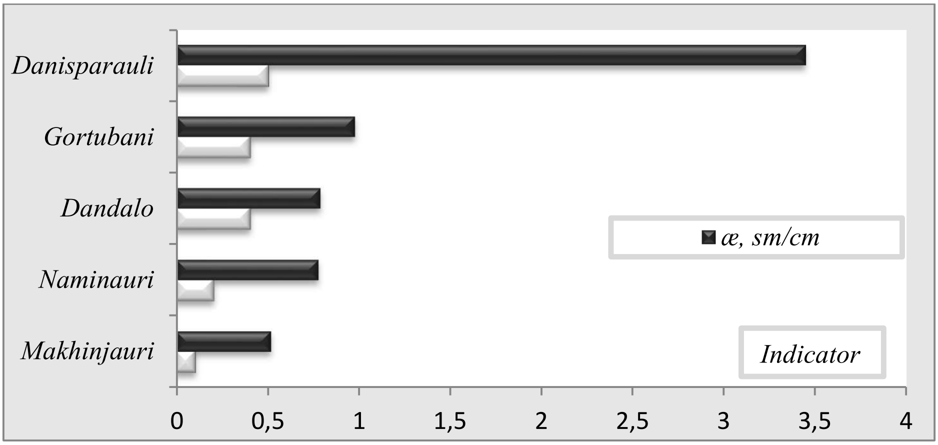

Fig. 1. Dry substances content and electrical conductivity of medicinal waters

When comparing the medicinal waters of different regions, but for the same purpose, it was found:

– Sulfur-containing waters (Dandalo, Makhinjauri), which are used by the population to treat fungal diseases: electrical conductivity, that is, the salt content of Dandalo water (Fig. 2), is 2 times and the amount of solids is 5 times higher than in water Makhinjauri;
– The waters of the balnearis (curative springs) of the Adigeni region (Gortubani and Naminauri) are used by the population for the treatment of joints and diseases of the gastrointestinal tract, as well as the water Gortubani for the treatment of ophthalmic diseases.

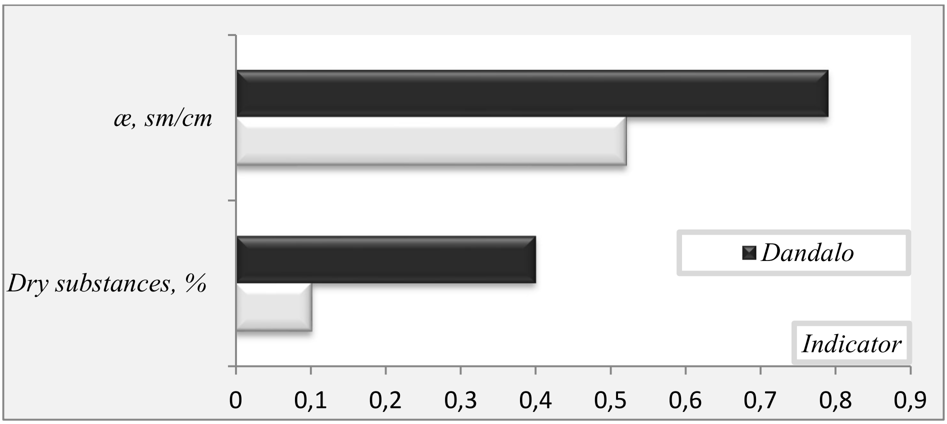

Fig. 2. Dry substances content and electrical conductivity of sulfur-containing waters

It was found that the electrical conductivity is 2.5 times, and the amount of solids is 4 times higher in the *Gortubani* water (Fig. 3).

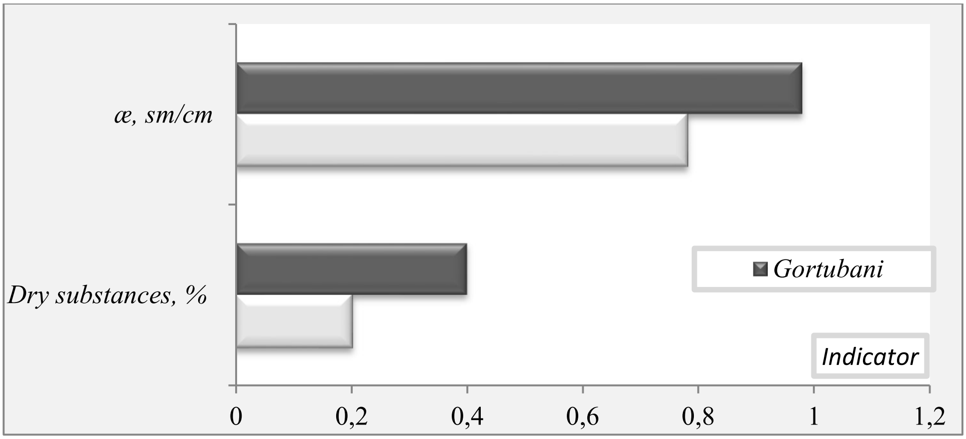

Fig. 3. Dry substances content and electrical conductivity of medicinal waters of Adigeni

From these data it follows that this water is quite salty, which means it cannot be used to treat joints as salt disagee with them. On the other hand, it can be used to treat ophthalmic diseases, in particular, eye inflammation, since saline solutions are quite strong antiseptics. But the question arises how justified is the use of saline solutions for this purpose.

Figure 4 compares the healing waters of the coastal strip (*Makhinjauri*) and mountain range (*Dandalo* and *Danisparauli*) of Georgia region Adjara.

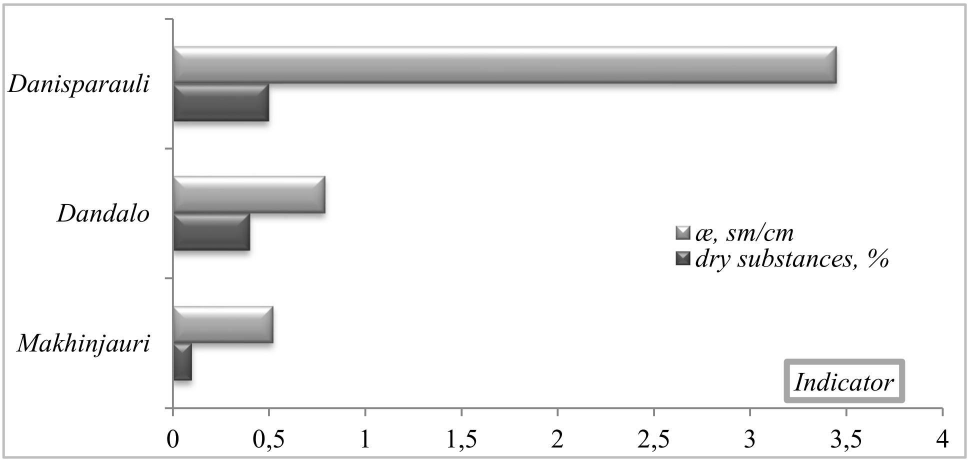

Fig. 4. Dry substances content and electrical conductivity of medicinal waters of Ajara

It was found: electrical conductivity and solids content are the highest in the mountain healing water *Danisparauli.*

An important indicator of the use of water as a medicinal one is acidity, i.e. the pH of the water. The data obtained are presented in Fig. 5–8.

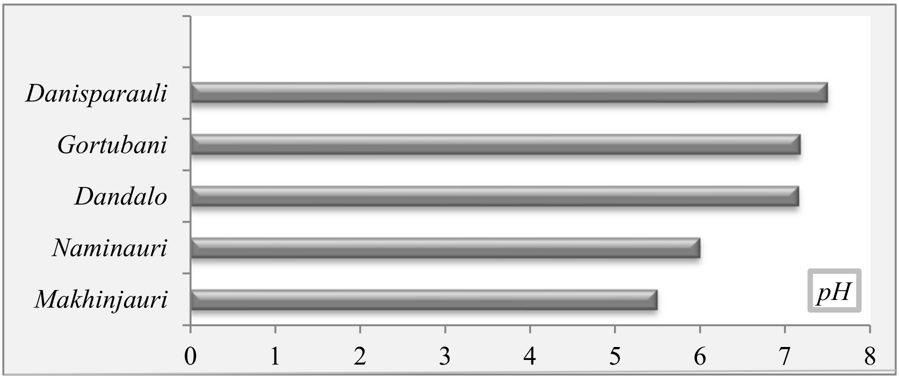

Fig. 5. pH of medicinal waters

It was found: the lowest acidity, i.e. a high pH > 7, is in the water *Danisparauli* which has a slightly alkaline reaction, the rest of the waters have an almost neutral medium and are arranged in the following order of increasing pH (Fig. 5):

Makhinjauri (5.5) → Naminauri (6.0) → Dandalo (7.16) → Gortubani (7.18) → Danisparauli (7.5).

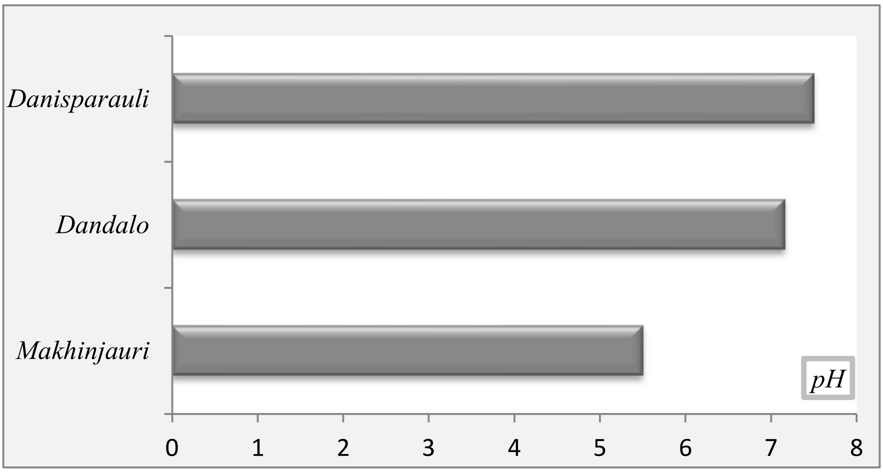

Fig. 6. pH of Adjarian medicinal waters

A comparison of the pH values of the medicinal waters of Adjara – *Makhinjauri, Danisparauli* and *Dandalo* (Fig. 6) shows that the waters *Danisparauli* and *Dandalo* have a slightly alkaline reaction and can be used to reduce stomach acidity and treat diseases of gastrointestinal tract.

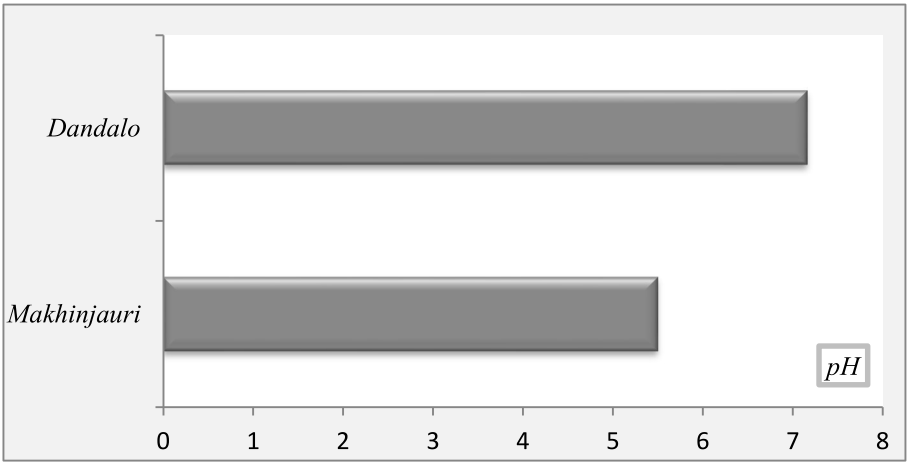

Fig. 7. pH of sulfur-containing waters.

As for the sulfur-containing waters of Adjara – *Makhinjauri* and *Dandalo,* which the population use to treat mycoses, the pH of the healing water *Makhinjauri* is lower than that of the water *Dandalo* (Fig. 7).

It is known that for the effective treatment of fungal diseases – mycoses, drugs are used that have an acidic and, in some cases, even a strongly acidic medium. Based on the data presented, for the treatment of mycoses, the *Makhinjauri* water will be more effective than the *Dandalo* water.

Figure 8 compares the pH values obtained for the medicinal waters of the Adigeni region*: Naminauri* and *Gortubani,* the *Gortubani* water has a higher pH, the medium is slightly alkaline, therefore it can be used to reduce the acidity of the stomach.

Then, the content of S^{-2} ions was determined in sulfur-containing waters (Fig. 9). *It was found:* the content of sulfide (S^{-2}) ions in the *Naminauri* water is 20% higher than in the *Makhinjauri* water. As follows from the above data, in the treatment of mycoses, a greater therapeutic effect will be obtained by using the *Naminauri* water.

Figure 10 shows data on the contents of Cl^-, NO_3^-, and NH_4^+ ions in the medicinal waters.

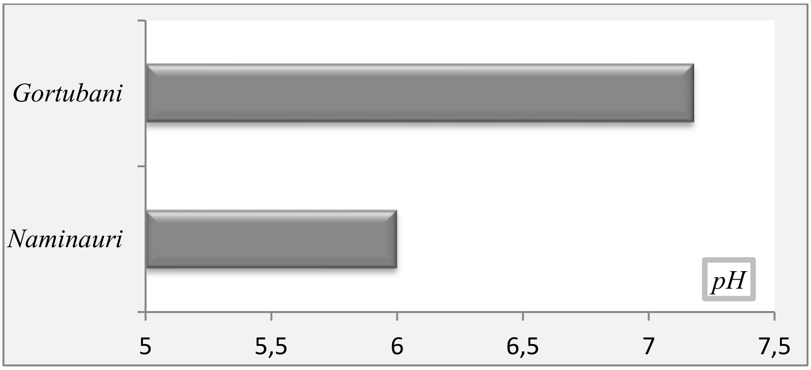

Fig. 8. pH of medicinal waters of Adigeni

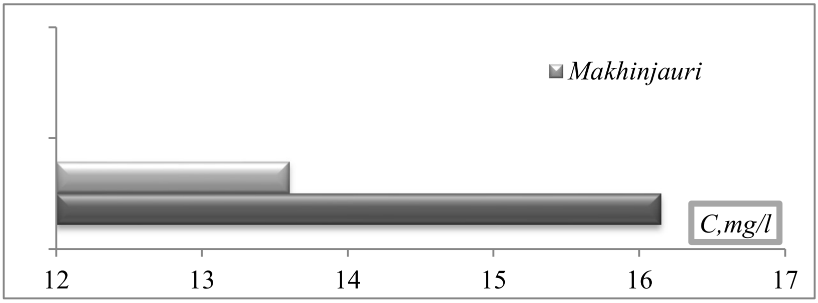

Fig. 9. Sulfide ion content of medicinal waters

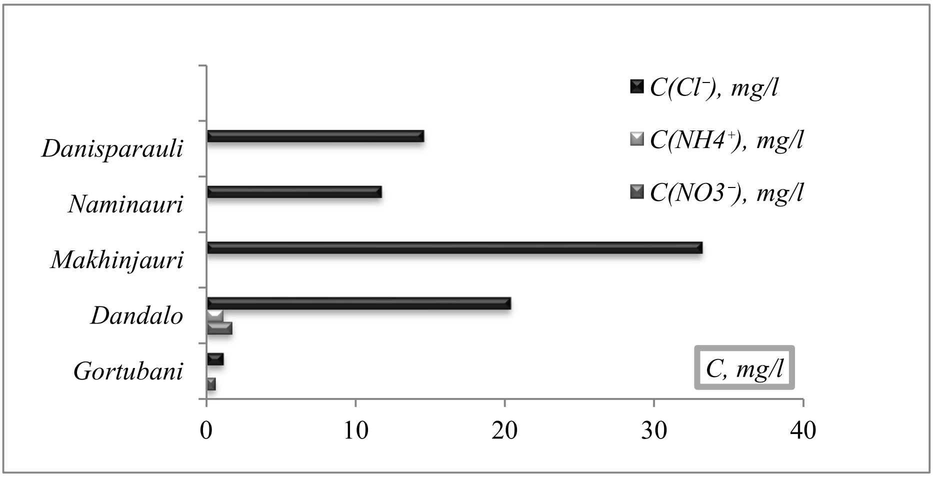

Fig.10. Content of chlorides, nitrates and ammonium in the medicinal waters

It was found: NO_3^- and NH_4^+ ions are present only in the *Gortubani and Dandalo* waters; moreover, in the *Dandalo* water, the content of NO_3^- ions (1.17 mg/l) is 11.4 times higher than in the *Gortubani* water (0.102 mg/l). The norm for the content of NH_4^+ ions in water is 0.5 mg/l. It was found that the NH_4^+ ions content in the *Dandalo* water is 2.5 times higher, and their content in the *Gortubani* water, on the contrary, is 5 times lower than normal.

The content of NO_3^- ions in the *Dandalo* water is 3 times higher (1.76) than in the *Gortubani* water (0.637 mg/l).

The norm for the content of NO_3^- ions in water is 50 mg/l. *It was found:* the NO_3^- ions content in the *Dandalo* water is 25 times, and in the *Gortubani* water is 75 times lower than normal. Cl^- ions are found in all the medicinal waters, and, in order of increasing their content, the waters are arranged as follows:

Gortubani (1.2) → Naminauri (11.8) → Danisparauli (14.6) → Dandalo (21) → Makhinjauri (33.2).

As follows from the above data, the most chlorinated is the *Makhinjauri* water, which corresponds to the identified pH value and confirms that this water can be an effective in treatment of fungal diseases. The chloride content norm is 250 mg/l. The chloride content in all the waters is 1–6 times lower than normal.

The content of sulfate SO_4^{-2} and hydrocarbonate HCO_3^- ions was determined in the medicinal waters (Fig. 11).

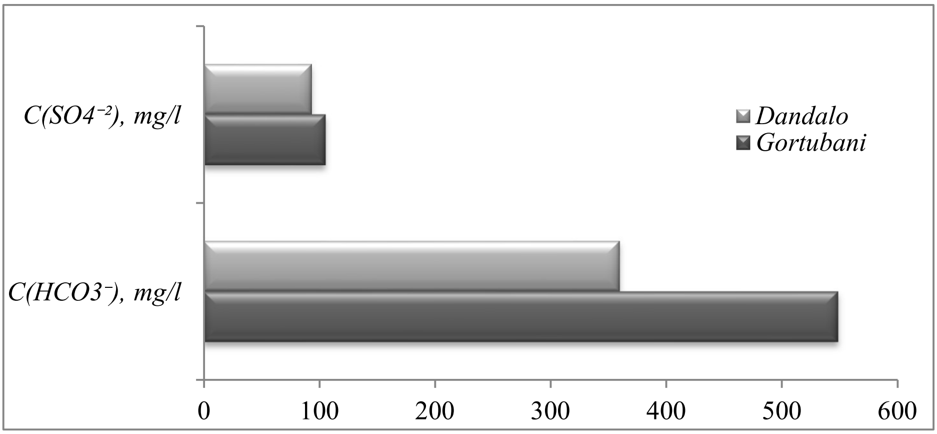

Fig. 11. Content of sulfates and bicarbonates in the medicinal waters

It was found: the content of SO_4^{-2} and HCO_3^- ions in the *Gortubani* water is higher than in the *Dandalo* water, but they are within the normal range. The norm of sulfates is 500 mg/l, and that of hydrocarbonates is 30–400 mg/l.

One of the main indicators of water is hardness (Fig.12). The norm for water hardness is 7–10 mg-equ./l.

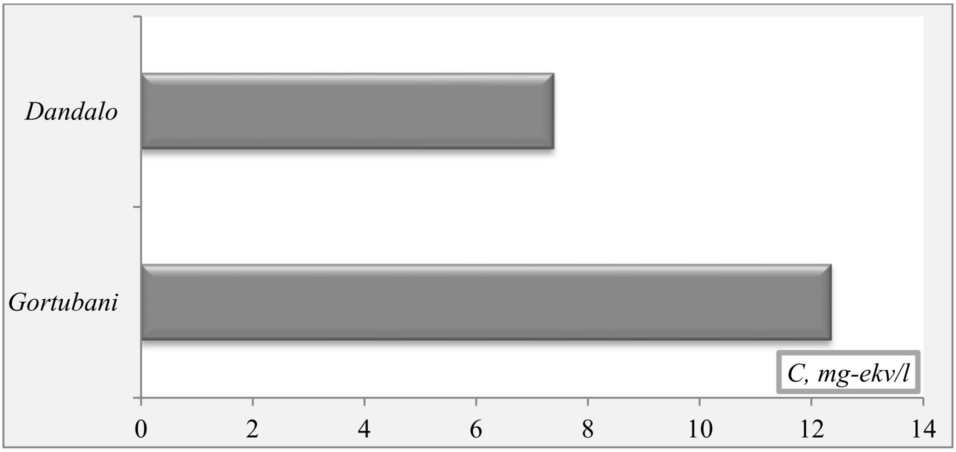

Fig. 12. Hardness of the medicinal waters

From the above data it follows that the hardness of the *Dandalo* water is within the established norms and amounts to 7.39 mg-equ./l, *Gortubani* is water of medium hardness, its hardness is 50% higher than normal. According to this indicator, the *Gortubani* water is an effective remedy for solving the problems of the gastrointestinal tract – calcium hydrocarbonate ($Ca(HCO_3)_2$) and magnesium hydrocarbonate ($Mg\ (HCO_3)_2$) reduce acidity.

The results presented in the diagrams are obtained by statistical data processing and are averaged.

4. Conclusion

The studies were conducted on the natural waters of Georgia: *Gortubani* and *Naminauri (*Adigeni region*), Danisparauli, Dandalo* and *Makhinjauri* (Adjara region) which exhibit medicinal properties.

The following water indicators were determined: titratable acidity, electrical conductivity, hardness, the content of solids, sulfates, chlorides, hydrocarbonates, nitrates, ammonium salts and etc. *It was found:* the water *Danisparauli* has the highest electrical conductivity and the lowest one is recorded for the *Makhinjauri* water, according to the increase in the electrical conductivity (sm/cm), the medicinal waters are arranged in the following order:

Makhinjauri (0.52) → Naminauri (0.78) → Dandalo (0.79) → Gortubani (0.98) → Danisparauli (3.45)

The salt content in the *Danisparauli* water is 7 times higher than in the *Makhinjauri* water, 3.5 times higher than in the *Gortubani* water and 3 times higher than in the *Dandalo* and *Naminauri* waters; The *Danisparauli* water cannot be used to treat joints and is a controversial issue about its use for the treatment of ophthalmic diseases.

The amount of solids, as well as electrical conductivity, is the highest in the *Danisparauli* water and the least in the *Makhinjauri* water. According to an increase in the amount of solids (%), the healing waters are arranged in the following order: *Makhinjauri (0.1) → Naminauri (0.2) → Dandalo (0.4) → Gortubani (0.4) → Danisparauli (0.5).*

The lowest acidity, *i.e.* a high pH > 7, is in the water *Danisparauli* which has a slightly alkaline reaction, the rest of the waters have a practically neutral medium and according to an increase in pH are arranged in the following order:

Makhinjauri (5.5) → Naminauri (6.0) → Dandalo (7.16) → Gortubani (7.18) → Danisparauli (7.5).

From a comparison of the pH values of the medicinal waters of Adjara – –*Makhinjauri, Danisparauli,* and *Dandalo*, it follows that the waters *Danisparauli* and Dandalo have a slightly alkaline reaction and can be used to reduce the acidity of the stomach and treat diseases of the gastrointestinal tract. The *Gortubani* water has a higher pH, the medium is slightly alkaline, therefore it can be used to reduce the acidity of the stomach.

The pH of the sulfur-containing medicinal water *Makhinjauri* is lower than that of the water *Dandalo,* that is, for the treatment of mycoses, the water *Makhinjauri* will be more effective than the water *Dandalo.*

The content of sulfide ions in the *Naminauri* water is 20% higher than in the *Makhinjauri* water and its use can produce a greater therapeutic effect in the treatment of mycoses.

It was found that NO_3^- and NH_4^+ ions are present only in the *Gortubani* and *Dandalo* waters, and in the *Dandalo* water, the content of NO_3^- ions (1.17 mg/l) is 11.4 times higher than in the *Gortubani* water (0.102 mg/l). The *Dandalo* water contains NO_3^- ions 25 times, and the *Gortubani* water 75 times, lower than normal.

It was found that the NH_4^+ ion content in the *Dandalo* water is 2.5 times higher, and in the *Gortubani* water, on the contrary, it is 5 times lower than normal.

Cl^- ions were found in all the medicinal waters, the chloride content in all the waters is 1–6 times lower than normal, and according to an increase in their content, the waters are arranged in an order:

Gortubani (1.2) → Naminauri (11.8) → Danisparauli (14.6) → Dandalo (21) → Makhinjauri (33.2).

The most chlorinated water – Makhinjauri, can be an effective treatment for fungal diseases.

The content of SO_4^{-2} and HCO_3^- ions in the *Gortubani* water is higher than in the *Dandalo* water, but they are within the normal range.

The hardness of the *Dandalo* water is within the established norms and amounts to 7.39 mg-equ./l. *Gortubani* is moderately hard water, its hardness is

50% higher than normal. According to this indicator, the *Gortubani* water can be an effective means for solving problems of the gastrointestinal tract.

It is likely that the difference in chemical and physico-chemical parameters of the studied sources is explained by the difference in their geographical location and, accordingly, the difference in soil composition, but this issue was not the subject of our study.

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Coefficient of flow rate for outlet cylindrical nozzles with lateral inflow installed in distributive pipelines

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Abstract

Results of experimental determination of values of the coefficient μ of flow rate of a nozzle with $(d/D)^2 = (8.99/26.01) = 0.119$ and $(d/D)^2 = (8.02/20.18) = 0.158$, where $(d/D)^2$ is the ratio of cross-section areas of the nozzles and of the distributive pipeline (DP); d is the inner diameter of the nozzle; D is the inner diameter of the DP. The butts of cylindrical nozzles near their lateral orthogonal inlets were blinded. The investigated nozzle was installed in the wall of a segment of DP with the possibility of rotation about its longitudinal axis. The angles β were assigned the following values: 0°, 45°, 90°, 135° and 180°.

It has been found that the value of the coefficient μ essentially depends on the angle β, on the Reynold's criterion $Re_d = v \cdot d/\nu$, and on the ratio $(d/D)^2$ of the areas. The greatest values of d the coefficient μ of the nozzles were obtained for $\beta = 0°$ for the both investigated values of $(d/D)^2$. When $Re_d = 2 \cdot 10^4$, the least throughput of nozzles, i.e. the least values of μ, for $(d/D)^2 = 0.119$ was obtained when $\beta = 135°$; and when $(d/D)^2 = 0.158$ for $\beta = 90°$. For a nozzle with $(d/D)^2 = 0.119$, with the increase in the angle β from: 0° to 135°, the value of the coefficient μ decreased by 14.6%. For a nozzle with $(d/D)^2 = 0.158$, with the increase in the angle β from: 0° to 90°, the value of the coefficient μ decreased by 12.3%.

Basing on the obtained results, it can be expected that for a long DP, which contains many nozzles, by variation of the angle β essential decrease in non-uniformity of water dispensation along the path can be achieved.

Keywords: outlet cylindrical nozzle with lateral inlet, coefficient of flow rate of inlet nozzle

1. Introduction

Pressure distributive pipelines (DPs) are important elements in different branches of engineering. Examples of such spheres of application are water supply; water removal (tubular distributing systems of purifying structures, fire-fighting systems); power industry (cooling of circulating waters of nuclear and thermal power plants, in sprinkle pools and in cooling houses); irrigation; ventilation (tide systems); agriculture aviation; oil, oil-chemical and chemical industries; and in other fields of application.

Because of hydraulic losses of energy, the head in long PDs deceases along the path. This causes non-uniformity of fluid dispensation along the path. The dispensation decreases in the direction of the stream. In overwhelming majority of industrial processes, the problem of ensuring the uniform fluid dispensation along the whole length of DP arises. The search for ways of reduction of the non-uniformity of operation of DP continues. The development of techniques of calculation of DPs proceeds. Widespread application of enforced flows with variable flow rate along the path under the absence of reliable techniques of calculating them indicates the urgency of this problem.

2. Literature review

There are described different ways of reduction of non-uniformity of fluid dispensation along a pressure distributive pipeline. Among them, there are reductions of the distances between nozzles along DP, increase in areas of outlet holes when approaching to the end of DP. It is considered that the speed v of outflow of jets out of a DP is proportional to the speed V of the main stream inside the DP (Idelchyk, 1992; Zakharchuk et al., 2006; Shvets et al., 1998). Therefore, to ensure a constant speed V along a DP, the reduction of its diameter in the directions of flow is suggested.

Hassan et al. (2014) have found that out of a tapered (conical cross-section) DP the non-uniformity of water dispensation along the path is less than that out of a cylindrical DP. The least uniformity of water dispensation was achieved in the case when the initial diameter D_{beg} twice greater diameter D_{end}. Further increase in the ratio D_{beg}/D_{end} caused irreversible increase in non-uniformity of water dispensation along the pass.

Lee et al. (2012) experimentally investigated the influence of thickness t of the wall of a DP of rectangular cross-section upon the non- uniformity of dispensation of water from it along the path. With the increase in the thickness t of the wall of a perforated DP from 2 to 10 mm, the coefficient ε of contraction of the jet at the outlet increased. The value of the coefficient ε also increased with the decrease in the total area $\Sigma\omega_{or}$ of all the outlet holes positioned in the wall of the DP. With the decrease in the value of $\Sigma\omega_{or}$, the non-uniformity of water dispensation out of DP along the path decreases; and the value of the coefficient μ of water rate through the outlet hole (orifice) stabilizes in the range of 0,66–0,68. The coefficient ε of contraction of the jet at its outlet from the hole (orifice) and the coefficient φ_{or} of the jet speed determine the value of the coefficient of fluid flow rate through a hole (orifice), because $\mu=\varepsilon\cdot\varphi$. Thus, with the increase in thickness t of the wale of DP and with the decrease in value of the ratio $\Sigma\omega_{or}/\Omega$ of the areas, the throughput of outlet holes (orifices) which are positioned in the wall of DP increases, here Ω is the cross-section area of the DP. It is known that it is not expedient to regulate the fluid dispensation out of DP along the path by means of the increase of thickness of its wall. It is sufficient to attach nozzles of the appropriate length to the outlet holes (orifices).

Abubakar (1977) investigated the influence of static pressure in an irrigation pipeline upon the coefficient μ of water flow rate out of orifices (holes) installed in the wall of the pipeline. He theoretically established that when the water is flowing through an orifice (hole) the value of the coefficient μ depends on the angle β: $\mu=f(\beta)$. The angle β, in its turn, was a function of the speed of the water stream and on pressure in the funnel of the outlet orifice.

Wang et al. (2011), Zeng et al. (2012), Kim et al. (2013) experimentally investigated the influence of geometrical parameters of branching of a jet from a DP in a heat exchanger on the non-uniformity of working fluid dispensation from the DP along the path.

Tapered pipelines or DPs with various distances between outlet holes (orifices) or with various areas of holes along the DP are implement in manufacturing of DPs. When the regime of operation of installed DPs changes, the nominal (design) regime of fluid dispensation becomes disturbed. The design of such DPs does not provide for a regulation of their geometric parameters in the course of operation.

It is possible to reduce the non-uniformity of fluid dispensation out of DP without any change in geometric characteristics of the DP. For this purpose, it is recommended to introduce very small amounts of polymer admixtures of chain-shaped molecules (Povkh et al. 1986, 1989). The non-uniformity of operation essentially decreases in such a case (Cherniuk et al. 2006).

Cherniuk and Ivaniv (2017) have suggested a way of regulation of fluid dispensation out of an equipped with cylindric nozzles with lateral orthogonal inflow of jet (Fig. 1) pressure DP along the path.

Cherniuk et al. (2020) have found that values of the coefficient μ of flow rate of such nozzles installed in the wall of DP change with regulation of the value of the angle β between the vector $\boldsymbol{V}$ of stream flow inside the DP and the vector $\boldsymbol{v}$ of the outflowing jet flow (Fig. 2).

The aim of this work is to experimentally establish values of the coefficient μ of flow rate of nozzles with lateral fluid inflow depending on the angle β in order to regulate the fluid dispensation along pressure pipelines.

3. Technique of experiment

An experimental set-up with gravitational water supply was applied. The operating heads on the nozzles were varied from 0.01 to 16.70 m. The butts of the cylindrical nozzles near their lateral inlets were blinded (Fig. 1).

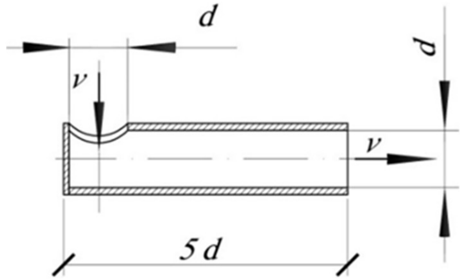

Fig. 1. Schematic diagram of cylindrical nozzle with orthogonal lateral inflow

We have investigated nozzles whose inner diameter was 8.99 and 8.02 mm. The former was installed in the wall of a DP whose diameter D = 26.01 mm, and the latter in a DP with D = 20.18 mm. The ratios $(d/D)^2$ of the areas of cross-sections of nozzles to those of DPs were equal to 0.119 and 0.158. The nozzle was installed in the wall of a 6D-long segment of DP with the possibility of its rotation about its longitudinal axis (Fig. 2). The angles β were assigned the following values: 0°, 45°, 90°, 135° and 180°.

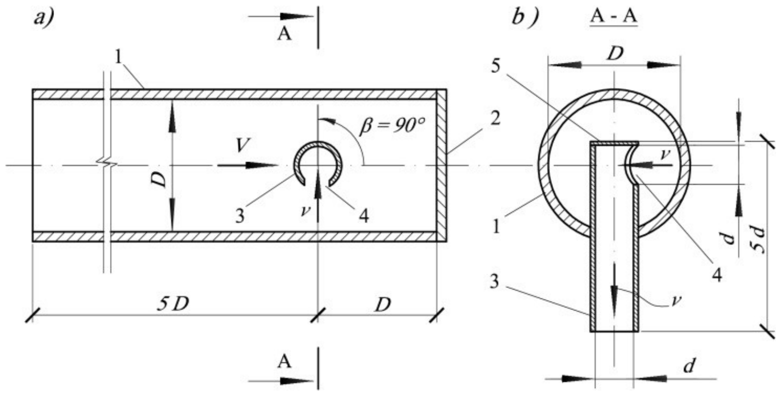

Fig. 2. Schematic diagram of outlet cylindrical nozzle with orthogonal lateral inflow for β = 90° positioned at the end of DP: a) longitudinal section; b) section A-A; 1 – wall of DP; 2 – butt blind of DP; 3 – nozzle; 4 – inlet hole of nozzle; 5 – blind near inlet butt of nozzle

To simulate such conditions of water inflow into cylindrical nozzles as those in the pressure DP, the inlet part *d* of a nozzle was inserted into the pipe segment *D* with one butt blind; in this case, the pipe-segment represented the terminal segment of the DP (Fig. 2). In fact, it was the operation of the last nozzle of the DP that was investigation.

4. Mathematical processing of experimental data

We determined the flow rate of the water which was flowing out of the nozzle according to the formula:

$$Q = \frac{W}{t} \tag{1}$$

where W is the volume of water which entered the gauge tank for the time t.

The coefficient μ of the flow rate of the nozzle was calculated according to the formula:

$$Q = \mu\omega\sqrt{2gH} \tag{2}$$

where Q is the flow rate of water through the nozzle, m^3/s; ω is the free cross-section area of the jet in the inlet hole end in body of the nozzle, m^2; g is the acceleration due to gravity = 9.81 m/s^2; H is the head of water at the inlet of the nozzle, m.

The kinematic viscosity ν of water we determined depending on the temperature of water, m^2/s.

The relative change in the coefficient μ of flow rate of water through the nozzle was determined according to the formula:

$$\Psi = \frac{\mu_{i^\circ} - \mu_{0^\circ}}{\mu_{0^\circ}} \cdot 100\% \tag{3}$$

where μ_{0° and μ_{i° are the coefficients of flow rate of the nozzle for the angles $\beta = 0°$ and $\beta = i°$, respectively; here $i° = 45°; 90°; 135°$ and $180°$.

5. Results of experimental investigations

In this work, result of experimental determination of the values of the coefficient μ of flow rate of nozzles for $(d/D)^2 = 0.119$ and 0.158 when $\beta = 0°, 45°, 90°, 135°$ and $180°$ are presented. The values of the coefficient μ essentially depend on the angle β, on the Reynolds` criterion $Re_d = vd/\nu$ (Fig. 3), and on the ratio $(d/D)^2$ of areas (Fig. 4).

From Fig. 3 and Fig. 4, it can be seen that the greatest throughput of cylindrical nozzles with lateral orthogonal inflow of water jet into a nozzle is obtained for $\beta = 0°$.

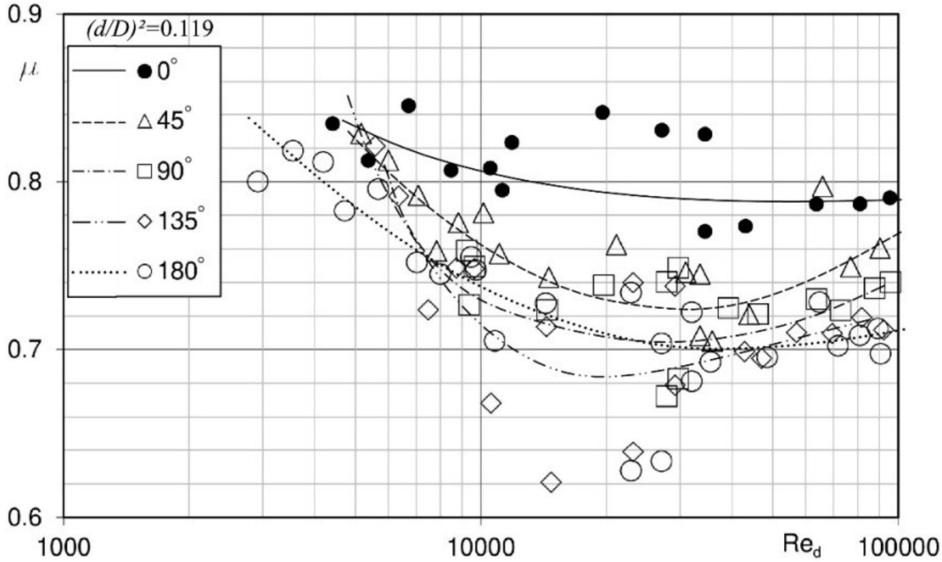

Fig. 3. Dependence $\mu = f(Re, \beta)$ for nozzles whose $(d/D)^2 = 0.119$ for different values of β; $Re_d = vd/\nu$ – Reynolds' criterion for water jet in nozzle

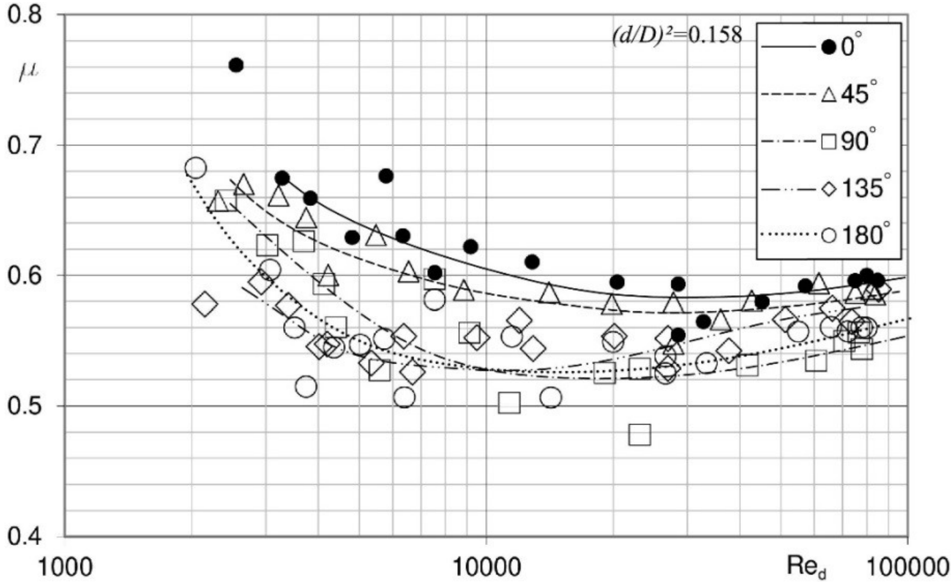

Fig. 4. Dependence $\mu = f(Re, \beta)$ for nozzles whose $(d/D)^2 = 0.158$ for different values of β; $Re_d = vd/\nu$ – Reynolds' criterion for water jet in nozzle

The value of the coefficient μ decreased with the increase in the angle β from 0° to 135° for $(d/D)^2$ = 0.119 (Fig. 5). Further, with the increase in the β the value of μ increased. For the nozzle with $(d/D)^2$ = 0.158, the least value μ, i.e. its least throughput, has been obtained for β = 90°. For the nozzle with $(d/D)^2$ = 0.119, with the increase in the angle β from 0° to 135° the value of the coefficient μ decreased by 14.6%. For the nozzle with $(d/D)^2$ = 0.158, with the increase in the angle β from 0° to 90° the value of the coefficient μ decreased by 12.3%.

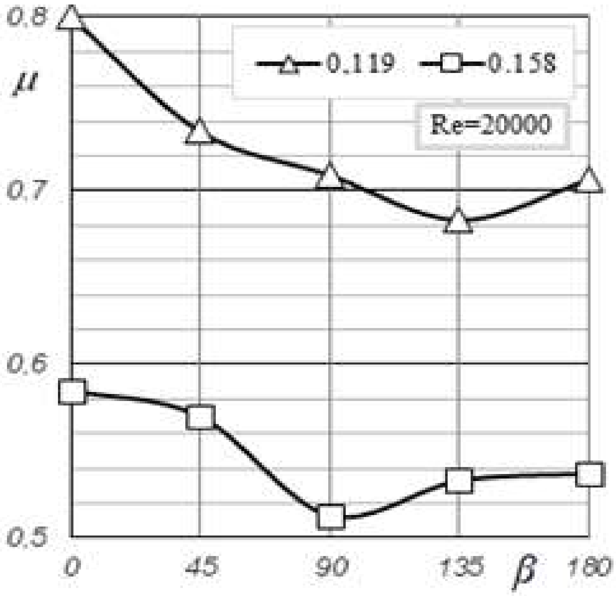

Fig. 5. Dependence of coefficient μ of flow rate of nozzles on angle β and on the ration $(d/D)^2$ of areas of cross-sections of nozzle and of DP for Re_d = 20000

In our prior work (Cherniuk et. al, 2020), we investigated nozzles with diameters d = 6.01 and 8.08 mm installed in DP of D = 20.18 and 16.13 mm for which $(d/D)^2$ was equal to 0.087 and 0.251, respectively. In Fig. 6 for the criterion $Re_d = 2 \cdot 10^4$, the dependences $\mu = f((d/D)^2)$ for all the carried out by us investigation are presented.

The greatest range of change of the μ (up to 22.1%) Cherniuk et. al (2020) have obtained for a nozzle of d = 8.08 mm, the nozzle was installed in a DP of D = 16.13 mm, when $(d/D)^2$ = 0.251 (Fig. 6).

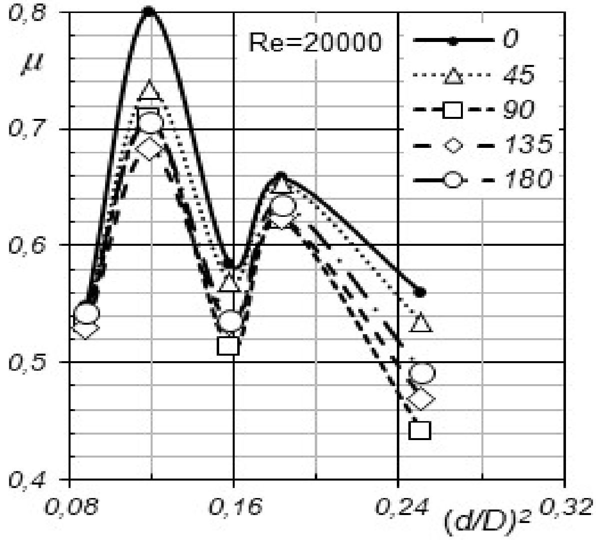

Fig. 6. Dependence of coefficient μ of flow rate of nozzles on rations $(d/D)^2$ for Reynolds' criterion $Re_d = 20000$ for different values of angle β

6. Conclusions

The dependence of values of the coefficient μ of flow rate of cylindrical nozzles with lateral orthogonal outflow on the angle β between the direction of the water stream and that of the outflowing jet in a distributive pipeline has been established. The experiments have been carried out for different values of the ration of cross-section areas of the nozzle to that of the pipe segment. In this work, by means of regulation of values of the angle β, the change in value of the coefficient μ up to 14.6% is obtained; in our prior investigation, such change was up to 22.1%, but only for a single nozzle installed in a pipe segment whose diameter was D and the length $6D$ (Fig. 2). For a longer distributive pipeline containing 10 or more nozzles, essential decrease in non-uniformity of fluid dispensation along the path can be achieved. The investigations of the authors of the article are aimed at finding such geometrical and hydraulic parameters under which this goal can be achieved.

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Project to improve the interactive environmental map of Ukraine: a new active way to slice statistical data on state of water resources

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Abstract

The article analyses the critical state of natural reservoirs and water resources on Ukrainian territory. An emphasis is done on analytical analysis towards the management of important painful issues of environmental protection (air, water, environmental finance), and the critical state of water resources. The processed data monitoring on the Danube River from different sampling points has shown high values for some indicators including biochemical oxygen demand for 5 days (BOD_5), common nitrogen (nitrate (NO_3^-) and/or nitrite (NO_2^-)), Total suspended solids (TSS), sulphate (SO_4^{2-}) and chloride (Cl^-) ions. As known, for example, the high BOD_5 indicates contamination of the reservoir with organic substances. Scientists from the Danube Institute of National University "Odessa Maritime Academy" have provided wide-ranging information on the water shortages prevention in modern society. The ways of lack (shortages) of water preventions are analysed. One of the modern environmental protection directions priority is shown – introduction of map conductors (water resources module is illustrated via the Open Access platform). Using the "Open Environment" geo-information system provided by the Luminate philanthropic organization, statistical data on the state of water resources (Danube River, inland, tributaries) have been compiled and analysed using the correlation analysis (implemented in MINITAB 19 software). All provided data are confirmed by mathematical statistics (interpretation, correction of water resources information indicators).

A correlation analysis method has been used to determine the relationship between water quality indicators from different sources. Pearson's correlation coefficient r (linear relationship between two values) has been used for statistical data processing. The conducted correlation analysis reveals the following: there is very high correlation (r = 0.95) between chloride and sulphate concentrations in Yalpug lake; there is no strong the moderate correlation in the place with ecologically clean water (Chop, Zakarpattya region); another pattern is observed in Vilkovo and Reni – the moderate correlation between nitrate and dissolved

oxygen concentrations is 0.668 and 0.634, respectively, the moderate correlation between chloride and sulphate concentrations is 0.575 and 0.557, respectively.

Keywords: "Open Environment" Geoinformation System (GIS), interactive map of Ukraine, water resources, Open Access Online Platform, Danube River, correlation analysis, Pearson's correlation coefficient *r*

1. Introduction

The 21st century is critical enough for the whole world! This is a century of crises. Global crises: deterioration of the natural state of the aquatic and air environment. And, humanity seems to achieve remarkable attractive results, not limiting the environment with low-quality impact, but (because of the modern anthropogenic interference) the natural ecological situation becomes a crisis day by day.

It is known that today the modern community (in Ukraine and abroad) is concerned about the deterioration of the state of natural environment. This community is primarily comprised of scientists, environmental protection experts, eco-activists, open-source experts, journalists. All of them are closely related to the problems of deep analytical analysis on the important issues of environmental protection management, in particular the state of water resources (Chwesik, 2005).

2. Ways to use the interactive environmental map of Ukraine: placing on the one platform environmental data on the state of water resources, air and finance. The republication of such data to implement the idea of active interaction between business, civil society and government in the sphere of environmental policy and environmental protection

2.1 Priority directions for overcoming water shortages

Two-thirds of our planet are covered with water. Then the question arises: why do people have lack of water.

So why do over 1 billion people not have access to clean water? Firstly, just over 3% of the water on earth is fresh water.

Secondly, 90% of water is used in agriculture. The remaining water goes to industry and household needs. By 2025 more than 2 billion people may meet the lack of water. So, here are some ways to overcome water shortages (UN Water, 2007; Conway, 2012):

- Rethink agriculture. Grow cereals that need less water. Use effective methods such as drip irrigation.
- Preserve groundwater. There are rich reserves of water underground. Effective management will save you from wasting (Castle et al., 2014).
- Purify water. Purified water can be used for industry and agriculture. This purified water will preserve the natural reserves of pure water (FAO, 2017).
- Desalinate. Removing salts and minerals from ocean water is an expensive process and not very popular, but it does attract a lot of investment (Ashley, 2009).
- Do small things. You can switch to more economical household appliances and use water wisely (Rachele, 2020).

Society's actions on the mentioned ways:

- Within the project (sustainable development goal: saving of marine resources, INRM educational platform) a pilot drip irrigation site is established in the Kherson region. It is one of the most efficient and rational ways of using fresh water in agriculture.
- Water erosion control helps to preserve the soil layer and improve soil infiltration. This contributes to the pollution reduction of reservoirs, improving the supply of plants with moisture and increasing the level of groundwater. Integrated natural resources management with extensive use of forest plantations and meadows allows to improve the level and quality of groundwater and natural reservoirs as well as to begin the process of self-purification.
- Inland waters preservation from chemical pollution is the key to prevent pollution of marine waters and combine the objectives of the "Clean Water and Proper Sanitation" and "Conservation of Marine Resources" educational platforms. Prevention of soil, groundwater, food contamination from chemicals is possible through optimization of crop rotation and improvement of soil cultivation methods. This, in turn, will reduce the use of mineral fertilizers and crop protection chemicals (https://healthy-soils.org.ua).
- Water desalination plants create dead zones in the ocean. There are more than 16.000 water desalination plants in the world (Root, 2019). And they produce more toxic dirt than drinkable aqua. As the first similar study has shown, every litre of drinking water extracted from the sea or another saltwater reservoir is accompanied by the production of one and a half litre of salt brine which is thrown back into the ocean. The extremely salty substance is even more toxic due to the chemicals used in the desalination process.

  It contains, for example, chlorine and copper, according to a research report on the site Phys.org. "The world produces less desalinated water than brine.

Almost all of it goes back to the environment, mostly to the ocean", explains study co-author Manzur Kadir from the Water Environment and Health Institute at the United Nations University of Ontario. The extra salinity in the aquatorium increases the temperature of coastal waters and reduces the amount of oxygen in them. That is why there are "dead zones" in the water areas. "It is difficult for marine organisms to breathe in such conditions. They need oxygen to survive.", explained Kadir (https://www.unian.ua/ecology).

– Areas of the future come into force: smart cities and smart homes. Today, if the city can't get smart, it continues to strive to meet the established goals. In its sense, a "smart" city is a coherent system of technologies and innovations used to interact with government agencies and obtain administrative services in the transport network and road traffic, energy and water supply, health care, housing. Although this is a suggestion of the European strategy, the humanity's desire is to create the most favourable, informative, intelligent systems by which the society will, unambiguously, reach a high level of development with the preservation of natural resources (emphasis is placed on smart) (Tretyak, 2018).

Water resources are planned to be redistributed in India. India's Water Minister told the BBC that the country should implement a project to divert the run-off part of the large rivers to arid regions. Water can be taken from the largest rivers – Brahmaputra and Ganges as well as from the Himalayan glaciers. Ecologists are outraged by this situation, in particular, no studies have been conducted on the future of rivers from which the Government of India plans to divert water (https://www.bbc.com, 2016).

Scientists are interested not only in the formation and collection of water on Earth. In fact, their research extends to the farthest places of the Universe. Scientists say that there is water on the Moon. But, unfortunately, the technologies of mankind are underdeveloped. There is a number of possible water sources on Mars but you still need to find a way to extract water (https://www.bbc.com, 2020).

On average, a single person uses about 9.000 Liters of water per year – that is enough to fill two gasoline tanks! (https://www.nationalgeographic.com) It is estimated that by 2025, more than 60% of people will have the limited access to fresh water.

New scientific research claims that the oceans play a much larger role in regulating the Earth's climate than previously thought. Scientists of the Southern Denmark University have submerged special robots at the bottom of the Mariana Trench – the deepest point of the ocean – to a depth of almost 11 km.

They have found that biomass accumulates in the basin. It sinks from less depth there and the bacteria are particularly active in decomposing carbon compounds at the bottom.

Scientists say that deep-water depressions play a greater role in regulating carbon dioxide volumes and, therefore, climate.

According to Professor Glud, even though these depressions make up only 2% of the ocean, they can be "disproportionately important" because they are likely to accumulate much more carbon as they work as a trap for biomass (https://www.bbc.com, 2011).

This is not the first time that the deep-water depressions have surprised scientists. Recent studies have found that there are more marine species living in a unfavourable environment than previously thought.

Therefore, modern technologies are able to "rethink" the appropriate environmental status throughout Ukraine.

Moreover, many different measures have been taken to improve the natural state of the environment to fulfil this mission. In particular, the cooperation of Ukrainian scientists and environmental experts with the European Union countries comes into force.

This helps to introduce the latest technologies (systematic, informational, analytical) properly and proactively; develop further the modern methods and methodologies for preserving living species. One of the modern environmental protection priority areas is the introduction of huge map conductors (Fig. 1) with complete information on the state of the air, water resources, and environmental finances.

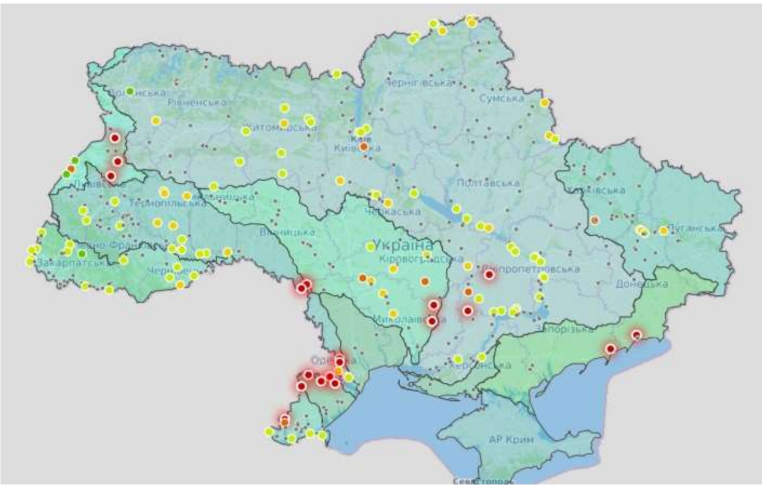

Fig. 1. Interactive map. Water Resources module (https://magneticonemt.com/en/)

This is a significant modern step related to the statistical data collection for each region, city, the natural state of rivers, seas, natural reservoirs in various key indicators (https://menr.gov.ua).

2.2. GIS "Open Environment"

It is well known that the current activity of environmental protection experts is aimed at the favourable on-line overview of the general ideas about GIS "Open Environment" with pilot maps "Water Resources", "Atmospheric Air" and "EcoFinance" (https://menr.gov.ua).

Thus, an interactive ecological map of Ukraine has been created. It integrates environmental data on the state of water resources, atmospheric air and finances on the same platform through the Open Access project. This system allows you to get a slice of data by year, region or pollutant (in three clicks).

The project was implemented by a group of experts under the leadership of the Ukrainian analytical centre "Open Society Foundation" the activity of which focuses on the public access to government data.

The project cooperates with the Ministry of Ecology and Natural Resources of Ukraine and public platforms which are interested in the republication of environmental data. This allows to realize the idea of business, civil society and government active interaction in the environmental policy and environmental protection field.

During the Summer 2019 developers and experts had to improve the system, in particular, test its capabilities with public activists, regional state administrations, local governments, and in the fall of 2019 the full integration is planned into the national system "Open Environment" (module of administrative services and system site are in the development process).

What is the difference between this system and other projects?

The system works with both government data that reflect the state of water and atmospheric pollution in Ukraine and alternative data collected by public environmental monitoring networks. Data on environmental tax, local and regional budgets expenses, financing volumes for environmental measures up to the district level are shown separately.

The project is joined by environmental protection experts, eco-activists, open data experts, IT start-ups, journalists; all of them are interested in green topics and working with the open data.

The creation of the "Open Environment" GIS has been made possible by the support, grant from the global philanthropic organization Luminate, part of the Omidyar Group. The project can be viewed on the Open Access site (https://openaccess.org.ua).

Additional information: "Open Society Foundation" is a non-governmental organization founded in 2001 to promote open society values in the Ukrainian political agenda, increase efficiency and accountability in public policy. It is a community of analysts, experts and managers who work with government authorities to analyse policy, develop and implement political recommendations in areas of competence, including proper governance, anti-corruption, transparency and efficiency of public finances and sustainable development.

The Foundation aims to develop innovative and anti-corruption tools for the environmental state monitoring. Thanks to these and other initiatives, the organization works to strengthen the capacity of civil society groups to ensure effective public control, broad participation and representation of interests in policy-making.

About the Luminate group: This is an independent philanthropic organization created on the basis of the Governance & Citizen Engagement initiative of the Omidyar Network, the activity of which aims to create opportunities for people to use the potential of the market to improve their living conditions. The Omidyar Network was created in 2004 by eBay founder Pierre Omidyar and his wife Pam. The organization invests and helps to strengthen innovative organizations to catalyse economic and social changes. The Luminate group has invested over $1 billion in businesses and non-profit organizations that promote economic development and encourage individual engagement through their initiatives including “Digital Identity”, “Education”, “New Technologies”, “Financial Integration”, “Government-citizen interaction”, “Property rights”.

Omidyar Network's most recent investments in Central and Eastern Europe include support for the 1991 Civic Tech Centre created by the IT organization SocialBoost, the EPF Foundation in Poland, and SeedStars start-ups competitions in various countries, including Ukraine, Georgia and the Baltic States.

For more information go to www.luminategroup.com and follow @luminategroup #PositiveReturns on Twitter (https://www.kyivsmartcity.com).

3. Materials and methods

The paper material is a huge interactive map of natural resources provided by the “Open Environment Foundation” which reflects data on the state of air, water (natural resources), environmental contributions and losses. Regarding these methods, this is a statistical on-line survey and information collection of the current state of the natural environment in Ukraine.

Especially, it concerns the Danube River internal state throughout Ukrainian territory (inland).

Data for the period from 2009 to 2019 were used for the correlation analysis. The following sites (in the Danube basin) were selected for the study: 1 – Vilkovo (109 observations); 2 – Reni (108 observations); 3 – Yalpug Lake (146 observations); 4 – Chop (111 observations) (Fig. 2).

The urgent task (the above mentioned point 2.1) was to cover a number of analytical and diverse issues: overcome water scarcity problems, redistribute water resources, regulate the climate of the Earth thanks to the scientific research concerning an ocean’s major role.

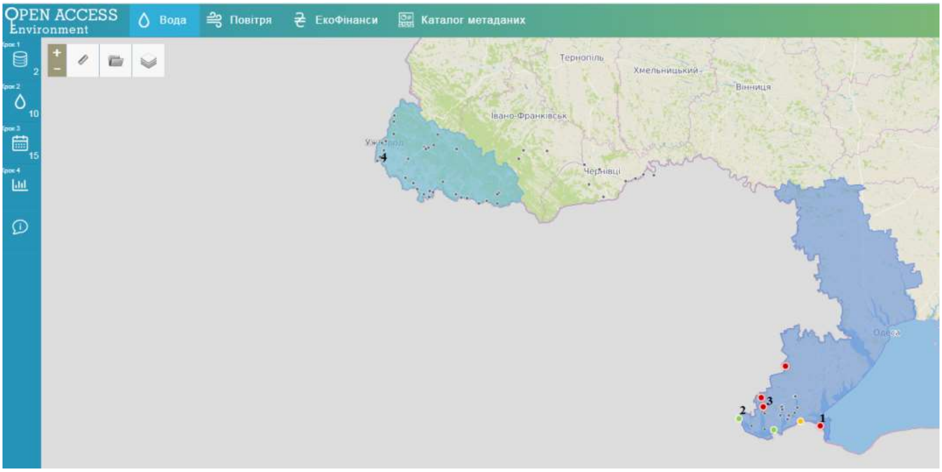

Fig. 2. Locations of water collection points in the Danube river basin

Currently, we, the scientists of the Danube Institute of National University "Odessa Maritime Academy", have been tasked with the analytical review of the interactive ecological map of Ukraine regarding the statistical data selection and sectioning on the state of water resources on the basis of correlation analysis. This analysis has been performed in the MINITAB 19 software (https://web.archive.org).

The purpose of correlation analysis is to provide some information about one variable with the help of another variable.

In cases when the goal is possible to achieve the variables are said to be correlated. The measure of the relationship between the experimental datasets are the numbers – the relationship coefficients.

3.1. The main tasks of correlation analysis

- Evaluation by sample data of correlation coefficients;
- Checking the significance of the correlation coefficients samples (correlation ratio);
- Formation of the confidence interval for the correlation coefficients.

Determination of the strength and direction of the relationship between variables is one of the major problems of data analysis. In the general case, the concept of correlation is used for this purpose.

The mathematical measure of the correlation of two random variables is the correlation coefficient. The given coefficient is calculated using Pearson correlation coefficient in our research. The Pearson correlation coefficient is used to measure the strength of a linear association between two variables, where the value $r = 1$ means a perfect positive correlation and the value $r = -1$ means a perfect negative correlation.

Requirements for Pearson's correlation coefficient:
- Scale of measurement should be interval or ratio;
- Variables should be approximately normally distributed;
- There should be no outliers in the data (https://www.socscistatistics.com).

Correlation coefficients whose magnitude are between 0.9 and 1.0 indicate variables which can be considered very highly correlated. Correlation coefficients whose magnitude are between 0.7 and 0.9 indicate variables which can be considered highly correlated. Correlation coefficients whose magnitude are between 0.5 and 0.7 indicate variables which can be considered moderately correlated. Correlation coefficients whose magnitude are between 0.3 and 0.5 indicate variables which have a low correlation. Correlation coefficients whose magnitude are less than 0.3 have little if any (linear) correlation (https://www.andrews.edu).

The following results of correlation analysis have been obtained for each water probe site.

The necessary conditions for calculating the Pearson's correlation coefficient r are done:
- The studied variables are measured in a ratio scale;
- The studied variables are normally distributed according to the Kolmogorov-Smirnov criteria;
- Identifying outliers in a data was calculated according to the three-sigma rule.

The three-sigma rule is a statistical rule which states that for a normal distribution, 99.7% data falls within three standard deviations of the mean (https://www.investopedia.com).

The main parameters that were considered during the analysis are presented in Tab. 1.

Table 1. The hydrochemical parameters of water

The hydrochemical parameters of water	Concentration/Unit	Variable
Biochemical oxygen demand for 5 days	mg/L	BOD_5
Total suspended solids	mg/L	TSS
Dissolved oxygen	mg/L	DO
Sulphate	mg/L	SO_4
Chloride	mg/L	Cl
Ammonium	mg/L	NH_4
Nitrate	mg/L	NO_3
Nitrite	mg/L	NO_2
Phosphate	mg/L	PO_4

Results of statistical analysis of water quality, Vilkovo.
The outliers were 6.6% (Tab. 2–5).

Table 2. Correlation matrix, Vilkovo

	BOD_5	TSS	DO	SO_4	Cl	NH_4	NO_3	NO_2
TSS	0.193							
DO	0.463	0.128						
SO_4	0.184	0.101	0.343					
Cl	0.149	0.024	0.438	0.563				
NH_4	0.184	0.202	0.139	0.331	0.138			
NO_3	0.337	0.137	0.670	0.377	0.352	0.315		
NO_2	–0.008	–0.163	–0.213	–0.151	–0.114	–0.013	–0.123	
PO_4	–0.164	0.027	–0.023	–0.019	–0.007	0.099	0.149	–0.279

Table 3. Moderate correlation (0.5–0.7), Vilkovo

Sample 1	Sample 2	*N*	Correlation	95% CI for ρ	*p*-value
NO_3	DO	99	0.670	(0.545; 0.766)	0,000
Cl	SO_4	99	0.563	(0.411; 0.684)	0.000

Table 4. Low correlation (0.3–0.5), Vilkovo

Sample 1	Sample 2	*N*	Correlation	95% CI for ρ	*p*-value
DO	BOD_5	99	0.463	(0.292; 0.605)	0.000
NO_3	BOD_5	99	0.337	(0.149; 0.501)	0.001
SO_4	DO	99	0.343	(0.156; 0.506)	0.001
Cl	DO	99	0.438	(0.263; 0.585)	0.000
NH_4	SO_4	99	0.331	(0.143; 0.496)	0.001
NO_3	SO_4	99	0.377	(0.194; 0.534)	0.000
NO_3	Cl	99	0.352	(0.166; 0.513)	0.000
NO_3	NH_4	99	0.315	(0.125; 0.482)	0.002

Table 5. The smallest and the biggest changes of the indicators concerning the normal level, Vilkovo

Variable	Concentration	
	Min	Max
BOD_5	0.170	2.570
TSS	0.140	17.130
DO	1.450	3.380
SO_4	0.260	0.900
Cl	0.060	1.090
NH_4	0.050	0.880
NO_3	0.020	0.270
PO_4	0.010	0.080

According to the Tab. 5, exceedance occurs on DO concentration indicators all the time. The more detailed analysis has shown the following – maximum emissions occurred on indicators in the following periods: BOD_5 concentration in 2.57 times 11.05.2010; TSS in 17.13 times 19.07.2016, DO concentration in 3.38 times 19.01.2010.

Results of statistical analysis of water quality, Reni.

The outliers were 7.4% (Tab. 6–9).

Table 6. Correlation matrix, Reni

	BOD_5	TSS	DO	SO_4	Cl	NH_4	NO_3	NO_2
TSS	–0.093							
DO	0.287	–0.001						
SO_4	0.198	–0.064	0.360					
Cl	0.101	–0.086	0.408	0.573				
NH_4	0.202	0.066	0.273	0.197	0.137			
NO_3	0.164	0.072	0.636	0.362	0.278	0.420		
NO_2	0.012	0.087	0.025	0.133	0.116	0.289	0.151	
PO_4	0.045	–0.065	0.231	0.078	0.171	0.068	0.162	–0.156

Table 7. Moderate correlation (0.5–0.7), Reni

Sample 1	Sample 2	N	Correlation	95% CI for ρ	p-value
NO_3	DO	100	0.636	(0.503; 0.740)	0.000
Cl	SO_4	100	0.573	(0.425; 0.692)	0.000

Table 8. Low correlation (0.3–0.5), Reni

Sample 1	Sample 2	N	Correlation	95% CI for ρ	p-value
SO_4	DO	100	0.360	(0.176; 0.520)	0.000
Cl	DO	100	0.408	(0.230; 0.559)	0.000
NO_3	SO_4	100	0.362	(0.179; 0.522)	0.000
NO_3	NH_4	100	0.420	(0.244; 0.570)	0.000

According to the Tab. 9, exceedance occurs on DO concentration indicators all the time. The more detailed analysis has shown the following – maximum emissions exceed the normal level in several times: on BOD_5 concentration indicators in 1.97 times 20.03.2012; TSS in 14.78 times 02.03.2010; DO concentration in 3.45 times 11.01.2012.

Table 9. The smallest and the biggest changes of indicators concerning the normal level, Reni

Variable	Concentration	
	Min	Max
BOD_5	0.200	1.970
TSS	0.110	14.780
DO	1.500	3.450
SO_4	0.230	0.670
Cl	0.050	1.070
NH_4	0.050	1.400
NO_3	0.040	0.260
PO_4	0.010	0.080

Results of statistical analysis of water quality, Yalpug.
The outliers were 19.2% (Tab. 10–13).

Table 10. Correlation matrix, Yalpug

	BOD_5	TSS	DO	SO_4	Cl	NH_4	NO_3	NO_2
TSS	0.121							
DO	–0.053	–0.333						
SO_4	–0.004	0.017	0.205					
Cl	0.080	0.091	0.225	0.948				
NH_4	0.409	0.355	–0.234	–0.028	0.062			
NO_3	–0.105	–0.070	0.164	0.254	0.203	–0.081		
NO_2	0.036	0.265	–0.238	–0.107	–0.051	0.075	0.061	
PO_4	–0.025	0.217	0.003	0.143	0.142	–0.043	–0.010	0.019

Table 11. Very high correlation (0.9–1), Yalpug

Sample 1	Sample 2	N	Correlation	95% CI for ρ	p-value
Cl	SO_4	118	0.948	(0.926; 0.964)	0.000

Table 12. Low correlation (0.3–0.5), Yalpug

Sample 1	Sample 2	N	Correlation	95% CI for ρ	p-value
NO_4	BOD_5	118	0.409	(0.247; 0.549)	0.000
NO_4	TSS	118	0.355	(0.186; 0.503)	0.000
TSS	DO	118	–0.333	(–0.484; –0.162)	0.000

Data of Tab. 13 show the constant exceedance on DO and Sulphate concentrations indicators. Maximum emissions are the following on indicators: BOD_5 concentration increased in 5 times 29.07.2019, TSS 12.4 times 15.08.2017, DO concentration in 4.85 times 20.02.2012, Sulphate concentration in 6.61 times 15.08.2017, Chloride concentration in 3.48 times 15.12.2009, Ammonium concentration in 1.8 times 19.08.2019.

Table 13. The smallest and the biggest changes of indicators concerning the normal level, Yalpug

Variable	Concentration	
	Min	Max
BOD_5	0.330	5.000
TSS	0.070	12.400
DO	1.000	4.850
SO_4	2.360	6.610
Cl	0.470	3.480
NO_4	0.060	1.800
NO_3	0.000	0.060
PO_4	0.000	0.390

Results of statistical analysis of water quality, Chop
The outliers were 11.7% (Tab. 14–16).

Table 14. Correlation matrix, Chop

	BOD_5	TSS	DO	SO_4	Cl	NH_4	NO_3	NO_2
TSS	0.133							
DO	–0.010	–0.336						
SO_4	0.165	–0.139	–0.105					
Cl	0.053	–0.027	–0.198	0.362				
NH_4	0.316	0.168	–0.364	0.135	0.129			
NO_3	0.039	0.060	0.165	0.005	–0.238	–0.038		
NO_2	0.240	0.343	–0.440	0.019	0.103	0.304	–0.103	
PO_4	0.042	0.214	–0.224	0.062	–0.004	0.051	–0.071	0.215

Table 15. Low correlation (0.3–0.5), Chop

Sample 1	Sample 2	*N*	Correlation	95% CI for ρ	*p*–value
NH_4	BOD_5	98	0.316	(0.125; 0.484)	0.002
DO	TSS	98	–0.336	(–0.501; –0.148)	0.001
NO_2	TSS	98	0.343	(0.155; 0.507)	0.001
NH_4	DO	98	–0.364	(–0.524; –0.178)	0.000
NO_2	DO	98	–0.440	(–0.587; –0.265)	0.000
Cl	SO_4	98	0.362	(0.176; 0.523)	0.000
NO_2	NH_4	98	0.304	(0.113; 0.474)	0.002

The constant exceedance occurs on DO concentration indicator. According to the detailed data analysis, the following comes out: BOD_5 concentration increased in 1.63 times 15.01.2010, TSS in 2.29 times 30.05.2013, DO concentration in 3.73 times 08.02.2010.

Table 16. The smallest and the biggest changes of indicators concerning the normal level, Chop

Variable	Concentration	
	Min	Max
BOD_5	0.470	1.630
TSS	0.140	2.290
DO	2.030	3.730
SO_4	0.040	0.780
Cl	0.020	0.610
NO_4	0.100	0.940
NO_3	0.030	0.160
PO_4	0.010	0.090

According to the data presented in the tables the diagrams of some water quality indicators have been built which significantly influence the nature of the correlations.

These diagrams are presented in Fig. 3–6.

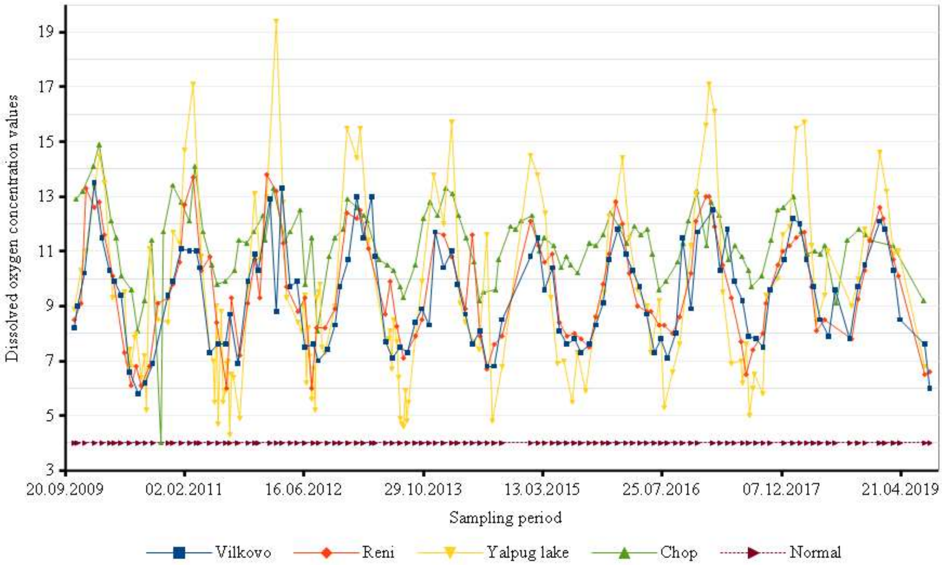

Fig. 3. Diagram indicator, Dissolved oxygen concentration

The visual diagram indicator (Fig. 3) shows the cycle (periodicity) of the indicator.

The given indicator exceeds the normal level in all water sampling sites.

It characterizes the viability of reservoirs, which in turn is one of the most important characteristics for summative assessment of environmental and sanitary conditions of an object.

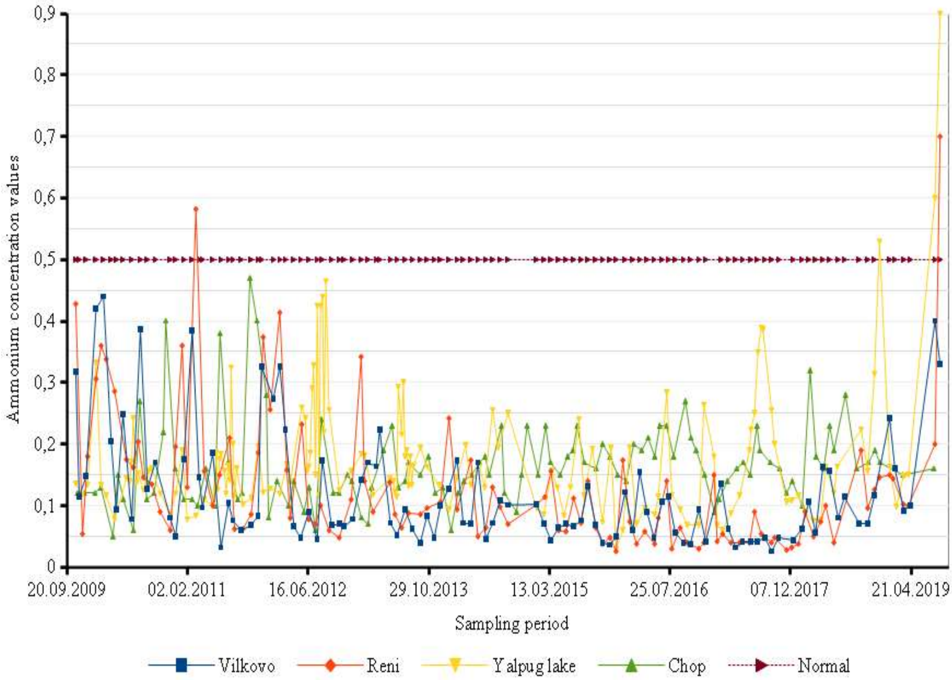

Fig. 4. Diagram indicator, Ammonium concentration

According to the visual diagram indicator, we can make the following conclusions:

– The given indicator has not exceeded the normal level in Vilkovo, Chop and Yalpug lake during the observations.
– Exceedance has been in 1.4 times 19.08.2019 in Reni (Fig. 4).

The diagram visualization reflects (Fig. 5) exceedance for the period from 2009 to 2019 at all water sampling sites.

The "most pleased" picture is seen in Chop (exceedance in 1.63 times) and the worst indicator (in 5 times) – in Yalpug Lake.

The visual diagram allows to make a positive conclusion that the indicator exceedance has not occurred at the water sampling sites during the whole period of the study (Fig. 6).

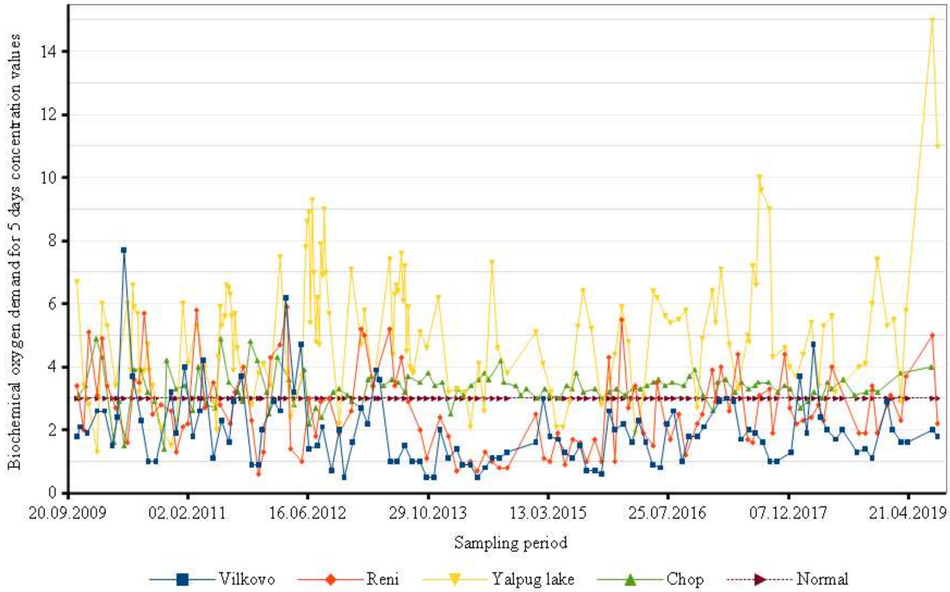

Fig. 5. Diagram indicator, BOD_5 concentration

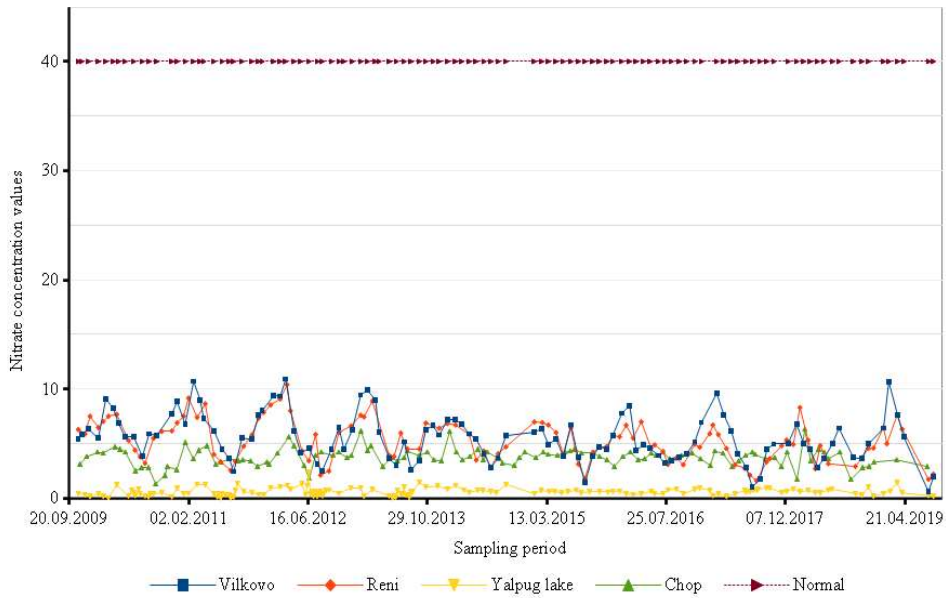

Fig. 6. Diagram indicator, Nitrate concentration

4. Results and discussion

In the southern part of Ukraine in Odessa, Kherson and Mykolaiv regions, a huge transport connection of seaports is involved. Odessa, Kherson, Mykolaiv are Ukrainian maritime "harbours". Moreover, these areas are the largest conductors of water, both potable and marine.

But it should be noted that representatives-scientists of the Danube Institute of National University "Odessa Maritime Academy" (DI NU "OMA") (Izmail), in the maritime industry, have an interest in the preservation of the world's water resources and solving problems about the implementation of protective and treatment facilities, equipment for water purification and disinfection (sewage, marine, drinking).

This is a top priority for the members of our higher educational institution (HEI) in the global scientific direction of natural water resources preservation (Bykovets et al., 2018; Danilyan et al., 2019).

We have conducted and analysed a statistical collection of on-line information on the internal state of the Danube River in all parts of Ukraine. Such a statistical survey gives a complete perception of ecological state of environment for every person. The new know-how enables not only scientists but also economists, business organizations to trace the state of the air environment, water and economic resources (investments).

We, scientists of DI NU "OMA", provide a fragment of correlation analysis – statistical data of 2009–2019 (29.07.2019–19.08.2019) for water sampling in some areas of the Danube River and its tributaries (Tisza River – the left and longest tributary of the Danube throughout Ukraine) (http://www.openenvironment.org.ua).

5. Conclusions

The statistical analysis allows to make some important conclusions:

- There is very high, positive correlation (r = 0.95) between Chloride and Sulphate concentrations in Yalpug lake.
- There is no strong and moderate correlation in the place with ecologically clean water (Chop, Zakarpattya region).
- Water quality indicators such as Nitrate and Phosphate concentrations have not been exceeded during the whole period.
- Water quality indicators such as BOD_5, TSS and DO concentrations have been exceeded during the whole period at all water sampling sites.

High values can be explained by the composition of the soil. In general, the process of forming the chemical composition of natural waters is too complex and is influenced by various factors. Among these factors are direct and indirect. Direct factors enrich the water with salts – soils, rocks, and indirect factors include the terrain and climatic zones.

- On solving environmental problems consideration should be given to the nature of emissions.

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Occurrence of cytostatic drugs in hospital wastewater

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Abstract

In recent years, a significant increase in the application of chemotherapeutic drugs is observed, along with their appearance in the environment (Santos et al., 2018; Souza et al., 2018).

For many years, there were no standards regulating the limitations on the introduction of medicines to the environment. Significant amounts of these pollutants were discharged with municipal wastewater to treatment plants, which were not adapted for their removal. It was shown that the standard technologies are characterized by low efficiency in terms of removing active substances of drugs and their metabolites. Therefore, it is necessary to implement additional steps in the technological system of treatment plants, based on advanced oxidation processes such as ozonation and UV irradiation (Olalla et al., 2018). Moreover, numerous substances negatively impact the biotechnological processes, inhibiting biochemical reactions and multiplication of utilized microorganisms. Many studies on micropollutants focus only on the efficiency of their removal, not accounting for the hindrance of the entire process (Avella et al., 2010).

Determinations of cisplatin, oxaliplatin, and carboplatin as well as their derivatives was carried out with ICP-MS method, using Agilent 8900 apparatus. The standard curve method and an external standard will be used. Mineralization in aqua regia will be performed in Mars microwave digestion system. In the case of the samples with high organic substances content, additional oxidizing media will be used if necessary (H_2O_2, $HClO_4$).

Concentration levels ranging from 0.7 to 185,7 $\mu g \cdot L^{-1}$ were obtained as a sum of analysed compounds.

Determinations of iphosphamide and cyclophosphamide was carried out with HPLC-MS/MS method, using Agilent 1200 series HPLC and Q-trap 4000 MS/MS system. Results showed that cyclophosphamide was present in hospital wastewater in the range 375–5141 $ng \cdot L^{-1}$, while iphosphamide was present in some months in effluents from only one wastewater treatment plant and hospital effluents in the range 56–1413 $ng \cdot L^{-1}$.

Results of our investigations (12 samples) are similar to the results presented.

Keywords: anticancer drugs, cytostatics, hospital wastewater

1. Introduction

Micropollutants, such as pharmaceuticals, constitute a new challenge for wastewater treatment plants and the industry. Medicines are designed to ensure their maximum biological activity. Cytotoxic agents, used in the treatment of cancer are one of the compounds characterized by strongest effect (Avella et al., 2010).

In recent years, a significant increase in the application of chemotherapeutic drugs is observed, along with their appearance in the environment (Santos et al., 2018; Souza et al., 2018).

For many years, there were no standards regulating the limitations on the introduction of medicines to the environment. Significant amounts of these pollutants were discharged with municipal wastewater to treatment plants, which were not adapted for their removal. It was shown that the standard technologies are characterized by low efficiency in terms of removing active substances of drugs and their metabolites. Therefore, it is necessary to implement additional steps in the technological system of treatment plants, based on advanced oxidation processes such as ozonation and UV irradiation (Olalla et al., 2018). Moreover, numerous substances negatively impact the biotechnological processes, inhibiting biochemical reactions and multiplication of utilized microorganisms. Many studies on micropollutants focus only on the efficiency of their removal, not accounting for the hindrance of the entire process (Avella et al., 2010).

One of the main issues in the studies on the presence and removal of micropollutants involve the problems with inadequacy of the analytic method, resulting from the presence of trace amounts of analytes in the compiled matrices, with composition varying in time. It is often necessary to carry out separation and enrichment prior to conducting the analysis. These operations may cause errors connected with incomplete recovery and introduction of pollutants, resulting in undesirable chemical reactions and interferences. Thus, a thorough validation of the employed analytic protocol seems necessary. Reference materials and isotope labelled substances play a special role in quality control.

It should be mentioned that the physicochemical properties of particles, characterized by high polarity, constitute an additional issue in terms of quantitative determinations (Kovalova et al., 2009). Therefore, it is necessary to employ dedicated sorbents for polar substances in the SPE method.

The cytotoxic agents drawing the greatest attention among scientists include 5-fluorouracil and platinum compounds (Cisplatin, oxaliplatin and carboplatin) (Mahnik et al., 2004; Kovalova et al., 2009; Mullot et al., 2009; Kosjek et al., 2013; Lin et al., 2014). However, there are few literature reports compared to the papers on antibiotics and nonsteroidal anti-inflammatory drugs. This gap in literature should be explained by the analytical difficulties; however, due to the high toxicity, this topic becomes increasingly popular.

The sources of therapeutic substances include the pharmaceutical industry, application by individual consumers, medicine, veterinary medicine, agriculture and animal husbandry (Kümmerer, 2009). Pharmaceuticals are discharged to hospital, municipal and industrial wastewater. Then, they spread in the environment, become bio-available and are retained in its elements.

The first documented observations on the occurrence of drugs in the environment appeared in 1981; in that study, clofibric acid was detected in aquatic environment in the concentration of 0.5–2 μg/l. In 1998, Thomas Terens made the first attempt in Europe to identify drugs in water, streams and wastewater in Germany. His monitoring studies confirmed the presence of painkillers, anti-inflammatory and psychotropic drugs as well as hormones (Czerwiński et al., 2015).

This issue was recognized globally, which led to its investigation by numerous scientific centers, also in Poland (Gdańsk University of Technology, Silesian University of Technology, Poznan University of Technology, and Lublin University of Technology).

Long-term exposure to trace amounts of cytotoxic agents may result in rash, skin irritation, hair loss, reduced number of white blood cells, and increased susceptibility to infections. Organ toxicity may occur as well. Most importantly, the exposure to chemotherapeutic drugs may damage and mutate DNA as well as induce carcinogenic effect (Mahnik et al., 2004; Kosjek et al., 2013; Smerkova et al., 2017; Gajski et al., 2018).

The first cytotoxic drug analyzed in the hospital wastewater corresponded to 5-fluorouracil (Kovalova et al., 2009). The exemplary determinations of cytotoxic agents were presented in Tab. 1.

The data presented in Tab. 1 indicate the presence of considered cytotoxic agents in hospital wastewater at different stages of their treatment. The authors cited in the Tab. mainly employed chromatography coupled with mass spectrometry as their analytic method. In turn, SPE was employed as the sample preparation method. As far as determining the platinum residues is concerned, virtually only the ICP-MS method is used.

The traditional methods of wastewater treatment are insufficient in the case of pharmaceuticals and their metabolites which are being constantly introduced to the environment. Therefore, more efficient methods of removing toxic compounds are sought by the academia. The application of deep oxidation processes seems to be a promising direction for future development.

Table 1. Concentrations of selected cytotoxic agents from hospital wastewater, treatment plant influent and treated wastewater, as reported in literature

Cytotoxic agent	Sample type	Analytical method	Result [µg/l]	Reference
5-fluorouracil	Hospital wastewater	CE	648–6083	Mahnik et al., 2007
5-fluorouracil	Hospital wastewater	GC/MS-MS	0.09–4.0	Mullet et al., 2009
5-fluorouracil	Hospital wastewater	GC/MS	92	Kosjek et al., 2013
5-fluorouracil	Hospital wastewater	GC/MS	35	Kosjek et al., 2013
5-fluorouracil	Hospital wastewater	GC/MS-MS	0.0069	Isidori et al., 2016
5-fluorouracil	Hospital wastewater	GC/MS-MS	0.0021	Isidori et al., 2016
5-fluorouracil	Treatment plant influent	GC/MS-MS	0.0031	Isidori et al., 2016
5-fluorouracil	Treatment plant influent	GC/MS-MS	0.0035	Isidori et al., 2016
Bleomycin	Hospital wastewater	LC/MS-MS	0.114–1.187	Olalla et al., 2018
Bleomycin	Hospital wastewater	LC/MS-MS	0.046–3.000	Olalla et al., 2018
Cyclophospamide	Hospital wastewater	GC/MS	0.019– 4.486	Steger-Hartmann et al., 1997
Cyclophospamide	Hospital wastewater	LC/MS-MS	1.080	Isidori et al., 2016
Cyclophospamide	Hospital wastewater	LC/MS-MS	22.100	Isidori et al., 2016
Cyclophospamide	Hospital wastewater	LC/MS-MS	0.032	Isidori et al., 2016
Cyclophospamide	Treatment plant influent	LC/MS-MS	0.027	Isidori et al., 2016
Cyclophospamide	Treatment plant influent	LC/MS-MS	0.027	Isidori et al., 2016
Cyclophospamide	Treatment plant influent	LC/MS-MS	0.019	Isidori et al., 2016
Cyclophospamide	Treatment plant influent	LC/MS-MS	0.006	Isidori et al., 2016
Cyclophospamide	Treated wastewater	LC/MS-MS	0.017	Isidori et al., 2016
Methotrexate	Hospital wastewater	LC/MS-MS	<LOD – 4.756	Olalla et al., 2018

Table 1 – continuation

Cytotoxic agent	Sample type	Analytical method	Result [µg/l]	Reference
Methotrexate	Hospital wastewater	LC/MS-MS	0.019	Isidori et al., 2016
Methotrexate	Hospital wastewater	LC/MS-MS	3.920	Isidori et al., 2016
Methotrexate	Hospital wastewater	LC/MS-MS	0.029	Isidori et al., 2016
Methotrexate	Treatment plant influent	LC/MS-MS	0.303	Isidori et al., 2016
Methotrexate	Treatment plant influent	LC/MS-MS	0.029	Isidori et al., 2016
Methotrexate	Treatment plant influent	LC/MS-MS	0.0290,0083	Isidori et al., 2016
Ifosfamide	Hospital wastewater	LC/MS-MS	<LOD – 0.031	Olalla et al., 2018
Ifosfamide	Hospital wastewater	LC/MS-MS	0.058–4.761	Olalla et al., 2018
Ifosfamide	Hospital wastewater	GC/MS-MS	0.048	Isidori et al., 2016
Doxorubicin	Hospital wastewater	HPLC	0–265	Mahnik et al., 2004
Doxorubicin	Hospital wastewater	DLLME HPLC-FLD	4.64	Souza et al., 2018
Doxorubicin	Hospital wastewater	DLLME HPLC-FLD	2.08	Souza et al., 2018
Epirubicin	Hospital wastewater	DLLME HPLC-FLD	6.22	Souza et al., 2018
Epirubicin	Hospital wastewater	DLLME HPLC-FLD	2.67	Souza et al., 2018
Pt	Hospital wastewater	ICP-MS	0.226	Isidori et al., 2016
Pt	Hospital wastewater	ICP-MS	0.352	Isidori et al., 2016
Pt	Treatment plant influent	ICP-MS	0.027	Isidori et al., 2016
Pt	Treatment plant influent	ICP-MS	0.023	Isidori et al., 2016

2. Materials and Methods

The places collection of samples were hospitals in Lubelskie Voivodship and additionally hospitals in Gdańsk and Szczecin.

For Pt analysis samples were digested in a Microwave 3000 solv (Anton Paar) digester in a HF mineralization vessels. HCl/HNO_3 mixture was used for the digestion. All acids were Ultrex grade (JT Baker), and water from Integral 5 MilliQ system (Millipore). Final analyses of digested samples were made on a Agilent 8900 ICP-MS/MS system. Detection limits for these analyses were estimated at low ppt levels.

HPLC analysis was performed by injection volume 50 µL of the sample onto the Lichrospher®100RP-18column (1254 mm) with particle size 5 µm (Merck,Germany). The flow rate was1000 µL/min. The mobile phase, under gradient conditions, was as follows: mobile phase A – methanol; mobile phase B – 10 mM ammonia and formic acid buffer adjusted to pH 3; time program: 0 min 20%A/80%B; 7min, 80%A/20%B; 9min: 80%A/20%B 10min: 20%A80%B and this mobile phase composition was maintained for 4 minutes. Total run time was 15 min.

MS/MS analysis was performed on the 4000 Q-Trap triple quadrupole mass spectrometer equipped with an electrospray ionization source (ESI) operating in positive ion mode. Analyst software (Applied Biosystems/MDS Sciex, v1.5) was used for the instrument control and data collection. The instrument was operated in multiple reaction monitoring (MRM) mode and the following ion transition (precursor/product) were monitored: m/z 261/140 and 261/92 for cyclophosphamide and for iphosphamide 544/361 and 544/397. The elctrospray voltage was 5000 V and dwell time was 200 msec. Curtain gas (CUR) 40 psi; collision energy (CE) 31V; declustering potential (DP) 80V; collision cel exist potentials (CEX) 22V were used for the analysis of CP and IP.

3. Results and discussion

Table 2 shows concentration of analysed cytostatic drugs in hospital effluents.

Concentration levels Pt ranging from 0.7 to 185.7 $\mu g \cdot L^{-1}$ were obtained as a sum of analysed compounds (cis-platine, carboplatine and oxaliplatine). Figure 1 shows weekly variability of cytostatics concentrations in haspital wastewater in Gdańsk.

Results showed that cyclofosfamide was present in hospital wastewater in the range 375–5141 $ng \cdot L^{-1}$, while ifosfamide was present in some months in effluents from only one wastewater treatment plant and hospital effluents in the range 56–1413 $ng \cdot L^{-1}$. These date are also presented in Fig. 2.

Table 2. Concentration of analysed cytostatic drugs in hospital effluents

Sample	Sampling point	Concentration Pt [µg/L]	Iphosphamide [ng/L]	Cyclophosphamide [ng/L]
1	PSK-4 Lublin	154.5 ± 5.9 (RSD 3.8%)	231±22	476±21
2	COZL	137.0 ± 19.8 (RSD 14.4%)	216±17	346±24
3	Staszica Lublin	126.2 ± 23.8 (RSD 18.9%)	143±17	98±11
4	Zamość	102.9 ± 14.2 (RSD 13.8%)	74±14	133±17
5	Chełm	85.4 ± 20.0 (RSD 23.4%)	45±13	212±17
6	PSK-4 Lublin II	185.7 ± 17.4 (RSD 9.4%)	219±21	622±34
7	Laborat. COZL	99.8 ± 16.6 (RSD 16.6%)	175±33	716±23
8	Szczecin Dąbie	54.1 ± 16.1 (RSD 29.8%)	427±32	548±48
9	Staszica II Lublin	82.6 ± 20.7 (RSD 25.0%)	143±14	219±43
10	COZL Lublin	92.1 ± 17.4 (RSD 18.9%)	622±29	841±31
11	Chełm II	95.1 ± 12.0 (RSD 12.6%)	78±14	324±21
12	Gdańsk GUM	134.7 ± 13.8 (RSD 10.3%)	411±18	683±26

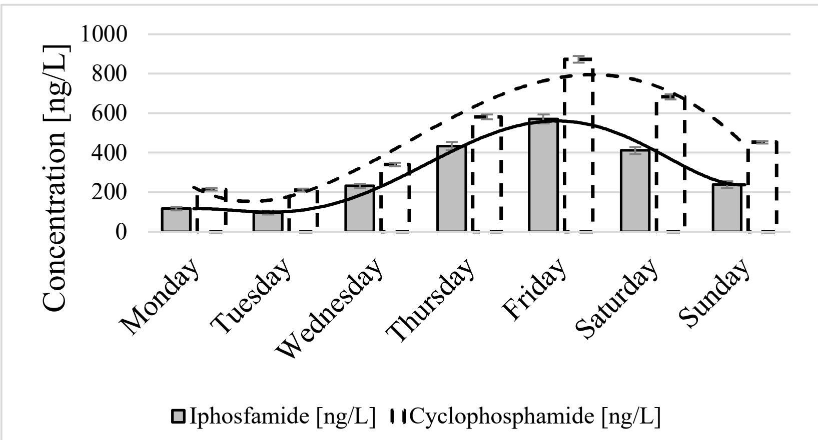

Fig. 1. Weekly variability of cytostatics concentrations in wastewater

Results of our investigations (12 samples) are similar to the results presented by other investigators.

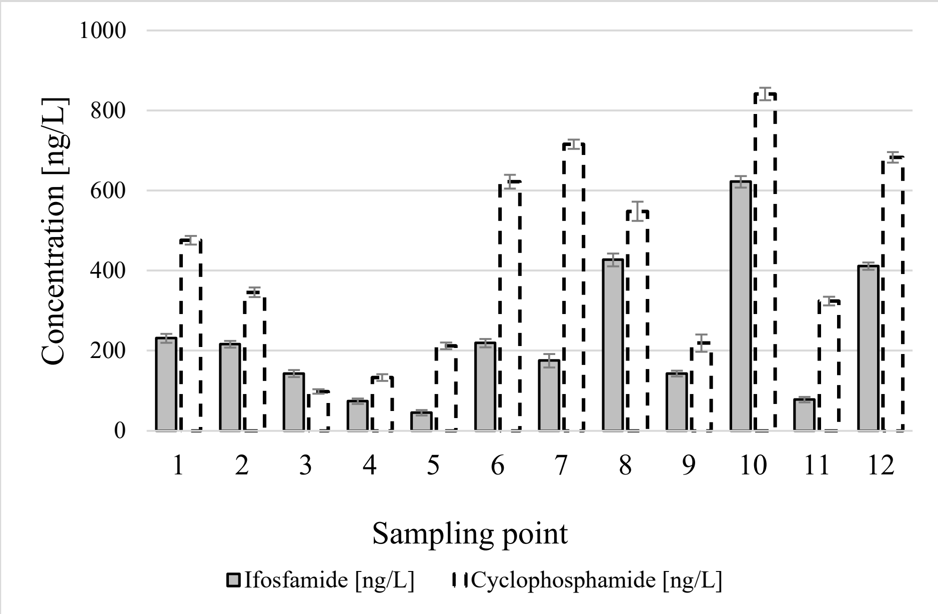

Fig. 2. Levels of analysed cytostatics in hospital wastewater in different sampling points

4. Summary and Conclusions

Hospital effluents are the most important source of cytostatic drugs in environment. In practice, precautionary mitigation approaches such as drug waste management should be adopted to prevent cytostatic residues from continuously admitted into the environment. Further fundamental understanding is required on the trace contaminants removal by various technical alternatives, such as advanced membrane bio-reactor and reverse/forward osmosis filtration, as well as advanced oxidation processes.

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Application of the chlorella type microalgae for the wastewater treatment

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Abstract

The results of experimental studies on the use of the Chlorella type microalgae for the wastewater treatment are presented. The influence of the main pollutants in particular anions HSO_3^-, NO_3^-, $H_2PO_4^-$ on the dynamics of wastewater treatment has been established. Analytical dependences of microalgae biomass growth rate depending on anions concentration HSO_3^-, NO_3^- and $H_2PO_4^-$ are obtained. The values of biomass growth coefficients at the corresponding anions concentrations are determined. On the basis of the obtained experimental research results, mathematical models have been constructed that allow to predict the maximum values of anions concentrations at which effective wastewater treatment by chlorophyllsynthesizing microalgae is possible. The technological scheme of wastewater treatment and the mechanism of the obtained application biomass are proposed.

Keywords: sulfur anion (HSO_3^-), nitrogen anion (NO_3^-), phosphorus anion ($H_2PO_4^-$), Chlorella, chlorophyllsynthesizing microalgae, wastewater treatment

1. Introduction

Global technogenic load causes significant environmental pollution, which is associated with the expansion of production and the imperfection of the technologies which are in use. This is especially related to emissions into the hydrosphere. Currently, the biological method of wastewater treatment is the promising one (Manakov and Pobedimskiy, 1990). The disadvantage of biological purification methods such as activated sludge, granular sludge, biofilm is that the necessary condition is oxygen enrichment, mixing, and as a consequence of carbon dioxide evolution. The advantage of our technology is that the sorption of sulfur anion (HSO_3^-), nitrogen anion (NO_3^-), phosphorus anion ($H_2PO_4^-$) and carbon dioxide (CO_2) by Chlorella microalgae occurs with the release of oxygen as photosynthesis product.

The problem of the current system of biological wastewater treatment in aerotanks is the enormous cost of oxygen for the bacterial processes of organic and mineral substances removal in wastewater, and carbon dioxide (CO_2), as a product of bacteria living abilities, is released into the air, it means that present existing treatment plants are the oxygen consumers and air pollutants with carbon dioxide (CO_2). It should also be noted that the biological feature of the bacteria is that they are narrowly specialized, that is, there is no one type of bacteria that could purify the entire spectrum of contaminants present in wastewater (Hubskyy, 2007).

Technology provides a method of wastewater treatment with different concentrations of contaminants using a specific strain of microalgae. Ecologically, this is justified by the fact that microalgae consume carbon dioxide (CO_2) and release oxygen for their living abilities (Statsenko and Vynohradova, 1992). Evolutionary microalgae are at a higher level of development than bacteria, and therefore many of their species are universal consumers of many organic and mineral substances which are pollutants of wastewater.

In the process of burning of fuel (solid, liquid, gaseous), besides carbon dioxide, sulfur, nitrogen and phosphorus oxides are released into the air. With precipitation, these pollutants return to the hydrosphere in the form of anions and cause acidification of reservoirs. Therefore, these anions were chosen for the experimental study.

By means of strain of the Chlorella type microalgae a high degree of biological purification from chemical contaminants is achieved. Biomass, accumulated in this way, can be used as organic „green" fertilizer or converted by biomethanization to methane gas (Zolotaryova et al., 2008). The use of this microalgae strain does not require reorganization or major construction of new treatment plants.

The literature contains little data on the effect of anions $\mathrm{HSO_3^-}$, $\mathrm{NO_3^-}$ and $\mathrm{H_2PO_4^-}$ on the dynamics of wastewater treatment by chlorophyllsynthesizing microalgae (Dyachok and Mandryk, 2018; Dyachok et al., 2019). Therefore, it is important to study the influence of these anions concentrations on the dynamics of wastewater treatment.

The aim of this work is to determine critical or maximum permissible concentrations of anions $\mathrm{HSO_3^-}$, $\mathrm{NO_3^-}$ and $\mathrm{H_2PO_4^-}$ in wastewater where the cultivation of the Chlorella type microalgae is possible.

2. Materials and Methods

In the process of the experimental research performing, culture of green microalgae – Chlorella was the object of observation. For this purpose, the culture of microalgae – Chlorella was placed into wastewater containing anions $\mathrm{HSO_3^-}$, $\mathrm{NO_3^-}$ and $\mathrm{H_2PO_4^-}$. Nutrients – carbon dioxide and mineral nutrients elements microalgae cells obtaine directly from the environment by absorbing them with their entire surface. As, like anions $\mathrm{HSO_3^-}$, $\mathrm{NO_3^-}$ and $\mathrm{H_2PO_4^-}$ are absorbed by microalgae, so their effect on the growth of chlorophyllsynthesizing microalgae was studied at different concentrations values of the corresponding anions.

To study the effect of anions HSO_3^- on the increase of chlorophyll-synthesizing microalgae the values of anion HSO_3^- concentration were investigated and indicated in the Fig. 1. To study the effect of anion NO_3^- and $H_2PO_4^-$ on the increase of chlorophyllsynthesizing microalgae the values of anion concentration are indicated in Fig. 3. and Fig. 5. Accordingly, the control solution, which did not contain the corresponding anions in three variants of research, it should be also noted that the conditions of the experiment involved the presence of natural light and temperature 30±5ºC.

The increase in the biomass of chlorophyllsynthesizing microalgae, under these conditions, was determined by photocolorimetric method using a blue light filter according to the law of Bouguer-Lambert-Behr (Poltorak and Chuhray, 1972). Since the optical absorption of light at a given wavelength is proportional to the concentration of microalgae, obtained experimental data on the accumulation of microalgae biomass depending on time within the studied anions HSO_3^-, NO_3^- and $H_2PO_4^-$ concentrations are proportional to the values of optical densities. The optical density value of the researched and control solutions was measured in relation to the comparison solution, in our case, the comparison solution was water.

3. Results and Discussion

During the experimental data processing, dependencies were obtained which illustrate the change in microalgae concentration over time at different values of anion HSO_3^- in solution with its single introduction (Fig. 1). The obtained data indicate that presence of the anion HSO_3^- in the wastewater significantly affects the growth of microalgae cells biomass in comparison with the control. Under the conditions of an increase in anion HSO_3^- concentrations in wastewater, the growth of microalgae biomass decreases. In the control sample, however, its stable growth is observed. Therefore, it is appropriate to assume that the anion HSO_3^- presence starting at concentrations of 0.001 mg/ml and above under the conditions of the experiment, there is a suppression of the wastewater treatment process with chlorophyllsynthesizing microalgae of the Chlorella type.

A more detailed data analysis in the Fig. 1 allows us to argue that the change in the number of microalgae cells per time unit under the experimental conditions is determined by the number of born and died cells. Quantitatively, this process can be described by a known equation (3), which is in the coordinates $ln\frac{C}{C_0} = f(t)$ allows you to determine the growth coefficient – μ (Dyachok et al., 2017).

The growth coefficient may be $\mu > 0$, under the conditions of a certain value activity of the inhibitor concentration (anion HSO_3^-) photosynthesis can gain negative value $\mu < 0$, as well as being equal to zero. Experimental research data (Fig. 1), in coordinates $ln\frac{C}{C_0} = f(t)$ (Dyachok et al., 2017) are graphically presented by the lines in Fig. 2.

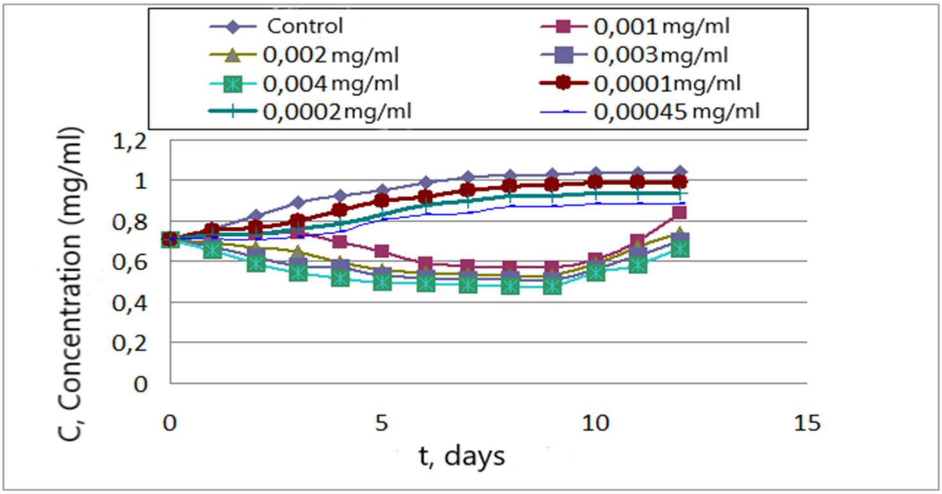

Fig. 1. The change in the concentration of microalgae cells over time at the corresponding values of anion HSO_3^- concentrations

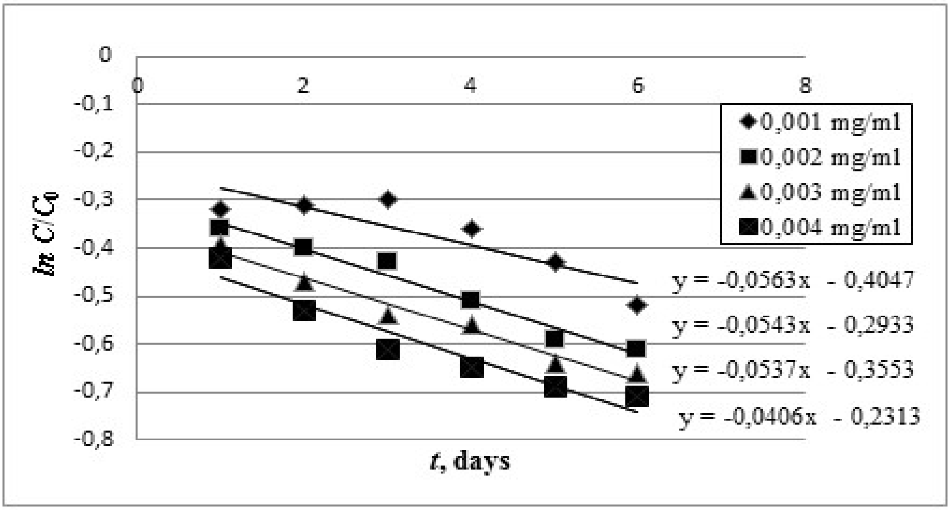

Fig. 2. The dependence of the logarithm change of the microalgae cells concentration on time at the corresponding anion HSO_3^- concentrations

At anion HSO_3^- concentration values in wastewater 0,001 mg/ml; 0,002 mg/ml; 0,003 mg/ml; 0,004 mg/ml, the growth rates are less than zero $\mu < 0$. The numerical values of the coefficients are respectively: $\mu_4 = -0{,}0563\ d^{-1}$; $\mu_5 = -0{,}0543\ d^{-1}$; $\mu_6 = -0{,}0537\ d^{-1}$; $\mu_7 = -0{,}0406\ d^{-1}$. Thus, the inhibitory properties of the anion HSO_3^- at given concentration values are obvious.

Subsequently, we studied the effect of anions NO_3^- and $H_2PO_4^-$ on the dynamics of microalgae growth. Based on the results of the experimental data and the calculated values, graphical dependences of the change in the concentration of microalgae cells on time at the corresponding concentrations of anions NO_3^- and $H_2PO_4^-$ in wastewater under the conditions of their single introduction fig. 3 and 5 were obtained. Analyzing the data (Figs. 3, 5), it should be noted that the growth of microalgae cell biomass over time also significantly depends on the anions NO_3^- and $H_2PO_4^-$ concentration compared to the control where anions NO_3^- and $H_2PO_4^-$ are absent. With increasing of anions NO_3^- and $H_2PO_4^-$ concentration, microalgae cell growth is increased compared to control. Such an increase in the values of the microalgae concentrations, only to a certain value of the concentration of the available anions NO_3^- and $H_2PO_4^-$. As can be seen in (Fig. 3) at the anion NO_3^- concentration, 68 mg/ml (4th sample) on the second day behaves in the same way as others, it means that the adaptation phase takes place up to two days, with a slight increase starting on the third day, which is higher on the 5th day than in the control sample, but from the sixth day there is a decline and the next five days there is a decrease in growth. At higher upper values of anion NO_3^- concentrations there is a dying of microalgae compared to the control.

The values of the growth coefficients – μ were found similarly, by the same methodology and they accordingly were: 0,075 d^{-1}; 0,076 d^{-1}; 0,077d^{-1}.

Concerning anion $H_2PO_4^-$ a similar pattern is observed only with other concentrations. As we can see (Fig. 5), the fifth sample, where the concentration is 0.1 mg/m^3, negative growth of microalgae biomass is observed. This indicates that this concentration of anion $H_2PO_4^-$ has a detrimental effect on the microalgae growth. At the same time at smaller values of anion $H_2PO_4^-$ concentrations there is an increase in the biomass of microalgae cells compared to the control. The main parameter is the value of the growth coefficients – μ it was determined according to the presented methodology Fig. 6. It should also be noted that in the experimental study, there is a change in the alkaline acid balance of the aquatic environment, namely from acidic (pH = 4.7) to neutral (pH = 6.8).

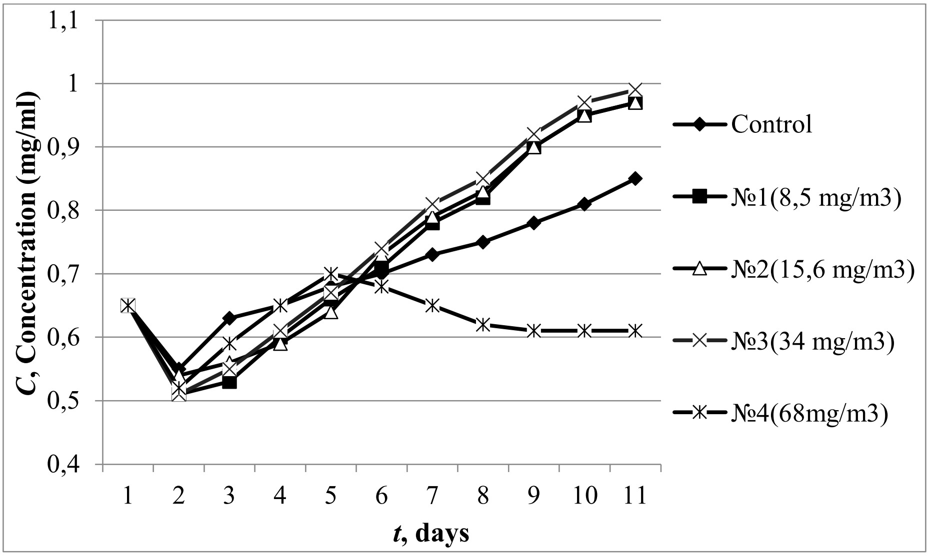

Fig. 3. The dependence of the change in the concentration of microalgae cells over time at the corresponding anion NO_3^- concentrations

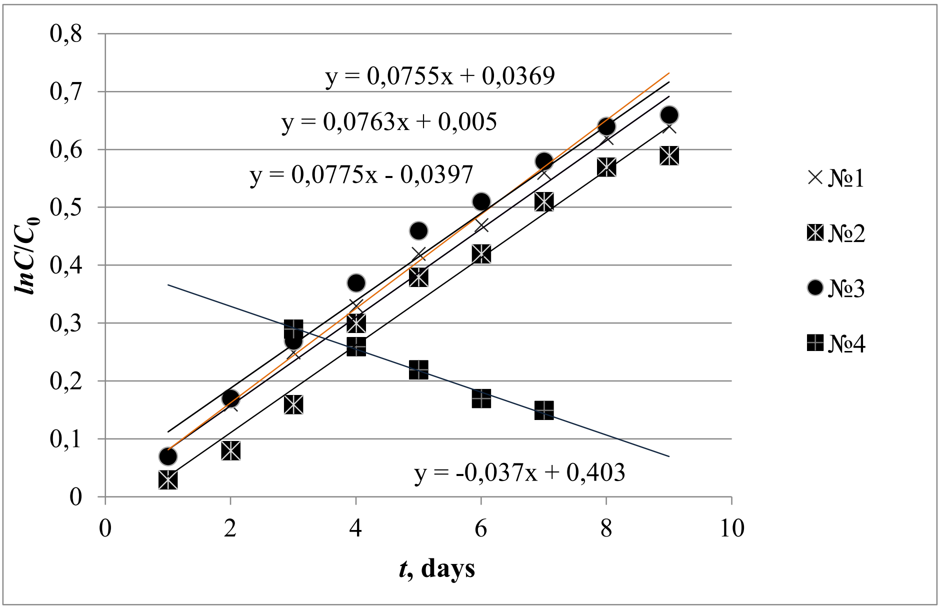

Fig. 4. Dependence of change in logarithm of suspension concentration of microalgae cell on time (at corresponding anion NO_3^- concentrations)

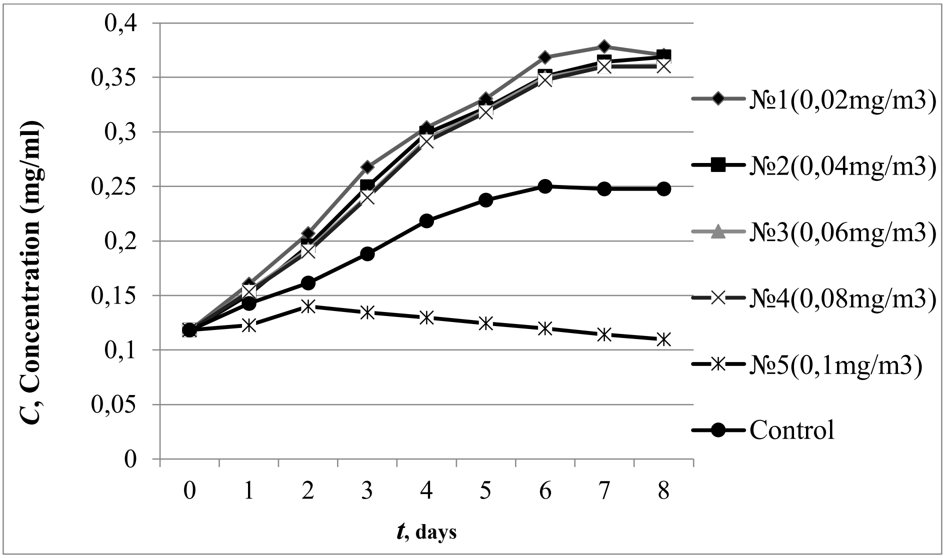

Fig. 5. The dependence of the change in the concentration of microalgae cells over time at the corresponding anion $H_2PO_4^-$ concentrations

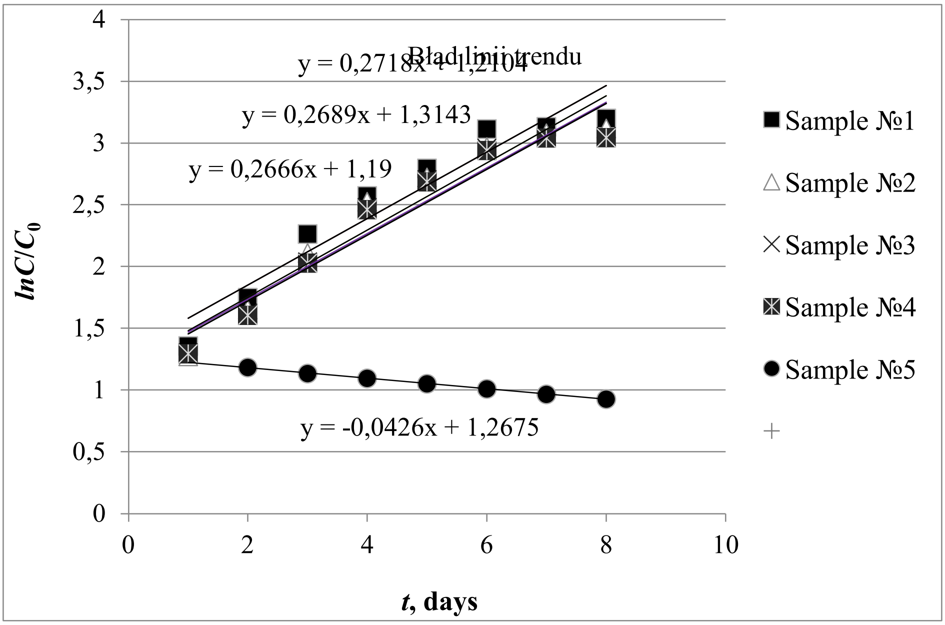

Fig. 6. Dependence of change in logarithm of suspension concentration of microalgae cells on time (at corresponding anion $H_2PO_4^-$) concentrations

For the analytical calculation of the optimum values of anions concentrations in wastewater to be purified using chlorophyllsynthesizing microalgae, a created mathematical model of microalgae biomass growth depending on the concentration of the corresponding anions, which looks like:

$$\begin{cases} \frac{dC}{dx} = \mu_1 C - \mu_2 C \\ \frac{dC}{dx} = \mu_1 C \\ x = 0, C = C_0 \end{cases} \tag{1}$$

where: x – concentration of anions HSO_3^-, NO_3^- and $H_2PO_4^-$; μ_1, μ_2 – growth coefficients at favorable and unfavorable values of anions HSO_3^-, NO_3^- and $H_2PO_4^-$ concentration; C – the concentration of microalgae in the culture medium.

Its solutions have several analytical expressions, one of them allows you to calculate the critical values of the corresponding anions concentrations according to the known values of the growth coefficients – μ;

$$x_{max} = \frac{ln\mu_2 - ln\mu_1}{(\mu_1 + \mu_2)} \tag{2}$$

Using the data of mathematical processing of the experimental studies results of the microalgae biomass growth, the corresponding values of the growth coefficients were calculated μ_1, μ_2. After substituting the obtained values for the anions NO_3^- and $H_2PO_4^-$ in equation (2) we calculate the optimum value of anion NO_3^- concentration to culture medium.

$$x_{max} = \frac{ln\,\mu_2 - ln\mu_1}{(\mu_1 + \mu_2)} = \frac{ln(-0{,}037) - ln\,0,076}{(0{,}076 - 0{,}037)} = 18{,}46\,mg/m^3 \tag{3}$$

Similarly, using equation (2), we calculate the optimal value of anion $H_2PO_4^-$ concentration in culture medium:

$$x_{max} = \frac{ln\,\mu_2 - ln\mu_1}{(\mu_1 + \mu_2)} = \frac{ln(-0{,}0426) - ln\,0,2425}{(0{,}2425 - 0{,}0426)} = 0{,}061\,mg/m^3 \tag{4}$$

According to the equations 3 and 4, the concentration of anions NO_3^- and $H_2PO_4^-$ is determined at which the maximum value of the microalgae biomass concentration in the culture medium is reached. To check the adequacy of the mathematical model and its solution, we build graphs of the dependence of anions NO_3^- and $H_2PO_4^-$ concentration on the growth coefficient μ.

From Fig. 7 and 8 it is seen that the maximum increase in the concentration of microalgae is achieved at the concentration of anion NO_3^- ≈ 18 mg/m^3 and anion $H_2PO_4^-$ ≈ 0,06 mg/m^3 concentration. This indicates that the mathematical model accurately describes the course of the study process, and the obtained solutions will allow to predict equipment for the implementation of wastewater treatment technology under the conditions of anions NO_3^- and $H_2PO_4^-$ presence (Fig. 9).

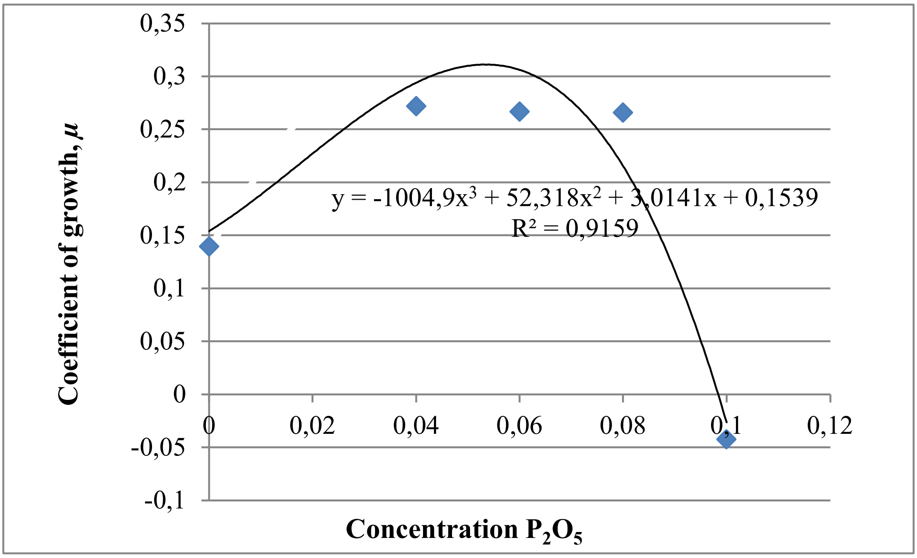

Fig. 7. Dependence of the microalgae growth coefficient μ on the concentration of anions $H_2PO_4^-$

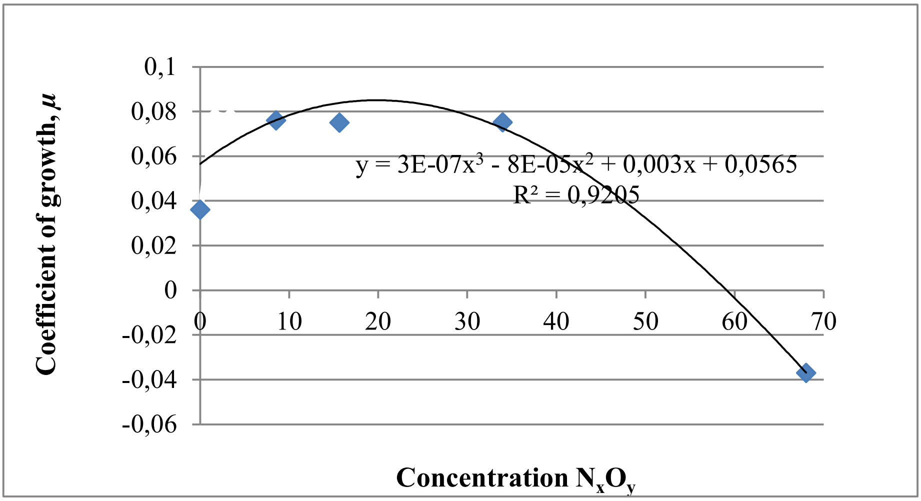

Fig. 8. Dependence of the microalgae growth coefficient μ on the concentration of anions NO_3^-

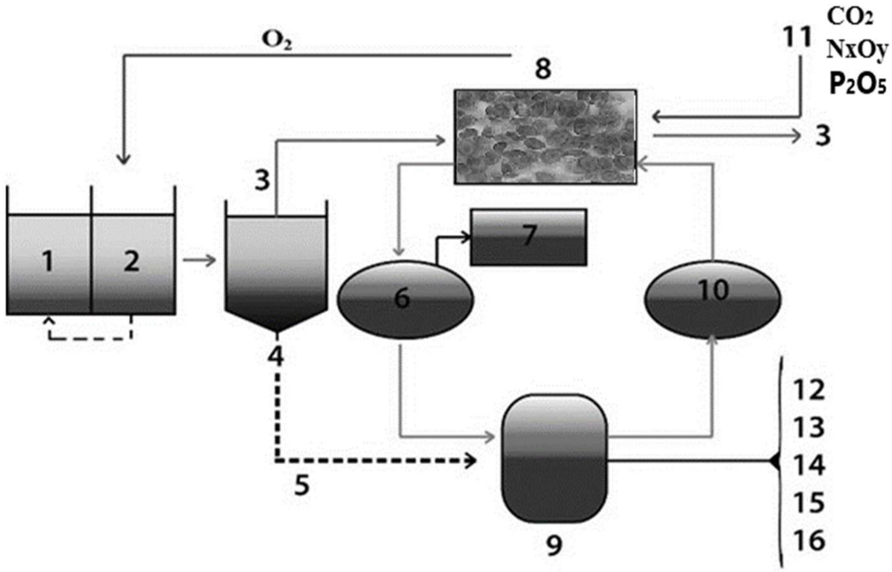

Fig. 9. Combined wastewater treatment scheme using Chlorella type microalgae: 1 – anoxide zone; 2 – oxide zone; 3 – wastewater after the process with activated sludge; 4 –secondary sedimentation tank; 5 – precipitate secondary sedimentation tank; 6 – microalgae biomass; 7 – tank; 8 – cultivation of the Chlorella type microalgae; 9 – hydrothermal liquefaction or anaerobic digestion; 10 – biogenes and CO_2; 11 – CO_2, P_2O_5 and NxOy from other systems; 12 – biochar; 13 – protein / nutritional supplements; 14 – fertilizers; 15 – soil amendment; 16 – biofuels

Figure 9 presents a scheme of wastewater treatment using the Chlorella type microalgae. The scheme consists of a biofilm reactor with a movable layer of nozzle for air sparging 1, and an open pond for the cultivation of microalgae as a biological reactor 2. Wastewater after the process with activated sludge 3, fall into the container 8, where the cultivation of the Chlorella type microalgae happens. The wastewater sludge enters the secondary sedimentation tank 4 and from there the precipitate of the second sludge 5 enters the hydrothermal liquefaction or anaerobic digestion 9. Since microalgae cultivation requires CO_2, there is an opportunity to use its emission at the enterprises of other industries (for example, power plants), reducing the emission into the atmosphere. Therefore, CO_2 , P_2O_5 and N_xO_y from other systems 11 fall into the tank 8 for the cultivation of microalgae. From the tank 8, the biomass of microalgae enters the tank 6, from which it enters the tank 9 for hydrothermal liquefaction or anaerobic digestion, or the tank 7 where organic „green" fertilizer is made from it. From the tank 9 biogenes and CO_2 enter the tank 10, and from it again into the tank of microalgae cultivation 8. Everything else after hydrothermal liquefaction or anaerobic digestion 9 is also converted into fertilizers 14, protein or nutritional supplements 13, soil ammendment 15, and biofuels 16 (https://hlorella.jimdo.com).

4. Summary and Conclusions

Chlorella type microalgae application is the one of the options for wastewater treatment, which in turn is a promising substrate for biofuel production, since biomass obtaining creates the potential for energy production.

Limit values of anions HSO_3^-, NO_3^- and $H_2PO_4^-$. concentration are set for the successful operation of this treatment plant.

The result of wastewater treatment by this method is changing of the alkaline acid balance from acidic to neutral after the experiment.

Based on the obtained experimental research results, mathematical models have been created that allow to predict the maximum values of anions NO_3^- and $H_2PO_4^-$. concentrations and at which effective wastewater treatment with chlorophyllsynthesizing microalgae is possible.

The scheme of wastewater treatment using chlorophyllsynthesizing microalgae of the Chlorella type is proposed.

The use of the Chlorella type microalgae for wastewater treatment creates new opportunities for the environmental safety improvement by designing and building a reliable system.

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Modeling of the destruction processes of antibiotics in drinking water by ultrasound method

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Abstract

The increase in the disposal of antibiotics demands for newer technologies for the purification of drink water. Advanced oxidation processes (AOPs) constitute a promising technology for the treatment of such waters. This study presents a general kinetics model ultrasound treatment drink water

Models developed to degrade organic pollutants. Typical methods such as Fenton/US and US in different antibiotics (ofloxacin, penicillin, enrofloxacin) are discussed. This work also highlights the application of US in treating antibiotics.

Keywords: reaction kinetics model, ultrasound; water sonolysis

1. Introduction

In Ukraine, at present, the problem of drinking water pollution is quite acute. The main source of drinking water is the Dnieper River. It is also used for the discharge of domestic and industrial wastewater. Existing schemes of water treatment in Ukraine include the stages of coagulation, sedimentation, filtration and chlorination. Thus, in some cases, secondary contamination occurs with iron cations and formed organochlorine compounds. In addition, unsatisfactory condition of pipelines leads to contamination by iron compounds at the stage of water transportation. Requirements for the quality of drinking water include the control of the content of certain organic substances, such as benzo (a) pyrene, benzene, pesticides, synthetic anionic surfactants, trichlorethylene, carbon tetrachloride. The content of antibiotics in water is not standardized.

On the other hand, the rapid growth of livestock and poultry production leads to the entry of medicines into water bodies. It is known that they have sufficient stability and negatively affect human health. The solution to this problem can be the use of local stations for additional purification of drinking water that purify drinking water from the entire range of organic compounds. Modern methods of purification from them are chemical, physical, biological methods, which are destructive. They are in the deep oxidation of organic compounds. For their implementation, energy costs are required. The traditional type of energy, which in the overwhelming majority of cases is currently used, is thermal energy. From a theoretical point of view, carrying out reactions with this method of supplying energy is not optimal, since typical values of the chemical breaking energies are several eV. Thermal heating is impossible in modern conditions. Therefore, the intensification of equilibrium processes has fundamental limitations. Another way is to conduct chemical processes in non-equilibrium conditions. Among these methods, called “Advanced oxidation processes”. Processes that use the effects of physical fields either directly in solution or over its surface are of particular interest. First, their use does not require chemical reagents. Secondly, a nonequilibrium system is the source of a large number of chemically active particles capable of leading to the decomposition of organic substances. The use of ultrasound in various processes, such as the purification of water and aqueous solutions from antibiotics can be very promising.

2. General information

A lot of work has been devoted to the investigation of the processes of purification of various waters by the excitation of cavitation phenomena by various methods and devices. It was convincingly shown that physicochemical processes in cavitation fields, regardless of the method of their excitation, are practically identical, that is, they occur according to the same mechanisms, although they differ in their energy indices.

Under the influence of US radiation, a rather high degree of neutralization of aromatic compounds and their substituted phenol, 2,4-dichlorophenol, bisphenol, diethyl phthalate etc. is achieved, especially in the case of the use of the Fenton reagent effective in an acidic environment (Liang et al., 2007; Guinea et al., 2009; Xiao et al., 2010; Garcia-Segura et al., 2012; Michael et al., 2012; Rodrigues-Silva et al., 2013; Barhoumi et al., 2015; Epold et al., 2015; Annabi et al., 2016; Gong et al., 2016; Özcan et al., 2016).

The use of cavitation in the presence of catalysts (dispersed iron or copper) provides a high degree of oxidation of phenol (Drijvers et al., 1999), and oxidation products of aromatic compounds are better subjected to biodegradation (Drijvers et al., 1999). With the help of ultrasonic radiation neutralized halogenated alkenes (Serpone et al., 1994; Nagata et al., 2000), intensify the purification of sewage from oil products by coagulation. Cavitation method disinfect water, including with the use of gaseous oxidants, UV radiation (Fischer et al., 1986).

During ultrasound treatment, cavitation bubbles are formed, the collapse of which causes significant local impulse increases in pressure and temperature and, accordingly, the heating of the entire volume of the treated medium. In addition, there is sonolysis of water, that is, its decomposition with the release of reactionary radical particles (Drijvers et al., 1999). These effects significantly intensify various processes – destruction, homogenization, chemical interaction, disinfection, etc. One of the active agents formed in the systems under study is hydrogen peroxide. According to existing concepts, hydrogen peroxide is formed in the process of local concentration of energy and decomposition of the water molecule, leading to the formation of radicals. No available direct methods make it possible to determine the concentration of radicals in solution and, especially, the actual velocities. The only way is numerical simulation methods. Despite the obvious difficulties of an adequate description, they remain the only tool to estimate the particle concentrations, the actual rates of their formation and death by elementary channels, to predict the course of the process in experimentally unexplored conditions, and to explain the observed regularities not qualitatively but quantitatively. Such works, known to us, are relatively few. In all studies, it is assumed that the action of ultrasound leads to initiation reactions.

Table 1 shows the main reactions that occur during sonication. The rate constants of these reactions are known (Yanagida et al., 1999; Liang et al., 2007; Guinea et al., 2009; Michael et al., 2010; Xiao et al., 2010; Garcia-Segura et al., 2012; Michael et al., 2012; 2013; Rodrigues-Silva et al., 2013; Bokare et al., 2014; Giri et al., 2014; Yahya et al., 2014; Barhoumi et al., 2015; Epold et al., 2015; Annabi et al., 2016; Gong et al., 2016; Özcan et al., 2016; Yahya et al., 2016). The scheme fully describes the entire set of experimental results on cavitation treatment of distilled water at pH 1–7.

Taking into account that the information on the rate constants of chemical reactions in the literature (Fischer et al., 1986; Susick et al., 1990; Kotronarou et al., 1991; Serpone et al., 1994; Francony and Petrier, 1996; Mason and Cordemans, 1996; Dahlem et al., 1998; Drijvers et al., 1999; Yanagida et al., 1999; Nagata et al., 2000; Liang et al., 2007; Guinea et al., 2009; Homem and Santos, 2011; Feng et al., 2013;Wang and Wang, 2016) is of a contradictory nature, the main one was estimated on the basis of experiments.

The modeling solution was affected by ultrasound in the apparatus. Being connected to the generator of ultrasonic fluctuations, the radiator of ultrasound dispergator UZDN is shipped in this vessel (Fig. 1).

The influence of ultrasound was investigated under frequencies 22 kHz.

The concentrations of peroxides in the modeling solution were determined through the different periods of time during investigations. Determination of hydrogen peroxide concentration by titration of the treated solution. The method is based on ion oxidation reactions with I^- peroxide, followed by iodine reduction with sodium thiosulfate using a starch solution.

Table 1. Reactions used in the calculation of concentration dependencies in water the treatment of ultrasound

Reaction	Rate constant, at 25 ° C	Reaction	Rate constant, at 25 ° C
$H_2O = H\cdot + OH\cdot$	$3{,}00\cdot10^{-7}$ $(8{,}00\cdot10^{-6})$ (s^{-1})	$2H\cdot = H_2$	$5{,}01\cdot10^{9}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$OH\cdot + H_2 = H_2O + H\cdot$	$3{,}60\cdot10^{7}$ $(l\cdot mol^{-1}\cdot s^{-1})$	$H\cdot + OH\text{-} = H_2O$	$2{,}19\cdot10^{7}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$H_2O = H^+ + OH\cdot$	$2{,}63\cdot10^{-8}$ (s^{-1})	$H\cdot + H_2O = H_2 + OH^-$	$6{,}17\cdot10^{8}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$H_2O_2 = OH\cdot + OH^-$	$1{,}29\cdot10^{10}$ (s^{-1})	$H\cdot + HO_2\cdot = H_2O_2$	$1{,}99\cdot10^{10}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$H\cdot + H_2O_2 = OH\cdot + H_2O$	$5{,}01\cdot10^{7}$ $(l\cdot mol^{-1}\cdot s^{-1})$	$2HO_2\cdot = H_2O_2 + O_2$	$8{,}511\cdot10^{5}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$H\cdot + H_2O = OH\cdot + H_2$	10^{10} $(l\cdot mol^{-1}\cdot s^{-1})$	$H^+ + OH^- = H_2O$	$1{,}48\cdot10^{11}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$OH\cdot + H_2O_2 = HO_2\cdot + H_2O$	$2{,}69\cdot10^{7}$ $(l\cdot mol^{-1}\cdot s^{-1})$	$2H_2O = H_2O_2 + H_2$	$1{,}99\cdot10^{6}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$OH\cdot + H_2 = H\cdot + H_2O$	$3{,}89\cdot10^{7}$ $(l\cdot mol^{-1}\cdot s^{-1})$	$Fe^{2+} + H_2O_2 = Fe^{3+} + OH\cdot + OH^-$	63 $(l\cdot mol^{-1}\cdot s^{-1})$
$OH\cdot + OH\cdot = H_2O_2$	$5{,}50\cdot10^{10}$ $(l\cdot mol^{-1}\cdot s^{-1})$	$Fe^{2+} + OH\cdot = Fe^{3} + OH^-$	$3{,}20\cdot10^{8}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$H_2O_2 = OH\cdot + OH\cdot$	$3{,}55\cdot10^{-9}$ (s^{-1})	$Fe^{3+} + H_2O_2 = Fe^{2+} + HO_2\cdot + H^+$	$1{,}50\cdot10^{-2}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$OH\cdot + HO_2\cdot = O_2 + H_2O$	10^{10} $(l\cdot mol^{-1}\cdot s^{-1})$	$Fe^{3} + HO_2\cdot = Fe^{2+} + O_2 + H^+$	$7{,}00\cdot10^{-7}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$OH\cdot = OH^-$	$3{,}02\cdot10^{10}$ (s^{-1})	$R_1H + OH\cdot = R_1\cdot + H_2O$	$2{,}30\cdot10^{-5}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$H^+ = H\cdot$	$2{,}29\cdot10^{10}$ (s^{-1})	$R_2H + OH\cdot = R_2\cdot + H_2O$	$7{,}95\cdot10^{9}$ $(l\cdot mol^{-1}\cdot s^{-1})$
$H_2O = H + OH^-$	$1{,}78\cdot10^{-5}$ (s^{-1})	$R_3H = R_3\cdot + H\cdot$	$2{,}00\cdot10^{-4}(s^{-1})$
$H\cdot + O_2 = HO_2\cdot$	$1{,}20\cdot10^{10}$ $(l\cdot mol^{-1}\cdot s^{-1})$		

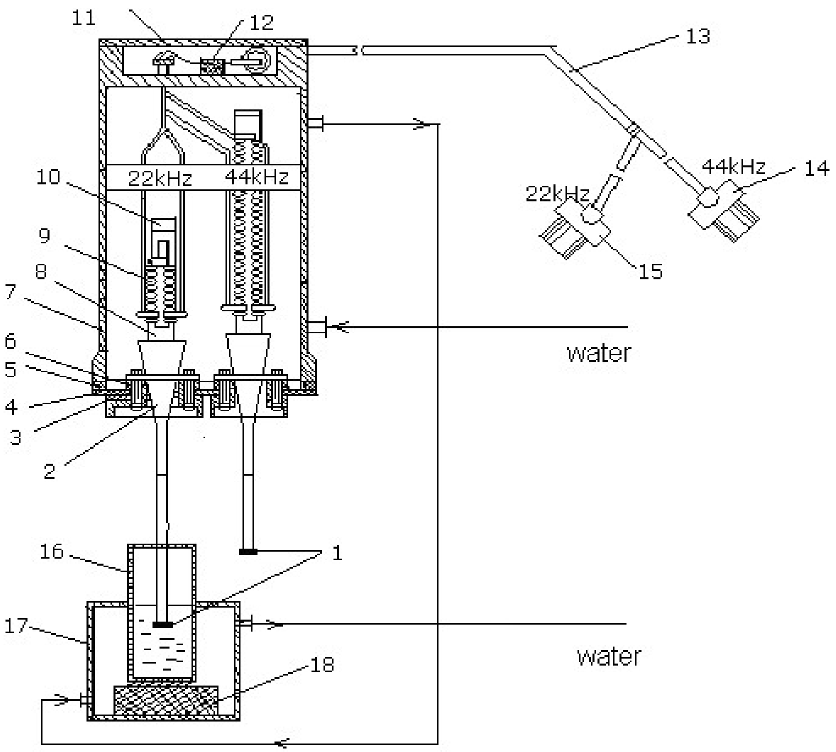

Fig. 1. Laboratory setup: 1 – conic nozzle,2 – concentrator, 3, 5, 6, 10, 18 – rubber gaskets, 4 – plank, 7– shroud, 8 – magnetostrictive transducer, 9 – coil, 11 – cover, 12 – stock of connections, 13 – cable, 14, 15 – connectors, 16 – ceramic glass, 17 – thermostatic shroud made of aluminium

3. Result and discussions

At the first stage kinetic curves of accumulation of oxidizing agents for tap water and distilled water were obtained. The calculated reaction rate constants were $3.0 \cdot 10^{-7}$ for distilled and $8.0 \cdot 10^{-6}$ mol^{-1} $L^{-1}s^{-1}$ for tap water.

In addition, it is obvious that in drinking water there are components that significantly affect the course of oxidation. In our model it is supposed to take into account the presence of Fe^{2+} cations, within the limits of the requirements for drinking water quality, as well as the rate constant of the first reaction, determined on the basis of experimental data.

In the presented model, the initial data for calculations are:

- the mechanism of the process, defined as a set of elementary reactions and their kinetic parameters, presented in Table 1;
- the composition of the reaction mixture at the initial time for tap water;
- process parameters;
- the limiting solubility of oxygen in water at a given temperature.

The solution of the system of equations was carried out using COMSOL 5.3. Calculations were carried out for a number of antibiotics widely used in veterinary medicine (ofloxacin, penicillin, enrofloxacin). The initial concentrations were 0.05 mmol/l.

Analysis of the obtained dependences shows that when ultrasonic treatment of distilled water the maximum concentration of OH radicals is reached in $4 \cdot 10^{-11}$ s and is $3 \cdot 10^{-8}$ M, whereas in the tap water (without taking into account the influence of iron ions and organic substances) the maximum concentration of OH- radicals is achieved for $3.8 \cdot 10^{-7}$ s and is $8.7 \cdot 10^{-13}$ M. In distilled water, the maximum concentration of peroxide is reached for $3.7 \cdot 10^{-10}$ s and is $4.7 \cdot 10^{-13}$ M. In tap water, the maximum concentration of peroxide (without the influence of iron ions and organic substances) is achieved for $3.7 \cdot 10^{-7}$ s and is $4.7 \cdot 10^{-13}$ M.

The rate constant of the reaction of decomposition of water into radicals does not affect the value of the maximum peroxide concentration, but affects the rate of its accumulation. In distilled water, the maximum concentration of peroxide is reached 1000 times faster than in the tap. In tap water, the rate of oxidation of iron (II) cations is slightly higher than in distilled water. Further calculations were carried out for model solutions (tap water containing iron cations and antibiotics).

Simulation of the decomposition of antibiotics has shown (Fig. 2–4) that ernofloxacin is not oxidized either in distilled water or in distilled water in the presence of iron under the action of ultrasound.

Penicillin in tap water and in distilled water is oxidized at approximately the same rate. Ofloxacin in tap water oxidizes slightly faster than in distilled water.

Analyzing Fig. 3–5, we can say that the greater the value of the rate constant of oxidation of organic substances, the more noticeable is the effect of impurities in tap water, and the more the oxidation rate in distilled water differs from the rate of oxidation in tap water.

The presence of impurities of organic substances has practically no effect on the rate of oxidation of iron in either distilled or tap water.

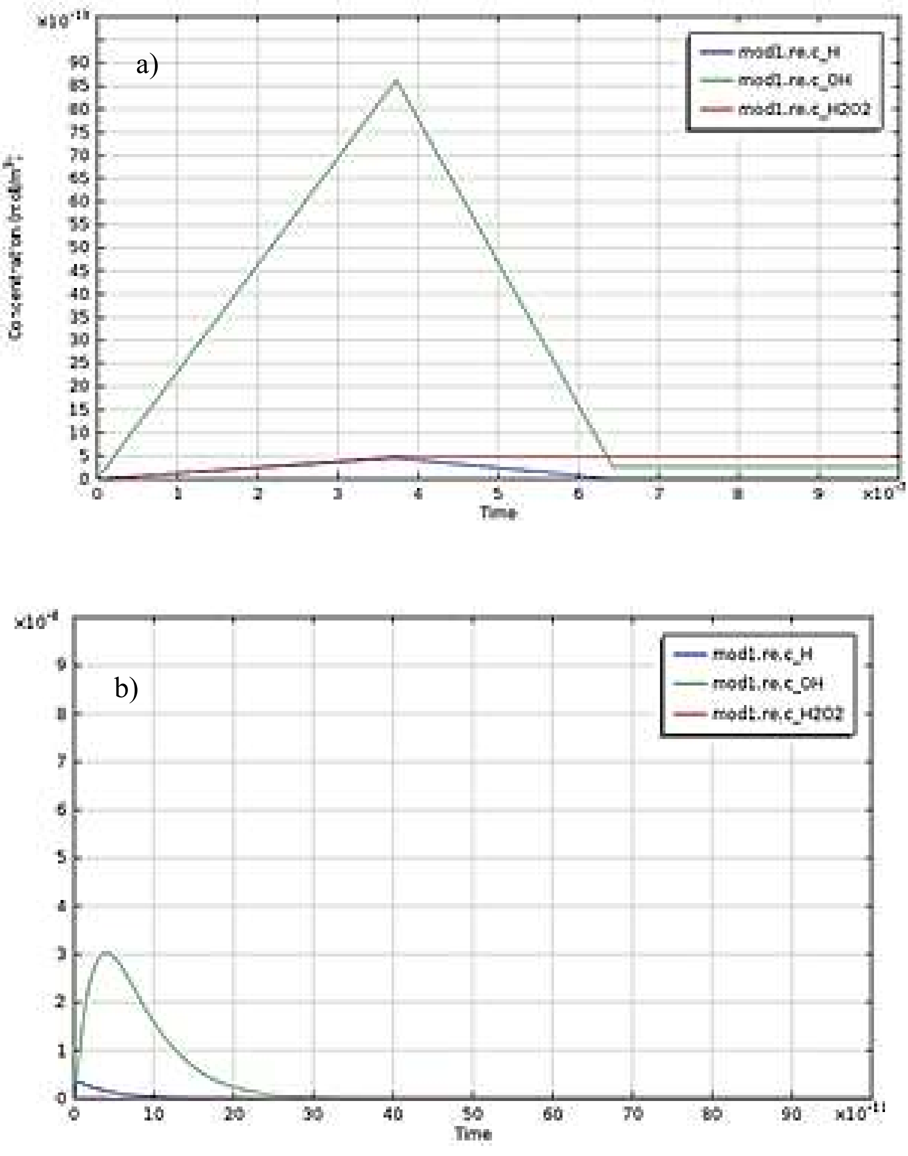

Fig. 2. Changes in the concentrations of the main reaction products in ultrasonic processing:
a) distilled water, b) tap water

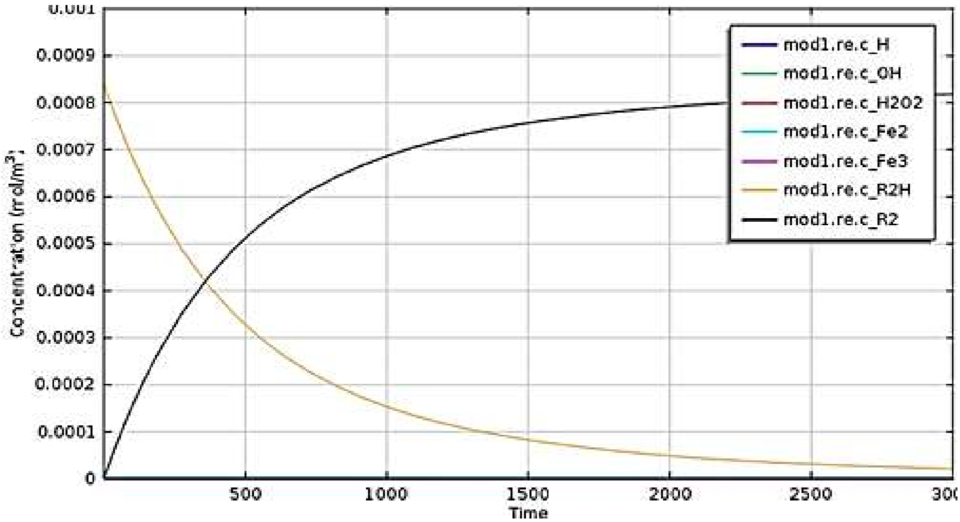

Fig 3. Enlarged views of the chemical reactions as a function of time R_2H- enrofloxacin R_2-radical

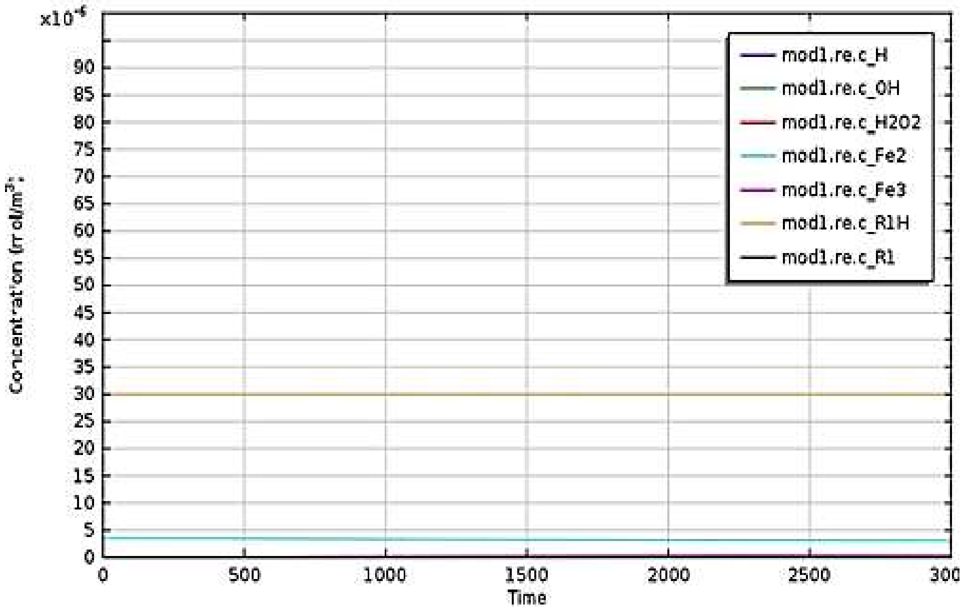

Fig 4. Enlarged views of the chemical reactions as a function of time R_1H-penicillin R_1-radical

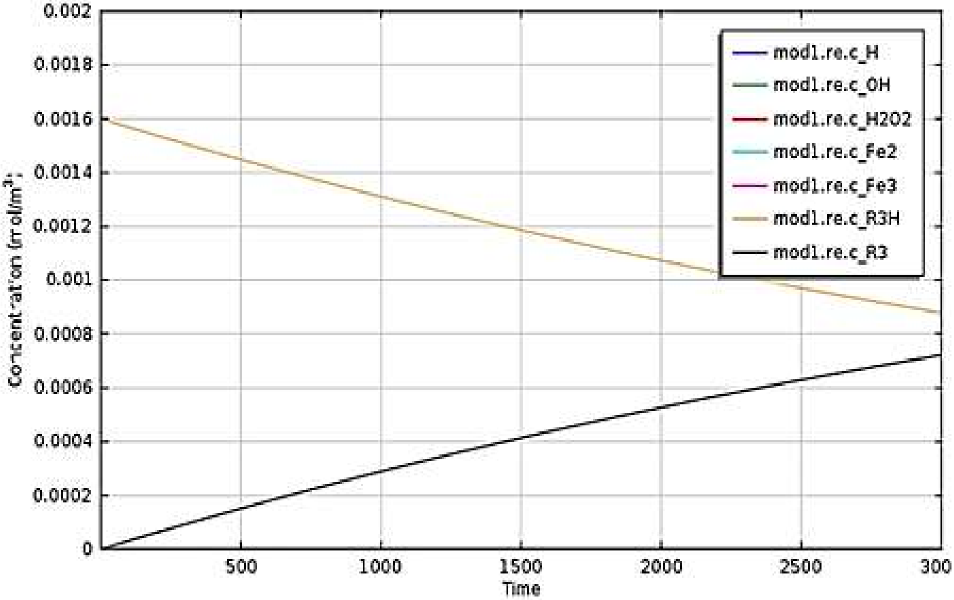

Fig 5. Enlarged views of the chemical reactions as a function of time R_3H-ofloxacin R_3-radical

The presence of impurities of organic substances has practically no effect on the rate of oxidation of iron in either distilled or tap water.

4. Conclusions

On the basis of experimental data, the rate constant for the formation of peroxides in distilled and tap water was determined.

A model describing the processes of peroxide accumulation in the presence of iron and without is constructed. A mathematical model is constructed that can be used to calculate the composition of water on ultrasonic treatment. The final composition of water containing antibiotics was determined. Numerical simulation showed that OH radicals are generated as the main oxidant species. The presented model in this article is suitable for predicting the influence of ultrasound on the decomposition of antibiotics in an aqueous medium.

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Purification of chromium containing waste water by magnetic sorbents

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Abstract

In the work shown that the use of magnetically controlled sorbents makes it possible to purify chromium (III) wastewater with high efficiency.

Obtained magnetic adsorbents are studied. The process of adsorption of chromium cations (III) by ferrite adsorbents was investigated. It is shown in the paper that the use of magnetically controlled sorbents makes it possible to purify chromium (III) wastewater with high efficiency. It was found that the removal of Cr (III) cations effected the adsorbents efficiency in the order of decreasing $NiFe_2O_4$> $(CrFe)_2O_3$> $MnFe_2O_4$> Fe_3O_4> $CoFe_2O_4$.

Keywords*:* magnetic sorbents, chromium, purification, waste water

1. Introduction

Chromium (III) compounds, especially chromium (VI), are toxic to humans and animals, therefore the development of new methods and technologies for wastewater treatment is very relevant.

There are many effective technologies for purification of chrome-containing wastewater from chromium cations: reagent, electrochemical, membrane. The application of sorption technologies is promising. In recent years, adsorption has shown promising and effective results in both drinking water and wastewater treatment technologies in the industry. A number of adsorbents have been synthesized and applied to the treatment of pollutants, such as metal cations, dyes, and pharmaceutical products in solutions (Pan et al., 2019; Nasr et al., 2019, Hashem et al., 2019, Tao et al., 2019).

However, these types of adsorbents have one common drawback – they require a long release from the solution, which increases operating costs. To prevent this problem, some researchers offer magnetic materials that can be promising adsorbents that can be easily separated from the solution using a magnetic field. Magnetic adsorbents (MA) can provide fast and efficient suspension separation.

Ferrites are magnetic materials with a cubic spinel structure that have a wide area of use. The properties of ferrites depend on the cationic composition, particle morphology, which is conditioned by the conditions of the technological process. Currently, many researchers are studying the effect of different synthesis parameters on the technological properties of ferrites. For example, nanomaterials of the $MeFe_2O_4$ composition (Me = Fe, Mn, Co, and Ni) with a particle size in the range of 50–10 nm were obtained by hydrophase methods (Coll et al., 2014; Kumar et al., 2018). Frolova (2019) presents the technology of spinel ferrite production by the plasma chemical method. Nanodispersed ferrites have a wide scope. A rather new trend is their use in environmental technologies related to the removal of heavy metals (Subramani and Jacangelo, 2015; Reddy and Yun, 2016).

This paper proposes a technology for the extraction of chromium cations by magnetic separation to solve the problem of environmental protection.

2. Experiment technique

The corresponding sulphates were used for the synthesis of magnetic sorbents. The $MeFe_2O_4$ nanoparticles (Me = Fe, Mn, Co, and Ni) were prepared by chemical precipitation from aqueous solution of ferric(II) sulphate, manganese(II) sulphate, nickel(II) sulphate, cobalt(II) sulphate by the method described in details in the publication of Frolova and Derhachov (2017). The resulting suspension was separated on a magnetic filter and dried at a temperature of 100–150°C for 2 hours.

X-ray analysis of the samples was performed on a DRON-2 diffractometer. Mode of operation of the X-ray source 40 kV, 30 mA. Scanning angle range 2θ: 10 to 90°, scanning step 0.0001°. Scanning electron microscopy images produced images of various magnifications.

The studies included the execution of several series of experiments with different ad-sorbents: magnetite adsorber (FFe), nickel ferrite adsorber (FNi), cobalt ferrite adsorbent (FCo), manganese ferrite adsorbent (FMn), chromium (FCr) adsorbent.

The sorption properties of MA samples were revealed by determining the degree of sorption of chromium (III) cations of different initial concentrations. The concentration of adsorbent in the model solutions also varied.

The degree of sorption was calculated by reducing the concentration of chromium cations in aqueous solution by the formulas:

$$\%S = \frac{(C_0 - C_t)}{C_0} 100\% \tag{1}$$

where: C_0 and C_t are the initial concentrations as well as the concentrations of metal ions after treatment in solutions, respectively (mol/l).

3. Results and discussion

Depending on the degree of sorption on the mass of adsorbents are of different nature. For magnetite, manganese ferrite and chromium, they are almost linear in nature and differ significantly in the maximum degree of extraction. When using magnetite, the maximum sorption capture was 70%, chromium ferrite – 90%, nickel ferrite – almost 100%. For cobalt and nickel ferrite, the course of the curve is logarithmic. In both experiments, the degree of trapping increased with increasing initial concentration of the solution.

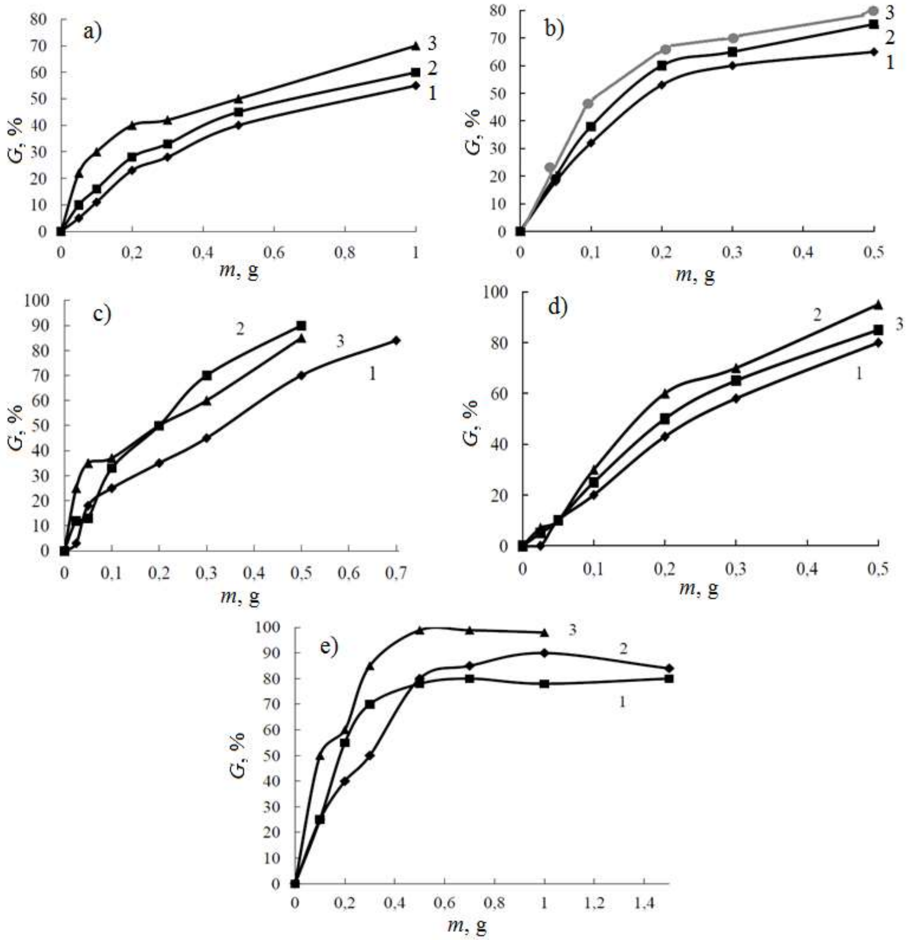

Fig. 1. Dependence of the degree of purification on the concentration of adsorbent (g/50 ml): a) FFe, b) FCo, c) FCr, d) FM, e) FNi

When using cobalt ferrite, the maximum sorption capture was 72%. As the initial concentration of the solution increases, the degree of trapping increases. The use of TNF leads to a degree of purification of 99.8%.

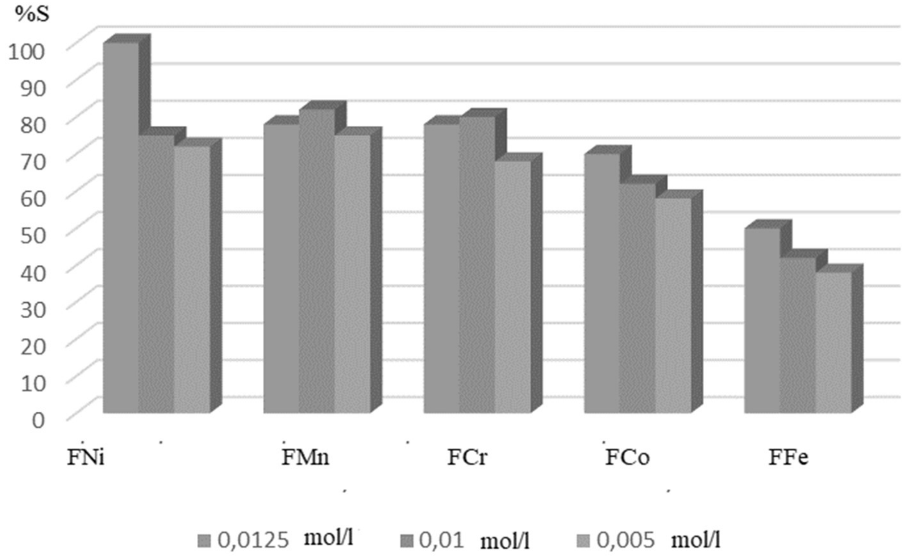

Fig. 2. Histogram of the distribution of the degree of purification (mass of adsorbent 0.5 g/50 ml)

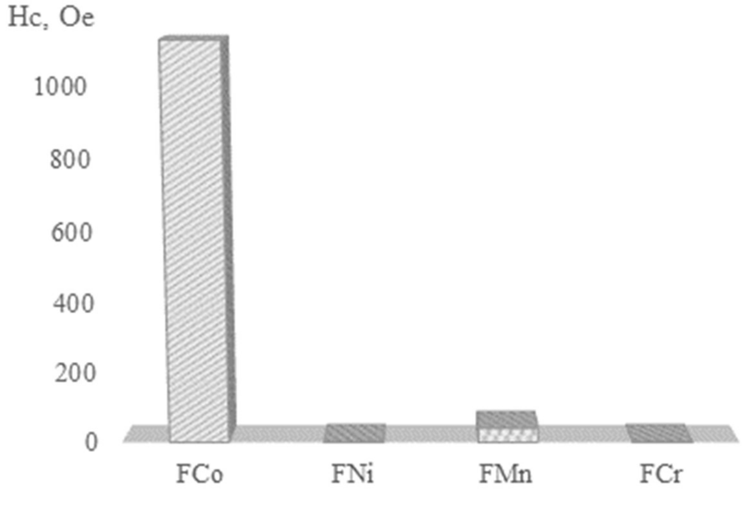

Fig. 3. Histogram distribution of the coercive force for ferrites

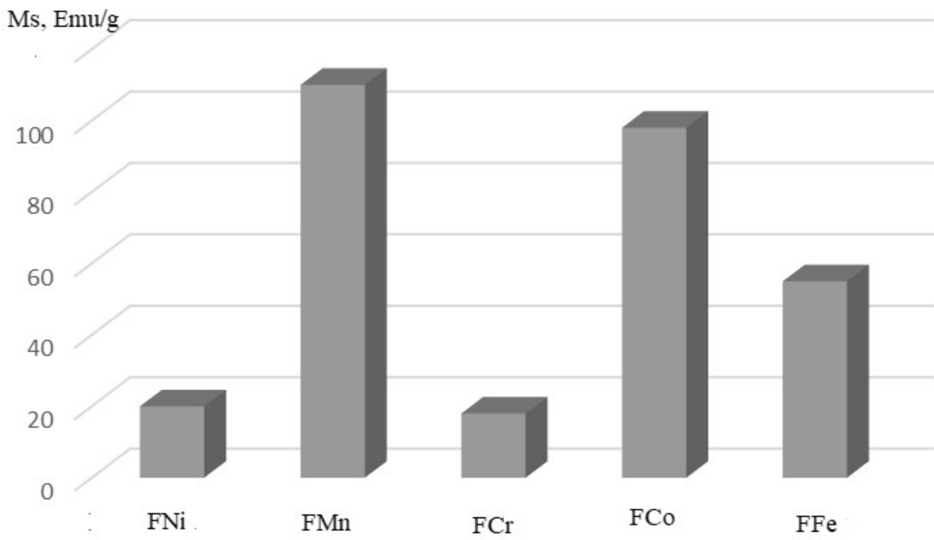

Fig. 4. Histogram distribution of magnetic saturation of the adsorbent type (mass of adsorbent 0.5 g/50 ml)

All adsorbents used are of a common nature. They are complex scales on the binder of iron. In the first stage, we investigated the X-ray phase composition of magnetic sorbents. All of them are of similar nature, so we give the characteristic of ferrite. As can be seen from the radiographs of Fig. 6. Is a crystalline substance having the general formula $MeFe_2O_4$. It can be assumed that the magnetic characteristics will provide ease of separation from the solution. This can provide a high adsorption capacity. Also important is the size and shape of these particles. As shown in Fig. 5, the size of the ferrite particles ranged from 40–90 nm, with most nanoparticles having a size <100 nm. As mentioned earlier, most magnetic nanoscale particles tend to aggregate due to their high surface energy and magnetic properties.

For removal of Cr(III), the adsorbent efficiency followed in the order of decrease as $NiFe_2O_4$>$(CrFe)_2O_3$> $MnFe_2O_4$> Fe_3O_4> $CoFe_2O_4$. The $NiFe_2O_4$ and $MnFe_2O_4$ sample showed maximum adsorption efficiency. For $CoFe_2O_4$, adsorption efficiency decreases. Comparison of histograms of dependence of adsorption properties with magnetic characteristics (Fig. 2 and Fig. 4) shows the independence of the obtained results.

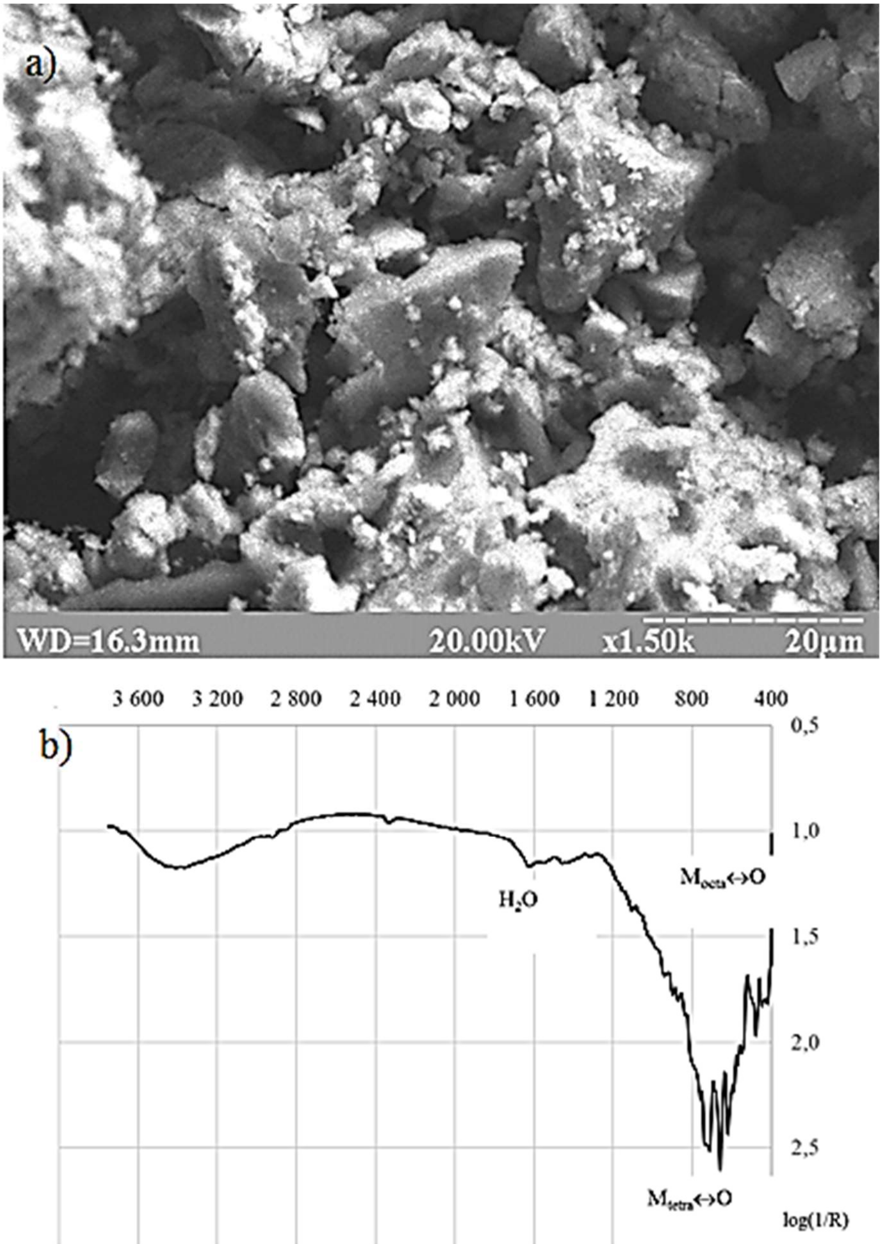

Fig. 5. SEM micrographs (a) and IR spectra of nickel ferrite (b)

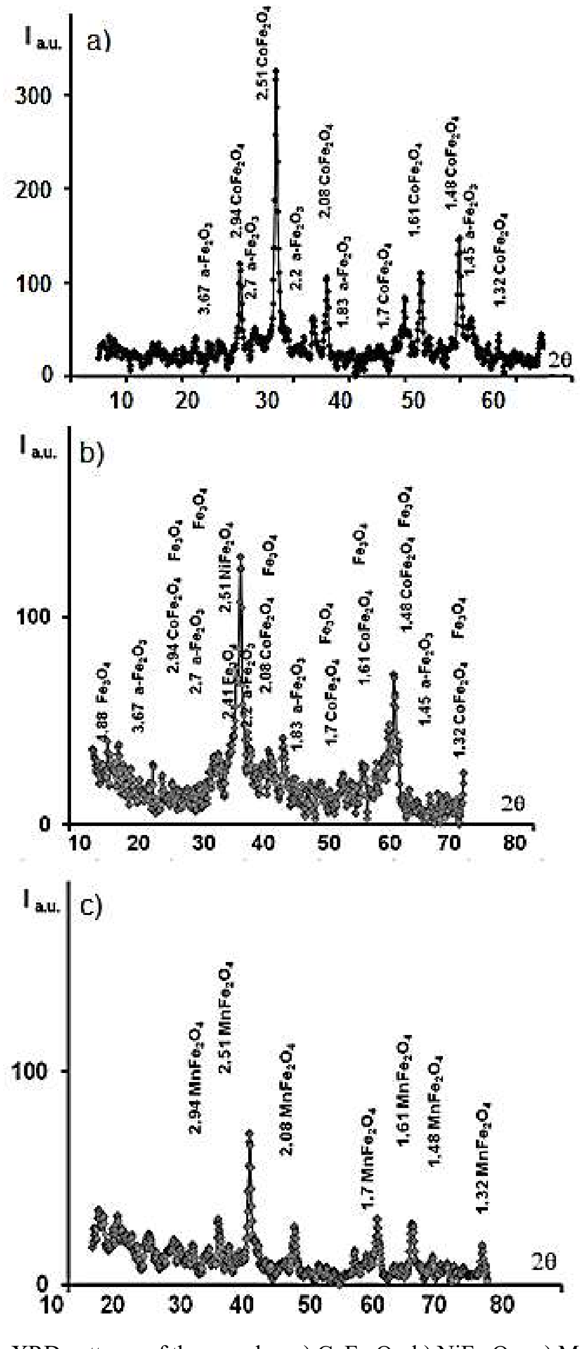

Fig. 6. XRD patterns of the samples: a) $CoFe_2O_4$, b) $NiFe_2O_4$, c) $MnFe_2O_4$

Because the adsorption process is due to ion exchange and interaction with the OH-- groups present on the surface. Co^{2+} ions have smaller ionic radii than Mn^{2+}, and ion exchange is easier by reducing energy barriers. When using cobalt ferrites, the adsorption activity is reduced by increasing the amount of $CoFe_2O_4$. Thus, the degree of adsorption is reduced. In addition, it can be assumed that with increasing spinel defect, the adsorption activity of the material increases.

4. Conclusions

Synthesized magnetically controlled sorbents based on cobalt, nickel, manganese, chromium, magnetite ferrites have high sorption capacity. It has been found that chromium sorption occurs at a faster rate: the equilibrium of the adsorption process is reached in a maximum of 10 minutes.

It is shown in the paper that the use of magnetically controlled sorbents makes it possible to purify chromium (III) wastewater with high efficiency.

The results obtained may form the basis for further research into the use of the latest adsorbents.

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Comparative economic analysis of domestic hot water preparation in a hotel and catering building including solar energy system

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Abstract

Thermal conversion of solar energy is often used for the preparation of domestic hot water due to possible reduction of fossil fuels consumption. According to Eurostat data, the total surface of installed solar collectors in the European Union in 2017 exceeded the amount of 52 million. However, application of solar collectors in multifamily buildings or service facilities raises many concerns mainly related to economic aspects including investment, maintenance and operation costs.

This paper presents the economic analysis of several variants of system designed to domestic hot water preparation in hotel and catering building, located in the Eastern Poland. The analysis includes a domestic hot water (DHW) installation, consisting of hot water and circulation, and three different sources of energy applied for hot water preparation: solid fuel boiler, gas boiler and gas boiler supported by solar collectors.

The performed economic analysis was based on popular indicators of investment cost efficiency: Dynamic Generation Cost (DGC), Net Present Value (NPV) and Benefit-Cost Rate (BCR). The required input data for determination of costs efficiency indicators were based on preliminary investment costs estimation as well as assumed operation and maintenance costs. Additionally, energy and economic benefits of solar installation were estimated by GetSolar software.

Keywords: solar energy system, cost efficiency, economic analyses

1. Introduction

The depletion of conventional energy sources, its rising costs and progressing degradation of natural environment, including serious climate changes, are major factors that indicate intensification of renewable energy usage in our everyday life. Despite the high investment costs associated with renewable energy sources (RES) implementation, renewables play a key role in the European energy policy as their development can contribute to greater energy independence and maintenance the EU leadership position of innovations at global level (Żelazna and Gołębiowska, 2015; Pacesila et al., 2016).

Available statistics confirm that the use of renewable energy in EU is growing continuously. In 2017, the share of renewable energy sources in gross final energy consumption was 17.5% while in 2010 it was approx. 13% and in 2015 – 16.7% (Eurostat, 2019). Moreover, according to the newest European Commissions framework, published in *Towards a sustainable Europe by 2030* (European Commision, 2019), in the next ten years, the total energy consumption should be covered by renewable energy in 32%.

Among renewable energy sources, solar energy is widely used in Europe. Solar energy conversion has increased rapidly in recent years, especially for electricity generation by using a photovoltaic cells. However, solar energy is also used to generate heat through solar thermal technologies. According to the European Commission data from 2018, 168 solar thermal energy projects worth 400 million Euros were founded in UE within the Horizon 2020 program framework. The total capacity of heat generation from solar energy achieved the level of 35 000 MWth (European Commision, 2018). According to the International Energy Agency data (IEA, 2019), solar thermal systems are the most commonly applied for domestic hot water (DWH) production in single family houses, as solar combi systems in single family and multi-family houses and in large DWH systems (multi-family houses, tourism and public sector) which represents 92% of the total installed water collectors capacity in Europe as well as worldwide.

In hotels buildings, special type of objects created to provide the variety of services, the energy demand may be significant and is composed mainly of electricity, space cooling and heating as well as hot water preparation (Kyriaki et al., 2015; Giama et al., 2018). For this reason, there is a great potential in conventional energy demand reduction in these kind of objects, requiring a proper energy management, services improvement and implementation of RES, which is the subject of interest of many researchers. Gallo et al. (2014) carried out the analyses in TRNSYS Simulation Studio for integration of solar thermal system, PV system and geothermal heat pumps in four different hotels located in Spain and Italy. One of the conclusion withdrawn from the conducted analyses was that important energy savings can be achieved for thermal demands. Kyriaki et al. (2017) performed an analysis of the solar thermal system in a hotel located in Greece including the comparison of two systems used for heating and DHW preparation: conventional with oil boiler and solar thermal systems. Achieved results showed that the alternative system produced almost 67% less carbon dioxide emissions than conventional one and was also cost effective. In Gima et al. (2018) the environmental impact of solar thermal systems for space heating and domestic hot water production in hotel buildings was evaluated using LCA methodology. Akzoun et al. (2018) estimated that the use of solar thermal systems in combination with air heat pumps or gas boilers could reduce the primary energy consumption in a hotel building located in Morocco (even up to 48%) decreasing simultaneously the level of carbon dioxide emission.

It seems that RES are the crucial requisites to achieved energy efficient and environmentally friendly hotel systems. However, taking into account the considerably high investment costs and required operation and maintenance expenses for professional servicing, decision-making process should be supported also by economic analysis including variable annual outflows and inflows of money generated by the investment, to select the most preferable solution including local climate condition and the type of services provided by the hotel. Generally, two dynamic methods of analysis are dedicated to properly assess the economic aspects of financial sustainability RES applications into DWH systems, taking into account the investment, operation and maintenance (O&M) cost, variable throughout the time duration of the studied investment. The first one covers cost-efficiency of investment, popularly determined by *DGC* (Dynamic Generation Cost) of annual ecological effect affected by investment and O&M costs and related too variable value of money. The second method, known as benefits-costs analysis reflected by two popular indicators *NPV* and *BCR*, covers comparisons of financial incomes and outcomes of the investment during proposed time duration. The proposed dynamic methods introduced to decision-making procedure allow introduction of economic factors into technical and technological analyses of possible, up-to-date and binding with local laws and standards, designs.

In this paper the economic analysis of three variants of the DWH system was carried out including conventional and renewable energy sources. The analysis was based on three indicators of investment cost efficiency: *DGC*, *NPV* and *BCR*. The required input data, including performance of the system, energy demand, energy savings, investment and maintenance costs, was obtained from the following computer software: GetSolar and NormaPRO.

2. Materials and methods

2.1. Building and general DHW installation characteristic

The hotel and catering building, considered in the following analysis, is a detached building located in Zamość (Poland) where total yearly horizontal irradiation is more than 1168 kWh/m^2 (www.solargis.com). The building is divided into three service sections: restaurant, hotel and banquet hall. On the ground floor of the building, there are a restaurant with kitchen, social and sanitary facilities and a banquet hall with sanitary facilities. The restaurant is designed for 30 guests and the banquet hall is intended for banquets and ceremonies for up to 100 guests. The hotel section with three hotel rooms for

6 guests is located in the attic utility above the restaurant. There is also a basement in the building where warehouse, laundry room and boiler room are located.

Domestic hot water installation is designed to provide hot water for the whole building. The installation consists of Wirsbo-PEX (crosslinked polyethylene) pipe system that can withstand a maximum heat temperature of 95°C and a maximum pressure of 10 bars. The domestic hot water daily demand is 560 dm^3 and the DHW tank volume is 750 dm^3. According to the requirements, the hot water temperature in the tank has to be set at 60°C.

The conducted analysis includes a DHW installation and three different sources of energy applied for hot water preparation:

- Variant I (V I): solid fuel boiler,
- Variant II (V II): gas boiler,
- Variant III (V III): gas boiler supported by solar collectors.

In Variant III, preparation of hot water is supported by solar thermal installation consisting of six flat plate solar collectors, solar pump station with safety valve and expansion tank as well as a bivalent water storage tank of capacity of 750 dm^3 that can cooperate with two energy sources.

2.2. Methodology of investment, operational and maintenance costs estimations

The investment, operation and maintenance costs of analyzed system variants, as well as performance of the solar installation, including fossil fuels consumption and solar gains, were estimated using various computer programs. The operational lifetime duration of the installation was assumed as 20 years, in relation to the average lifetime of the solar collectors.

To assess the investment and system maintenance costs the Norma PRO software was used. In the estimation of the investment costs for all variants, the following actions were included:

- four replacements of circulation pump, filter and water meter during the whole assumed operation period,
- periodic inspections of boiler room – every four years,
- in case of installation with solar collectors (V III): fourfold solar heat transfer fluid replenishments/exchangs and single external pipes insulation exchange.

The amount of conventional energy carriers required to provide the hot water in Variant I and Variant II was estimated on the basis on GetSolar software as well as the detailed simulation of the performance of the system with gas boiler supported by solar collectors (Variant III).

2.3. Methodology of economic analysis

The performed economic analysis was based on popular indicators of investment cost efficiency: Dynamic Generation Cost (*DGC*), Net Present Value (*NPV*) and Benefit-Cost Rate (*BCR*).

The Dynamic Generation Cost (*DGC*) expresses the discounted revenues equal to discounted costs of investment. In other words, *DGC* shows the technical cost (in Euro) of obtaining an ecological effect unit. In the considered case, the ecological effect is a preparation of a hot water thus this cost is expressed in Euro per 1 m^3 of DHW. The lower value of *DGC* indicator, the more acceptable economically investment is. The DGC value is determined from the following equation (Rączka, 2002):

$$DGC = p_{EE} = \frac{\sum_{0}^{t=n} \frac{IC_t - EC_t}{(1+i)^t}}{\sum_{0}^{t=n} \frac{EE_t}{(1+i)^t}} \tag{1}$$

where: IC_t – investment costs in a given year (in Euro), EC_t – exploitation costs in a given year (in Euro), t – year of investment time duration (it changes from 0 to n, where n is the last assessed year of investment activity; t is expressed in years), I – discount rate (%), p_{EE} – price of the ecological unit effect of the investment (Euro·m^{-3}), EE_t – ecological unit in given year (m^3).

It should be noted, that in in the presented formula, the time horizon of the analysis must be equal to the lifetime of the investment.

Net Present Value indicator shows a difference between the present value of cash inflows (benefits) and the present value of cash outflows (including operational cost and investment costs) over a period of time (Berry, 2007). When NPV value is equal or greater than zero ($NPV \geq 0$), an investment will be profitable. Otherwise, it will generate net losses. *NPV* can be calculated as follows (Miłaszewski, 2003; Widomski et al., 2017):

$$NPV = \sum_{t=0}^{n} \frac{R_t}{(1+i)^t} \tag{2}$$

where: R_t – net cash inflows-outflows for a given year (Euro), i – discount rate (%), t – year of investment time duration (year) , n – the last assessed year of the investment activity (year).

Benefit-Cost Rate presents dimensionless ratio of benefits to costs of an investment in a certain period. The value of *BCR* indicator for profitable investment should be higher than 1 ($BCR \geq 1$). *BCR* may be calculated using the following formula (Miłaszewski, 2003; Widomski et al., 2017):

$$BCR = \frac{PV_b}{PV_c} \tag{3}$$

where: PV_b – present value of benefits (Euro), PV_c – present value of costs (Euro).

In Variant III, the possible savings resulting from the reduction of natural gas consumption for DHW preparation were assumed as investment benefits (incomes).

Solar installation payback period in Variant III was estimated by dividing investment costs of the solar installation supporting the operation of gas boiler by the annual savings resulting from the reduction of conventional fuel consumption. The calculating formula is as following (Lewandowski, 2010):

$$PP = \frac{IC}{IA} \tag{4}$$

where: PP – payback period (years), IC – investment costs (Euro), IA – annual incomes/savings (Euros).

3. Results

The results of the investment, operation and maintenance costs calculations conducted in Norma PRO and GetSolar software, for all variants of the DWH installation for the considered hotel and catering building are presented in Tab. 1.

Tab. 1. The investment and operational cost of variants considered in analyses

Installation variant	Investment costs [Euro]	Annual operation and maintenance costs [Euro]
V I	10 607	882
V II	11 089	821
V III	18 454	608

The highest investment cost are connected with Variant III, as it is the most complex system including solar collectors and all crucial devices for additional energy source – solar energy. However the O&M costs for this system are the lowest which is triggered by lower consumption of fuels. Nevertheless, the best economical choice for the investor, taking into account the sole total costs of the system, is a system in Variant II that is DWH system with condensing gas boiler as an energy sources.

The detailed analysis of solar installation performance in Variant III is presented in Fig. 1 and Fig. 2 showing the results of GetSolar simulation including the amount of solar energy gained for DHW preparation (kWh), conventional energy required for additional DWH heating (kWh), solar installation efficiency (%) and the coverage ratio of the solar installation calculated by dividing the solar gains by heat required for DHW heating.

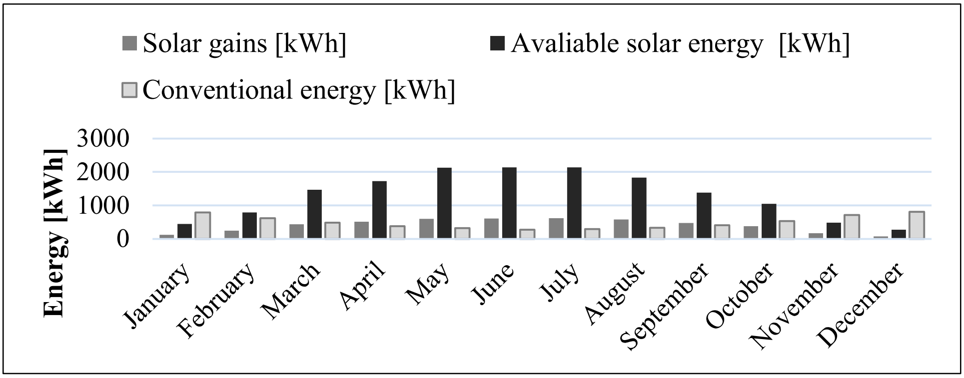

Fig. 1. Simulation results from GetSolar including the amount of available solar energy, solar gains and conventional energy required for additional DWH heating.

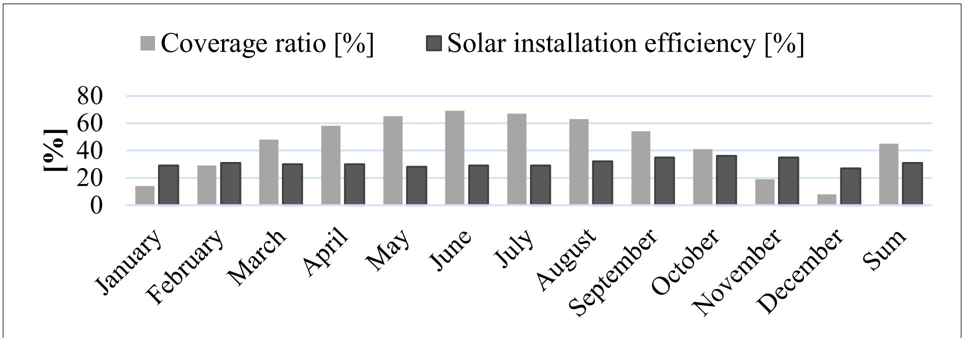

Fig. 2. Simulation results in GetSolar including the solar installation efficiency and the coverage ratio (solar gains / heat demand for DHW heating)

Calculation conducted in GetSolar computer programmer showed that 4864 kWh of solar energy could be gain during the year by the solar installation and the annual efficiency of the system, which is a ratio of solar gains and solar irradiation, is equal to 31%. Solar system, considered in Variant III, allows to provide 45% of the total energy required for DHV preparation and save 591 m^3 of natural gas during the year.

The conventional energy consumption in different variants is presented in Tab. 2. Installation with solar collectors (V III) allows to save 5940 kWh of conventional fuel (natural gas) required to the domestic water heating during the year and thus save 1123 kg of carbon dioxide emission.

Tab. 2. Energy required to the DWH preparation in different variants

	Energy carrier used for DWH preparation	Annual energy carriers demand
V I	pellets	3215 kg
V II	natural gas	1313 m^3
V III	natural gas and solar radiation energy	m^3 (n. gas)

On the basis of obtained results (investment, operation and maintenance), economic indicators were determined for different variants: *DGC*, *NPV* and *BCR* (see Tab. 3). In must be noted, that in Variant III an external founding was not included.

The obtained results of *DGC* calculations for all tested variants show that the lowest cost of unit effect of investment, i.e. 1 cubic meter of hot water, 8.59 Euro per 1 m^3, was obtained for variant II including gas boiler as source of heat. The similar vale was determined for the other tested traditional energy source, solid fuel boiler utilizing pellets. The highest value of *DGC* was observed for system utilizing RES. In this case, the cost of unit effect was nearly 20% higher than in variants using traditional sources of heat, reaching level of approx. 10.5 Euro per 1 m^3. Such high value of technical cost of 1 m^3 of hot water may discourage the potential investors from investing in RES. The determined values of *NPV* and *BCR* showed that none of the proposed variants would be economically profitable, thus each of them may be stated as financially ineffective. Only possible savings available due to reduced fuel consumption would positively affect benefits/cost ratio in case of variant V III.

Tab. 3. *DGC*, *NVP* and *BRC* indicator values for different systems

Installation variant	*DGC*	*NPV*	*BCR*
	[Euro/m^3]	[Euro]	[-]
V I	8.70	–24256	0.0
V II	8.59	–23832	0.0
V III	10.49	–24103	0.144

The above discussed obtained values of economic efficiency indicators suggest that the outside (governmental or EU) founding allowing to reduce part of investment costs is required to increase economic attractiveness and social acceptance of local investors, required for sustainable investment (Carbajales-Dale et al., 2014; Kumar et al., 2017).

In Figure 3 the determined relation between outside founding rate and cost-efficiency of investment presented by *DGC* values which would increase the interest of local investors is presented. It is visible, then founding rate equal to approx. 70% of total investment costs is required to reduce *DCG* to level presented by the studied traditional heat sources, utilizing solid or gas fuel. In our opinion, reaching this threshold of outside founding combined with proecological education would allow financial acceptance of local investors.

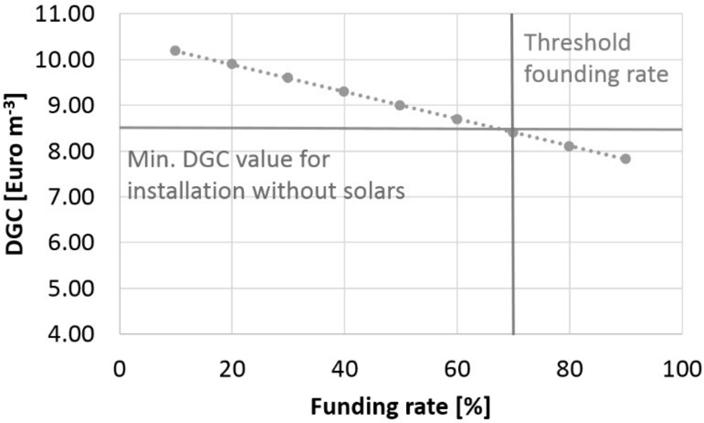

Fig. 3. DGC value change along with increasing external funding rate

The determined payback time for the solar installation in Variant III, assuming that all cost are covered by investor, is 27.5 years. Thus, in this specific case, the obtained payback time, without any outside financial support, is longer than lifetime duration of the assessed investment. The determined minimal outside founding rate allowing to reduce payback period duration below 20 years was approx. 28%. On the other hand, the calculated payback period for the minimal founding rate (70%) allowing to level the unit technical costs (*DGC*) of traditional and alternative DHW installations achieved the level of 8.25 years. However, it should be underlined that calculations of payback period, as static economic indicator, do not include O&M costs and variable value of money.

4. Conclusions

The performed sustainable economic analyses of three DHW systems with applied different energy sources allowed to formulate the following conclusions:

– Obtained values of *DGC* indicator show that solar installation generates the highest cost of the obtained effect, thus, traditional DHW installations are more cost-effective and more attractive to potential investors.
– Application of solar installation in Variant III has a positive environmental results resulting from reduction of natural gas consumption (591 $m^3 \cdot a^{-1}$) and carbon dioxide emission (1120 $kg \cdot a^{-1}$).

- The performed financial analyses showed that considered installation of solar panel as additional source of Energy for DHW preparation is financially ineffective. The determined payback period for solar installation without any outside financial support is longer than 27 years, thus is longer that assumed life duration of investment. Its reduction is possible only due to the partial external founding. So, in our opinion, the significant external financial support of medium size solar installations seems to be a sine qua non condition to consider the investment as cost-efficient from the investor's perspective.
- According to the performed calculation, the necessary founding rate allowing to reduce cost of unit effect of DHW installation with RES applied due to reduction in costs of solar systems installation should be higher than approx. 70% to increase the attractiveness of these systems for the investors.

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The study of the level of environmental consciousness and the efficiency of environmental education students

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Abstract

A leading role of the ecological culture of society in solving the problems of the modern ecological crisis, the importance of environmental education in the formation of the ecological world outlook of young people, especially students, to ensure the successful sustainable development of the state, determines the relevance of research. The purpose of the work is to assess the level of environmental consciousness of students, the impact on it of environmental education during the period of study at universities.

The research was carried out by questioning, testing students of the National Metallurgical Academy of Ukraine of different courses and directions of training with the following analysis of their results. During the research methods M. Rokeach, ”Dominant” and ”Naturafil” were used. These techniques are proven, fairly versatile, easy to use and very popular in practice. As a result, the structure of value orientations and the place of nature in the student values system, the degree of priority of their relation to nature, the indicators of the formation of environmental consciousness on individual components and in general, the dynamics of its changes during the study at the academy was determined. It is established that evaluation of the importance of instrumental and terminal values in different groups of students is close to each other and they attribute nature to secondary values. This is confirmed by the diagnostic data based on the modified ”Dominant” techniques, where nature takes place in a group with average dominance.

Most students have an average level of intensity in relation to nature, but environmentalists have a percentage of high levels are about 2 times more likely than other students and less than a percentage of levels with a reduced attitude to nature. Ecologists have a close connection between the time of training and the level of components of environmental consciousness. Other students do not have such positive dynamics. At the senior courses there is even a decline in the level of attitude to nature. This gives evidence of the urgent need to adjust the content of technical disciplines and strengthen their environmental component.

Keywords: environmental consciousness, environmental education

1. Introduction

Solving modern environmental problems largely depends on the level of morality in society and its ecological culture. In addition to environmental education – knowledge, skills, ecological culture are characterized by the harmony of human relations and nature; awareness of its place in nature and activities in its protection, preservation of ecological balance (Curry, 2011). This is the way of life support, in which society shapes the needs and ways of their realization, which do not create threats of life on Earth. It can be seen as the main indicator of intelligence and civilization of the individual and society as a whole (Aikens et al., 2016; Ivanov et al., 2018). A modern specialist in any profile should have not only a high level of professional knowledge, but also an ecological world outlook. This allows him to analyze and evaluate his own production activity in relation to its action on the natural environment, to make informed decisions in its work, to avoid any damage to nature, or to minimize this damage (Bonnett, 2012; Żeber-Dzikowska et al., 2016). The formation of the ecological culture of society is a priority direction of the state strategy of sustainable development (Kopnina and Meijers, 2014; Babenko et al., 2017). The sooner people will begin to critically assess the results of their activities and measure their goals with the resources available at the disposal of nature, the sooner it will be possible to move to correct already accepted and to prevent future mistakes.

The ecological culture of a person is determined by ecological education, ecological consciousness and ecological activity (Cherdymova et al., 2018). Ecological education includes environmental knowledge, skills. Environmental activities are ecological behaviors, participation in environmental events (Shelest et al., 2017). It is determined by environmental beliefs, values, responsibility, moral attitude towards the natural world, love for nature.

The purpose of ecological education is to form a worldview that directs society to a co-evolutionary path of the development of nature and man and to overcome the consumer attitude to nature (Liu and Guo, 2018). Ecological consciousness is not hereditary; its norms and rules are assimilated throughout life through learning, purposeful work and human activities.

Extremely important is the formation of the ecological consciousness of youth, which determines the future of the country and stimulates the sustainable development. This is especially true of environmental education and the upbringing of the most active and numerical part of it – student youth when studying at a high school (Jadhav et al., 2014; Khinkanina and Serova 2016; Ramirez, 2017). In addition to study of the scientific foundations of nature use, at this stage, the necessary persuasion and skills behavior in the natural environment and a responsible attitude towards nature. It contributes to the future development of a specialist in the ecological style of thinking, a humane attitude towards nature, an active life position on environmental issues.

Diagnostics and detailed analysis of the level of ecological consciousness and trends in its changes can promptly identify the weak and strong points of the educational process and take measures to improve it. Naturally, the formation of a modern ecological worldview of students is possible only at a high level of the ecological culture of the teacher and his ability to implement the environmentalization of the learning process. This should become an important qualification of the teacher (Popova, 2013). Increasing the level of environmental consciousness of students is the most objective integral indicator of the effectiveness of the teaching staff of higher educational institutions in this direction. The listed aspects determine the relevance of the topic research, the purpose of which was to assess the level of environmental consciousness and culture of students and the impact on them of environmental education during the period of study at a higher educational institution.

2. Materials and methods

The object of the study was the structure of value orientations of students of different specialties and training directions on the example of the National Metallurgical Academy of Ukraine. The subject of the study was to determine the place of nature in the system of values of students and the effectiveness of the formation of their ecological consciousness during the study period.

Experimental studies were carried out by questioning, testing, analyzing their results with the involvement of the apparatus of mathematical statistics. The following techniques were used in the study, which are proven, fairly versatile, easy to use and widely used in practice (Dzhamalova et al., 2019; Slinkova et al., 2015; Maravić et al., 2014):

– Technique for the study of value orientations of M. Rokeach, based on the procedure of direct ranking of terminal and instrumental values (Rokeach 1979, Vauclair 2011). Each of the subjects was offered two lists of these values (18 in each) and he performed their ranking, placing opposite each corresponding rank from 1 to 18. The list of terminal values allows us to reveal the domination of the investigated values of personal life, professional self-realization. Terminal values are the conviction of people about the purpose and the end state to which they are trying to get closer (for example, happiness, welfare, knowledge, etc.). The instrumental list allows to establish the tendencies of the benefits of the values of communication, self-affirmation, ethical, business, etc. It is an idea of the desirable behaviors for achieving terminal values (for example, responsibility, courage, talent, self-control, etc.).

The research involved 160 students, among them 99 environmental students and 61 students of technical specialties – metallurgists, mechanics, power engineers. 102 girls and 58 boys were interviewed.

- Express method for the diagnosis of the dominance of the subjective relationship to the "Dominant" nature (Deryabo & Yasvin 1995). The method was used in the main version and in the modified. In the first series of testing, each subject chose three of the most and the least important concepts for him from the 9 proposed; They were assigned ranks 1, 2, 3, and 9, 8, 7 respectively, and three unselected – the middle rank 5. In the modified version, each person similarly evaluated these concepts in an emotional, informational, practical plan, and based on the calculation of the average rank, determined their priority. The rank obtained by a certain notion allows us to judge the dominance of the relation to it: if it is the top three of the ranks, then it is a question of the high dominance of the ratio, if the average is about the average, if the lower one is, accordingly, a ratio with low dominance.

  The total sample size was 124 people, 67 of them students-environmentalists, and 57 students of technical specialties.
- A method for diagnosing the level of development of the intensity of the subjective relation to the nature of non-pragmatic modality and its structure "Naturafil" (Panov et al., 2004). The survey was conducted in writing and the respondents indicated on their form 25–30 minutes of their answers to the proposed 50 questions (on a "yes – no" basis).

Of the total of 10 questions corresponded to the perceptive-affective, cognitive and practical components. The perceptually-affective component determines the relation to the nature of the aesthetic and ethical nature. The cognitive component evaluates the degree of motivation and orientation of cognitive activity in relation to objects of nature. Practical component determines readiness and aspiration for practical interaction: perception of the world of nature as a source of material benefits; a component of actions that diagnoses the person's activity to change the attitude of the environment to nature. Another 10 points were additionally foreseen to determine the level of naturalistic erudition.

The survey data were compared with a control card (key); in the case of a match with the key she was given 1 point, and for non-conformity – 0. Then the amount of points for each scale was determined and there was a parameter of the intensity of the subjective relation to nature as the sum of points on the four basic scales. The results for each scale (from 0 to 10 points) were translated into a standard scale of states, where the estimates acquire values from 1 to 9 with a mathematical expectation of $M = 5$ and a standard deviation of $s = 2$. Similarly, the intensity parameter was translated into a standard T-scale with $M = 50$ and $s = 10$. According to the results presented on standard scales, the interpretation of indicators of the intensity of the relation to nature – from extremely low to very high – was performed using the estimation table.

In the study 180 people took part in this method, including 108 environmentalists and 72 students of other specialties.

3. Results and discussion

Analysis of the structure of student value orientations

The histograms of the average rank of instrumental and terminal values on the 18-point scale, obtained from the results of the research according to *M.* Rokeach`s method are giving Fig. 1 and Fig. 2. If conditionally to assume that the values of paramount importance were occupied by the first 6 places, secondary values took from 7 to 12 places, while others are non-essential values, then we get the distribution presented in Tab. 1.

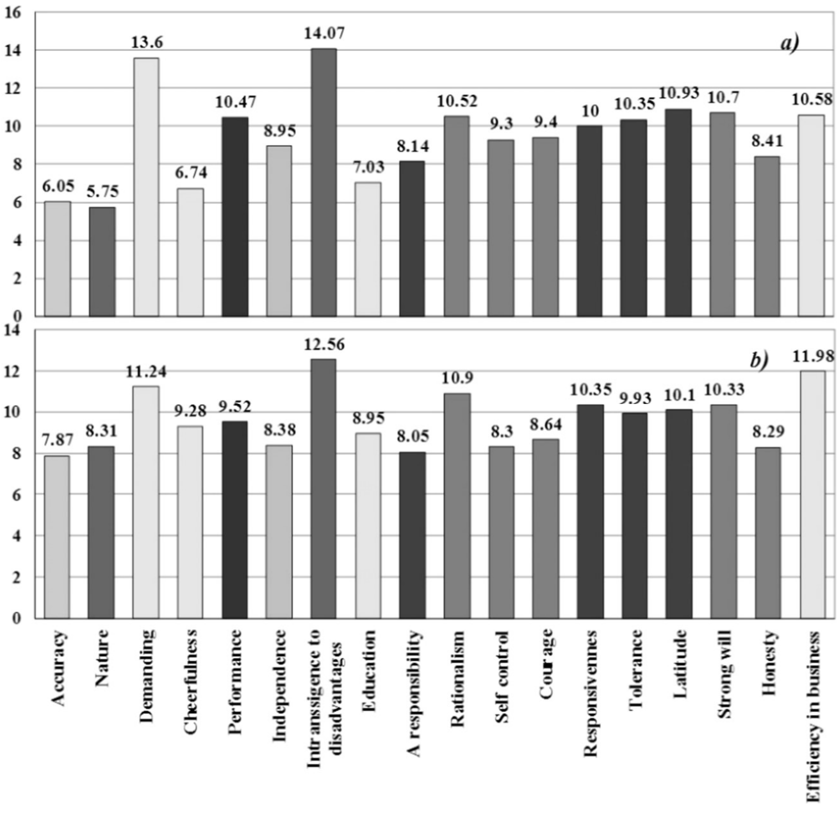

Fig. 1. The average rank of instrumental values of: a) environmental students, b) technical students

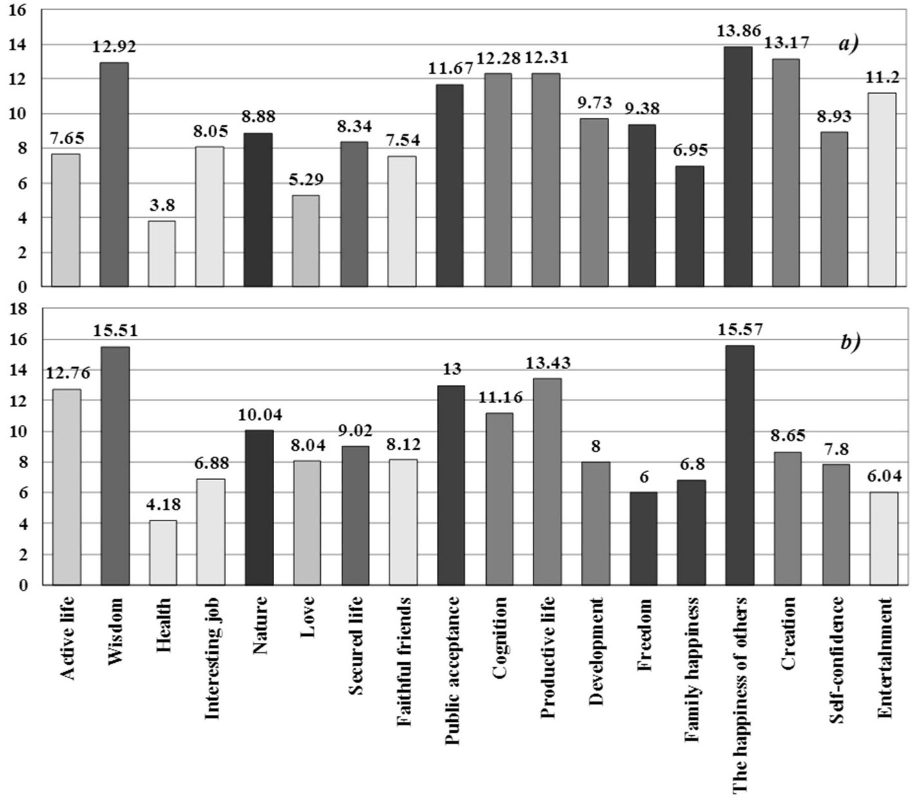

Fig. 2. Average rank of terminal values of: a) environmental students, b) technical students

In the main assessment of the importance of both instrumental and terminal values to different groups of students are close to each other. A significant difference in the views on individual values, such as love or sensitivity, can be explained by the different composition of groups by gender: environmentalists are mostly girls, while others are boys.

Among instrumental values there is some agreement on the attribution of paramount values by good manners and accuracy, responsibility and honesty; to secondary values – the courage to defend their thoughts, tolerance and diligence; to the inessential – intransigence to flaws, efficiency in business and rationalism, firm will and high demands. These results largely correlate with the data of similar studies with students from other universities and specialties (Blyznyuk, 2017; Zvereva, 2015; Slezackova et al., 2018).

Table 1. Distribution of value orientations of: a) environmental students, b) technical students

The place	Instrumental values		Terminal values	
	a)	b)	a)	b)
Values that are a paramount importance				
1	Good manners	Accuracy	Health	Health
2	Accuracy	Responsibility	Love	Freedom
3	Cheerfulness	Honesty	Happiness in the family	Pleasure
4	Education	Self-control	Faithful friends	Happiness in the family
5	Responsibility	Mannerliness	The active life	The interesting job
6	Honesty	Independence	The interesting job	Self-confidence
	The secondary values			
7	Independence	Courage	The wealthy life	Development
8	Self-control	Education	Nature	Love
9	Courage	Cheerfulness	Self-confidence	Faithful friends
10	Responsiveness	Diligence	Freedom	Creation
11	Tolerance	Tolerance	Development	The wealthy life
12	Diligence	Breadth of views	Pleasure	Nature
	Unimportant values			
13	Rationalism	The firm will	Public acceptance	Cognition
14	Business efficiency	Responsiveness	Cognition	The active life
15	Firm will	Rationalism	Productive life	Public acceptance
16	Breadth of views	Exactingness	Wisdom	Productive life
17	Exactingness	Business efficiency	Creation	Wisdom
18	Intolerance to deficiencies	Intolerance to deficiencies	The happiness of others	The happiness of others

The main places among the terminal values occupy health and happy family life. Students attribute nature to secondary values: it is 8th place in ecologists, 12th in future engineers. Among the inessential values with averaged rank 11.67 and 13 in these groups ”Social recognition”, which testifies to the low level of ambition of respondents regarding their social status ”Happiness of others” is in the last place with the highest average rank (13.86 and 15.57), which can reflect today's realities of dehumanization of our society. Students attribute ”Public acceptance” to inessential values with an average rank of 11.67 and 13 that indicates a low level of ambition among respondents regarding their social status. ”Happiness of others” is in the last place with the highest average rank (13.86 and 15.57) that can reflect today's realities of dehumanization of our socjety (Fig.1).

To assess the degree of communication of the average rankings of different groups of students, according to Tab. 1, the coefficient of Spirmen's double-rank correlation is determined that plays the role of the coefficient of objectivity. For instrumental values its value is r = 0.833; for terminal r = 0.585. The estimated values of Student's t-criterion for these groups of values are respectively t_p = 6.02 and t_p = 2.8555. The table values of this criterion for the number of degrees of freedom f = 16 are t_T = 2.58 with a confidence probability P = 98% and t_T = 2.92 at P = 99% (Bobyliev et al. 2014). This quantitatively confirms the high degree of coherence of ranking results between groups of students of environmentalists and students of technical specialties lists of instrumental and terminal values (Fig. 2, Tab. 1).

The determination of the degree of priority of the relation to nature in the minds of students

Tables 2–4 show the meanings of the rankings in relation to the various categories of diagnostic objects obtained from the data of the general sample and separately for the students of ecology and other students, according to the ”Dominant” method. According to this, the places occupied with the relation to themselves, education, work and material values, while the attitude toward nature takes 6th place in the group with average dominance with a rank of 5.16 for a simplified technique and 5th place with a rank of 4.99 for modified. In the rating of environmental students, this category occupied the same places as from other students for both 6 variants methodology took place (Tab. 2–4).

These data correspond to the distribution of the proportion of the ratio with the highest dominance (rank 1) for the considered categories of objects (Fig. 3). Environmental students gave the rank 1 in the 7 questionnaires to the category ”Nature”. The category ”I myself” in 10 cases received rank 1, that is 14.93% of the volume of this sample, while the category ”Job” and ”Education” in 9 questionnaires (13.43%). Thus, the 1–3 place, that divides these three categories into ranking, indicates a high dominance of them.

Students of technical specialties ranked 1 most often – 8 times for material values, morality and attitude towards themselves, which is 14.03% of the 57 respondents. This rank was assigned to the categories ”Nature” and ”Job” (12.28%) in 7 cases. In the general sample of the category ”Job” and ”Material values” that received the highest rank in 14 questionnaires (12.9%), they occupy

2–3rd place, yielding only to themselves (18 questionnaires or 14.52% of the total number of respondents).

Table 2. Averaged – a), and normalized – b), ranks of categories of objects according to the main and modified diagnostic options according to the Dominant method (a total sample)

The object category	The main option		The modified option				
			The average rank			a)	b)
	a)	b)	Emotional	Informational	Practical		
I myself	4.17	1	3.79	3.8	4.45	4.02	1
Education	4.21	2	4.89	3.94	3.78	4.2	2
Job	4.46	3	4.28	4.85	4.48	4.54	3
Material values	4.94	4	5.01	4.42	4.71	4.71	4
Morality	5.0	5	4.33	5.2	6.61	5.38	7
Nature	5.16	6	5.69	4.94	4.35	4.99	5
State	5.32	7	6.33	5.77	4.88	5.66	8
Sex	5.41	8	4.45	5.71	5.06	5.07	6
Others	6.33	9	6.23	6.37	6.68	6.43	9

Table 3. Averaged – a), and normalized – b), ranks of object categories by basic and modified Dominant diagnostics (environmental students)

The object category	The main option		Modified option				
			The average rank			a)	b)
	a)	b)	Emotional	Informational	Practical		
I myself	4.25	2	3.52	3.43	5.17	4.04	1
Education	4.17	1	5.43	3.46	3.25	4.05	2
Job	4.31	3	4.21	4.25	4.69	4.38	3
Material values	5.37	7	5.34	5.45	5.12	5.3	6
Morality	5.57	8	4.58	5.93	6.69	5.73	8
Nature	5.25	6	5.52	4.96	4.48	4.96	5
State	4.99	5	5.78	5.6	4.66	5.35	7
Sex	4.63	4	4.1	5.43	4.46	4.66	4
Others	6.46	9	6.52	6.49	6.48	6.5	9

According to the data of both the general sample and separately for different groups of students, the practical consideration of nature is more important than informational or emotional. The dominance of the attitude toward nature as an object of benefit to environmental students is characterized by rank 3, and to other students by rank 2, while the level of their emotional attitude has a rank 7th, and informational – 4 and 6. By the magnitude of the average rank from environmentalists the emotional component prevails, and information and practical components being stated to dominate for the students of technical specialist (Fig. 3).

Table 4. Average (a) and normalized (b) rank categories of objects according to the basic and modified variant of diagnostics by the method of "Dominant" (other specialties).

The object category	Main option		Modified option				
			Average rank			*a*)	*b*)
	a)	*b*)	Emotional	Informational	Practical		
I myself	4.07	1	4.12	4.23	3.58	3.97	2
Education	4.26	2	4.25	4.51	4.41	4.39	3
Job	4.63	5	4.37	4.56	4.25	4.73	4
Material values	4.44	4	4.39	3.21	4.23	3.94	1
Morality	4.33	3	4.03	4.35	6.52	4.97	5
Nature	5.05	6	6.12	4.91	4.21	5.08	6
State	5.71	7	6.98	5.96	5.14	6.03	8
Sex	6.33	9	4.86	6.04	5.75	5.55	7
Others	6.18	8	5.88	6.23	6.91	6.34	9

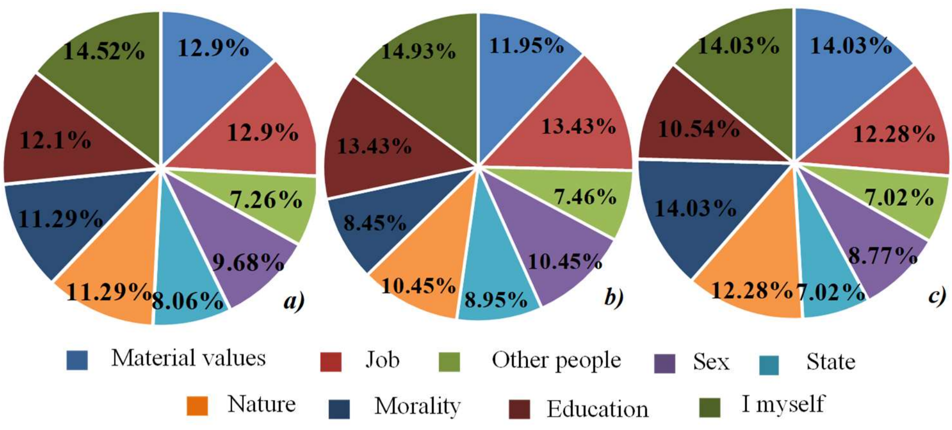

Fig. 3. The distribution of the proportion of the highest dominant relationship by types of object categories

Monitoring the quality of environmental education students

The summarized results of the investigation of the level of the intensity of the attitude toward nature of the students with the "Naturafil" – the technique is given in Fig. 4.

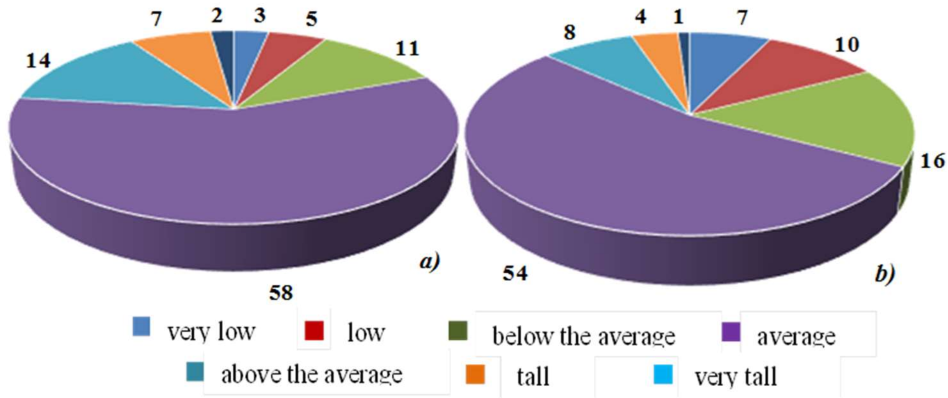

Fig. 4. The level of subjective attitude towards the nature of environmental students (a) and students of technical specialties (b)

The majority of students are shown to have an average intensity of attitude toward nature: from environmentalists, 58%, for other students, 54%. As compared with environmentalists students of technical specialties are approximately 2 times lower for such levels as very high, high and above average. At the same time, they have a significantly higher percentage of levels with a reduced intensity of attitude toward nature.

On individual scales both the students of ecologists and students of technical specialties also prevail on the average level. Ecologists for perceptually-affective, practical scale and scale of deeds have a very low level of only 1–2%, and cognitive – 6%. According to the scale of naturalistic erudition, students show a higher level than on other scales: higher than average – 17%, high – – 16%, very high – 12%.

The students of technical specialties in the first three scales do not have a very high level of intensity of the relation to nature. At the same time, they are well-developed in naturalistic erudition: 18% of those polled are above average on this scale; high – 20%; very high – 26%. This indicates that all students of the academy that were the objects of research have sufficiently high-quality basic knowledge about objects of nature, but future specialists in technology and production technology are much lower than other components of ecological consciousness.

The change in the components of the students' environmental consciousness during the study period is shown in Fig. 5 and Fig. 6. It confirms that the ecologists have a positive trend on all scales. The results of the regression analysis show a significant increase in the level of intensity relative to nature.

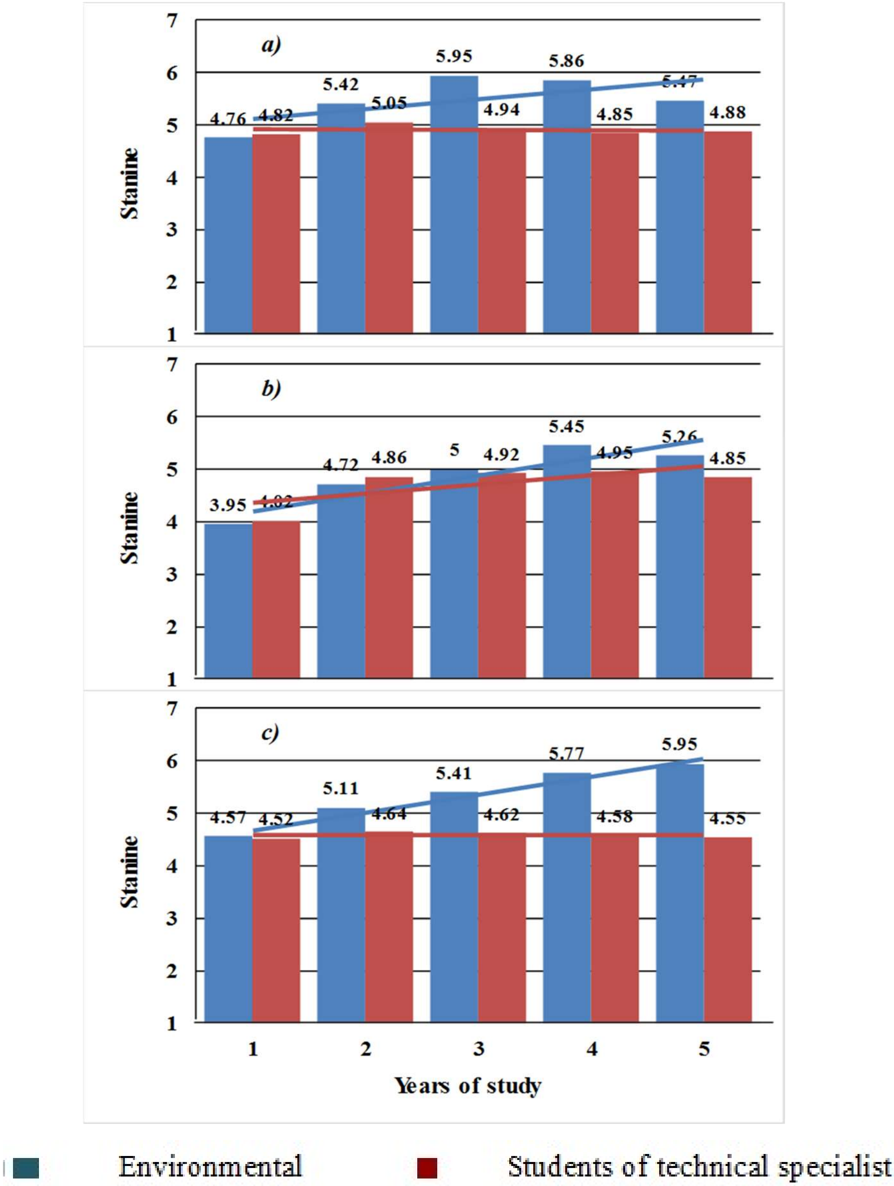

Fig. 5. Changing the level of intensity of subjective attitude towards the nature of environmental students in courses in: a) perceptual-affective, b) cognitive, c) practical scale

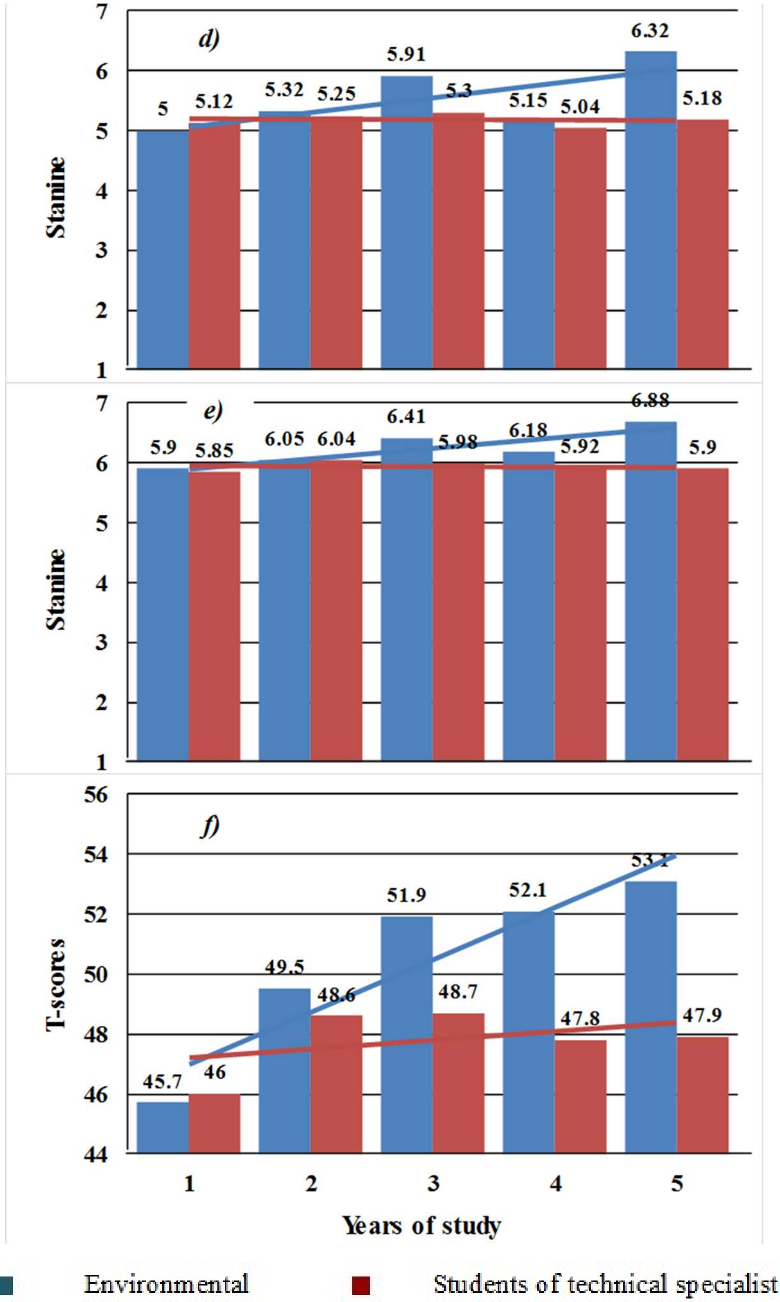

Fig. 6. Changing the level of intensity of subjective attitude towards the nature of students during study: d) in the scale of actions, e) naturalistic erudition, f) the generalized indicator

There is a close relationship between training time and component level. This is evidenced by the high correlation coefficients for cognitive and practical scales, action scales and naturalistic erudition on a generalized basis. The calculated values of the *t*-criterion for them significantly exceed the Student's *t* test criterion $t = 2.353$ for the number of degrees of freedom $f = 3$, that confirms their significance with a 95% confidence level (Bobyliev et al., 2014).

On a perceptual-affective scale, we have a relatively low correlation coefficient, and according to the calculated value of the *t*-criterion, we can consider it significant only with a confidence level of 85%, for which the tabular value $t = 1.25$.

Other students have a similar positive dynamic in the formation of environmental consciousness but of a much lower intensity, observed only for the cognitive component and the naturalistic erudition index. Analysis by the *t*-test shows that the correlation coefficients between the indicated components of consciousness and the period of study are significant with a fairly low confidence level of 85%.

The impact on the generalized indicator of the nature of the length of study at the academy is insignificant; there is no correlation between it and the practical component, and the negative coefficients of linear effects in the regression equations for the last two components indicate a tendency for some decrease in the attitude towards nature, especially in the higher years. This indicates the urgent need to adjust the content of technical disciplines, enhancing their environmental component.

Conclusions

Upbringing of environmental culture in society is a key condition for solving ecological problems and sustainable development of the state. Environmental education is a powerful tool for creating a system of values and environmental awareness of student youth and one of the priority directions of the activity of higher education. Diagnosing the level of environmental consciousness of students and trends in its changes in the learning process creates the necessary feedback in the system of ecological education and provides an opportunity to timely implement measures for its improvement and efficiency improvement.

The system of values in different groups of students is close to each other. The main instrumental values are good manners and accuracy, responsibility and honesty, and nonessential - irreconcilability to shortcomings and efficiency in business, rationalism and high demands. Among the terminal values, the main sites occupy health, happy family life and interesting work. The respondents attribute nature to secondary values, but to the inessential – public recognition and productive life, wisdom and happiness of others.

On the dominance of the relationship the nature has rank 5–6. This is an average dominance that inferior to attitude to yourself and education, work and material values. More important is the practical component of the attitude toward nature than informational or emotional. At the same time, ecologists dominate the emotional component, and students of technical specialties – informational and practical.

Table 5. Characteristics of influence on the level of Y intensity of subjective attitude to the nature of study time X = 1, 2,…, 5 years in the academy for groups of students of: a) ecologists, b) other specialties (linear model)

Dependency (parameter)	Groups of students	Scale for assessing the level of intensity in relation to nature		
		perceptive-affective	cognitive	practical
Regression equation	a)	$Y = 0.186X + 4.93$	$Y = 0.335X + 3.87$	$Y = 0.342X + 4.34$
	b)	$Y = -0.008X + 4.93$	$Y = 0.175X + 4.2$	$Y = 4.58$
r_{xy} correlation coefficient	a)	0.624	0.904	0.984
	b)	– 0.139	0.703	0
t-criterion for r_{xy}	a)	1.385	3.656	9.922
	b)	0.243	1.713	0
Dependency (parameter)	Groups of students	Scale for assessing the level of intensity in relation to nature		
		the scale of actions	naturalistic erudition	a generalized indicator
Regression equation	a)	$Y = 0.247X + 4.8$	$Y = 0.169X + 5.74$	$Y = 1.74X + 45.2$
	b)	$Y = -0.009X + 5.21$	$Y = 0.158X + 5.3$	$Y = 0.3X + 46.9$
r_{xy} correlation coefficient	a)	0.843	0.865	0.923
	b)	– 0.138	0.608	0.438
t-criterion for r_{xy}	a)	2.714	3.05	4.247
	b)	0.241	1.328	0.843

The majority of students have an average intensity of attitude toward nature. Compared with ecologists, other students have about 2 times lower rates for high levels and a much higher percentage of levels with a lower intensity of attitude toward nature. At the same time, all students have a good naturalistic erudition, indicating that they have received sufficiently high-quality basic knowledge about objects of nature.

The positive trend and the close relationship between the time of training of environmental students in the academy and the level of components of their environmental consciousness testifies to the effectiveness of the graduation department in shaping their ecological culture. The students of technical specialties do not have such a positive dynamics, and in the senior courses there is even a decline in the level of attitude towards nature. This necessitates the urgent need to adjust the contents of technical disciplines and increase the environmental component in corresponding issue departments.

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Evaluation of Turkey's Wastewater Management Performance in Terms of Several Variables

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Abstract

Water is one of the most important sources of life. Especially in recent years, where the effects of globalization on human life have intensified, it is estimated that the water reserve will not be able to meet the future demand. In this context, water use and wastewater management are gaining great importance. Even its utilization as a "potential energy source", has come to the agenda and wastewater is no longer regarded as a waste that needs to be disposed of. In this study, a situation assesment is made for Turkey according to the total number of municipalities, the number and total populations of municipalities providing sewer service and the amount of waste water discharge. The assesment is done according to the real data obtained from Turkish Statistical Institute. As a summary, Turkey's wastewater management performance and progress are evaluated within the results of this study.

Keywords: municipalities, population, sewer, Turkey, wastewater management

1. Introduction

The availability of water today and in the future is an issue that everyone should be interested in. Management of water resources for the future increases the need for today's efforts to use water more efficiently and to maintain water quality. Pollutants in the environment make the necessary resources unusable for our health. Turkey is in the process of growth and the consequent rapid population growth, industrial, environmental problems caused by urban and agricultural activities effect the limited water resources negatively. Thus the water to become a strategic commodity. Therefore, the conservation of the existing water resources and the reuse of wastewater are of great importance (Aslan, 2007).

Turkey is not a country rich in water. According to the annual amount of water per capita, our country is experiencing water scarcity. The annual amount of usable water per capita is around 1,519 m^3. Turkey Statistical Institute (TSI) has predicted that by 2030 Turkey's population will rise up to 100 million. In this case, it can be said that the amount of usable water per capita for 2030 will be around 1,120 m^3/year. It is possible to estimate the pressures on water resources with the effect of factors such as current growth rate and changes in water consumption habits. In addition, all these estimates will be available if the available resources are transferred to the next 20 years without being destroyed. Therefore, if Turkey's next generation will use healthy and adequate resources, today's water resources must be used rationally (State Hydraulic Works, 2019).

There are interesting studies in the literature due to the importance of the topic. For example, a decision analysis process was applied to identify the priority areas to address sewage pollution in West Maui, with the objective of reducing nearshore coral reef exposure to pollution (Barnes et al., 2019). A critical review on ammonium recovery from wastewater for sustainable wastewater management review study was presented by (Ye et al., 2018). The internet of things is applied for wastewater management by (Edmondson et al., 2018). They presented the Smart Sewer Asset Information Model for an existing sewerage network. The model incorporates distributed smart sensors to enable real-time monitoring and reporting of sewer asset performance. Recently, the performance and management of five wastewater treatment plants in rural areas of Bolivia was analyzed. Pollutants' concentrations, wastewater flows, hydraulic and organic loads and hydraulic retention times were determined in three small and two very small treatment plants (Cossio et al., 2018).

Using a combination of expert interviews and a constellation analysis, the condition of Iran's wastewater sector was investigated in order to illustrate the main problem areas, understand the interplay of problem factors and identify promising approaches for overcoming the main obstacles. The main problem areas involve organizational, legal and management deficiencies, a lack of financial means and the status of, and approach to, water resources (Mohajeri and Deirich, 2017). For further reading, following papers could be examined; (Raff and Earnhart, 2018; Machado et al., 2017; Capodaglio, 2017).

2. Materials and Methods

In this section of the study, the data obtained from Turkish Statictical Institute website is used for the interpretations. Since the open source existing data covers 2004–2016, the comments will be about that time period.

3. Results and Discussion

Below, Tab. 1 shows the municipal indicators of Turkey between the years 2004–2016.

Table 1. Total and range of population according to municipalities

	2004	2006	2008	2010	2012	2014	2016
Turkey population	67803927	70586256	70586256	73722988	75627384	77695904	79814871
Total number of municipalities	3225	3225	3225	2950	2950	1396	1397
Total municipal population	53935050	58581515	58581515	61571332	63743047	72505107	74911343
Number of municipalities served by sewerage system	2226	2321	2421	2235	2300	1309	1338
Municipal population served by sewerage system	46149479	50856943	51673078	54017052	58754795	65071589	67227191
Rate of population served by sewerage system in total population (%)	68	72	73	73	78	84	84
Rate of population served by sewerage system in total municipal population (%)	86	87	88	88	92	90	90

As it could be seen, total population and municipal population increases year by year. The increase in the total population living in the municipality to be faster than the increase in Turkey's total population can be explained by the increasing migration from rural to urban. Decrease of total number of municipalities by 2014 is because of the legal regulation that envisages the transformation of the municipalities in the neighborhoods close to the city centers. Therefore, although there seems to be a decrease in the number of municipalities, this indicator gives misleading results. In this case, although the number of municipalities served by sewerage network seems to have decreased, it is seen that the population living in municipalities is increasing.

Numerical information concerning Turkey's wastewater treatment plant is presented in Tab. 2 below.

When the numbers presented in Tab. 2 are examined, it's seen that number and total capacity of wastewater treatment plants quickly increased. Advanced plants' capacity increasions are the highest. Amount of wastewater treated by treatment plants also shows a promising increase. The data of natural wastewater treatment plants were not availeble for 2004 and 2006 years.

Table 3 includes the information about distribution of wastewater treatment plants by municipalities.

As the number of municipalities increases, it is seen that the wastewater treatment services offered by the municipalities increase. This situation shows that municipalisation in Turkey, is successful in terms of reflection on the wastewater treatment services. As a common form of public administration, the municipality does not only provide name but also services promisingly.

Amount of wastewater discharged from municipal sewerage by receiving bodies for the years between 2004–2016 are given in Tab. 4 below.

As the amount of water discharged increases, it is seen that the amount discharged by treatment decreases. Considering the first two bodies, the seas and the rivers in terms of the amount of water discharged, it is noteworthy that the treated part in the total amount of water discharged to these bodies increases. It is also seen that the amount of water discharged into the land decreases dramatically. In addition to that, the treated part in this decreased amount increases. In each channel in the table, it's possible to say that Turkey presents well performance in wastewater discharge and treatment.

At this point, it is considered useful to consider the amount of wastewater discharge per capita of municipalities in the light of the information presented above. Hence, numbers of the amount of wastewater discharge per capita of municipalities are presented in addition to number of municipalities having marine outfalls within the Tab. 5 below.

Table 2. Wastewater treatment plants

	2004	2006	2008	2010	2012	2014	2016
Number of wastewater treatment plants (pieces)	172	184	236	326	460	604	881
Physical (pieces)	35	26	29	39	57	49	55
Biological (pieces)	133	135	158	199	244	345	492
Advanced (pieces)	4	23	32	53	70	92	135
Natural (pieces)	...	...	17	35	89	118	199
Total capacity of wastewater treatment plants (1000 m^3/year)	3410352	3648198	4143140	5293204	5562075	5940579	5941049
Physical (1000 m^3/year)	1384634	1329470	1537719	1838627	1904642	1823038	1802239
Biological (1000 m3/year)	1750532	1510835	1594640	1732674	1703694	2074215	1748095
Advanced (1000 m^3/year)	275186	807893	1000814	1709415	1918697	1984915	2365775
Natural (1000 m^3/year)	...	...	9967	12488	35042	58411	24940
Amount of wastewater treated by wastewater treatment plants (1000 m^3/year)	1901040	2140494	2251581	2719151	3256980	3483787	3842350
Physical (1000 m^3/year)	598769	714404	735710	751101	929334	869248	906221
Biological (1000 m^3/year)	1071217	926581	861428	931356	1072873	1155353	1214977
Advanced (1000 m^3/year)	231054	499509	648536	1031616	1245977	1450494	1708361
Natural (1000 m^3/year)	...	...	5906	5079	8795	8692	12791

Table 3. Wastewater treatment plants by municipalities

	2004	2006	2008	2010	2012	2014	2016
Number of municipalities served by wastewater treatment plants	319	362	442	438	536	513	581
Municipal population served by wastewater treatment plants	24369119	29643258	32518318	38050717	43543737	49358266	56016738
Rate of population served by wastewater treatment plants in total population (%)	36	42	46	52	58	64	70
Rate of population served by wastewater treatment plants in total municipal population (%)	45	51	56	62	68	68	75

Table 4. Discharged wastewater from municipal sewerage by receiving bodies

	2004	2006	2008	2010	2012	2014	2016
	Amount	Amount	Amount	Amount	Amount	Amount	Amount
Amount of wastewater discharged (1000 m^3)	**2922783**	**3366894**	**3261455**	**3582131**	**4072563**	**4296851**	**4484075**
Treated (1000 m^3)	1901040	2140494	2251581	2719151	3260396	3483846	3842350
Untreated (1000 m^3)	1021743	1226400	1009874	862979	812167	813005	641724
Sea (1000 m^3)	**1178001**	**1522695**	**1458461**	**1498728**	**1843115**	**1915294**	**1812650**

Table 4 – continuation

	2004	2006	2008	2010	2012	2014	2016
Treated (1000 m^3)	1003736	1215440	1231880	1347977	1718588	1759461	1724792
Untreated (1000 m^3)	174265	307255	226581	150751	124528	155833	87858
Lake/Artificial lake (1000 m^3)	**43006**	**46415**	**67193**	**76024**	**75116**	**93596**	**78551**
Treated (1000 m^3)	25283	28166	48295	37881	36748	47893	53262
Untreated (1000 m^3)	17723	18249	18899	38143	38368	45703	25289
River (1000 m^3)	**1380516**	**1410614**	**1404164**	**1741078**	**1817352**	**1898895**	**2153123**
Treated (1000 m^3)	713395	705561	778293	1180630	1276456	1409633	1728000
Untreated (1000 m^3)	667121	705054	625871	560448	540896	489262	425122
Dam (1000 m^3)	**99551**	**121532**	**115405**	**130224**	**114199**	**120781**	**126325**
Treated (1000 m^3)	52563	84015	84375	83409	63296	61 843	76660
Untreated (1000 m^3)	46988	37517	31030	46816	50903	58 938	49665
Land (1000 m^3)	**40007**	**120525**	**50374**	**35091**	**35770**	**17 954**	**20063**
Treated (1000 m^3)	6420	12011	14108	9166	8999	8367	14036
Untreated (1000 m^3)	33586	108514	36266	25925	26771	9587	6027
Other (1000 m^3)	**181702**	**145113**	**165857**	**100985**	**187011**	**250332**	**293363**
Treated (1000 m^3)	99642	95301	94631	60088	156309	196649	245601
Untreated (1000 m^3)	82059	49813	71226	40897	30701	53683	47762

Table 5. Discharged wastewater per capita and marine outfalling municipalities

	2004	2006	2008	2010	2012	2014	2016
Amount of wastewater discharged per capita in municipalities (liters/capita-day)	174	181	173	182	190	181	183
Number of municipalities having marine outfalls	73	77	92	80	80	36	36

When Tab. 5 is examined, it is seen that the amount of wastewater discharge per capita has a certain stability. Considering the increasing water consumption, it is possible to say that these values are normal. In addition, the decrease in the number of municipalities that have marine outfalls is a very good indicator.

4. Summary and conclusions

It is a known fact that the population living in the world is increasing rapidly. This increases the demand for water, which is an essential requirement for the survival of life. Despite the increase in the population and consequently the demand for water, water reserves in the world are being used in a rough way and water resources are decreasing. In this case, efficiency and efficiency in water use and wastewater management become very important for the sustainability of life in the world.

Turkey, especially in the confusion experienced in recent years in neighboring regions together, is one of the very fast growing countries in terms of population. Taking into account the share of young population in the total, the population of Turkey is expected to continue to rise. Although Turkey is acountry, where is not considered poor in terms of water resources, its population and economic growth makes it necessary to take water use and wastewater management in the agenda.

In this study, applications regarding Turkey's wastewater management was presented with the review at the municipal level. In the study prepared from the statistics between 2004 and 2016, it is possible to say that Turkey's wastewater management have improved and on the right track.

For future studies, Turkey's performance in wastewater management examined in this study should be compared with the performance of different countries. This study examined only the distance covered over the years in the scope of the management of wastewater in Turkey. Comparison of different countries will enable more accurate evaluations.

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Wastewater treatment by flotation

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Abstract

Flotation is widely used for urban and, especially, industrial wastewater treatment, sludge thickening etc. However, the study of flotation wastewater treatment usually comes down to performing simple laboratory experiments on real wastewater and applying the obtained results in the design of industrial flotation facilities. Attempts to use well-designed theoretical approaches from the practice of flotation enrichment to the flotation chambers calculation require the consideration of dozens factors not established for wastewater and do not provide at least approximate match of the calculations results to the results of even simple laboratory studies of flotation treatment.

To resolve the contradiction “theory-practice” it is proposed to consider flotation as a probabilistic interaction process of normally distributed particles of wastewater pollution and normally distributed air bubbles with taking into account the normal distribution of the fractional flotation efficiency function. On the basis of this approach a linear dependence between the initial concentrations of contaminants and the amount of the same contaminants removed during the process of the flotation treatment, the dependence between the loading on the surface of the flotation zone by dry matter and the residual concentrations of contaminants is theoretically established. It was develoved a series of vertical circular settlers-flotators with diameters of 2.4, 4.0, 6.0 and 7.2 m with productivity of 5–140 m^3/h with the preliminary removal of large particles by short time settling and compatible ascending flow of air bubbles and pollution particles to maximize their contact in the flotation zone.

Efficiency studies of the settlers-flotators usage, which were carried out in the production conditions on wastewater of meat processing plants, poultry farms, butter factory, concentrated apple juice production enterprises, confirmed the high efficiency of non-reagent pressure flotation wastewater treatment and easy operation of these facilities.

Keywords: wastewater, flotation, wastewater contaminants, bubble-particle interaction, settlers-flotators

1. Introduction

Flotation is a complex physicochemical process that has been used on an industrial scale for mineral enrichment for over a hundred years. However, independent theoretical studies of the process of flotation wastewater treatment were almost never conducted, which was replaced by the use of basic theoretical approaches borrowed from the theory of flotation enrichment. As it was mentioned by A. I. Matsnev (1976), "the transfer of the theoretical dependences of the flotation process from the practice of enrichment to the practice of wastewater treatment is quite acceptable, but it is necessary to take into account, firstly, the specific features of the wastewater composition, and secondly, fundamentally other problems that are solved in wastewater treatment". That's why such transfer may be carried out with significant warnings, which need to be taken into account:

- the differences in the nature of the flotationable particles (mainly mineral particles in ore enrichment and mainly organic particles of wastewater contamination) and their features (density, hydrophobicity, hydrophilicity, wetting angle etc.);
- differences in particle shape and surface structure;
- differences in the features of the dispersion medium (pH, ionic force, surface tension, concentrations of surfactants and their nature, temperature);
- differences in the method of bubble generation during flotation (only impeller or foam enrichment flotation and preferably pressure flotation for sewage treatment);
- mechanism of flotocomplexes formation.

According to modern ideas (Derjagin at al., 1986; Grau, 2006; Meshcheryakov, 1990; Pyke, 2004), the elementary act of flotation is considered as a multi-stage process, and its probability is represented as a product of probabilities, which are characterizing, respectively, the processes of collision of a particle with the surface of the bubble (P_c), fixing on it (P_a) and possible subsequent tearing (P_d)

$$P = P_c \cdot P_a \cdot (1 - P_d) \quad (1)$$

In literature instead of the probability of a collision P_c, the concept of the so-called collision efficiency *E* or *Ec* is often used. Based on the analysis of models of Sutherland, Gaudin, Iohn and Lattrell, Duhin, Rulev, and more sophisticated models of I. Langmuir-K. Blodgett, D. Anfrunz and D. Kitchener, W. Weber and K. Paddock, G. Schulze, A. Nguyen and others we can conclude that the collision efficiency can be approximated as proportion to the ratio $(d_p/d_b)^n$, in which d_p is the diameter of the particle and d_b is the diameter of the bubble. According to various researchers, the value of the degree index varies within 1–2, depending on the ratio of the densities of particles and liquid – D. Ray and

G. Ratcliff, bubble size – Z. Jang and P. Haltham (Han, 2002) and mode of fluid flow on the surface of the bubble – R. Yoon and G. Luttrell.

Figure 1 shows the results of experimental determination of the collision efficiency of quartz spherical particles of different diameters with bubbles with diameter of 0.77 μm, and also the values of the collision efficiency calculated by the mentioned models. As it can be seen from the figure, even in the quite simple case, the values of the collision efficiency calculated by different models differ significantly from each other and from the experimental results, what points on their imperfection.

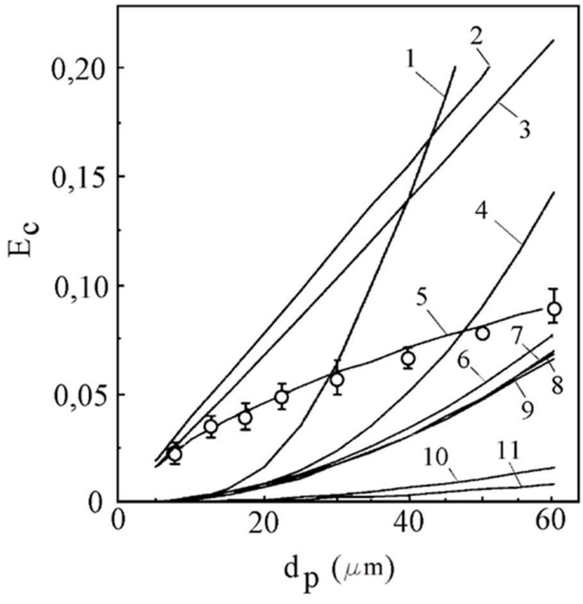

Fig. 1. Experimental quartz (circles) and calculated (lines) collision efficiencies E_c as a function of particle size at bubble diameter 0.77 μm for models: 1 – Langmuir – Blodgett; 2 – Sutherland; 3 – Weber – Paddock (1); 4 – Schulze; 5 – Sutherland's general equation; 6 – Weber – Paddock (2); 7 – Yoon – Luttrell; 8 – Anfruns – Kitchener; 9 – Nguyen; 10 – Flint – Hovarth; 11 – Gaudin (Dai, 2000; Pyke, 2004)

According to R. Yoon and G. Luttrell, the bubble-particle adhesion probability is a function of the particle and bubble sizes, and according to E. Woodburn et al., the probability of particle separation from the bubble depends on the particle diameter.

Summarizing the above mentioned, we can conclude that the sizes of particles and bubbles have a decisive influence on both the flotation process in general and its subprocesses, what is completely consistent with the well-known theory of academician L.A. Kulsky, according to which the phase-dispersed state of impurities determines their behavior in the process of water treatment. However, taking into account only the diameters of a single spherical particle and a bubble cannot adequately describe the diversity of interactions of large number particles with bubbles generated by flotation wastewater treatment, in particular because:

– with high quantity of bubbles the liquid velocity distribution near their surface is significantly deviated compared to a single bubble;
– there are different mechanisms of interaction with the bubble for small (0.5–30 μm), medium (30–70 μm) and large (more than 70 μm) particles;
– there are not obtained optimal ratios between particle size and bubble in terms of obtaining the most stable flotation complexes;
– it is obtained that a large number of particles can not float at all as one bubble.

However, most basic flotation studies, have focused on relatively simple systems of rest. The accuracy of theoretical results predictions of the particle-bubble interaction is greatly reduced due to the unresolved issues of the heterogeneity of the collisions distribution on the entire surface of the upper half of the bubble, determining the stage of inhibition of the bubble surface and determining the values of the Hamaker constant when applying thermodynamic approach to flotation process consideration. Collision theories based on the theoretical consideration of smooth particles are likely always make incorrect predictions, as uneven or angular particles facilitate the drainage and tearing of the film.

It is theoretically possible that the formation of flotocomplexes under pressure flotation can be carried out as a result of the pushing of particles with bubbles, the separation of bubbles from the supersaturated solution directly on the surface of the particles and the capture of the floating bubbles by aggregates of particles. However, B.V. Deryagin, N.F. Meshcheryakov, V.A. Proskuryakov and L.I. Shmidt, E.A. Stakhov express different, often opposite points of view on the prevailing mechanisms of flotocomplexes formation under conditions of pressure flotation (Proskuryakov at al., 1977; Stakhov, 1983; Derjagin at al., 1986; Meshcheryakov, 1990).

It should be emphasized that the obtained theoretical models of the flotation process are quite complex, require the experimental determination of a considerable number of different constants and do not allow to unambiguously determine the efficiency of flotation removal of particles depending on their diameter and other factors, what narrows the possibility of their practical application. There are no simple calculation formulas for determining flotation efficiency.

Studies performed by E.A. Stakhov (1983), R.T. Rodríguez and J. Rubio (2003), O.K. Edzwald (1995), De Rijk, Rikaart and Harthoff, Han et al. (2002)

and others have shown that at saturation pressures of 0.3–0.6 MPa, typical for pressure flotation wastewater treatment, the predominant quantity of bubbles have a diameter of 40–90 microns. It was obtained that the dispersed compositions of particles and bubbles, as well as the function of the fractional flotation efficiency, are logarithmically normally distributed.

Thus, while the flotation models constructing, among other factors, the features of the particle and bubble ensembles, which are involved in the process, must be taken into account. Obviously, when considering these group features, statistical methods should be taken as a basis, what combined with the probabilistic nature of the flotation process gives grounds to consider flotation as a stochastic process and, on that basis, to research its effectiveness.

The total effectiveness of wstewater treatment in the flotation chamber η is expressed as a percentage of the weight of the detained suspension $\mathrm{m_r}$ to the mass of the suspension $\mathrm{m_{en}}$, what entered the chamber

$$\eta = 100\left(\frac{m_r}{m_{en}}\right) = 100\left[\frac{m_{en} - m_{ex}}{m_{en}}\right], \% \tag{2}$$

where m_{ex} – the mass of the suspension removed from the flotation chamber with the treated wastewater.

The fractional purification rate η_{fi} is equal to the ratio of the mass of any i-th suspension fraction, detained in the flotation chamber (Δm_{ri}), to the mass of the same suspension fraction, what entered the chamber (Δm_{eni}):

$$\eta_{fi} = 100\left(\frac{\Delta m_{ri}}{\Delta m_{eni}}\right), \% \tag{3}$$

The total purification rate can be approximately calculated as the sum of the fractional purification rates productions η_{fi} on the respective suspension fractions, what entered the chamber ΔR_i:

$$\eta = \frac{1}{100}\sum_{i=1}^{n} \Delta R_i \, \eta_{fi} \tag{4}$$

When reducing ΔR_i to elementary fractions dR, the exact value of the total purification effectiveness is expressed by the following integral:

$$\eta = \int_0^{\infty} n_f\,(\delta) dR(\delta) \tag{5}$$

The integration by the Allander method of equation (5) takes into account logarithmically normal laws of particle size distribution of contaminants and distribution of fractional effectiveness of purification (Kouzov,1987), allows to obtain the equation for determination of the total purification effectiveness

$$\eta = F\left(\frac{lg\delta_{50} - lg\delta_{\eta=50}}{\sqrt{lg\ ^2\sigma + lg\ ^2\sigma_\eta}}\right) = F(t) \qquad (6)$$

$$F(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{x} exp\left(-\frac{t^2}{2}\right) dt \qquad (7)$$

where $F(t)$ is a function of normal distribution.

Equations (6) and (7) give a possibility of determination of the flotation purification efficiency with taking into account the dispersed composition of particles of wastewater contamination. The parameters $\delta_{\eta=50}$ and σ_η of the treatment distribution efficiency function depend on the design of the flotation chamber and the factors that determine its hydrodynamic characteristics, particularly the air mass flow, the size of the bubbles generated in the flotation chamber, etc. Obviously that for the flotation chamber with known sizes and fixed conditions for the air bubbles formation, the parameters are unchanged. On other hand, for the wastewater of the particular city or enterprise there are constant parameters of the particle size distribution function depending on δ_{50} and σ. In these conditions both the value of the argument t and the value of the normal distribution function (6) of the treatment efficiency will be obviously constants, that means $\eta = const$. With taking into account equation (2) in this case we can write

$$100\left(\frac{m_r}{m_{en}}\right) = const\ or\ \frac{m_r}{m_{en}} = const \qquad (8)$$

Thus, there must be a linear dependence between the amount of suspension entering the flotation chamber and the amount of suspension removed there.

2. Materials and Methods

On the basis of theoretical analysis of the floating process laws in pressure flotation flotocomplexes units, which include particles of contaminants with different dispersion rate, and also one or more bubbles, theoretically substantiated feasibility of pre-flotation treatment by short-term clarifying for the removal of the largest particles from the wastewater, flotation of which is more difficult, and also setted values of the recirculation factor and the fluid velocity in the air separation area (Kovalchuk, 2004). On the basis of the achieved results it was develoved a series of vertical settlers-flotators with diameters of 2.4, 4.0, 6.0 and 7.2 m

(Fig. 2) with productivity of 5–140 m^3/h, in which waste water firstly gets short-term settling, then then pressure flotation with recirculation of the working fluid, which is taken directly from the edifice and not from special intermediate tanks of working fluid. Using of vertical settlers-flotators with short-term settling of wastewater and compatible upward flow direction of air bubbles and contaminant particles in the flotation zone allows:

- to increase the overall efficiency of suspension removal by pre-deposition of large, poorly flotated particles;
- to ensure maximal effective contact with air bubbles during flotation;
- to simplify the process of removing sludge and sediment by arranging a conical bottom and a relatively small area of settlers-flotators with circular shape.

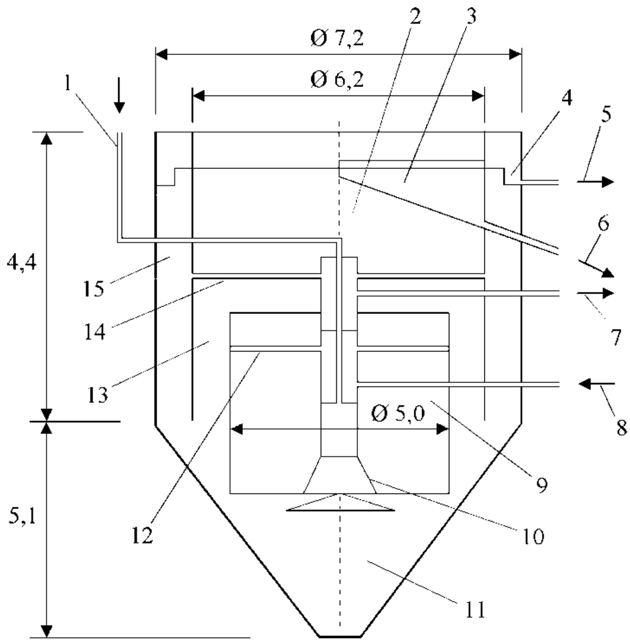

Fig. 2. The scheme of the settler-flotator with a diameter of 7.2 m: 1– supply pipeline; 2 – flotation zone; 3 – tray for collecting flotation sludge; 4 – ring drainage tray; 5 – treated wastewater; 6 – flotation sludge; 7 – extraction of working fluid; 8 – working fluid supply; 9 – settling zone; 10 – distribution device; 11 – silt zone; 12 – working fluid distribution pipelines; 13 – air separation zone; 14 – working fluid intake pipelines; 15 – additional settling zone. A radial scraper is not conventionally shown

The general technological scheme of flotation treatment involves the preliminary removal of large waste from the wastewater on the grates or sieves, and the sand – in the sand traps. The saturation of the working fluid with air is carried out with the use of flotation pumps, a pressure tank and a water-air ejector (Kovalchuk, 2009; Fig. 3a). In many cases, the pressure tank was arranged from a large metal pipe (Fig. 3b). Removal of the flotation sludge into the radial tray was carried out periodically by radial scraper, which was actuated by a gear motor. The wastewater treated in the settlers-flotators then run to the biological treatment facilities.

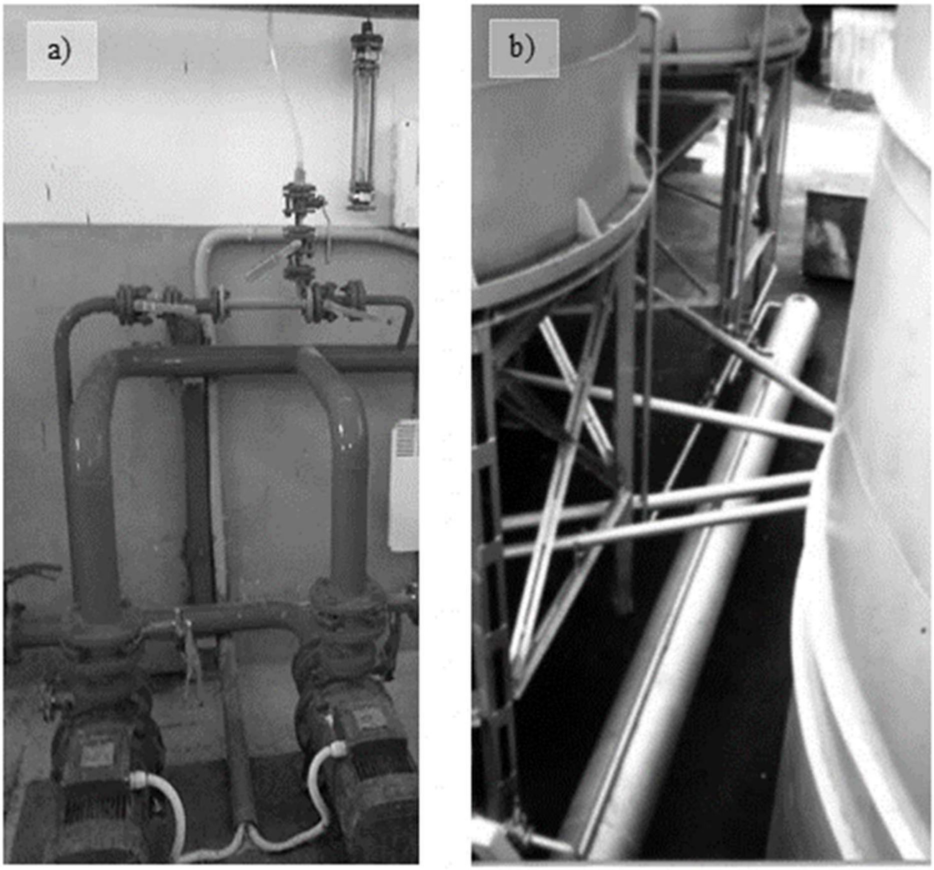

Fig. 3. a) Flotation pumps, water-air ejector and rotameter at the treatment plants of the Zolotonosha butter factory, b) Pressure tank made from large diameter pipe at the wastewater treatment plant of Chernihiv Meat Processing Plant "Rhythm"

Research of non-reagent flotation wastewater treatment was carried out by analysis of input and output samples, and also by control of technological parameters of the work of settlers-flotator with diameter of 7.2 m (Chernihiv Meat Processing Plant "Rhythm", Belotserkovsky Meat Processing Plant "Polis", poultry farm "Oril-Leader", Morozovsky poultry farm, enterprise of concentrated apple juice production "Bukofruit" (Fig. 4), Zolotonosha butter factory), 6.0 m (Nizhyn Meat Processing Plant, Tarasovets Poultry Farm), 4.0 m (Concentrated Apple Juice Company "Gold Trans International") and 2.4 m (Meat Processing Complex "Rosana", Novgorod-Siversky Meat Processing Plant) (Kovalchuk, 2000; Kovalchuk, 2000a; Kovalchuk, 2004; Kovalchuk at al. 2013; Kovalchuk, 2018).

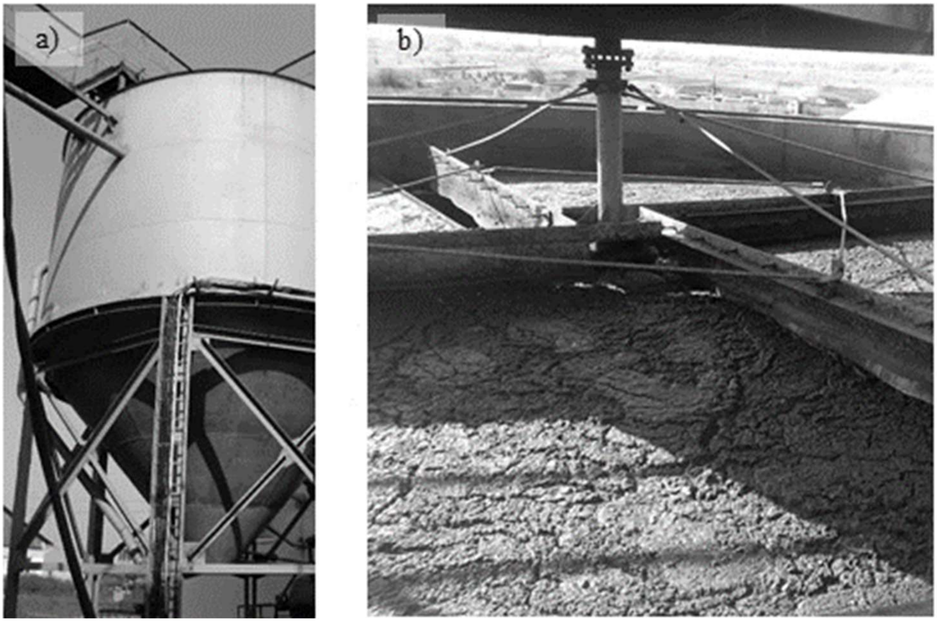

Fig. 4. a) Settler-flotator with diameter of 7.2 m, b) Removal of flotation sludge from the surface of settler-flotator

Measurements of wastewater quantities during production research were carried out with the help of turbine water meters brand VT, which passed the state verification. Determination of the pollutants concentration was carried out in shaken and settled samples of untreated and treated wastewater after each stage of treatment. Wastewater sampling was performed in accordance with the KND 211.1.0.009-94 (Sampling, 1995). There were collected one-off and daily-average wastewater samples. There were selected samples of sludge and flotation sludge from settlers-flotators. The list of hydrochemical parameters, what was determined in the taken sewage samples, was corresponded to the complete program (Annex A) according to KND 211.1.2.008-94 (Rules, 1995).

Determination of fats concentrations in sewage was carried out according to the conventional method (Methodology 1977).

The technological parameters of settlers-flotators operation were determined by the following formulas:

– surface hydraulic load of the flotation chamber ($m^3/(m^2 \cdot h)$)

$$N^h = \frac{(1+\alpha)Q_h}{F} \tag{9}$$

– surface load of the flotation chamber by dry matter ($kg^3/(m^2 \cdot h)$)

$$N^{dm} = \frac{Q_h \cdot C_{en}^{SS}}{F} \tag{10}$$

– specific air flow rate per unit mass of dry matter, what is extracted from wastewater (l/kg)

$$q_{air} = \frac{\alpha \cdot a}{C_{en}^{SS} + \alpha C_{ex}^{SS}} \tag{11}$$

where: Q_h – hourly quantity of treated wastewater [m^3/h], F – area of the flotation chamber surface [m^2], α – recirculation factor [-], a – air solubility [l/m^3], C_{en}^{SS} – suspended solids concentration in the wastewater, what is entering the flotation chamber, [mg/dm^3], C_{ex}^{SS} – concentration of suspended solids in treated wastewater [mg/dm^3].

The basic technological parameters of settlers-flotators operation on treatment plants of some enterprises are given in the Tab. 1.

Table 1. Technological parameters of settlers-flotators operation

Parameter	Technological parameters of settlers-flotators operation at treatment wastewater of enterprises				
	Chernihiv Meat Proce-ssing Plant “Rhythm”	Nizhyn Meat Processing Plant	Belotserkov-sky Meat Processing Plant “Polis”	Poultry farm „Oril-Leader”	Morozov-sky poultry farm
Hydraulic load [$m^3/(m^2.h)$]	2.0–4.0	3.3–4.7	1.66–3.32	3.54	3.54
Load by dry matter [$kg/m^2.h)$]	0.6–24	0.7–17.4	0.24–2.64	3.1	22.1
Recirculation factor [–]	0.83–1.6	0.5–0.74	0.5–1	0.5	0.5
The saturation pressure [MPa]	0.43	0.3–0.34	0.43	0.42	0.42

Determination of the dispersed composition of the investigated wastewater was carried out by optical microscopy method, which involves translating the obtained optical images into digital form and their subsequent computer analysis. The particle density for the transition from their size to mass was determined by the pycnometer method. The function of the fractional flotation efficiency of the settlers-flotators of one diameter was determined on the basis of equations (5) and (6).

3. Results and Discussion

Experimental studies have found that the optical diameters of contamination particles of meat plants are 1–80 microns in size, and the largest number of particles has diameter of 3–5 microns; the contamination particle diameters of poultry farms are in the range of 1–100 microns, and the largest number of particles has size of 2–4 microns. Contamination median particle diameters of meat plants are in the range of 26.7–42.9 microns and poultry farms are 27.4–32.4 microns. The log standard deviation for meat plants and poultry farms is quite narrow – 0.37–0.44. Based on the studies of the dispersed composition of the pollution particles and the efficiency of meat processing plants wastewater treatment in the investigated settler-flotator with a diameter of 7.2 m, the parameters values of the function of the fractional efficiency of flotation wastewater treatment $\delta_{\eta=50}$ and $\lg \sigma_\eta$ are obtained, which are, respectively, 3.6 μm and 0.6 (Kovalchuk, 2008).

As it is shown by the results analisys of the flotation wastewater treatment at all the above-mentioned enterprises, there is a linear dependence between the concentrations of suspended solids in treated wastewater C_{en}^{SS} and the amount of suspended solids, which are taken during the flotation proces $C_{en}^{SS} - C_{ex}^{SS}$, where C_{ex}^{SS} – the concentration of suspended solids in treated wastewater. The presence of such dependence indicates that the flotation of enterprises wastewater occurs according to the laws of free flotation, and the increase of air supply will not increase the efficiency of pollution removal from wastewater. Figures 5–7 show the dependence between the concentrations of suspended solids in treated wastewater and the amount of suspended solids, what are removed during the flotation process for wastewater of Chernihiv Meat Processing Plant “Rhythm” and Nizhyn Meat Processing Plant, Belotserkovsky Meat Processing Plant “Polis”, enterprise of concentrated apple juice production “Gold Trans International” and “Bukofruit”.

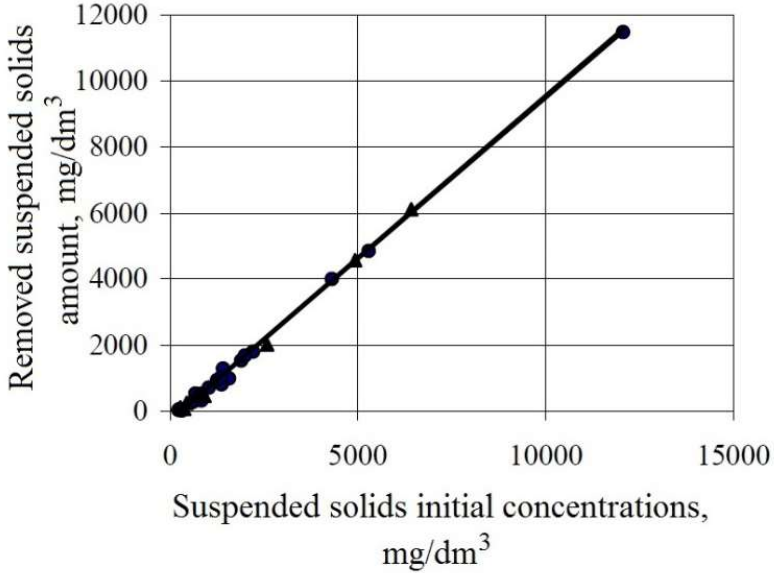

Fig. 5. Dependence of the suspended matter amount, what are removed during flotation sewage treatment at Chernihiv Meat Processing Plant "Rhythm" (●) and Nizhyn Meat Factory (▲), from their initial concentrations

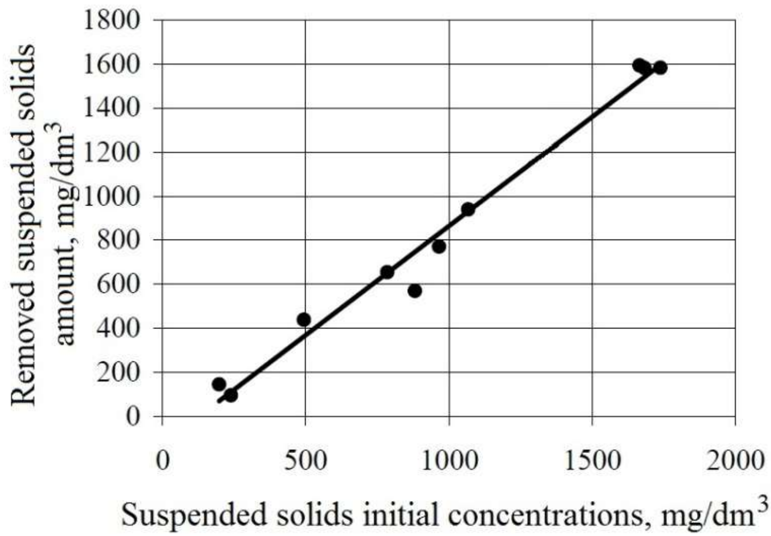

Fig. 6. Dependence of the suspended matter amount, what are removed during flotation sewage treatment at Belotserkovsky Meat Processing Plant "Polis", from their initial concentrations

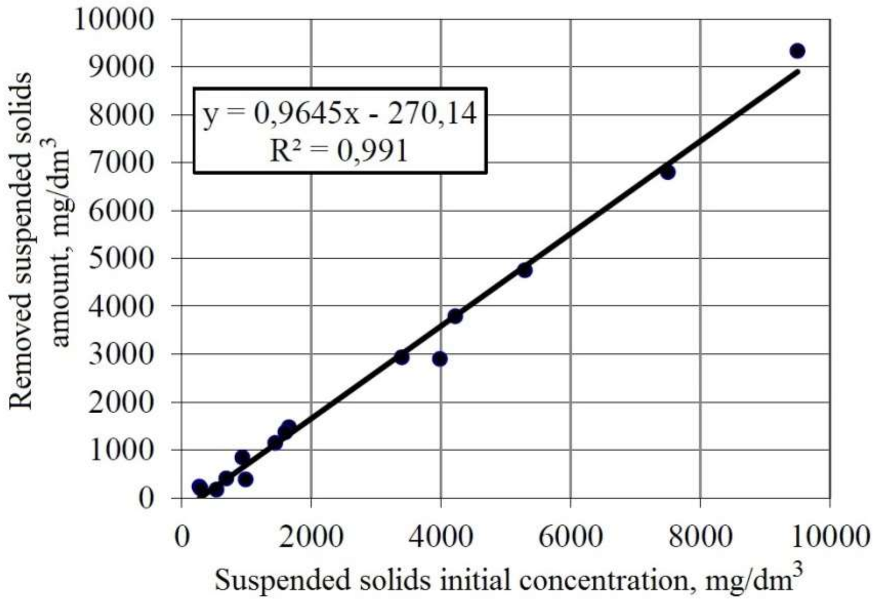

Fig. 7. Dependence of the suspended matter amount, what are removed during flotation sewage treatment at enterprise of concentrated apple juice production "Gold Trans International" and "Bukofruit", from their initial concentrations

It is known that the concentrations of suspended solids correlate with the concentrations of other wastewater contaminants. That's why, it is totally understandable that similar linear dependencies should also be for concentrations of other wastewater contaminants, in particular fats (Fig. 8), COD (Fig. 9), BOD_{20} (Fig. 10) and BOD_5 (Fig. 11). Taking into account the fact that the coefficients of obtained linear dependencies by these indicators for Chernihiv Meat-Processing Plant "Rhythm" and Nizhyn Meat Processing Plant were quite close, then, as a result of the joint processing of the experimental data, the general analitical linear dependencies between the number of initial and removed sewage pollutants in the process of flotation wastewater treatment were obtained for both enterprises and are shown in Tab. 2.

The practical value of the obtained analytical dependences is that they allow to determine with sufficient accuracy the indices of the treated wastewater pollution by the indices of the untreated runoff pollution (by concentrations of suspended solids and fats, COD, BOD_{20}, BOD_5), what not allow to do none of the existing methods of flotation chambers calculating.

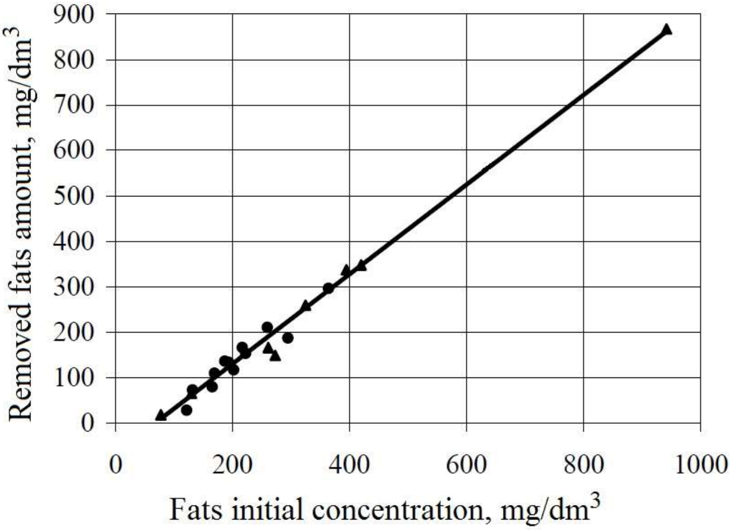

Fig. 8. Dependence of the fats amount, what are removed during flotation sewage treatment at Chernihiv Meat-Processing Plant "Rhythm" (●) and Nizhyn Meat Processing Plant (▲), from their initial concentrations

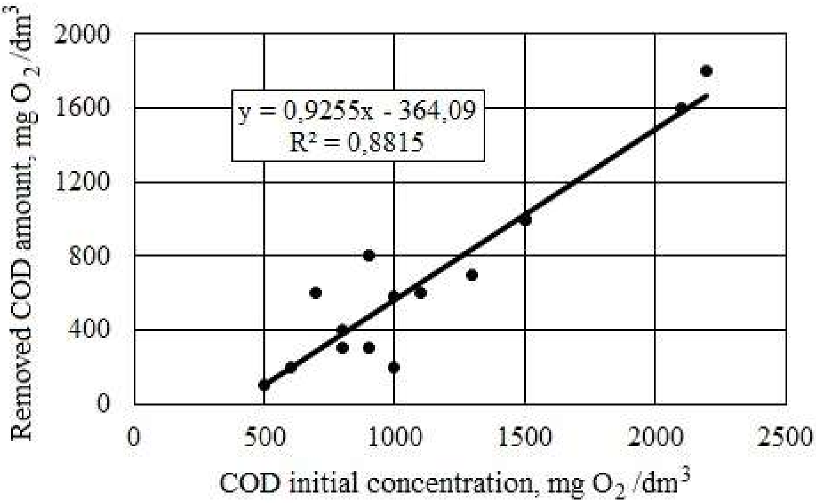

Fig. 9. Dependence of COD amount, what are removed during flotation wastewater treatment at Zolotonosha butter fact

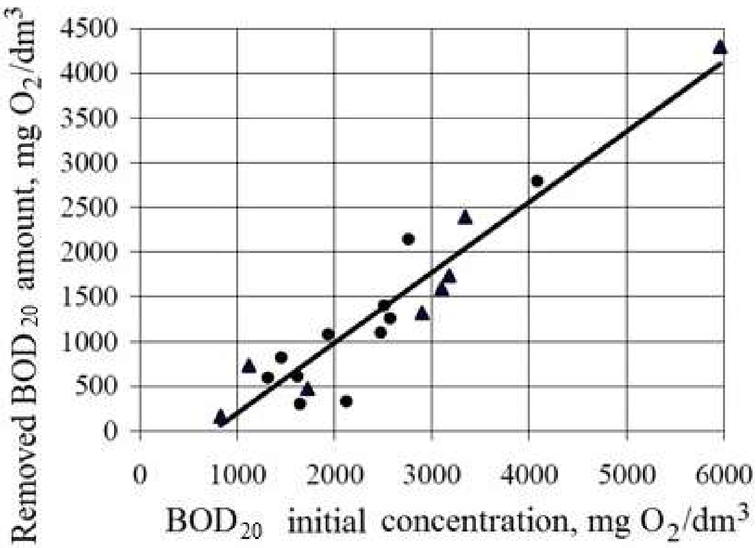

Fig. 10. Dependence of the BOD_{20} amount, what are removed during flotation sewage treatment at Chernihiv Meat Processing Plant "Rhythm" (●) and Nizhyn Meat Processing Plant (▲), from their initial concentration

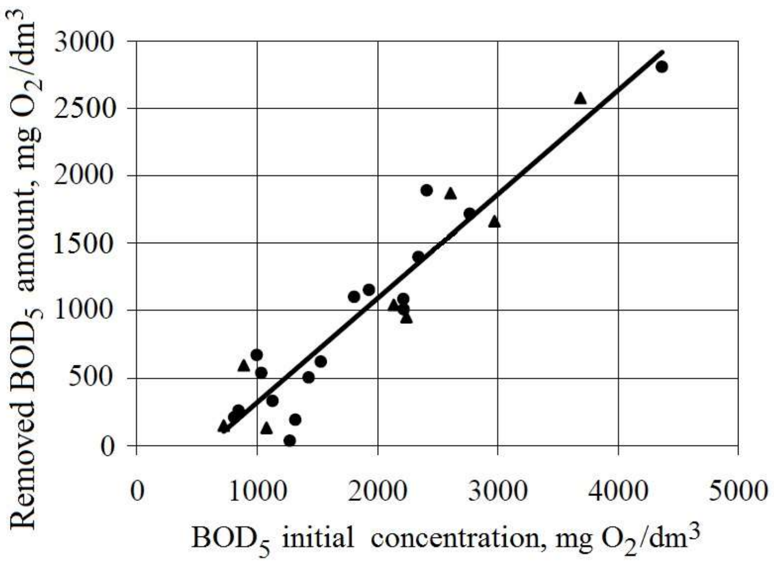

Fig. 11. Dependence of the BOD_5 amount, what are removed during flotation sewage treatment at Chernihiv Meat Processing Plant "Rhythm" (●) and Nizhyn Meat Processing Plant (▲), from their initial concentrations

Table 2. Analitical dependences of the pollution amount, what are removed during flotation wastewater treatment from their initial concentrations in wastewater of some Meat Processing Plants

Analitical dependences	R^2
Chernihiv Meat Processing Plant "Rhythm" and Nizhyn Meat Processing Plant	
$C_{en}^{SS} - C_{ex}^{SS} = 0.976C_{en}^{SS} - 287.4$, mg/dm^3	0.998
$C_{en}^{fat} - C_{ex}^{fat} = 0.993C_{en}^{fat} - 71.2$, mg/dm^3	0.998
$C_{en}^{BOD_{20}} - C_{ex}^{BOD_{20}} = 0.809C_{en}^{BOD_{20}} - 660.9$, mg O_2/dm^3	0.897
$C_{en}^{BOD_5} - C_{ex}^{BOD_5} = 0.773C_{en}^{BOD_5} - 463.4$, mg O_2/dm^3	0.896
$C_{en}^{BOD} - C_{ex}^{BOD} = 0.886C_{en}^{BOD} - 1065.5$, mg O_2/dm^3	0.967

The avarage values of the flotation treatment efficiency and the average concentrations of contamination of the treated sewage at meat processing enterprises are given in the tables, accordingly, Tab. 3 and Tab. 4, and at the enterprises of the concentrated apple juice production – in Tab. 5.

Table 3. Average values of the flotation treatment efficiency of wastewater from meat processing enterprises

Parameter	Flotation treatment efficiency [%], for enterprises						
	Chernihiv Meat Proce-ssing Plant "Rhythm"	Nizhyn Meat Processi ng Plant	Belotserkov-sky Meat Processing Plant "Polis"	Novgorod-Siversky Meat Processing Plant	Meat Processing Complex "Rosana"	Poultry farm "Oril-Leader"	Morozov-sky poultry farm
Suspended solids	81.8	83.9	85.8	59.7	35.5	76.8	95.7
COD	57.3	51.9	65.5	47.3	39.5	67.1	76.0
BOD_{20}	41.8	51.4	61.1	45.2	50.7	49.0	74.2
BOD_5	51.1	48.6	55.8	52.8	43.7	53.8	63.8
Fats	86.1	75.8	87.8	77.3	65.6	76.8	93.0

The efficiency of flotation removal of suspended solids and fats from fats contaminated wastewater should be considered separately. Accordingly, to the obtained results, the achieved efficiency of the suspended solids removal during flotation wastewater treatment of meat-processing plants was 35.5–85.8%, and fats: 65.6–87.8%. While using flotation treatment for wastewater of slaughterhouses poultry farms the same indicators were respectively 76.8–95.7% and 76.8–93.0%. Conducted research have shown that it is impossible to completely remove fats from sewage of meat-processing plants with only one flotation treatment. Obviously, a thin emulsified fat, which is not subject to flotation, is left in the treated wastewater.

Table 4. Average wastewater quality of meat processing plants and slaughterhouses of poultry farms before and after flotation treatment

Parameter	Contamitant wastewater concentrations [mg/dm^3], untreated/treated				
	Chernihiv Meat Proce-ssing Plant "Rhythm"	Nizhyn Meat Processing Plant	Belotserkov-sky Meat Processing Plant "Polis"	Novgorod-Siversky Meat Proces-sing Plant	Meat Processing Complex "Rosana"
Suspended solids	1793/326	1816/292	972/135	884/205	6235/270
COD	3430/1463	2664/1282	2249/719	2471/812	6687/1606
BOD_5	1697/830	1878/966	1206/373	1153/533	2639/955
BOD_{20}	1788/1040	2569/1248	1779/517	1513/772	4682/1208
Fats	483/67	405/98	367/69	175/40.6	1341/94.4
pH	6.80/6.81	6.5/6.68	6.84/6.69	6.67/6.69	7.00/6.83

Table 5. Average values of the flotation treatment efficiency of wastewater from concentrated apple juice production enterprises

Parameter	Average contamitant wastewater concentrations [mg/dm^3], untreated/treated		Average efficiency of wastewater treatment [%]	
	"Gold Trans International"	"Buko-fruit"	"Gold Trans International"	"Buko-fruit"
Suspended solids	1464/296	1654/288	79.8	82.3
COD	7413/3022	9094/3947	59.2	56.6
BOD_5	- / -	4910/2567	-	47.7
BOD_{20}	5145/2563	5941/3207	50.2	46.0
Ammonia nitrogen	14/123.2	21.6/139.2	-	-
Nitrites	- / -	0.31/0.25	-	19.4
Nitrates	- / -	1.62/0.53	-	67.3
Phosphates	2/65.1	3.9/67.4	-	-

Simultaneously with the fats and suspended solids removal, flotation treatment reduced COD of wastewater from meat-processing enterprises (mixed samples, Tab. 3) by 39.5–76.0% (an average is 57.8%), BOD_5 – by 43.7–63.8% (an average is 52.8%), BOD_{20} – by 41.8–74.2% (an average is 57.8%), which improved their next biological treatment in aerotanks. The efficiency of flotation wastewater treatment from the Zolotonosha butter factory for COD was 10.9–67.8% with the maximum concentration of suspended solids in treated sewage

210 mg/dm3. The average efficiency of flotation wastewater treatment from the concentrated apple juice production enterprises was 81.0% for suspended solids, 57.9% – for COD, 48.1% – for BOD_{20} (Tab. 5).

Analysis of own results of flotation wastewater treatment from the enterprises listed above, as well as the results of flotation wastewater treatment of various industries (oil refineries, meat canning plants, fish processing factories, paper mills, vegetable oil production, canning of fruits and vegetables, soap making, gluing making, leather factories, washing and steaming stations, technical fiber factories, artificial fibers, etc. – in total 156 enterprises), published in open press, confirmed the existence of a clear correlation between the concentrations of suspended solids in wastewater, what are entering into the flotation chamber, and the mass of suspended solids, what are removed during the flotation process $C_{en}^{SS} - C_{ex}^{SS}$ (Fig. 12), which was theoretically foreseen earlier. Based on the obtained dependence there were found practically valuable dependencies between the main technological parameters of the flotation process:

$$C_{en}^{SS} - C_{ex}^{SS} = 0.963\, C_{en}^{SS} - 130 \text{ [mg/dm}^3\text{]} \quad (12)$$

$$\eta = 96.3 - 13000/C_{en}^{SS} \text{ [\%]} \quad (13)$$

$$\eta = 96.3 - 13\, N^h/N^{dm} \text{ [\%]} \quad (14)$$

$$C_{ex}^{SS} = 130 + 0.037 C_{en}^{SS} \text{ [mg/dm}^3\text{]} \quad (15)$$

$$C_{ex}^{SS} = 13\, N^{dm}/N^h + 130 \text{ [mg/dm}^3\text{]} \quad (16)$$

where: η – flotation treatment efficiency [%], N^h – hydraulic load on the flotation chamber surface [$m^3/(m^2 \cdot h)$], N^{dm} – load on the flotation chamber surface by dry matter [$kg/(m^2 \cdot h)$].

Obtained dependencies can be taken as a basis in the analysis of the influence of technological parameters of the flotation process on its efficiency.

As it was shown by the results of the work of the settler-flotator at Chernihiv Meat Processing Plant “Rhythm”, with increasing the load on the surface of the flotation zone by dry matter the removal efficiency of the suspended solids is asymptotically increasing (Fig. 13), reaching maximum values of 94–97% with loads of 5–8 $kg/(m^2 \cdot h)$. The removal efficiency of suspended solids did not decrease, even with increasing dry matter load up to 24 $kg/(m^2 \cdot h)$, what indicates the sufficiency of the air amount, that supplied with the working fluid.

Along with the experimental points in Fig. 13–17 are the curves, what are calculated by the equations and pointed hydraulic loads values are shown in the same figures.

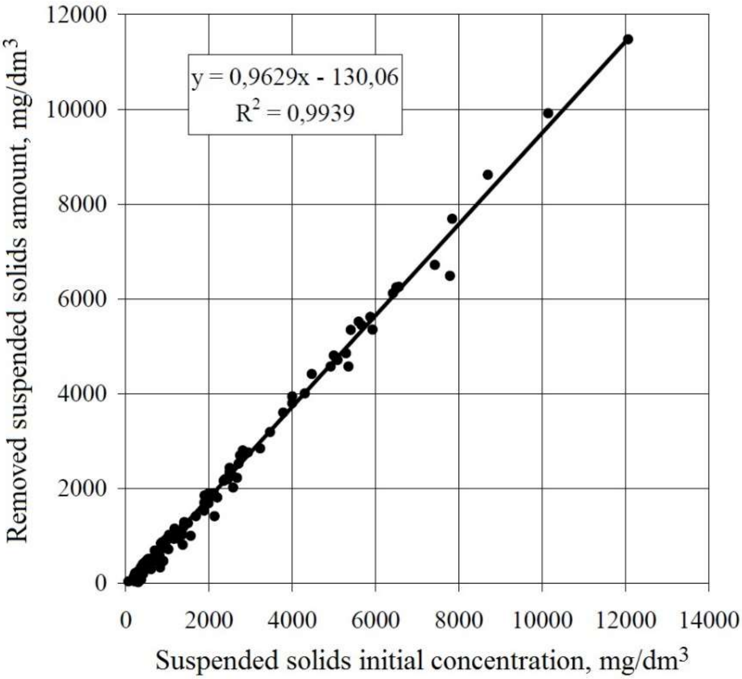

Fig. 12. Dependence of the suspended matter amount removed during the flotation treatment of different categories wastewaters from their initial concentrations

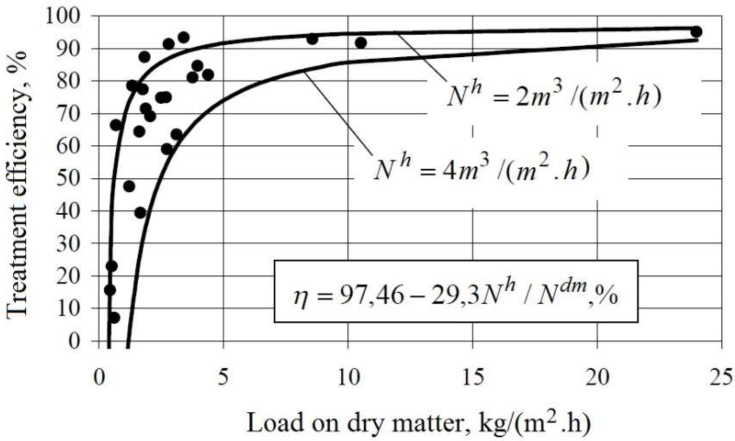

Fig. 13. Dependence of flotation treatment efficiency of sewage from Chernihiv Meat-Processing Plant "Rhythm" by suspended solids from load on dry matter

At the same time as the load on the flotation zone surface increased, the concentrations of suspended solids in the treated wastewater increased (Fig. 14). Obviously, the optimum value of the load on the flotation zone surface by dry matter in this case can be obtained, taking the maximum permissible concentration of suspended solids in the wastewater after the settler-flotator. For example, with maximum concentration of suspended solids in treated wastewater 300 mg/dm^3 the load on the flotation zone surface by dry matter should not exceed 2.5 kg/(m^2·h).

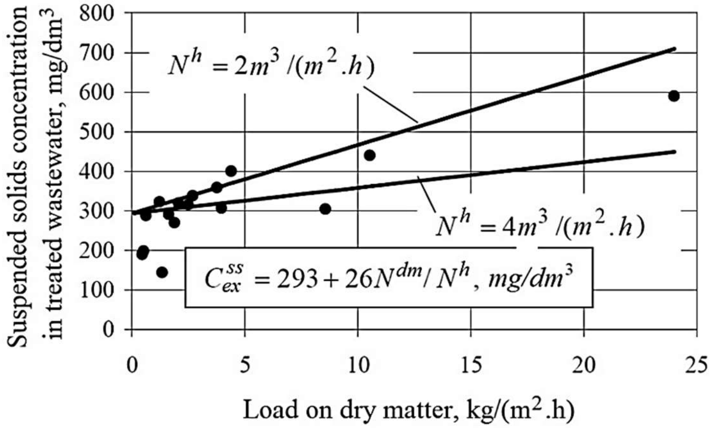

Fig. 14. Dependence of the suspended solids concentrations in the outlet of the settler-flotator of the Chernihiv Meat Processing Plant "Rhythm" on the load by dry matter load

The dependence of the fats removal efficiency on the load on the flotation zone surface by the dry matter, what is presented in Fig. 15, shows that maximum fats removal efficiency values are also achieved at loads 5–8 kg/(m^2·h). The average residual fats concentrations were 67 mg/dm^3.

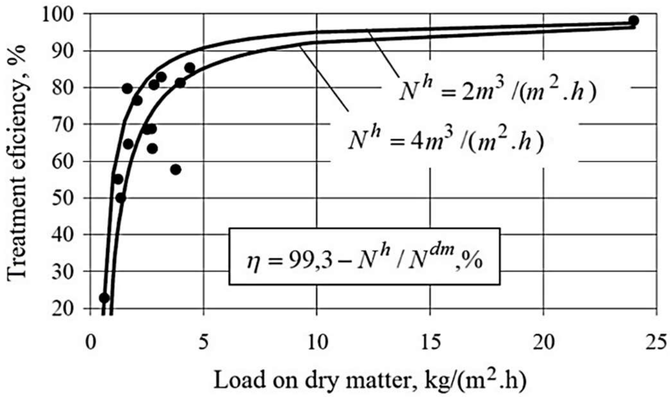

Fig. 15. Dependence of flotation treatment efficiency of sewage from Chernihiv Meat Processing Plant "Rhythm" on fat from the load by dry matter

Approximately the same nature of the dependence of the suspended solids removal efficiency from loading on the flotation zone surface by dry matter was obtained during the research on settler-flotator operation at the Nizhyn Meat Processing Plant (Fig. 16). Quality indicators of untreated and treated wastewater are given in Tab. 4.

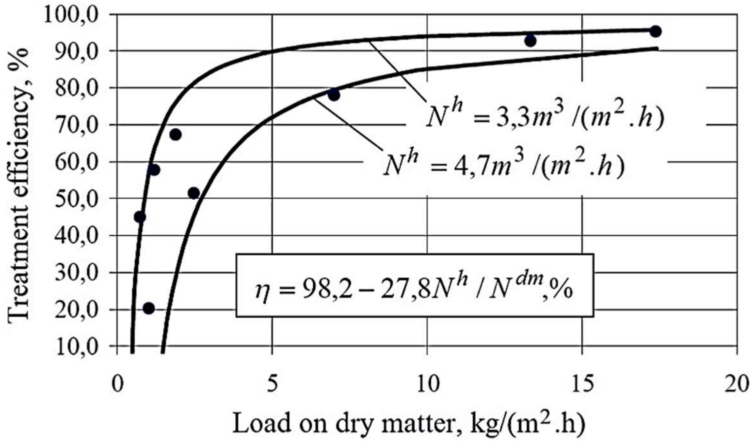

Fig. 16. Dependence of flotation treatment efficiency of wastewater from the Nizhyn Meat Processing Plant on suspended solids on the load by dry matter

During the research at Nizhyn Meat Processing Plant, the hydraulic load on the flotation zone surface was 3.3–4.7 $m^3/(m^2\cdot h)$ and load on dry matter was within the range 0.73–17.4 $kg/(m^2\cdot h)$. As the load on dry matter increases, the effect of sewage treatment on suspended solids increases, but the residual concentrations of the suspended solids in the treated wastewater increase almost linearly. Based on the maximum concentration of suspended solids after the settler-flotator of 300 mg/dm^3, the load on the flotation zone on dry matter should not exceed 2.2 $kg/(m^2\cdot h)$. The dependence of treatment efficiency of wastewater from Bilotserkivsky meat-processing plant "Polis" on suspended solids from the load on dry matter is shown in Fig. 17.

It is known that the pressure with which the working fluid is saturated with air determines the size of the bubbles, what are released in the flotation chamber. Beside that, the saturation pressure also determines the amount of air that dissolves in the working fluid, and together with the recirculation coefficient of the working fluid, – the specific air flow rate per unit mass of dry matter of insoluble wastewater contaminants that is subject to flotation (Fig. 18).

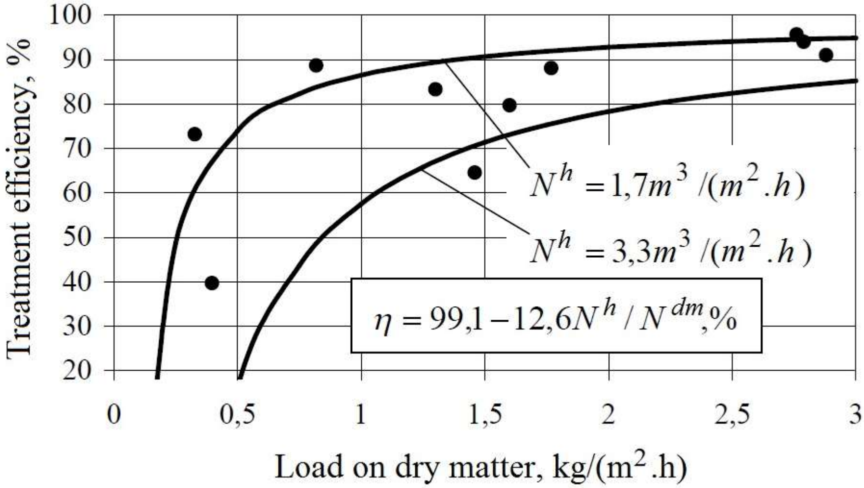

Fig. 17. Dependence of flotation efficiency treatment of sewage at Bilotserkivsky meat processing plant "Polis" on suspended substances from load on dry matter

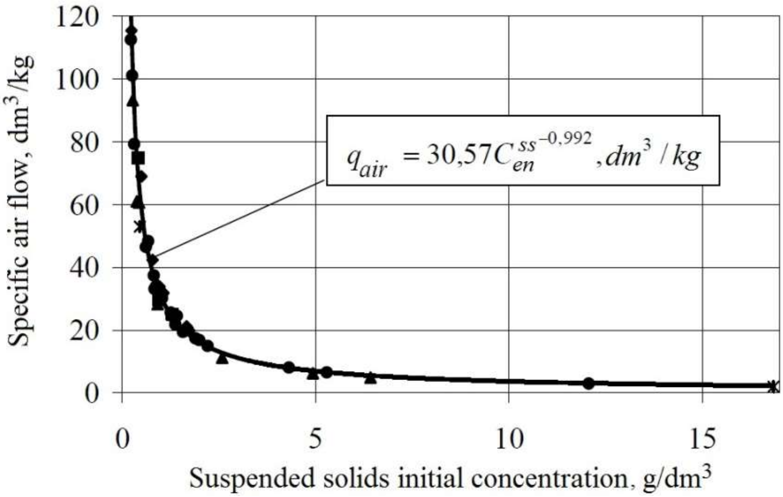

Fig. 18. The dependence of the specific air flow on the initial concentration of suspended solids: ● – Chernihiv Meat-Processing Plant "Rhythm"; ▲ – Nizhyn Meat Processng Plant; ♦ - Bilotserkivsky meat processing plant "Polis"; ■ – Poultry farm “Oril-Leader”; * - Morozovsky poultry farm

As it can be seen from the figure, the specific air flow decreases with increasing of insoluble pollution concentration. This type of dependence can be explained by the increased probability of collision and fixing bubbles and particles with increasing their quantity in unit of volume (Matsnev, 1976; Ulrich at al. 2007). The obtained practically valuable experimental dependence appeared to be quite close to the analogous dependence obtained by A.I. Matsnev (1976), and is well described by the following equation (R^2 = 0.995):

$$q_{air} = 30.57 {C_{en}^{SS}}^{-0.992} \tag{17}$$

where: q_{air} – specific air flow per unit mass of dry matter, what is subjected to flotation [dm^3/kg]; C_{en}^{SS} – concentration of suspended solids in the wastewater, what are entering the flotation chamber [g/dm^3].

The amount of sediment, what is generated in the settlers-flotators installed at the meat-processing plants, is 1–4% of the treated wastewater flow. The humidity of the sediment is 91.4–97.3%, the ash content is 20.2-35.5%, the specific filtration resistance is 98–784.10^{10} cm/h. The average daily amount of generated flotation sludge is 1.7–2.5% of treated wastewater quantity for meat processing plants and 0.8–1% for poultry farms. The humidity of flotation sludge is in the range of 83.9–94.1%, and the ash content is 11.7–16.7%. The content of ether-soluble substances in the flotation sludge is 21.6–29.4% by mass of dry matter, which points on the feasibility of its disposal in the shops of technical factories to obtain meat-bone meal or technical fat.

During the research of mechanical sludge dewatering on OGSh-501U-01 centrifuges, what was performed at Chernihiv Meat Processing Plant "Rhythm", it was obtained that the main technological parameters should be taken as follows: rotor speed – 3000 turn/min, the radius of fugate draining – 200 mm; hourly centrifuge productivity – 7–10 m^3/h. The cake humidity is 80% on average (Kovalchuk, 1997).

Summarizing the long-term observations of the settlers-flotators, we can conclude that their operation, and also the flotation pumps operation, water ejectors and all units of working fluid preparation, was reliable and stable.

At treatment plant of Chernihiv Meat Processing Plant "Rhythm" a metal settler-flotator is located outdoors. To prevent pipelines and fittings freezing of the settler-flotator in winter during heavy frosts, a continuous round-the-clock circulation of the working fluid was carried out. Due to the entering warm sewage into the settler-flotator, the freezing of the flotation sludge was not observed in winter. As the settler-flotator of the Nizhyn Meat Processing Plant was located in the heated building, its operation in winter did not cause any particular problems. The same can be said about the settlers-flotators of the Meat Processing Complex "Rosana" and the Novgorod-Siversky Meat Processing Plant, which tanks in winter were heated by the heat of treated sewage due to the placement of the first-stage aeration.

Flotation can be successfully used in the intensification of the primary wastewater treatment process in so-called flotation biocoagulators, and also in the intensification of the biological wastewater treatment process in so-called flotation aerotansks-clarifiers.

An example of the practical application of the flotation biocoagulation method can be wastewater treatment plants in Rivne (Fig. 19 and Fig. 20), which are used for wastewater treatment of the city and a number of industrial enterprises (Kovalchuk, 2002). The commissioning of flotation biocoagulators has allowed to send in them about 70% of all treated wastewater and increase the productivity of wastewater treatment plants from 19.5 to 25–27 thousand m^3/day with high treatment quality. Technological scheme of wastewater treatment in flotation biocoagulators, what were operated in the period from 1974 to 1995.

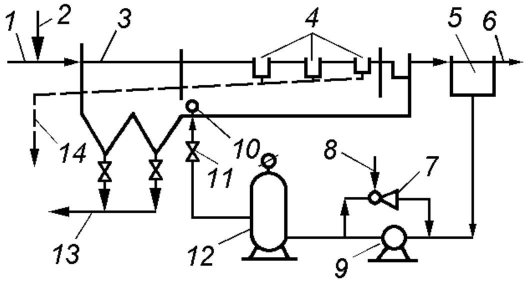

Fig. 19. Scheme of horizontal settler conversion of into a flotation biocoagulator:
1 – wastewater tray; 2 – pipeline of excess activated sludge; 3 – chamber for wastewater previous clarifying; 4 – trays for removal of flotation sludge; 5 – intermediate capacity; 6 – treated wastewater tray; 7 – water jet ejector; 8 – air supply; 9 – pump; 10 – preassure tank; 11 – pressure relief valve; 12 – pipeline for drainage of flotation sludge

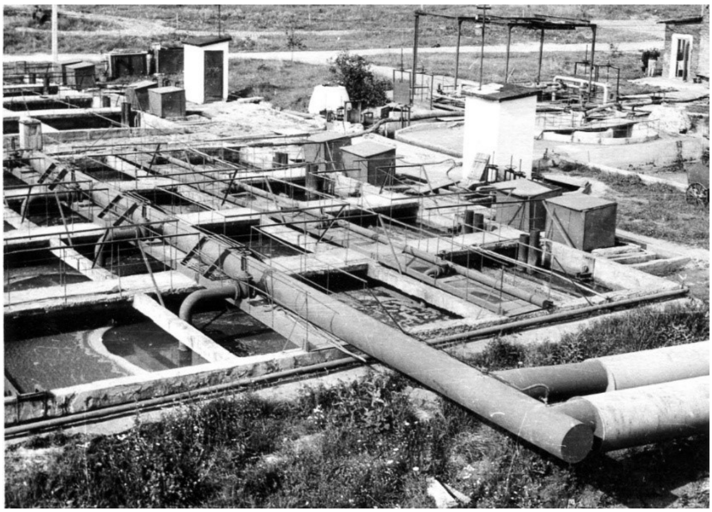

Fig. 20. Flotation biocoagulator at wastewater treatment plant in Rivne

The mode of wastewater treatment in flotation biocoagulators is characterized by the following indicators: the stay duration in the flotation chamber of the working fluid mixture and treated wastewater is 35–40 min, recirculation factor 0.5–0.7; saturation pressure of working fluid with air 0.45–0.5 MPa; air dose is 2–3% of the total flow of working fluid and treated wastewater; dose of excess activated sludge 190–210 g/m^3.

Flotation biocoagulation reduced concentrations of suspended solids in wastewater (average values) from 520 to 250 mg/dm^3, COD of mixed samles – from 437 to 280 mg/dm^3, BOD_5 – from 185 to 115 mg/dm^3. The humidity of the flotation sludge was about 90%, what allowed to abandon the use of gravitational sludge thickeners.

4. Summary and Conclusions

- On the basis of theoretical provisions summarizing of wastewater treatment by flotation, it was made the evaluation of the main flotation process models and the possibilities of their practical application, it was substantiated the feasibility of applying a probabilistic-statistical approach in considering the flotation process.
- Based on perceptions of the probabilistic-statistical nature of the flotation process a linear dependence between the amount of suspended matter entering the flotation chamber and the amount of suspended solids removed there is theoretically substantiated and experimentally confirmed. This made possibility to obtain practically valuable dependence s between the initial and final concentrations of suspended solids and other contaminants, the flotation treatment efficiency, the load on the flotation chamber surface by dry matter and the hydraulic load.
- With using optical microscopy method, it was experimentally investigated the dispersed composition of wastewater contamination particles of several meat-processing enterprises, the median particle diameters and logarithms of their standard deviation are determined, it was obtained the values of the parameters of the fractional efficiency function of the sewage treatment in a flotation chamber with a diameter of 7.2 m.
- It is justified the reasonable expediency of application for the wastewater treatment vertical circular flotation chambers with the preliminary removal of large particles with short-term settling and compatible ascending flow direction of air bubbles and particles of contaminants to ensure their maximum effective contact in the flotation zone. This made it possible to

increase the overall efficiency of the removal of suspended solids, fats and other contaminants, to simplify the process of removing sludge and sediment.

– It was develoved a series of vertical settlers-flotators with diameters of 2.4, 4.0, 6.0 and 7.2 m and productivity of 5–140 m^3/h. Research of the usage efficiency of the settlers-flotatators, which were carried out in the productional conditions on sewage of meat-processing plants, poultry farms, butter factory, concentrated apple juice production enterprises, confirmed the high efficiency of non-reagent flotation treatment. The dependences between the initial concentration of the suspended solids and the specific air flow rate during flotation, the loading on the flotation zone surface by dry matter and the residual concentrations of the suspended solids and fats were also clarified.

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Threats of contamination of drinking water by water from the fire protection systems

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Abstract

In accordance with applicable regulations, drinking water should be protected against secondary pollution. This is especially important when not only drinking water installations but also fire protection installations use one water supply. In the case of fire protection installations, the risk of water contamination is significant due to the higher pressure in the sprinkler systems. Adding right class backflow preventer to the water supply pipe will generate a significant loss of pressure. While in newly specified sprinkler systems additional pressure head may be taken into account at the calculation stage, it may be a problem in modernized existing installations.

Key words: sprinkler systems, secondary water contamination, backflow preventer, pressure loss

1. Introduction

One of the acceptable sources of water for fire protection *systems* is a water supply network.

Due to the specificity of the operation of fire-fighting installations and the applicable procedures for its operation and maintenance, direct connection of this type of installation to the water supply network can pose a threat to the quality of drinking water.

2. Possible hazards of drinking water contamination from fire protection systems

One of the types of fire protection installations are installations filled with water (Malesińska, 2018). This means that the water is kept in these installations for years (depending on the requirements of the regulations according to which the fire protection installation was made). Due to the changing conditions in the environment of such installations, water parameters such as temperature, oxygen content, chemical and biological composition are also changing. In addition, a certain amount of water is pumped in periodically to maintain the required pressure in a non-working installation. For these reasons, the water filling fire protection systems may have much worse quality parameters than the parameters of drinking water. According to the conducted studies (Duranceau and Foster,1998), the following were observed:

- exceeding the allowable concentration of lead and cadmium as well as iron and manganese,
- the presence of oil in water that is used when cutting steel pipes,
- change of smell and color of water,
- increased total organic carbon concentration on the high pressure side of the sprinkler check valve,
- change of dissolved oxygen in the horizontal pipe as a function of distance from the sprinkler valve of a given section,
- pathogenic bacteria, including coliforms, which most likely contaminated pipes during installation.

In addition, the following substances can be found in fire protection installations (Malesńska, 2018):

- against water freezing,
- foaming agents,
- disinfectants (prevention of biological corrosion).

In accordance with EN 1717: 2003, due to possible admixtures and dangers associated with stagnation, water from sprinkler systems can be classified into fluid categories 3, 4 or 5. The possibilities of protecting water against contamination according to the standard, depending on the fluid category, are listed in Tab. 1.

Contamination prevention devices from various manufacturers are available on the market. In addition, protections even in the same class may differ in technical solutions, which significantly affects the amount of generated pressure loss. Figure 1 compares the pressure loss head of anti-contamination fittings from one manufacturer for selected diameters and flows.

The letters on the graph are in line with the names in Tab. 1.

As can be seen the smallest pressure loss is 1 m water column. In this case, it is possible that the pressure reserve with which the fire protection systems are specified will cover the additional pressure loss and thus the installation of the anti-contamination fittings will not adversely affect the operation of the installation. However, in such situations it should always be confirmed by appropriate calculations. An extreme case in the reported head pressure loss is a 20 m high water column. To ensure reliable operation of the fire protection system, a pressure reduction of 20 m is not permitted. This affects the amount of discharge from the sprinkler located, in terms of hydraulic parameters, in the most unfavorable position. Reducing the volume of water flowing out will reduce the density. Density is one of the basic design parameters of the sprinkler system, closely related to the fire hazard class. A reduction of this parameter in an already existing sprinkler system is not permitted.

Table 1. Protection against contamination for selected fluid categories (EN 1717:2003)

Name	Safety device	Fluid category		
		3	4	5
AA	Unobstructed free outlet			
AB	Free outlet with a non-circular overflow (unrestricted)			
AC	Free outlet with vented immersion tube and overflow			
AD	Free outlet with injector			
AF	Air interrupion with circulat overflow			
AG	Air interrupion with overflow checked by vacuum measurement			
BA	Pipe separator with controllable medium pressure zone			
CA	Pipe separator with different not measurable pressure zones			
DA	Pipe aerator in flow form			
DB	Pipe interruptor with moveable parts			
DC	Pipe interruptor with permanent connection to the atmosphere			
GA	Pipe separator, not flow-controlled			
GB	Pipe separator, flow-controlled			
LB	Pressurized aerator, combined with downstream backflow preventer			

– protection is provided
– protection is provided only for pressure equal to atmospheric pressure

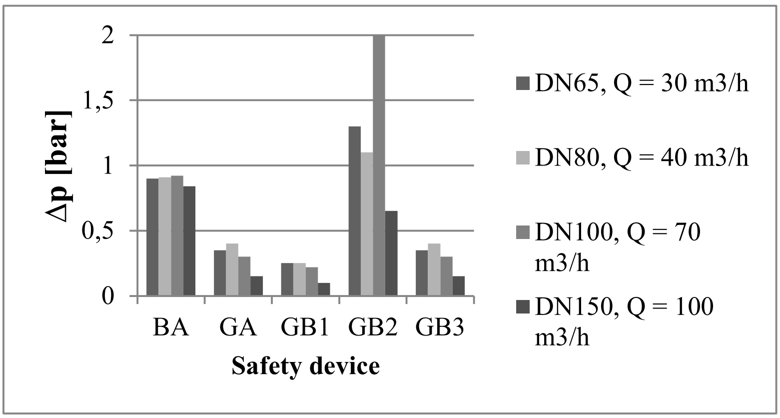

Fig. 1. Summary of the pressure losses (own study)

Summary

Reported cases of contamination of drinking water by water from a fire protection system were associated, among others, with damage to the check valve or with a significant decrease in water pressure in the water supply network. Currently, the installation of drinking water is protected from contamination by backflow preventers. Newly designed fire protection installations should not be a threat to the quality of drinking water, and an additional pressure head, necessary to cover the loss on the backflow preventer valve, is included in the required pressure head for proper operation of the fire protection system at a given fire hazard at the stage of hydraulic calculations. The problem arises in the case of existing fire protection installations in which the appropriate class of contamination protection has not been applied (design requirements from 10–15 years ago). Modernization of such systems requires taking into account the current levels of contamination protection. However, this involves the introduction of an additional local loss of pressure up to 10 m water column. In the case of an existing fire protection system, such a pressure loss may lead to the installation losing its ability to extinguish or control the flame in a given fire hazard. In order to maintain the planned efficiency of the fire protection installation, it will often be necessary to rebuild the installation, which may be associated with significant costs.

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Improvement of technical control process of wastewater at the industrial enterprise

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Abstract

The EU legislation places the great emphasis on issues of groundwater and surface water quality. This requires to monitor wastewater quality, because mainly wastewater is the reason of the deterioration of the quality of water resources. Therefore, it is timely to conduct investigations and search for better methods for controlling the concentration of substances in liquids.

The main aim of the article was to develop, on the basis of established dependencies, the concept of a new electrical method for determining concentrations of substances in a multicomponent fluid, and to develop methods for the operational determination and control of wastewater characteristics on the basis of the proposed electrical method, the concentrations of substances in a multicomponent fluid. The investigations covered physicochemical studies with elements of conductometry, dielcommetry and imitation spectroscopy using a primary transducer – capacitive sensor. The concept of the method bases on the dependence of the liquid composition on its dielectric constant. The proposed method advantages include i.a. the possibility of determining the lowest concentration of a substance, measurements in actual time, small measurement time as well as usefulness for a wide range of controlled substances.

The methods of an operational control of the concentration of controlled substances in technical liquids and treated wastewater consist of two main steps: study of the control model and the actual process for controlling the object itself. The methods enables automating the express control of the composition of liquids and can be developed and used in real production conditions and in combination with the current production and environmental standards of a specific enterprise. Moreover, they will contribute to the saving material resources and will minimize the impact of liquid waste on the environment.

Keywords: wastewater, industrial control, electrophysical characteristics of liquids, imitation, conductivity sensor, operational control, electrolytes, non-electrolytes, control of fluid composition, maximum permissible concentration (MPC)

1. Introduction

Wastewater – industrial, agricultural and domestic, as a type of treated liquid water waste, is the main source of man-made load and deterioration of surface water that does not have time to recover. Therefore, higher requirements are envisaged for regulatory provision of wastewater quality characteristics and methods of their control.

Directive 2000/60/EC of the European Parliament and of the Water Policies Council at local level is aimed at preventing the deterioration and improvement of aquatic ecosystems, promoting the long-term protection of water resources, ensuring a gradual reduction of surface and groundwater pollution, and facilitating mitigation and impacts. The purpose of EU water law is to achieve sustainable use of EU water resources, including the provision of satisfactory qualitative and quantitative status for surface and groundwater.

The legislation lays the foundation for a comprehensive water management system and requires EU Member States to set up appropriate administrative structures, develop plans and have a modern monitoring system. In addition, it determines the quality standards of surface and groundwater in the environment, as well as for specific types of water use (e.g. drinking supply or bathing), emission standards for individual pollutants (e.g. nitrates), technological standards (e.g. for urban wastewater treatment). The main common disadvantages of water quality are:

- the use of MPC as a limit value; at the same time, the MPC (maximum permissible concentration) is not an environmental quantity, but a sanitary and toxicological quantity;
- mainly situations monitor only one component – chemical;
- physical and biotic components are usually ignored;
- the parameters that characterize the processes, properties and phenomena of the controlled object are not taken into account;
- weak scientific validity of indicators;
- insufficient sensitivity of definition of indicators;
- weak correlation with other indicators (risks, security indicators);
- lack of validity for decision making.

This means that objective monitoring of surface water variables is impossible in practice. Technogenic pollution should be monitored at the enterprises for compliance with the established standard characteristics.

The fulfillment of these requirements during the production and treatment of liquid waste is not possible without the introduction of operational control methods of normalized substances concentrations. Implementation of standard analytical definitions for the rapid and automated control of multicomponent liquids composition, which are real objects, are complicated by the length of the analysis or lack of selectivity.

Therefore, research of improving operational methods of controlling solubility in liquids during technological processes and environmental monitoring is timely and relevant.

The fundamentally greater efficiency of new physical methods can be illustrated by the illustrative example given by the famous German chemist M.F. von Stackelberg: ”One gram atom is a powder, but a charge of one farad can give the whole globe a potential of 160 million volts”.

The standard electrical conductometric method is intended for rapid studies in binary solutions of concentrations of substances that affect the conductivity of a liquid. This method makes it impossible to determine the concentration of an individual controlled substance in a multicomponent fluid by the measured value of the specific conductivity, with one electromagnetic field defined for all liquids at a standard frequency. Investigation of the electrical properties of aqueous solutions, such as liquid dielectrics, and the analysis of the components of complex electrical parameters at different frequencies of the electromagnetic signal, allow us to develop a theory of the relationship between the electrical properties of liquids and their composition. Also, interest in such research is enhanced by the improvement of experimental equipment.

The results of studies using RLC meters make it possible to determine the dependences of the electrical parameters of liquids in a wide range of electromagnetic field frequencies on the chemical nature and the concentrations of their constituents. The use of set electrical parameters, which correspond to the normalized component concentrations, improves the informativeness of conductometric studies of multicomponent liquids. This makes it possible to expand the list of controlled substances on which the various electrical properties of liquids depend, to increase the selectivity, precision and efficiency of the analysis.

The introduction of an electrical method for the rapid determination of liquids characteristics will quickly determine the required level of industrial water treatment; to predict the future quality of the return water of the enterprise; promptly monitor the normalized parameters of the treated wastewater for compliance with the regulations related to production and specific categories of water use.

Therefore, the objects of research are the electrical properties of binary and multicomponent liquids and real wastewater.

The subject of research is the normalized characteristics of wastewater, in particular dissolved substances, their concentration in water and methods of their control.

The purpose of scientific research is to improve the dielectric and conductometric method for of measuring and controlling the concentrations of constituents of multicomponent liquids by electrical parameters, and also, to formulate recommendations and develop draft regulatory documents for methods for of standard wastewater characteristics operational control. The purpose of the study is:

– to analyze the current situation of the regulatory framework for wastewater control;
– to analyze the main features, tendencies and prospects of development of modern electric methods for control of composition of liquids;
– to determine the dependences between substances concentrations of different electrical nature in a liquid and complex component of conductivity in an electromagnetic field of a wide frequency range;
– to develop, on the basis of established dependencies, the concept of a new electrical method for determining concentrations of substances in a multicomponent fluid;
– to develop methods for the operational determination and control of wastewater characteristics on the basis of the proposed electrical method, the concentrations of substances in a multicomponent fluid;
– to develop a draft standard for the method for determining and controlling the normalized characteristics of wastewater quality.

The scientific novelty of the obtained results is the development of normative and technical bases for the improvement of electrical methods for determining the composition of multicomponent liquids.

Practical application of the obtained scientific results will enable:

– to establish the concentration of a substance in a multicomponent fluid according to the measured values of the admittance;
– to control at a certain, experimentally set frequency the maximum permissible concentration of the controlled substance in the multicomponent mixture according to the value of the reactive conductivity component determined during the measurement by the sign;
– to expand the list of substances whose identification or concentration is electrically controlled;
– to implement a new approach to the method for dielectric and conductometric measurements for the operational control of the composition of technical fluids and standard characteristics of wastewater;
– to recommend directions for improvement of environmental regulations on wastewater.

2. Theoretical thesis

In addition to state control, the composition of water is monitored by every enterprise that uses water and discharges wastewater into reservoirs. For this purpose there are created the posts of factory or special laboratories at the enterprises, which are equipped with the necessary equipment for carrying out the analyzes. Physical, chemical, biological and organoleptic methods are used in wastewater control.

Analyzing the characteristics and methods of monitoring water object has revealed a number of contradictions that are inherent in enterprises that discharge wastewater into reservoirs.

The rigorous approach to pollution control is undoubtedly justified, but the complexity and duration of the experiments make it impossible to have the required speed of control and objective assessment in real time. There is a need for constant monitoring directly near the sources of discharge into natural water sources, since under these conditions the constituents and their normalized concentrations are always known. Due to the fact that the equipment and methods for treatment are outdated, and because of the large number of constituents in the industries themselves, it is economically advantageous to control their composition from specific production leaks (e.g. from a galvanic plant) before analyzing and treating the total wastewater mixture.

The normalized characteristics of regional wastewater meet the requirements of national regulations, especially their quantitative composition. However, regional water sources differ in their characteristics and ecological status and have 5 quality categories according to Ukrainian national standards (in some countries 7 quality categories).

The paper proposes that enterprises and urban treatment plants promptly, in real time, control the product of purification and, if necessary, return it for further purification to obtain the required characteristics of a certain quality category of natural source.

At different industries, even with the same production technology, the composition of wastewater, its output and the mode of drainage is very different. The quality of the processed raw material, its physicochemical properties and especially the chemical composition greatly influence the composition of industrial wastewater. Each enterprise's passport lists normalized MAC values and Maximum allowable discharge of substance (MAD) of treated wastewater. Unlike domestic wastewater, which today has the same qualitative and quantitative composition as industrial wastewater, only industrial wastewater is strictly regulated. In addition, in some countries, liquid waste from healthcare facilities is not regulated, which in today's context can be a source of dustrie's treatment to remove all contaminants that interfere with the return of treated water to the circulating water supply system or discharge them to an urban wastewater treatment plant. The required degree of treatment of industrial wastewater is determined by the conditions of their acceptance into the city's drainage system.

In order to carry out standard control procedures, it is important to observe the two-component requirement of the composition of the test solution. Moreover, the composition of such a solution contains a substance whose concentration is to be measured. Therefore, the study of multicomponent mixtures is quite problematic.

Even all analytical methods are unable to capture the diversity of modern pollutants. Operational and automated control of the composition of multicomponent liquids, which are real liquid wastes, is complicated by the length of time of analysis in industrial chemical laboratories. In addition, methodological errors of existing laboratory studies of concentrations of controlled substances for the enterprise can reach up to 50%, and in some cases up to 100%.

Standard laboratory (or, in the case of chromatography – portable) measurements, these are the so-called indirect and destructive measurements, which have a number of significant drawbacks that make it impossible to use them directly in the production process.

The authors propose an advanced electrical method that uses complex coupled electrical quantities, such as resistance and conductivity, as an informative parameter, allowing real-time monitoring directly. This creates the ability to automate such controls. At the same time, only the electrical method for controlling the composition of liquids will allow the creation of robotic systems for monitoring wastewater treatment.

Non-destructive methods for the study of liquids wich are based on the use of conductometry and dielometry are known. However, such methods are used as generalizations that are not selective for non-electrolytes or weak electrolytes, to which certain substances of inorganic composition and preferably all of organic composition are attributed. Only an imitation method, which is actually based on conductometric and dielometric methods, can theoretically be suitable for the study of liquids of different chemical nature.

The standard conductometric method is based on the measurement of electrical conductivity of entire measuring system, which depends on the concentration of only those substances that are electrolytes and affect the electric current. At the same time, the liquid should be only two-component.

The standard dielectric method is a method where the electrical parameter is an informative parameter, because of the generalization of this indicator it makes it difficult to control the composition of multicomponent liquids. Instead, the complex electrical parameters of the imitation method would give more information about the composition of such liquids.

Modern imitation spectroscopy is used for semiconductor, dielectric, ion-electronic materials and electrochemical systems analysis. The specific physical mechanisms of systems response to the applied sine wave signal in different external physical fields are studied. The basic methods of finding the kinetic parameters of the charge transfer process and the identification of energy relief are determined by the imitation parameters of the kinetic parameters (Macdonald and Cook, 1985; Hixson, 1988; Barsoukov and Macdonald, 2005; Hryhorchak and Ponedilok, 2011).

Based on this theoretical analysis, it is proposed to investigate the composition of objects of a non-electric nature, in particular liquid, which is wastewater, by imaging spectroscopy. Namely, physicochemical studies with elements of conductometry, dielcommetry and imitation spectroscopy were performed using a primary transducer – capacitive sensor.

Here is a description of just some of the scientific findings that illustrate the possibility of developing a new approach to imitation studies of objects of a non-electric nature, which are multicomponent fluids containing electrolytes and non-electrolytes.

3. Conditions and course of research

The essence of the proposed research method is the dependence of the liquid composition on its dielectric constant. Some fluid can be considered as a dielectric substance that has the accumulate, store and distribute electrical energy potential.

There is no absolute difference between the dielectric and the resistive state of a substance, because of the same substance may be a dielectric and a conductor, depending on the conditions. The basic concept that explains the physical nature of a substance's behavior and enables it to be interpreted as a conductor or dielectric is the Maxwell time of dielectric relaxation, which is determined by the equation:

$$\tau = \varepsilon_0 \cdot \varepsilon \cdot \rho \tag{1}$$

where: ε_0 – dielectric steel, ε – the relative dielectric constant of the medium between the covers, ρ – resistivity.

If the material is subjected to a pulse voltage over time t, then at $t < \tau$, the substance can be considered as a dielectric, and in the case of inequality, the material will be considered as a conductor with some resistive properties. For the case of AC comparing τ and $\frac{1}{\omega}$, where ω – AC frequency, that is, at $\tau > \frac{1}{\omega}$ it is a dielectric, and at $\tau < \frac{1}{\omega}$ – the conductor. Therefore, the electrical properties of the substances depend on the frequency of AC. This means that in the Maxwell time of dielectric relaxation, one can understand the physical nature of a substance, which has the corresponding meanings ε and ρ and is located between the plates of the flat capacitor.

A simple substitution diagram for a real capacitor consists of a parallel coupling of a capacitor and a resistor. Dielectric AC losses are conductivity and polarization losses.

In the case of AC, the polarization losses are determined by the equation:

$$P = U^2 \omega C tg\delta \tag{2}$$

where: P – power losses, δ – dielectric loss angle, $tg\ \delta = \frac{I_G}{I_B}$ – ratio of active current to reactive, U – electric field voltage, C – electric capacitance of a flat capacitor, ω – AC frequency.

Other losses in liquids are due to the presence of weakly polar groups in the molecules and the presence of ionic impurities.

It should be noted that the dielectric loss in any material depends on the temperature, frequency, field strength and nature of the material.

Therefore, the frequency dependence of losses is a characteristic of the material and is determined for each substance – solvent, not only by its properties, but also by the presence of impurities.

As a rule, losses are maximal at one or more frequencies, depending on the type of molecule. Highs are due to the rotation of polar molecules in a liquid dielectric. Such a study of losses frequency behavior is known as "dielectric spectroscopy", which allows to determine the structure of substances. The dielectric properties depend on the polarization mechanism with a certain frequency and time of the process.

Electron polarization occurs in a neutral atom when the electron cloud shifts relative to its nucleus.

Atomic polarization occurs when an electron cloud is deformed by the action of a field.

Relaxation effects arising from the rotation or vibration of elementary particles – atoms, ions or electrons – are observed in the vicinity of their characteristic absorption frequencies.

Therefore, the fundamental characteristic of dielectrics is the dielectric constant characterizing the processes of electric polarization.

According to Debye's theory, the relaxation time of particles depends on their size, solvation processes and other local factors. Therefore, considering complex systems such as multicomponent fluids, where there are solvent molecules, the solution itself, their self-associates and solvation complexes, the anomalous dispersion region corresponds to more than one relaxation time, but a set of values τ. Each of these values corresponds to the independent relaxation of elementary particles of different types.

To consider different polarization mechanisms independently of one another is incorrect, given that they influence each other.

Carrying out rapid chemical analysis of the composition of liquids in production is a complex and costly task. Therefore, a method is required to satisfy the following requirements:

- low cost of technical means and methodological support;
- minimal analysis costs;
- prompt decision making on compliance/ non-compliance with regulatory requirements;
- the ability to identify the controlled components and determine their concentrations, or to establish the conformity of the test sample comparison standard;
- existence of criteria of conformity of the test sample of the standard must be scientifically substantiated.

A number of factors described below have been taken into account to formulate the conditions for the experimental studies.

The physicochemical properties of aqueous multicomponent liquids with need to be taken into account in electromagnetic studies are due to the particular molecular and intermolecular structure of constituents, in particular electrolyte ions, polar and nonpolar molecules of organic matter and complex compounds.

Measurements of the impulse and impedance parameters of the bipolar poles were used to carry out the research, which made it possible to analyze objects of both electrical and non-electrical nature. If the capacitance, inductance, resistance, conductivity for objects of an electrical nature are manifested under the action of a test signal in the form of parameters independently, so for objects of a non-electric nature the characteristics of the properties are manifested only in interaction with the primary transducers – sensors.

The primary converter may be a sensitive element in the form of a capacitor, an inductor, or a resistor that interacts with the control object. The electrical characteristics of the object cause the changing of reactive and active components of the dielectric constant of the imaging sensor environment.

An electrochemical cell for classical conductometry was adopted as the basis of the converter design. It can also be considered as a capacitive primary converter.

The conductometric method is based on the use of the dependence of the resistance of the electrolytic converter on the composition and concentration of impurities. Usually such converters are used to measure the electrical conductivity of the electrolytes at which the concentration is determined. However, it should be borne in mind that the electrical conductivity of the electrolyte solution depends not only on the concentration, but also on the temperature, which requires a mandatory temperature correction.

A capacitive transducer was chosen because of the wide range of conductometric method wich has an applications in modern manufacturing plants, which use a set of electrochemical methods of analysis of liquids based on the measurement of electrical conductivity, which is proportional to the concentration of the constituent of the solution. Concentration of a defining substance is the main normative characteristic in product safety standards, including the ecology.

Capacitive primary converters are chosen because in classical physicochemistry. In the tested analytical control, this type of sensor is the most studied in terms of the design of the primary transducer and the electrical characteristics of the object – binary liquids. It will allow to sufficiently plan and substantiate the experimental conditions, theoretically expect the experimental data, as well as logically analyze the results.

A simple contact conductometric converter consists of two electrodes immersed in the test liquid. The resistance between the electrodes depends on the electrical properties of the solution, the relative location of the electrode covers, and on the permittivity of the medium between them. The electric capacitance of a flat capacitor is determined by the formula:

$$C = \varepsilon_0 \cdot \varepsilon S / \delta \tag{3}$$

where ε_0 – dielectric steel; ε – the relative dielectric constant of the medium between the covers; S – active cover area; δ – the distance between the covers.

Measurements of resistance between electrodes were carried out on alternating current to ensure the principles of non-destructive method.

In capacitive primary converters there are considerable forces of attraction between the plates, which is determined by the electric field energy derivative by the coordinate of movement of the moving plate:

$$F = \frac{dW}{d\delta} = \frac{d}{d\delta}\left(\frac{CU^2}{2}\right) \tag{4}$$

where: W – electric field energy, δ – the distance between the covers, C – electric capacitance of a flat capacitor, U – electric field voltage.

You can get the necessary conversion function by profiling the plates by changing the area of the electrodes in the converter.

In addition, the capacitance between the electrodes depends on the level of the liquid, since the dielectric constant of the fluid differs from the dielectric constant of air.

During the experiments, primary converters of different sizes, made of different materials, were studied. The electrodes of the sensor were copper, stainless steel, graphite carbon, in the form of wire or plates. The design provided the possibility of changing the distance between electrodes. The conductive electrodes were investigated with a stable lacquer coating of plates and wire as a non-contact sensor and an uncoated contact sensor.

Such a sensor needs shielding to eliminate the influence of non-informative parameters. They characterize the spurious capacitance of the electrodes, the capacitance of the connecting wires, the external electromagnetic field, and the like.

The experiments were performed in the frequency range from 50 Hz to 1000 kHz. The change in active G and reactive B components of conductivity was estimated using RLC meters (Fig. 1).

Multiple equilateral measurements of electrical parameters for an empty sensor were slight changes in the values of the active and reactive conductivity components.

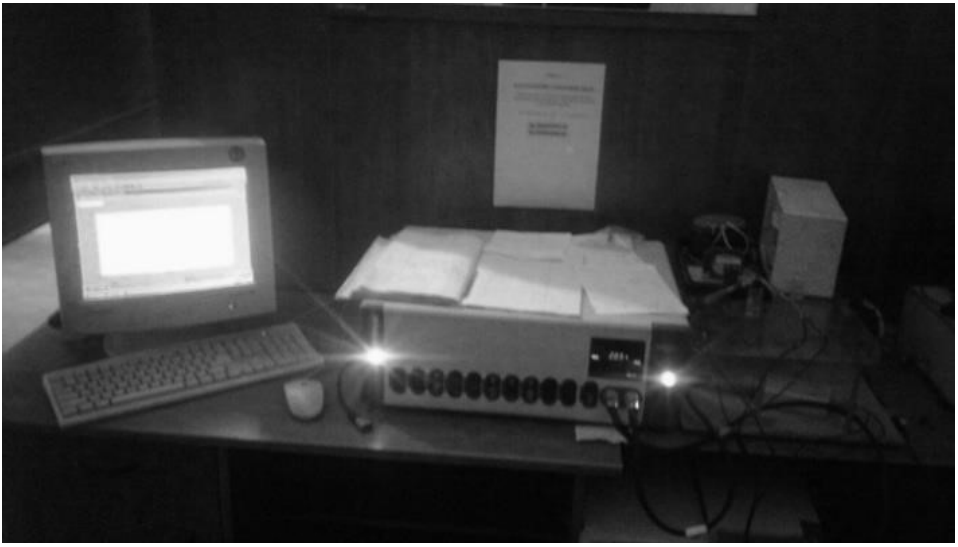

Fig. 1. Measuring research system

As a result of the experimental studies, experimental dependences (Fig. 2) of the frequency components were obtained, according to which the physical and chemical properties of the investigated liquids were performed.

Since the experimental study lasts from two seconds to one minute, each of the experiment was planned to solve a specific problem, provided that the effects of temperature were neglected. The time of the experiment depends on the time of measurement and presentation of the results on the display. Usually, long-term analysis would require a thermostat. The thermostat conditions are well understood and easy to implement.

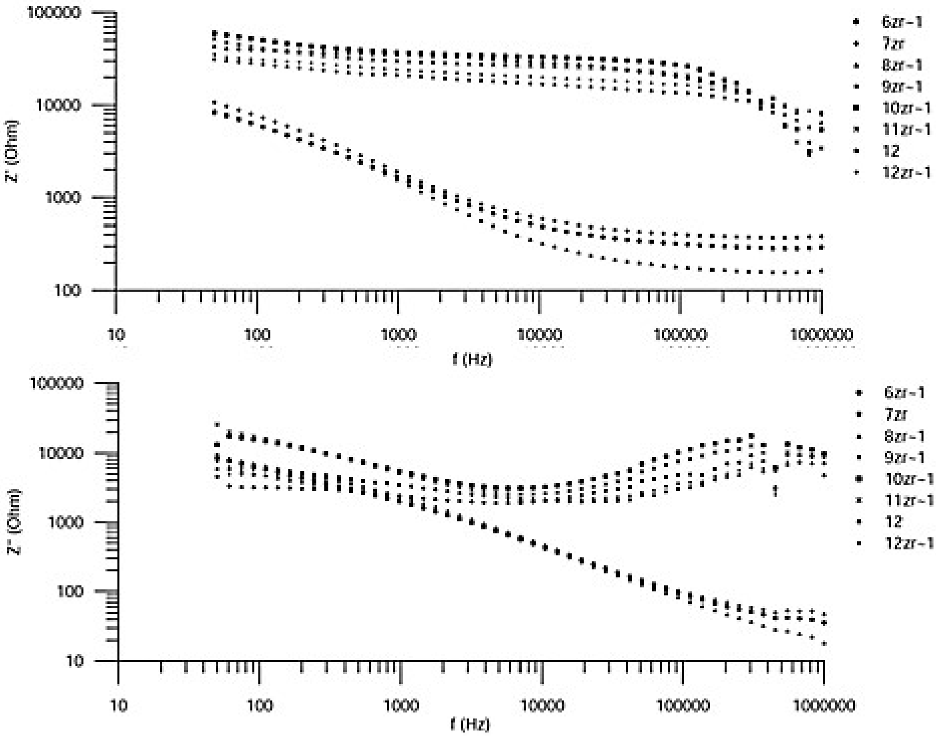

Fig. 2. Results of the study of the dependence of active *Z*'and reactive *Z*'' component of the measurement conductivity on the frequency of the test signal; 6zr- 8zr – change in electrolyte concentration in solution; 9zr-12zr – change in concentration of non-electrolyte in solution

According to the results of experimental studies, a number of ways of analyze have been developed. They can be in practical use in enterprises and can be implemented in regulatory documents – methods for monitoring wastewater characteristics, in particular:

- the method for controlling the maximum permissible concentration of the pollutant by the sign of the measured value of the reactive conductivity component;
- a method for express qualitative and quantitative control of the composition of the electrolyte in a liquid complex mixture with a possible change in the composition of the matrix;
- a method for express identification and determination of the concentration of copper sulfate and control of its MPC in complex mixtures using modified electrodes;

– a method for express identification and determination of the composition of high-carbon substances in complex liquids-mixtures by controlling the composition of alcohols of the homologous series.

All the described methods allow for automated rapid control of the composition of liquids and are offered for use in automatic environmental monitoring lines. An electronic measuring unit can be made”intelligen” by incorporating a microprocessor. With the help of appropriate software, the functions of the electrochemical sensor can be greatly expanded. It helps in:

– processing of data during the calibration (calibration) of selective electrodes;
– construction of calibration graphs (Fig. 3);

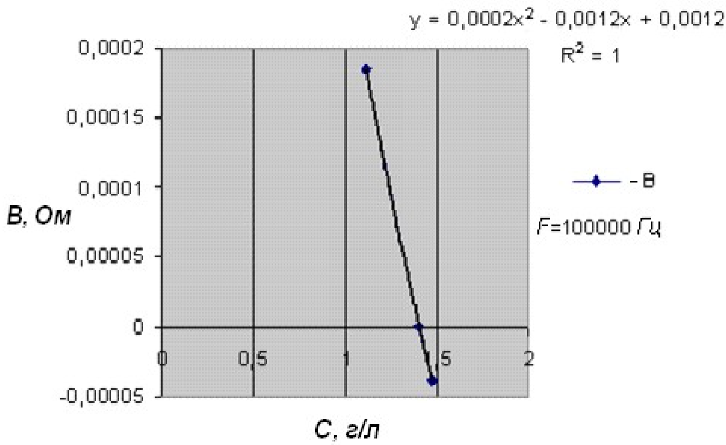

Fig. 3. Approximation of the dependence of the reactive conductivity component on the concentration of the KCl solution at an electromagnetic field frequency of 100 kHz and a constant volume of fluid in the converter

– memorizing the calibration information received;
– automatic calculation according to the measurement of the difference of potentials of concentrations of ions taking into account the actual temperature of the test solution and its dilution with corrective additives and other related data;
– fixation of date and time of measurement;
– the accumulation, processing and transfer of data (for example, in any user-specified units) is not an external computer or network.

Methods of operational control of the concentration of controlled substances in technical liquids and treated wastewater consist of two main steps: study of the control model – liquids with the maximum permissible concentration of the controlled substance, which are performed under laboratory conditions; and the actual process for controlling the object itself.

In the first stage, the method of liquid research is applied. This method uses the dependence of the active or reactive conductivity component on the volume of the multicomponent fluid in the converter, the concentration of the controlled substance, the frequency of the electromagnetic field, the concentrations of the matrix and the temperature. To control the composition of the electrolytes experimentally determined:

- the volume of controlled multicomponent fluid in the converter V;
- generator setting frequency $F_{control}$.

To control the composition of non-electrolytes, the values of active $G_{control}$ are experimentally obtained and reactive $B_{control}$ components of conductivity at a certain frequency $F_{control}$ generator setup.

The second step is the process of operational control of the normalized concentrations of controls.

The steps for implementing the process of operational control of the normalized electrolyte concentration on the real object are presented in Fig. 4.

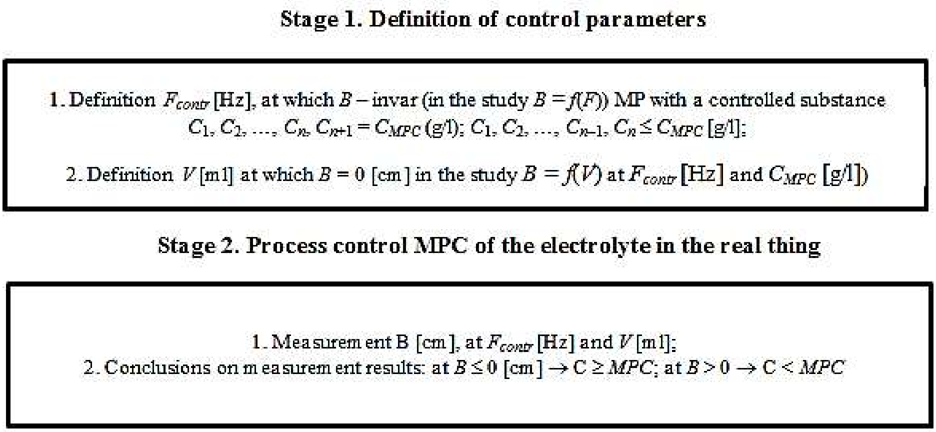

Fig. 4. Stages of control of electrolyte composition on the real object

Conclusions on exceeding the MPC of a controlled substance are based on determining the sign of the measured values of the reactive conductivity component.

For example, the method by which the proposed method for electrolytes is implemented provides a number of requirements for:

- experimental determination of the dependence of the active and reactive constituents of the solution conductivity of the test liquid reference sample on the frequency of the electromagnetic field in the range of 50 Hz–1000 KHz;

- determination of the volume of the test solution in the carbon converter, which causes a change in the polarity of the reactive component of conductivity;
- determining the frequency of the selective control substance in the reference sample at which the reactive component is zero at the normalized maximum permissible concentration of the substance;
- adjustment of a specified volume of fluid and frequency of the transducer signal that is used as an element of control of the automated control system in responding to an indicator signal of exceeding a certain concentration of a substance;
- comparison of experimentally obtained indicators of the active and reactive conductivity component with the previously studied solution of the reference sample;
- forming a conclusion about the qualitative and quantitative composition of the liquid.

Consider a specific example. This is a technique for controlling the leakage from a galvanic bath of a copper sulfate liquid into a wastewater collector of the plant's overall production for subsequent process control and purification. For automated control, the system must be configured to signal that the concentration limit is exceeded, for example, 2.8 g/l. The algorithm provides:

- "Tuning" the converter to a specific liquid (according to its composition) and to a certain regulatory concentration (maximum permissible concentration) of the controlled component through reference studies;
- connection of the converter as an element of control to the automated control system of production processes;
- responding to an indicator signal of exceeding a certain concentration of the component.

The first step of the algorithm control is to test experimentally the volume of a liquid with a given concentration of a controlled substance (for example, 2.8 g/l), It will change the sign of the reactive component of the capacity of the carbon transducer at a certain selective value for the substance of the signal frequency at the point of comparison. This is accomplished by researching and plotting a nomogram of the volume of a reference fluid with certain concentrations of solute from the value of the reactive conductivity component. By measuring the dependences of the reactive component of the conductivity of aqueous solutions characteristic points are established. At these points, the reactivity of the conductivity for the copper sulfate at different concentrations takes the same value. The coordinates of these points can be controlled by changing the amount of substance between the electrode covers. Namely the volume of the liquid under study. When changing the volume of fluid, you can lower the first (at the lowest concentration) dependence on the intersection with the abscissa. This is the essence of the proposed zero method of controlling the characteristics of liquids (Macdonald and Cook, 1985; Stolyarchuk et al., 2005; 2007; 2009; 2010; 2011; Mikhalieva et al., 2013; 2016). Subsequent dependencies with are greater than the required concentrations of the controlled substance will intersect in the vicinity of the same point, within the error of determining the concentration. Experimentally determined volume – 345 ml; frequency at which the zero value of the reactive component is observed, 15000 Hz. These are necessary and sufficient characteristics of the converter, which is easy to change (adjust) if necessary, depending on the liquid, the controlled substance and its maximum permissible concentrations.

Further, after the connection of the transducer with the test liquid to the automated control system, changing the polarity of the reactive conductivity component of the analyte will indicate that the impurity concentration in it exceeded the MPC (in this case, the specified concentration exceeded 2.8 g/l).

The last step involves appropriate guidance on the results of control.

Figure 5 shows the layout of the measurement system for laboratory testing and the operational control of concentrations of controlled substances, consisting of a computer, a converter, and an RLC meter. The system must be customized to the specific converter of the controlled substance and the MPC of the controlled substances and used to construct the specific methodology.

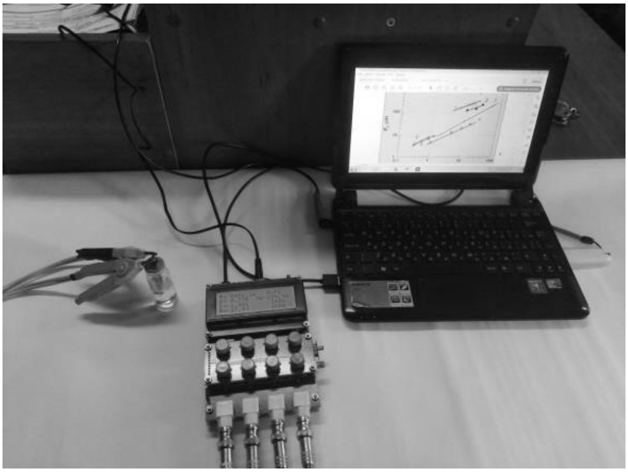

Fig. 5. Measurement systems for controlling concentrations of controlled substances

It is obvious that, depending on the chemical nature of the controlled substance, in particular whether electrolytes or non-electrolytes are being investigated, the methods for control will differ (Macdonald and Cook, 1985; Stolyarchuk et al., 2005; 2007; 2009; 2010; 2011; Mikhalieva et al., 2013; 2016).

4. Conclusions

Methods for operational control of the concentration of controlled substances in technical liquids and treated wastewater, consist of two main stages:

- study of the control model – liquids with the maximum permissible concentration of the controlled substance performed in laboratory conditions;
- the actual process of control for a real object.

The proposed electrical method for studying the composition of liquids has several advantages over existing ones, in particular:

- the lowest concentration of a substance that can be determined by the developed methods – 0.01–0.001 mg/l;
- measurements are made in real time (no sampling and concentration);
- the accuracy of the analysis is (1.0–10.0)% and sufficient for the needs of industry;
- an important advantage of the method is the small measurement time, which does not exceed a few seconds;
- the simplicity of the design of the primary transducer enables rapid mass analysis for a wide range of controlled substances.

The developed methods allow to automate the express control of the composition of liquids and can be developed and used in real production conditions and in combination with the current production and environmental standards of a specific enterprise; will contribute to the saving of material resources and will minimize the impact of liquid waste on the environment.

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Calibration of hydraulic model of the selected municipal water supply network

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Abstract

Availability of numerous computer models allowing numerical simulation of water supply systems and possible integration among GIS (Geographic Information System), SCADA (Supervisory Control And Data Acqusition) and CIS (Customer Information System) databases results in increased application of modeling by water supply companies in systems operation and management.

The available pieces of simulation software based on mathematical models allow reflecting operation of water supply network and simulation of variable random events, possible on the network, without interference in real, existing systems. One of the most important aspects of practical application of numerical simulations is calibration of models, usually based on minimization of differences between results of calculations and values measured empirically, possible due to determination of physical and operational characteristics of the water supply system.

This paper contains calibration results of hydraulic model of the selected municipal water supply network. The tested hydraulic model was developed in Epanet 2.0, basing on data provided by the local water supply company and water demand determined due to domestic watermeters readings. The calibration was performed by trial-and-error method using results of pressure measurements in the selected points of network. The characteristics of pipelines selected to calibration covered pipe material roughness, pipe diameter and hydraulic characteristics of applied pumps.

The performed calibration of model representing the real water supply network revealed several problems including availability of in-situ measurements results and validation of fitting degree of tested variables in calibration module of Epanet 2.0. The performed statistical analysis allowed assessment of model data fitting in several nodes of the developed model.

Keywords: water distribution, hydraulic model, calibration, Epanet

1. Introduction

Water supply companies are nowadays prone to frequently apply results of numerical modeling in everyday management and operation services planning for water distribution networks. It is possible due to wide availability of pieces of modeling software and possibility of integration among various GIS (Geographic Information System), SCADA (Supervisory Control And Data Acqusition) and CIS (Customer Information System) databases (Zimoch, 2008; Bałut and Bylka, 2013; Zimoch and Bartkiewicz, 2017; 2018).

The available modeling software packages are based on mathematical models and allow to reflect operation conditions of water supply network and simulation of different random events possible on the network without interference with the real objects.

There are two known categories of models, in relation to time — steady simulation, with all parameters of modeled phenomena constant during time duration in time; and extended period simulations (EPS), reflecting the behavior of the system over time.

The quality of obtained results of numerical simulations is strongly dependent to quality of the model itself. Mapping of water supply distribution structure, proper description of its physical characteristics, determination of water demands patterns or denotation of water supply characteristics directly affect quality of numerical modeling results. The proper calibration of the developed model is required to fully use the possibilities offered by numerical software. The calibration process is commonly classified as the most important and most difficult stage of water supply networks numerical modeling.

Literature reports provide different definitions of calibration process. According to Cesario (1995) calibration is a process of model adjustment allowing to simulate conditions in the system for the assumed time duration at required degree of accuracy. Walski et al. (2003) defined calibration as process of comparison of model results to in situ observations, and, if required, adjustment of data describing the system until predicted behavior match the observed one in the reality for the wide variety of operation conditions. Osfeld et al. (2012) assumed that calibration is a process of comparing model results with field data and making the appropriate adjustments so that both results agree. On the other hand calibration depends on minimization of differences between the results of simulation and measurements, by determination of physical and operational characteristics of tested water supply system (Bhave, 1988; Boulos and Ormsbee, 1991; Sudoł, 2004; Bhave and Gupta, 2006; Bylka, 2013).

The following input data may be corrected during calibration of water supply network hydraulic model: pipelines roughness, values and patterns of water demand and pumps characteristics (Ormsbee and Lingireddy, 1997; Price and Ostfeld, 2014; Kowalska et al., 2017; Zimoch and Bartkiewicz; 2017). Calibration process may be performed by several methods, including iterations, open and implicit (Alves et al., 2014; Okeya et al., 2014; Lippacher et al., 2019). Difficulties in reaching the satisfactory agreement between results of calculations and measured values may result from limits of the applied computational method, inaccuracy of measurement equipment or simplifications of the developed model. According to Walski et al. (2003; 2007) the highest uncertainty of input data concerns pipe roughness and water demand. Pipe material roughness may be affected by pipe diameter, material itself, its age and water quality, whereas, water demand is related to patterns of water use and location of uptake points (Wlaski et al., 2003; 2007; Kowalska et al., 2017; Bartkiewicz and Zimoch, 2018).

Convergence criteria for iteration should be set individually, in relation to the assumed purpose of the model, its size and function, the literature guidelines should be treated only as recommendations (AWWA, 1999; Walski et al., 2003).

This paper presents calibration results of selected municipal water supply network hydraulic model. The tested hydraulic model of water supply network was developed in Epanet 2.0 software basing on data obtained from the local water supply company and read-outs of domestic watermeters. The applied calibration was performed by trial and errors method for in situ measurements of water pressure in selected nodes of the network. The characteristics selected for calibration process covered inter alia pipe material roughness, pipe diameters and hydraulic characteristics of pumps.

2. Materials and Methods

2.1. Description of the network

The municipal water supply system providing drinking water for population over 40000 and several industrial facilities was selected to this study. The studied network is being supplied by two water supply stations drawing groundwater by six deep drilled wells. The water supply station WTP 1 delivers water to the city and to the tertiary pumping station, while WTP 2 station transfers water only to the 3rd degree pumping station. Diameters of pipelines in the network vary between 100 mm and 400 mm for the main transit lines, while domestic connections utilize pipelines 32 mm – 65 mm. The discussed water supply network consists mainly of cast iron, high density polyethylene (PE-HD) and polyvinyl chloride (PVC) pipelines, while household connections are made of PE-HD, PVC and galvanized steel. The total length of pipelines in the network, including connections, equals approx. 244 km. The oldest cast iron pipelines were built in 1972.

2.2. Hydraulic model

Our research was performed on the hydraulic model of tested water distribution network developed in EPANET 2.0 software by EPA, US. (United States Environmental Protection Agency). The model was prepared by the outside firm on the order of the water supply company and consisted of 622 nodes, 715 lines, 6 water intakes, 3 water reservoirs and 14 pressure or flow regulation valves, located after reservoirs and pumping stations (see Fig. 1). The range of applied diameters was 64–400 mm. Regardless the material and age of the given pipeline, the unified value of roughness equal 0.5 mm was set to all lines in the model. Number of pumps in each water station was reflected directly, with simplified, one-point, characteristics (Tab. 1).

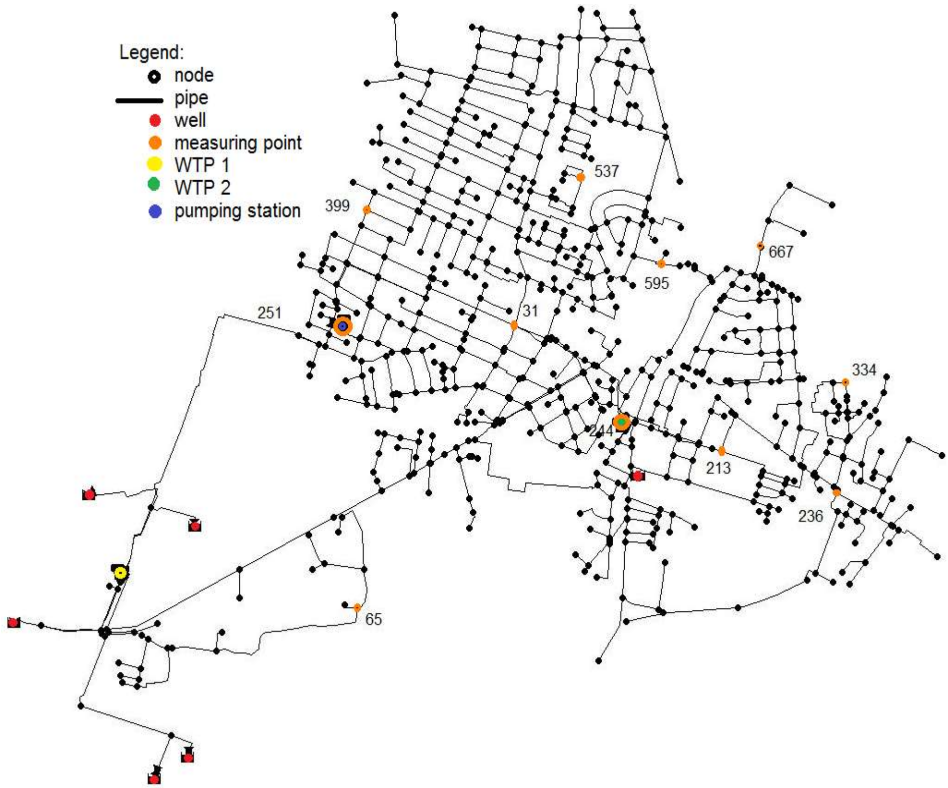

Fig. 1. Scheme of the water supply network

Table 1. Pumps characteristics

Pumping station	Number of pumps	Pumps characteristics		Remarks
		Pressure head [m H_2O]	Vol. flow rate [dm^3/s]	
WTP 1	4	36	25	To 3rd degree pumping station
	2	65	24	To water supply system
WTP 2	4	50	14	To 3rd degree pumping station
3rd degree pumping station	3	50	42	To water supply system

The computational water demands, set at the nodes of model, were based on domestic watermeters read-outs, while water demand pattern was based on read-outs of water flow meters localized in water supply stations. The water demand pattern based on water demand by housing was assigned to all nodes of the shared model (Fig. 2).

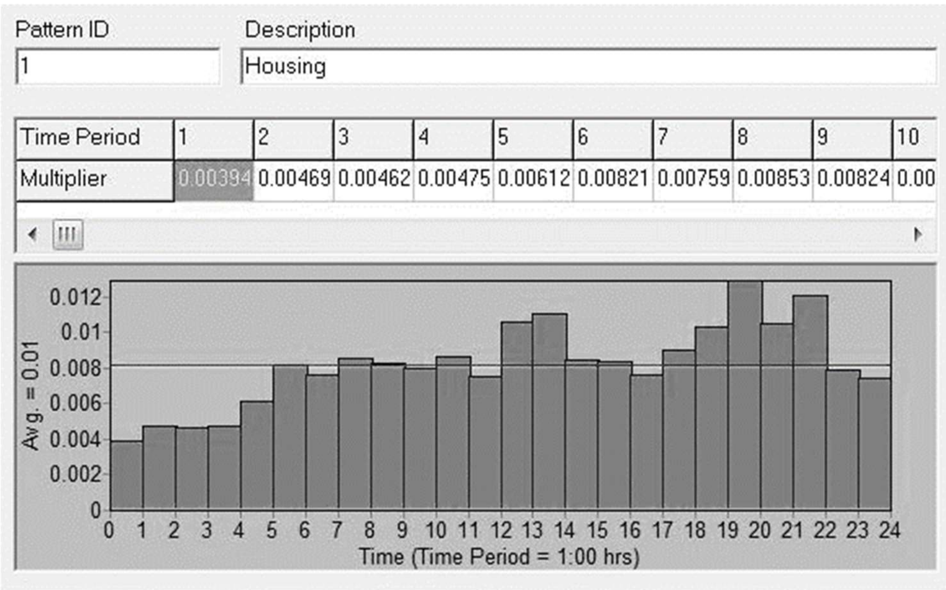

Fig. 2. Water demand pattern for housing

2.3. Methodology of research

The measurements of water pressure in 9 nodes of the tested water supply network as well as at exits of two water supply stations (WTP 2 and pumping station 3rd degree) were performed to allow calibration of the model (Fig. 1). Pressure meters, CellBox-H with data loggers, were instead in below and four over ground fire hydrants. Additionally, data covering water pressure and volumetric flow rate at WTP 1 and 3rd degree pumping station were obtained from the management of the network. Duration of the measurements on the water distribution pipelines was equal 4 days, however, the results from 48 hours were assumed as credible.

During the first step of the presented studies the tested model was calibrated by Epanet 2.0 software with assigned singular water demand. After introduction of the calibration file, based on water pressure measurements, the significant divergence between modeling and measurements results was reported by calibration module of Epanet 2.0 software.

The obtained coefficient of determination $R^2 = 0.541$ showed weak agreement between model and real conditions. In order to improve the above agreement the tested model was modified by addition of some pipelines constructed after development of the model and additional water demand pattern for services (Fig. 3). Basing on the available GIS maps, the elevations of water distribution system nodes were corrected, with accuracy to 1 cm.

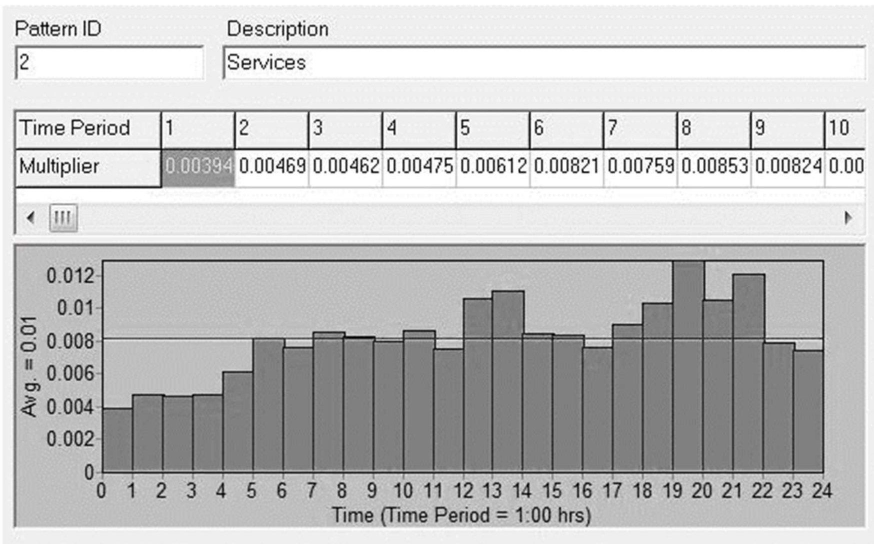

Fig. 3. Water demand pattern for services

Additionally, the manner of pumps implementation was alerted. Basing on the read-outs from the water supply stations, the alternative singular, three-points characteristics of pumps were developed. The characteristics of alternative pumps are presented in Fig. 4.

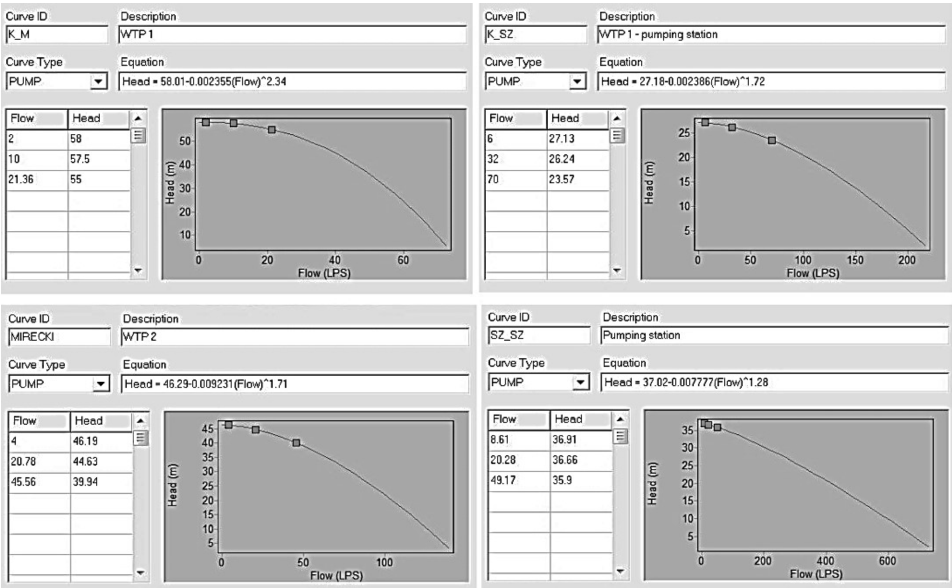

Fig. 4. Characteristics of replacement pumps

Then, after upgrade of the model, the further process of calibration was performed by trial and error methods, until the best possible agreement between measured field data and results of calculations. During the calibration the values of pipe material roughness and pressure head at pumping station were alerted manually. New values of roughness were assigned in relation to pipe material, $k = 1.5$ mm for cast iron and steel pipes and $k = 0.15$ mm for plastic pipes respectively.

3. Results and Discussion

Figures 5 and 6 present comparison of measured and determined numerically in Epanet 2.0 values of pressure head before and after calibration, respectively.

Analysis of results presented in Figures 5 and 6 shows that the performed calibration based on adjustment of pressure head values in the selected nodes of network allowed increased agreement between modeled and field data.

Table 2 shows comparison of mean values of pressure head determined during numerical simulation after calibration and measured during in situ studies. It is visible that process of model calibration allowed comparable values of pressure head, calculated and measured. However, application of mean values to analysis significantly affects the degree of agreement between discussed values. The RMSE determined by the software equal to 1.055 mH_2O suggests good fit of model results to real values, while the AWWA (1999) guidelines suggests RMSE equal or lower than 1.4 mH_2O.

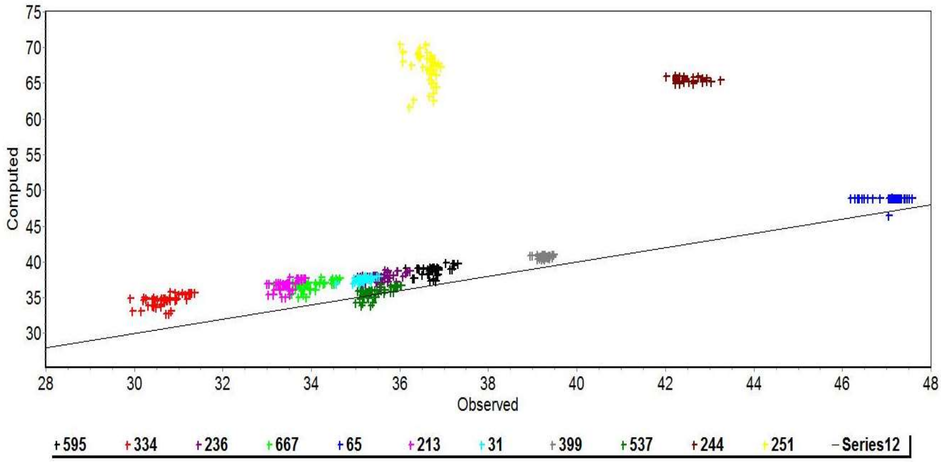

Fig. 5. Comparison of measured and calculated in Epanet 2.0 values of pressure head before model calibration

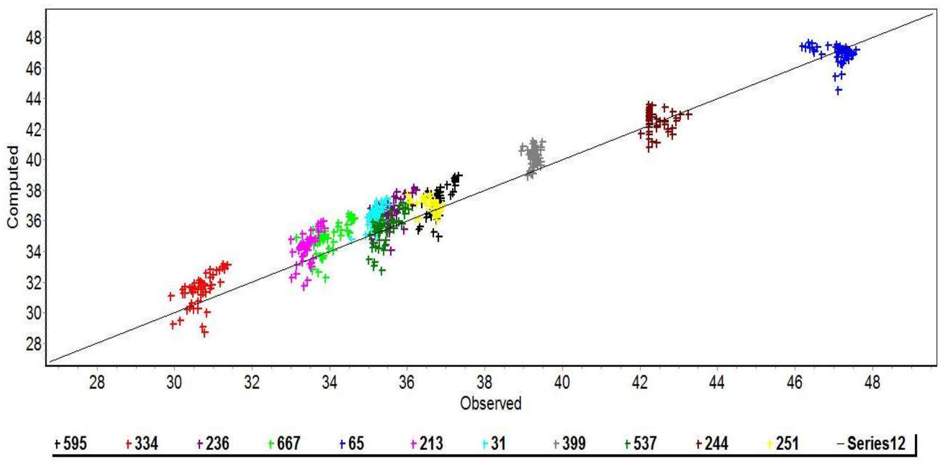

Fig. 6. Comparison of measured and calculated in Epanet 2.0 values of pressure head after model calibration

Table 2. Calibration statistics for pressure head values

Location	Number observation	Observed mean	Computed mean	Mean Error	RMS Error
595	47	36.79	37.38	0.885	0.955
334	47	30.67	31.43	1.053	1.180
236	47	35.57	36.56	1.118	1.312
667	47	33.98	34.83	1.047	1.117
65	47	47.08	46.93	0.578	0.761
213	47	33.44	34.31	1.111	1.239
31	47	35.18	36.36	1.187	1.294
399	47	39.27	40.25	0.995	1.125
537	47	35.44	35.43	0.670	0.877
244	47	42.43	42.47	0.581	0.706
251	47	36.6	36.97	0.514	0.660
Network	517	36.95	37.54	0.891	1.055

Figure 7 presents comparison of pressure head values measured in situ as well as modeled, after and before calibration.

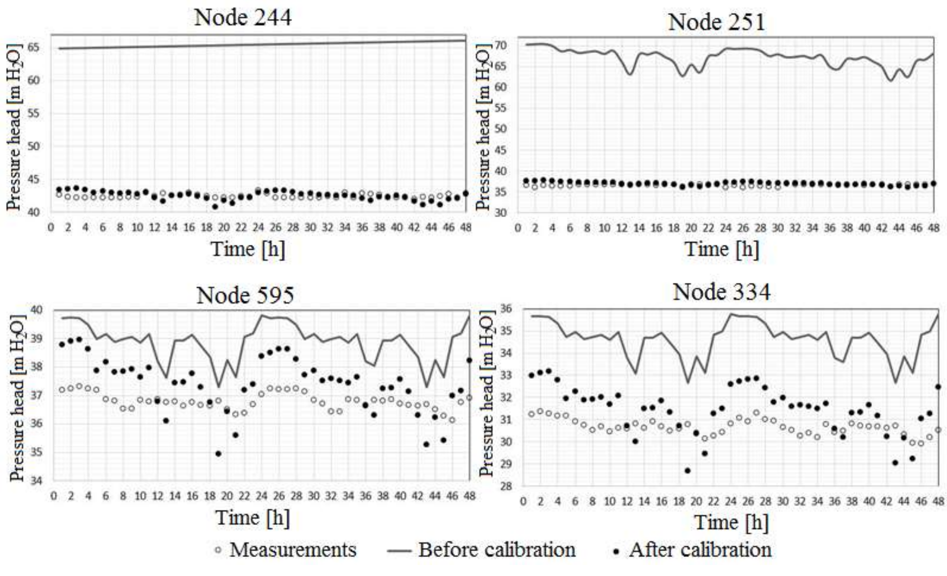

Fig. 7. Comparison of results of measured and calculated pressure head changes before and after model calibration for selected nodes: 244, 251, 595 and 334

Taking into account the fact that coefficient of determination for calibration results in Epanet 2.0 software is determined for mean values of obtained results for the whole network (Rossman, 2000), the proper assessment of variables agreement is difficult. Thus, the additional calculations of correlation and determination coefficients for values determined and measured for the selected nodes of the studied network were performed in Statistica software. Table 3 presents comparisons of validation results determined by means of Statistica and Epanet 2.0.

Table 3. Comparison of R and R^2 values calculated in Statistica and Epanet 2.0

Node	Statistica				Epanet 2.0			
	Before calibration		After calibration		Before calibration		After calibration	
	R	R^2	R	R^2	R	R^2	R	R^2
31	0.6188	0.3829	0.6914	0.4780	0.7355	0.541	0.998	0.997
236	0.4113	0.1692	0.5245	0.2751				
334	0.6049	0.3659	0.7226	0.5221				
595	0.6277	0.3940	0.7136	0.5092				
65	–0.0062	0.0000	–0.2819	0.0795				
213	0.5244	0.2745	0.6216	0.3863				
244	0.0082	0.0000	0.0022	0.0000				
251	–0.4238	0.1796	–0.4708	0.2216				
399	0.2128	0.0453	0.0880	0.0008				
537	0.6488	0.4209	0.7185	0.5162				
667	0.5999	0.3599	0.6965	0.4851				

Despite the outliers removal, the unsatisfactory fit degree between calculated and measured results for selected nodes of network was noted. The coefficient of correlation R determined in Statistica for most of the tested nodes after calibration of the model varied in range 0.0022–0.7226. The negative R values (–0.2819 and –0.4708) were obtained for two studied nodes. The strong positive correlations, R = 0.6–0.8, were observed for only six points. For the remaining ones a low (R = 0.2 – 0.4) or moderate (R = 0.4–0.6) relationship was obtained. For nodes 244 and 399, no relationship was observed between the compared values.

Figure 8 shows linear regression, with applied ellipse method of outliers removal, determined for pressure head values measured and calculated for selected nodes of the network.

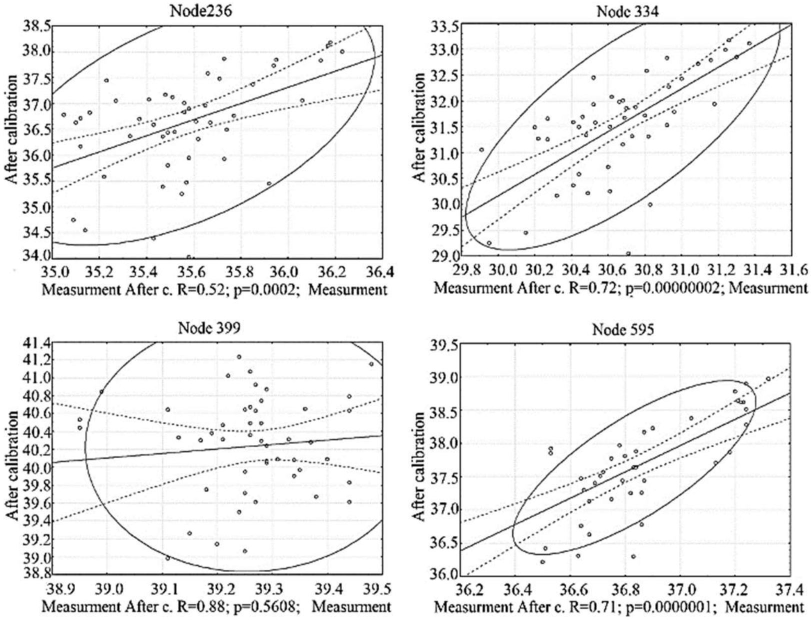

Fig. 8. Comparison of results of pressure head measured and calculated for selected nodes

4. Summary and Conclusions

The performed calibration of model representing the real water supply network revealed several problems including availability of in-situ measurements results and validation of fitting degree of tested variables in calibration module of Epanet 2.0. The performed statistical analysis allowed assessment of model data fitting in several nodes of the developed model.

An attempt to calibrate the model of the municipal water supply network resulted in a better match of the values of modeled pressure head in relation to the real conditions.

Due to the inability to carry out the simultaneous measurements of flow rates at selected nodes, the performed calibration is not fully satisfactory.

The coefficients of determination specified in Epanet and Statistica provide very divergent information about the match of the obtained results. The value of R^2 = 0.997 calculated on the basis of averaged values indicates a satisfactory effect of the model calibration process. According to AWWA guidelines, the calculated RMS Error less than 1.4 m H_2O also confirms the satisfactory effect.

Taking into account the values of the R^2 calculated for each of the nodes in the Statistica program, an unsatisfactory degree of model matching to the actual conditions prevailing in the network was obtained.

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Preparation of aqueous solutions of polyacrylamide in Taylor-Couette flow

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Abstract

The results of experimental studies of the effect of rotor eccentricity relative to the stator and the presence of polyacrylamide solutions on the friction coefficient in the Taylor-Couette flow are presented. The annular gap between the rotor with a diameter of 113 mm and a stator with a diameter of 142 mm was filled with aqueous solutions of polyacrylamide mass concentration of 100 ppm. The annular gap between the surfaces of the cylinders, which corresponded to their coaxial location, was transformed into a closed confuser-diffuser when changing the position of the outer cylinder relative to the inner one. The dependence of the friction coefficient on the Reynolds number and on the width of the gap between the rotor and stator at their axial location and the concentration of aqueous solutions of polyacrylamide is revealed. With an increase in the Reynolds number, a decrease in the friction coefficient was observed for the studied concentration of the polyacrylamide solution compared to water. For the same Reynolds number at a concentration of a polyacrylamide solution of 100 ppm, a decrease in the friction coefficient as compared to water was obtained. With a decrease in the gap width, an increase in the friction coefficient for the studied concentration of the polyacrylamide solution is obtained. In studies of aqueous solutions of polyacrylamide, compared with water, the first critical Reynolds number has a smaller value. Moreover, the value of the friction coefficient corresponding to this Reynolds number is larger. The results indicate the possibility of preparing aqueous solutions of polyacrylamide in the proposed mixer using a motor with adjustable speed.

Keywords: eccentric cylinders, rotor, coefficient of friction, torque, Taylor-Couette flow, Reynolds number

1. Introduction

The environmental safety of wastewater transport systems is a very pressing issue (Alekseev et al., 1991). As the stormwater drainage system is limited in its flow rate, under extreme congestion during periods of intense rain there is a problem of its operation. The use of hydrodynamically active polymers (HAP) leads to the restoration of the normal functioning of the pipelines by increasing their throughput due to the reduction of hydraulic friction (Zhuk and Orel, 1995; Hart et al., 2011; Andrade et al., 2015; Khadom and Abdul-Hadi, 2014). The periodicity and short duration of the use of HAP in such situations make their application justified.

It is advisable to use HAP as a solution only where their rate of dissolution matters. In the preparation of aqueous solutions of HAP use paddle mixers with a small number of revolutions. In this case, their destruction occurs as a result of mechanical destruction of molecules (Kozlov, 1987; Povkh, 1982; Kaboorani and Riedl, 2015; Rowin et al., 2018). This leads to a reduction or complete cessation of the action of the HAP on hydraulic resistance.

In order to prevent the destruction of HAP molecules, a mixer was proposed (Cherniuk and Pitsyshyn, 2017), which contains a drive rotor located in cylindrical containers, which is fixed with the possibility of rotation about the material axis, which does not coincide with the geometrical axis of the container. The mixer is equipped with a reversible drive to rotate the container relative to the material axis located on the outer lateral surface of the container, and limiters of movement of the container.

The purpose of this work is to study the preparation of aqueous solutions of HAP in the Taylor-Couette flow, which takes place in the proposed mixer.

The fluid flow arising between two rotating concentric cylinders is known as the Taylor-Couette flow, in which a closed geometry avoids the degradation of the HAP solution by the stirrer blades.

In the Taylor-Couette flow with the angular velocity change of the inner or outer cylinder, there are several flow modes – from laminar to turbulent.

In his experiments, Taylor (1923) focused on the primary instabilities of the Taylor-Couette flow, a toroidal vortex that consistently extended to the axis of the cylinder and were much smaller under highly turbulent modes. Davey (1962) numerically determined the torque acting on cylinders in the flow with Taylor vortices. Cole (1976) observed the second critical Reynolds number and performed flow visualization with a further increase in angular velocity. Outside the first critical Reynolds number, a wavy vortex flow was observed. Measurement of torque proved that Taylor vortex flow becomes unstable at this critical point that is confirmed by experiments in different ranges of heights and radii ratio cylinders (Huisman et al., 2013; Adebayo et al., 2018; Adebayo and Rona, 2015; Campolo et al., 2015).

To study the effect of reducing friction in the Taylor-Couette flow the rotation of the internal cylinder Jones and Marshall (1969) used aqueous solutions of polyacrylamide (PAM) low concentrations.

Groisman and Steinberg (1996) found a significant influence of PAM solutions on the structure and stability of the Taylor-Couette flow. Two new vibrational structures were visualized, which were explained by the fluid elasticity. Yi and Kim (1997) observed a decrease in the critical Taylor number in the Taylor-Couette flow with increasing PAM concentration.

Researchers (Campolo, 2015; Sugiyama et al., 2008; Koeltzsch et al., 2003; Ashrafi, 2011; Labkovich, 2017) also investigated the reduction of resistance in Taylor-Couette flow using other polymers, surfactants, etc.

In (Dutcher and Muller, 2009; Greidanus et al., 2011; Srinivasan et al., 2009; Eskin, 2014; Greidanus, 2015) investigated solutions of various applications in the Taylor-Couette system with different modifications of cylinder surfaces.

2. Materials and methods

The object of study is the flow of aqueous solutions of HAP in the proposed mixer.

Experimental stand. Experimental studies were performed at the experimental stand (Popadiuk et al., 2018) (Fig. 1).

The stator 1 with a diameter of 142 mm is fixed on the plate 2, which is mounted with the possibility of reciprocating movement on the support plate 4. In the stator cavity is located a smooth stainless steel rotor 5 with a diameter of 113 mm, which is connected to the electric motor 7, which is rigidly fixed relative to the base plate. Motor shaft 6 passed through a hole in a sealed cover 8, which is fixed on the stator. The stator 15.3 cm high is a metal frame 9 with windows, in the middle of which a transparent cylinder 10 is rigidly attached. The movement of the stator and its inconsistency with the rotor is controlled by an arrow attached to the movable plate relative to the scale 14 on the base plate 4.

The annular gap between the rotor and stator surfaces, which corresponded to their concentric arrangement, changed to a closed confuser-diffuser when the stator position changed (Fig. 2).

In studies used a direct current motor, so the stand is equipped with a device for rectifying alternating current (AC) to direct current (DC). A tachometer of the TCh 10-P model (Ukraine) was used to measure the velocity of rotation of the rotor. The rotor rotated at an angular velocity $\Omega_i = 80–300\ \text{min}^{-1}$.

Dimensional torque *G* was used for scaling torque, which was compared with studies (Bhambri and Fleck. 2016; Lewis and Swinney, 1999; Wendt, 1933) (Tab. 1).

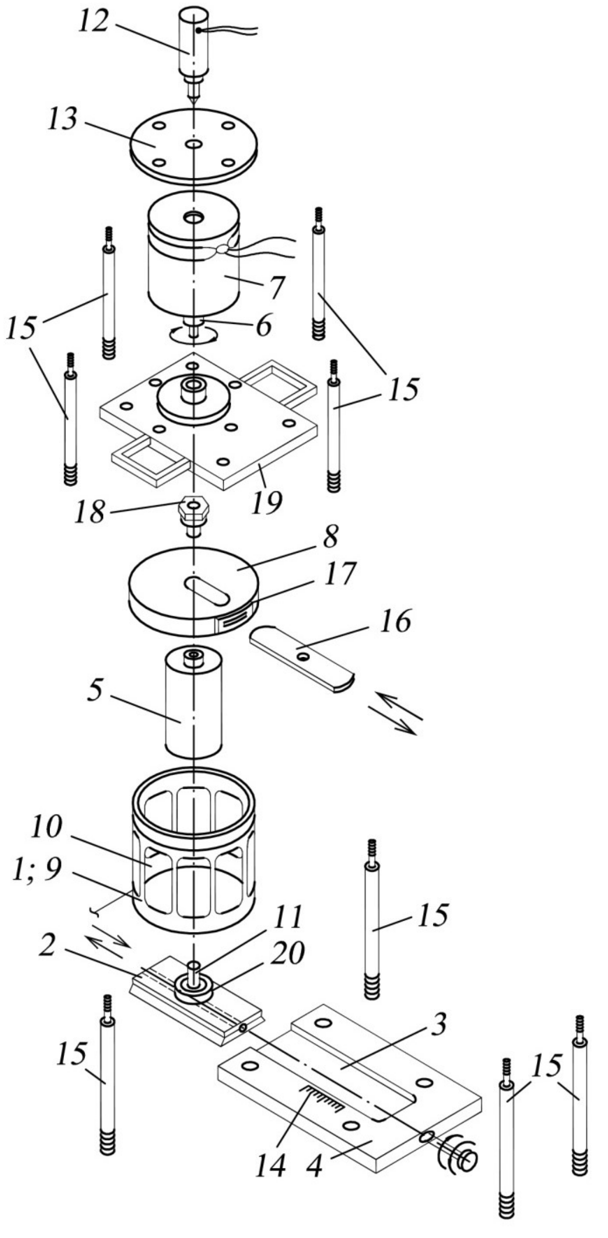

Fig. 1. Scheme of the experimental stand: 1 – stator; 2 – movable plate; 3 – groove; 4 – base plate; 5 – rotor; 6 – shaft; 7 – electric motor; 8 – cover; 9 – metal frame; 10 – transparent cylinder; 11 – axis; 12 – tachometer; 13 – plate; 14 – scale; 15 – stand; 16 – sealing plate; 17 – seals; 18 – intermediate sleeve; 19 – plate; 20 – clamp

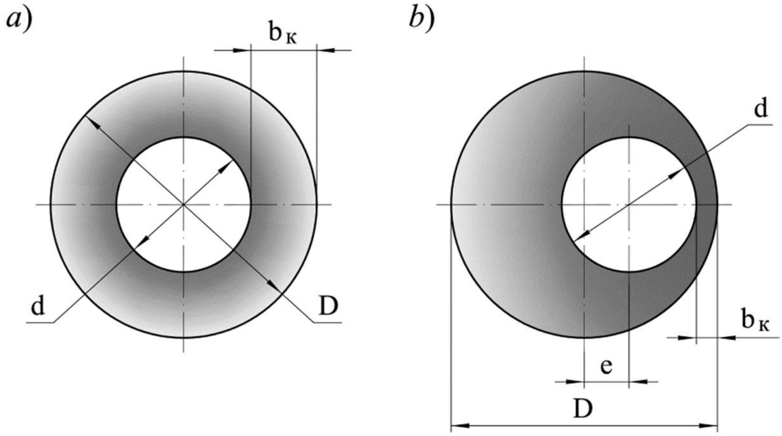

Fig. 2. Schemes of rotor and stator arrangement: a – coaxial; b – axial; e – eccentricity; b_k – the width of the gap at the coaxial (concentric) arrangement of the rotor, b_e – at the axial (eccentric)

Table 1. The parameters of the studied ratios of the "rotor-stator"

Ratio of rotor and stator radii, η	Reynolds number range, *Re*	Dimensional torque, *G*	The authors of the research
0.724	$2.5{\cdot}10^3$–$1{\cdot}10^6$	0.1–2000	Lewis and Swinney, 1999
0.76	$8{\cdot}10^4$–$2.9{\cdot}10^5$	60–600	Bhambri and Fleck, 2016
0.5; 0.68; 0.85;0.94	$1{\cdot}10^4$–$1{\cdot}10^5$	2–70	Wendt, 1933
0.8	$9{\cdot}10^4$–$2.8{\cdot}10^5$	300–500	own research

Selection of working fluid. Water solutions of PAM (molecular weight $1.8{\cdot}10^6$) with a mass concentration of 100 ppm were investigated. The original PAM used for the preparation of solutions was 8% technical gel (TU 6-01-1049-92, Ukraine). In the preparation of aqueous solutions of PAM used laboratory mixer MM3M (Ukraine). The specific gravity of an aqueous solution of PAM was determined by densimeters, and viscosity – by a viscometric method.

Calculation formulas. Torque T [N·m] acting on the inner cylinder (rotor) was determined by dependence:

$$T = \frac{N \cdot 30}{\pi \cdot n} \tag{1}$$

where: N – the power consumption of the electric motor [W], n – the number of rotations of the rotor [min^{-1}].

Dimensionless torque on inner cylinder between rotor and stator (Bhambri and Fleck, 2016) was determined by dependence:

$$G = \frac{T}{\rho \nu^2 L} \tag{2}$$

where: ρ – the density of the fluid [kg/m^3], ν – the kinematic viscosity [m^2/s], L – the height of the inner cylinder, m.

The coefficient of friction between the rotor and the stator (Bhambri and Fleck, 2016) was determined by dependence:

$$C_f = \frac{G}{Re^2} \tag{3}$$

where: Re – the Reynolds number.

The Reynolds number was determined by the formula (Bhambri and Fleck, 2016):

$$Re = \frac{\Omega_i r_i (r_o - r_i)}{\nu} \tag{4}$$

where: Ω_i – the angular velocity of the inner cylinder [min^{-1}], r_o – is the radius of the outer cylinder [m], r_i – the radius of the inner cylinder [m].

The ratio of the radii of the cylinders was calculated by the formula (Bhambri and Fleck, 2016):

$$\eta = \frac{r_i}{r_o} \tag{5}$$

3. Results and discussion

The experiments were first performed using water as a working fluid in the Reynolds number range from $9 \cdot 10^4$ to $2.8 \cdot 10^5$. The dimensionless torque G observed in our studies for the ratio of the radii of cylinders η=0.8 (Fig. 3) was in good agreement with the results. Thus, comparing the results of own research with results of (Bhambri and Fleck, 2016), the equality of dispersions for Fisher F-test significance level of 0.02 and the equality of homogeneity of sample averages for Student's t-test significance level of 5% are obtained.

Figure 4 presents a dimensionless torque G at $Re = 1 \cdot 10^5$ for different values of the ratio of the radii of the rotor and stator η. The solid line describes the theoretical dimensionless torque G obtained by Wendt (Wendt, 1933) for Re=1·10^5:

$$G = 0.23 \cdot \frac{\eta^{2/3}}{(1-\eta)^{7/4}} \cdot Re^{1.7} \quad (6)$$

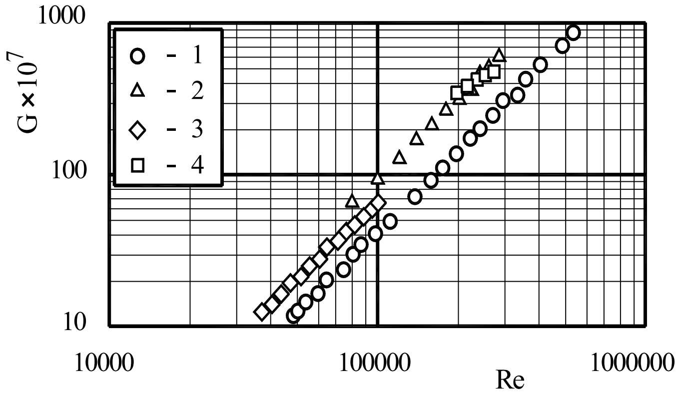

Fig. 3. Experimental values of dimensionless torque G at different values of Reynolds number Re, obtained in this study compared with previous results: 1 – study of (Lewis and Swinney (1999), 2 – study of Bhambri and Fleck (2016), 3 – study of Wendt (1933), 4 – results obtained in this study

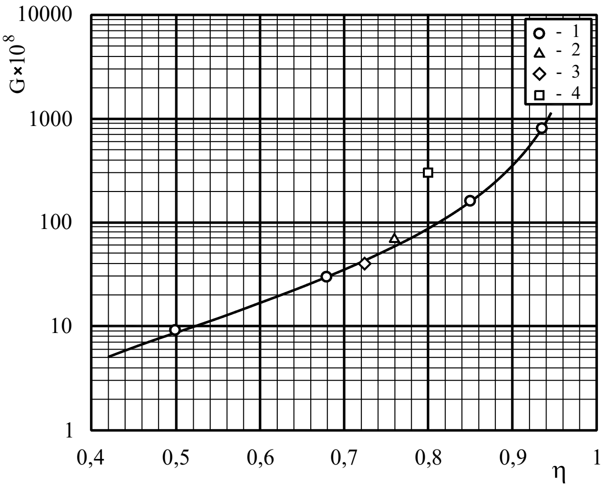

Fig. 4. Comparison of dimensionless torque G for different radii ratios η at Re =1·105:
1 – study of Wendt (1933), 2 – study of Bhambri and Fleck (2016), 3 – study of Lathrop (1992), 4 – own studies

The results of our studies and the results of studies (Bhambri and Fleck, 2016; Wendt, 1933; Lathrop et al., 1992) (Fig. 4) do not coincide, since the heights of the cylinders under study were different.

Figure 5 presents the results of experimental studies of the influence of water and aqueous solutions of PAM with a concentration of C=100 ppm on dimensionless rotor torque for $b_e/b_k = 1.0$ at different values of angular velocity. Each point represents the average of three repeated measurements. As the angular velocity increases, the difference between dimensionless torque for water and for aqueous solutions of PAM increases. This is in good agreement with the results obtained by Popadiuk et al. (2018).

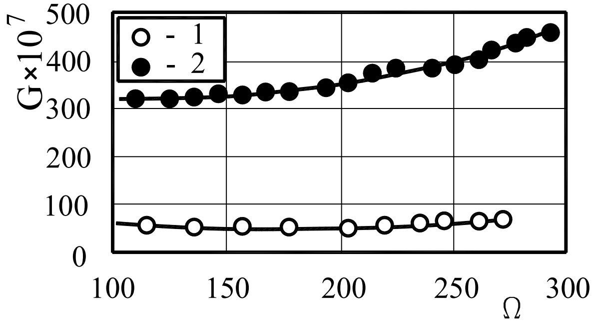

Fig. 5. The dependence of dimensionless torque G on the angular velocity of rotation of the inner cylinder for water (1) and aqueous solutions of PAM mass concentration C=100 ppm at a relative width of the $b_e/b_k = 1.0$

With the unconscious arrangement of the cylinders (Fig. 2b), the experiments were carried out at b_e/b_k equalled 1.0, 0.7 and 0.41.

Figure 6 presents the dependence of the coefficient of friction C_f on the Reynolds number Re for water and aqueous solutions of PAM with a mass concentration of C=100 ppm at relative widths b_e/b_k equalled 1.0, 0.7 and 0.41.

The dependence of the friction coefficient C_f on the Reynolds number Re at laminar modes for values of the relative width b_e/b_k=1,0; 0.7; 0.41 does not change to the first critical Reynolds number for the eccentric arrangement of cylinders for both water and aqueous solutions of PAM with a mass concentration of C=100 ppm (Fig. 6).

In studies of aqueous solutions of PAM, compared to water, the first critical Reynolds number has a smaller value. At the same time the value of the friction coefficient C_f corresponding to this Reynolds number Re is larger. This allows the preparation of aqueous solutions of PAM at smaller rotations of the inner cylinder for the same consumption of electricity. Therefore, the mixer can be equipped with an engine with adjustable speed.

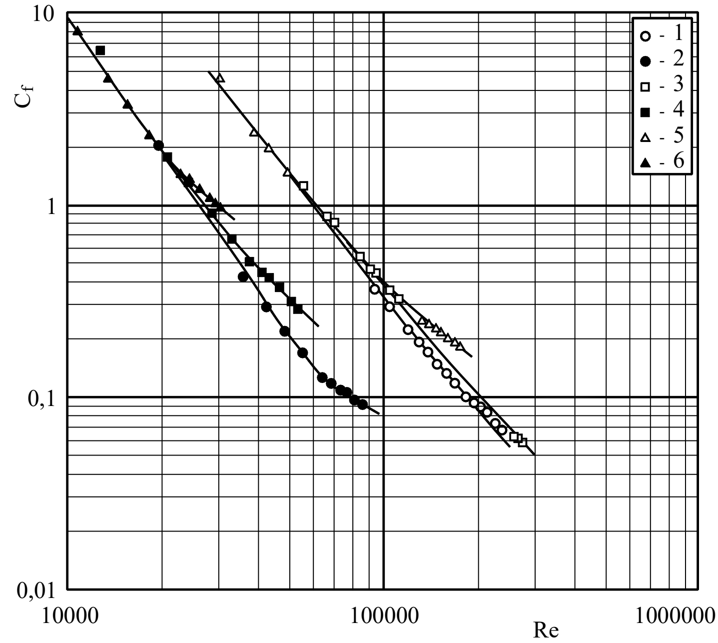

Fig. 6. The dependence of the coefficient of friction in the gap between the rotor and the stator on the Reynolds number Re for water at the relative width of the $b_e/b_k = 1.0$ (1), at $b_e/b_k = 0.7$ (3), at $b_e/b_k = 0.41$ (5) and aqueous solutions of PAM with a mass concentration of C = 0,01% at $b_e/b_k = 1.0$ (2), at $b_e/b_k = 0.7$ (4), at $b_e/b_k = 0.41$ (6)

Figure 6 shows that in concentric arrangement of cylinders, both for water and for aqueous solutions of PAM, there is one formation that covers laminar and turbulent modes after the first critical Reynolds number.

For the eccentric arrangement of the cylinders, the branching of the dependence curves C_f=f(Re) for the values of b_e/b_k = 0.7 and 0.41 is observed after the first critical Reynolds number Re. Moreover, the value of the first critical Reynolds number is less than the same value at concentric arrangement of cylinders.

The decrease in the width of the gap leads to an increase in the coefficient of friction for the same value of Reynolds number Re for both water and aqueous solutions of PAM.

For the eccentric arrangement of the cylinders, the first critical Reynolds number Re is the same for $b_e/b_k = 0.7$ and for $b_e/b_k = 0.41$.

The increase of the slope of the curve C_f=f(Re) for aqueous solutions of PAM with a concentration of C=100 ppm, compared with water, is consistent with studies (Kalashnikov, 1998; Sreenivasan and White, 2000; White et al., 2004).

Experiments were conducted to find out the efficiency of an aqueous PAM solution with a concentration of C=100 ppm with a maximum value of angular velocity Ω_i= 300 min^{-1}, which corresponded to the Reynolds number Re=$3\cdot10^4$. After ten minutes of stirring, the effectiveness of the solution did not change.

Experiments were conducted to find out the efficiency of an aqueous PAM solution with a concentration of C=100 ppm with a maximum value of angular velocity Ω_i= 300 min^{-1}, which corresponded to the Reynolds number Re=$3\cdot10^4$. After ten minutes of stirring, the effectiveness of the solution did not change.

4. Conclusions

The dependence of the friction coefficient on the Reynolds number and on the width of the gap between the rotor and stator at their axial location and the concentration of aqueous solutions of polyacrylamide is revealed. The dependence of the friction coefficient on the Reynolds number at the laminar mode for values of a relative width b_e/b_k=1.0; 0.7; 0.41 does not change to the first critical Reynolds number for the eccentric arrangement of cylinders. At the same values of Reynolds number for the aqueous solution of PAM with a concentration of C=100 ppm obtained a decrease in the friction coefficient compared with water. By decreasing the width of the gap, an increase in the friction coefficient was obtained for the investigated concentration of an aqueous solution of PAM. The results obtained indicate the possibility of preparing aqueous solutions of PAM in the proposed mixer using an electric motor with adjustable speed.

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Modernization of the water treatment process from heavy metals

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Abstract

One of the most important pollutants of wastewater is heavy metals. Sources of heavy metals are enterprises of the chemical, metallurgical industry and other removal of heavy metals ions from discharges, in particular galvanic plants, is one of the most difficult tasks of wastewater treatment. There are many methods of treatment, but their disadvantages include insignificant performance, significant energy costs, generation of secondary chemical pollutants, etc. Today there are many methods of purification: physical, physicochemical, combined, but to their general disadvantages are insufficient productivity, significant energy costs, and most importantly, the generation of secondary chemical pollutants of water. Therefore, the modernization of existing methods of purification of heavy metal wastewater remains an urgent task for researchers.

Subject of research is: process of wastewater treatment of galvanic manufactures with the help of an electro spark method. Object of research: wastewater of galvanic production. The aim of the research is to improve the method of treatment of the galvanic sewage with the help of the electro spark method.

The method of investigation is an electro spark method, the essence of which is the short-term electrical pulses through the waste water through the electrodes submerged in the solution. The pulsed electric discharge in the liquid is accompanied by a sharp increase in pressure (up to 100–200 MPa), the influence of strong electromagnetic and acoustic fields, cavitations, which creates a powerful flow of fluid that converges and diverges, a sharp increase in temperature, and so on. The electrical discharge, in fact, the explosion in the aqueous phase causes complex physical and chemical processes in it, which leads to the decomposition of organic impurities present in sewage, the improvement of the coagulation of colloidal and suspended matter, the deposition of suspensions and chemical compounds.

Determination of the concentration of general Chromium, Zinc and Cuprum in sewage was carried out using a photocolorimetric method. Some results of the analysis are presented.

It is practical to achieve the degree of purification of the galvanic wastewater is characterized by such excessive concentrations of heavy metals: Zn^{2+} – completely removed (less than 0.001 mg/l), do not need further purification; Cr^{6+} + Cr^{3+} – up to 0.0002 mg/l, do not need further purification; Cu^{2+} – up to 0.003 mg/l, conditions that the concentration can be reduced to 0.001 mg/l with increasing specific energy processing

The results of the experimental data show that purification of galvanic wastewater from heavy metals to the norms of the MPC by electro spark method is quite possible. This method has a high degree of effectiveness purification and prospects for technological implementation.

Keywords: heavy metals, water treatment, galvanic processes electro spark method

1. Introduction

Issues of water status and quality are among the priorities in the environmental policy of European countries (Bharti and Katyal, 2011; Mitryasova et al., 2018a; b). Wastewaters, which contains heavy metals has environmental risk. Therefore, the question of finding effective wastewater treatment methods containing heavy metals is an urgent issue. Among many methods coagulation methods for wastewater treatment from heavy metal ions are the most effective and used (Kulskij, 1980; Zapolskij and Baran, 1987; Filatova and Soboleva, 2012; Dudarev and Pomazkina, 2012; Solozhenkin et al., 2003). Reagent coagulation is based on the hydrolysis of polyvalent metals salts (aluminum and iron), which lead to the formation of highly dispersed oxides and hydroxides of these elements, which can actively adsorb impurities of heavy metal ions from water (Kulskij, 1980; Zapolskij and Baran, 1987).

In electro coagulation methods of treatment of galvanic wastewater adsorption-active hydroxides of iron or aluminum are formed by electro erosion by electrolytic dissolution of steel or, respectively, aluminum anodes. In this case, phenomena such as water electrolysis, particles' polarization, electrophoresis, redox processes and the interaction of electrolysis products with each other can occur in the electrolyzer (Filatova and Soboleva, 2012; Dudarev and Pomazkina, 2012). Galvanic coagulation consists in passing wastewater through a galvanic coagulator that contains an active anode and cathode mixture, for example, iron and aluminum chips, iron chips and coke (Solozhenkin et al., 2003) etc.

Electrospark discharge in metal-containing reactors is an effective method for producing coagulatively active metal oxides and hydroxides (Levchenko, 1992;

Yushchishina et al., 2005; Khajnaczkij et al., 2005). The method is proposed as an alternative to existing methods for cleaning electroplating. It was shown that it is possible in principle to purify multicomponent galvanic wastewater from heavy metal ions, such as Cr^{6+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} (Khajnaczkij et al., 2005a, 2005b). In this case, the main attention is directed to expanding the capabilities of the method, that is aimed primarily at component treatment of galvanic wastwater, by increasing the operating voltage from 300–600 V to 3–15 kV and by using monometallic metal loading (granules of one metal) (Levchenko, 1992). This allowed the treatment of concentrated galvanic wastwater containing Cr^{6+} to 1000 mg/dm^3. However, the further implementation of this method turned out to be economically inexpedient due to the high cost and limited resource of high-voltage equipment, its increased danger and low process productivity.

The purpose of this work is to study the influence of technological parameters (specific energy, characteristics of the electric pulses and their frequency, schemes of channel of purified water) on the efficiency of the process of treatment of multi component galvanic wastewater in reactors with combined metal loading and by using low-voltage (up to 1000 V) electrical equipment.

2. Materials and Methods

The raw material for the treatment is real wastewater after various galvanic production operations, which is supplied to the treatment facilities of a machine-building enterprise (State Enterprise "Zorya Gas Turbine Engineering and Production Complex Mashproekt", Ukraine). Galvanic wastewater are multicomponent composition containing ions (Cr^{6+}, Ni^{2+}, Cu^{2+} and Zn^{2+}).

A mixture of iron and aluminum granules with a diameter from 4 to 6 mm is selected as the material for metal loading. This choice is due to the following reasons:

- the positive result of complex water purification from heavy metal ions during high-voltage electric discharges in reactors with granular metal loading and the use of these materials (Khajnaczkij et al., 2005a);
- the traditional use of steel or aluminum electrolytically soluble anodes during the implementation of the electrocoagulation method for treatment galvanic wastewater (Filatova and Soboleva, 2012; Dudarev and Pomazkina, 2012);
- experience in stabilizing spatially distributed discharges in a layer of aluminum and iron granules with using low-voltage (up to 1000 V) electrical equipment (Shcherb et al., 2017; Shherba et al., 1993; Petrichenko et al., 2016).

Figure 1 shows the appearance of a laboratory installation for the purification of galvanic wastewater.

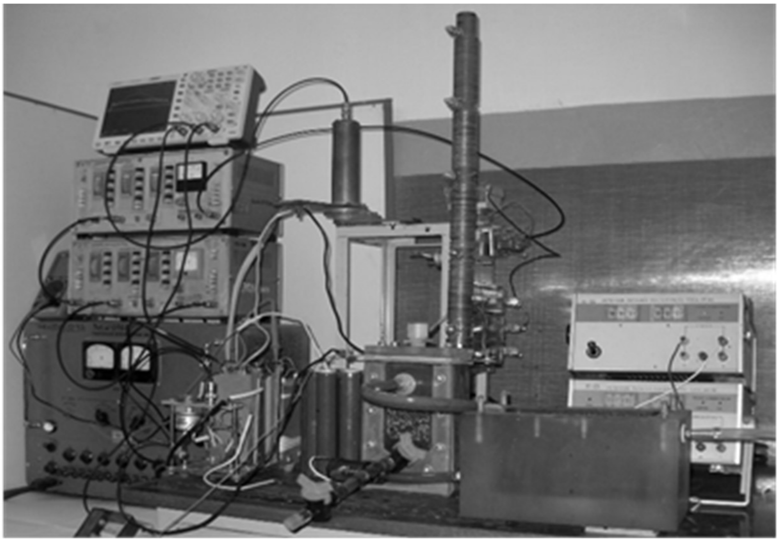

Fig. 1. A laboratory installation for the purification of galvanic wastewater

The layer of granules of metal loading in the form of a rectangular parallelepiped is characterized by the following sizes: length (l) – distance between the electrodes; width (b), which was equal to the width of the electrodes and height (h), which varied depending on the scheme of implementation of the fluid flow. The distance between the electrodes was chosen in such a way as to ensure stable breakdown along the shortest chain of contacts between the granules from one electrode to another at a given capacitance of the capacitor bank (Shcherba et al., 2017; Petrichenko et al., 2016) and order to optimize the phase composition of electroerosion particles (Zaharchenko, 2012).

The discharge current and voltage at the interelectrode gap are recorded with an OWON XDS 3202E oscilloscope, using a divider and shunt of own manufacture.

The experimental reactor (Fig. 2a, position 4) is made in the form of a rectangular hollow parallelepiped with flat steel electrodes (position 7), a perforated bottom (position 9) and a prism-shaped cavity under it.

The tank (position 1) was filled with galvanic wastewater. The shut-off valve (position 6) was set to the turned off position. When the pump (position 2) was turned on by a valve (position 3), the required volumetric flow rate of the liquid was established.

The galvanic wastewater is entered the reactor passing through the holes of the perforated bottom, then through the metal loading layer (Fig. 3b, position 8), in which multichannel spark discharges between metal granules formed at a given frequency.

After that, through the nozzle, depending on the position of the valve (position 5), the treated galvanic wastewater are poured into a container for next analysis, or returned to a repeated treatment cycle.

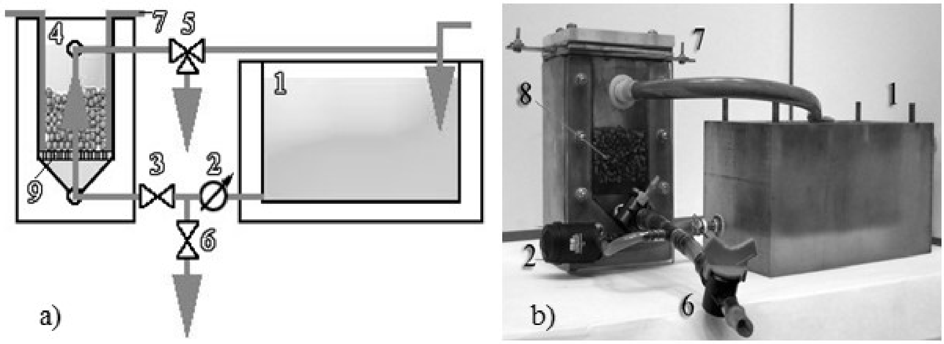

Fig. 2. The reactor: a) the hydraulic scheme, b) the appearance

The determination of the content of heavy metals in the start and treated water was carried out in accordance with the current regulatory documents of the Ministry of Environmental Protection of Ukraine (MVV № 081/12-0178-05; MVV № 081/12-0173-05; MVV № 081/12-0114-03; KND 211.1.4.035-95). Photocolorimetric method was used to determine heavy metals. The hydrogen index (pH) of the start galvanic wastewaters and the treated liquid was measured with an ionomer I-160 M. The tests were performed in 30 replicates. The uncertainty of measurements is 0.5%.

The efficiency of the galvanic wastewaters treatment process was studied by varying the specific processing energy, the amount of stored energy, pulse parameters, and the height of the metal load.

3. Results and Discussion

The choice of the range of variation of parameters and processing schemes is based on the following assumptions. The specific energy is varied taking into account the data given in (Khajnaczkij et al., 2005a; b; Nazaryan and Efimov, 1983), which relate to the purification from highly concentrated solutions of heavy metal ions (from 8500 mg/dm^3 – total content of heavy metals and up to 600 mg/dm^3 Cr^{6+}, respectively) with high-voltage electric discharges in reactors with granular metal loading in a column electro coagulator.

The data relate both to the purification of a multi component mixture of heavy metal ions of real galvanic wastewater, and to single-component model solutions (Khajnaczkij et al., 2005b). The specific energy spending in the considered cases depend from the concentration of pollutants and are to several hundred kJ/dm^3. The energy spending of polycomponent solution purification by the electrospark method is 18 kJ/dm^3 at ion concentrations up to 30 mg/dm^3 (Levchenko, 1992).

The influence of various technological, electrical, and energy parameters on the results of treatment the galvanic wastewater is presented in Tab. 1.

Table 1. The results of treatment the galvanic wastewater from various technological, electrical and energy parameters

Parameters	No. of sample	Parameter' s value	The concentration of heavy metal ions [mg/dm^3]				pH	Color
			Ni^{2+}	Zn^{2+}	Cr^{6+}+ Cr^{3+}	Cu^{2+}		
Original galvanic wastewater	0	-	1,20	0,26	1,27	0,06	7,45	yellowish
Influence of the specific energy on the purification degree of the galvanic wastewater at a pulse duration of 38 μs and energy per pulse W = 4.5 J								
Specific energy, kJ/dm^3	1	130	0,03	0	0,0002	0,003	7,34	colorless
	2	65	0,054	0,03	0,0023	0,01	8,19	colorless
Influence of the pulse duration on the degree of purification of the galvanic wastewater at fixed energy in the pulse (W = 4.5 J) and specific energy (Wsp = 130 KJ/dm^3)								
Pulse duration, μs	3	38	0,02	0	0,0002	0,003	7,34	colorless
	4	200	0,02	0	0,0002	0,003	7,33	colorless
Influence of energy in a pulse on the degree of purification of galvanic galvanic wastewater at a fixed specific energy (W = 130 KJ/dm^3) and a slight change in the pulse duration (from 38 to 40 μs)								
The stored energy in a pulse, J	5	4,5	0,03	0	0,0002	0,003	7,34	colorless
	6	5,5	0,025	0,04	0,0017	0,005	7,97	colorless
Influence of the metal loading height on the degree of purification of galvanic galvanic wastewater at a fixed all other parameters (W=130 J/dm^3; pulse duration 38 μs; Wsp = 4,5 J)								
The metal loading height	7	*h*	0,03	0	0,0002	0,003	7,34	colorless
	8	*h*/2	0,146	0,15	0,0026	0,015	7,842	colorless

The authors (Filatova and Soboleva, 2012; Dudarev and Pomazkina, 2012) are able to reduce the energy consumption of the electrocoagulation method of purification from Nickel, Copper, Zinc and Iron ions at initial concentrations of 15–20 mg/dm^3 to values of 1 kJ/dm^3. The treatment efficiency in these experiments is 77–98%. At the same time, the authors emphasize the fact that sorption, for example, Nickel ions, from wastewater is possible at a concentration above 0,15 mg/dm^3, which corresponds to the threshold for coagulation of this ion.

The maximum allowable concentrations of the studied metals in galvanic wastewaters for different countries are presented in Tab. 2.

Table 2. The maximum allowable concentrations of the studied metals in galvanic wastewaters for different countries

Country	Ni^{2+}, mg/dm^3	Zn^{2+}, mg/dm^3	Cr^{3+}, mg/dm^3	Cu^{2+}, mg/dm^3	ΣFe, mg/dm^3
USA	2.38	1.48	- (Cr^{3+})	2.07	-
European Union	0.5	0.5	0.5 (Cr^{3+})	0.5	-
Austria	0.5	2.0	0.5 (Cr^{3+})	0.5	-
Germany	0.5	2.0	- (Cr^{3+})	0.5	3.0
Russia	0.5	2.0	1.0 (Cr^{3+})	0.5	3.0
Belarus	0.44	5.0	2.5 (Cr^{3+})	1.0	3.3
Ukraine	0.5	1.0	2.5 (Cr^{3+})	0.5	2.5

Analysis and comparison of the tables' data allows us to draw the following conclusions. Flow-through treatment of galvanic wastewaters to MPC standards using the electric spark method using granular metal loading and a low-voltage (up to 1000V) source of discharge currents is possible and technologically feasible. This electrospark method allows to achieve high results of wastewater treatment from galvanic industries from heavy metals.

The achieved degree of galvanic wastewaters purification in the case of moderate concentrations of heavy metal ions (Ni^{2+}, Zn^{2+}, Cr^{6+}+Cr^{3+}, Cu^{2+}, ΣFe) is higher, sometimes by several times in comparison with the MPC standards in different countries of the world. The thresholds were not found.

4. Summary and Conclusions

Research has been carried out on the purification of multicomponent galvanic wastewaters by the electric spark method using combined metal loading (Fe, Al) and low-voltage (up to 1000 V) equipment. It is shown that the degree of purification depends on the specific energy, the height of the metal loading of the reactor, and weakly depends from the pulse energy and the speed of its input. The concentrations of heavy metals (Ni^{2+}, Zn^{2+}, Cr^{6+}+Cr^{3+}, Cu^{2+}, ΣFe) in the treated water are significantly lower than their MPC values regulated in different countries.

The main influence on the degree of galvanic wastewaters purification under the conditions of choosing the parameters of the discharge pulse, so that efficiency ~ 0,8–0,85, has a specific energy, which at moderate concentrations of pollutants can be less than 65 kJ/dm^3 (18 kW·h/m^3) and metal loading height. Other variable technological parameters can serve either as a scaling tool or as methods for regulating the operation of electrical equipment.

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Development of the water-green frame of the Vinnytsya

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Abstract

The irrational use of coastal territories and the lack of necessary communication between parts of the city located on different shores is acommon problem for cities located in riverine areas and crossed by rivers. Several cities can be included into this number in Ukraine, first of all, such big cities as Kyiv, Dnipro, Zaporizhzhia, Sumy, Uzhhorod. One of the peculiarities of the development of many cities, unfortunately, is the deterioration of their ecological state, the reduction of the percentage of the landscaped territories and recreational areas. By changing the application of riverine areas would help to solve many of the urgent urban problems.

In modern Ukrainian cities, which mentally are gradually moving away from socialist urban paradigms, a rapid development of public spaces can be observed. The surroundings of coastal river territories can serve as one of the examples of such public spaces. New public spaces over water reservoirs are quickly becoming an integral part of the city, opening up new potential and opportunities for development and recreation of the population, while forming a new appearance of the city. Therefore, it is necessary to find urban solutions for the usage of coastal territories to improve the quality of urban space.

The purpose of the article is to determine the basic spatial and functional principles of the revitalization of coastal river territories and to formulate recommendations for their urban development on the example of the city of Vinnytsia.

Keywords: coastal river territories, development, public spaces, urban design, urban planning, water-green frame, Vinnytsya

1. Introduction

The General Scheme of Planning of the Territory of Ukraine (https://zakon.rada.gov.ua, 2002), defines the territories whose development requires state support, in particular territories with significant environmental recreational, sanatory, historical and cultural potential, which are mainly river basins;, the Law of Ukraine “On Local Self-Government in Ukraine” (https://zakon.rada.gov.ua, 1997) established that land and other natural resources, which are communal property of territorial communities, are the material and financial basis of local self-government. Accordingly, the rational and effective use of the land of the settlement is the basis for the sustainable development of the territory, attracting investment for the development of settlements, increasing of the budget revenues. Smaller mono-functional post-Soviet cities, which see a new factor in the development of water reservoirs are especially favourable for this purpose (Petryshyn et al., 2020).

In 1995, the Water Code of Ukraine was adopted (https://zakon.help/), which defined the classification of the Ukrainian rivers according to the catchment area of the river basin.

Depending upon the class of the river, its water and coastal protection strips are determined. The State Building Norms of Ukraine (Derzhavni Budivelni Normy, 2019) set the normative dimensions of coastal protective strips of existing settlements and such norms in design of new ones. Within the existing settlement, the coastal protection strips are established against water cut in a limited period depending upon the length of the river (up to 50 km – not less than 20 m, from 50 to 100 km – up to 50 m, more than 100 km – 100 m). The coastal protection strip establishes a special regime of economic and other activities to prevent pollution, contamination, mudding and depletion of water reservoirs, as well as to preserve the environment for existing species. The riverain territories are potential recreational landscapes, closed by transport communications, development and the river itself, combining valuable natural and aesthetic resources that require a special approach to the designing of landscaping and gardening (Fedoseeva, 2013). The riverain territory is considered as a unique urban planning subsystem, which is in the structure of the urbanized urban environment of the city and at the same time it is the area adjacent to the natural component i.e. the river. It can be considered as an environmental stabilizer of the urban environment provided it is released from industrial zones and transport corridors and the formation of a system of landscaped open spaces (Vadimov, 2000).

At the urban level, embankments form complex systems of varying capacity and configuration. At the local level, they are creations of the architectural and landscape art that combine into a single whole the water and plant components, small architectural forms, landscaping elements, urban equipment and communications. The local level makes it possible to "feel" every corner of the object visually and tactile, which is enhanced by the level of detailing of the territory.

The modern experience of world urban science underscores the value of water in the city. The priority of preservation of the environment is a good basis for reviewing attitudes towards riverine ecosystems. Analysis of design developments on the verge for the 20th and 21 centuries showed a fundamental change in the focus of urban research. The priority is not the creation of new highly urbanized waterfront spaces, but the ecological and rehabilitation concept of coastal zone development (Vadimov, 2000). The accentuation of the new role of the water reservoir (river) in the planning and compositional structure of cities contributes to their self-identification (Petryshyn et al., 2012).

Many urbanists and researchers of related scientific fields and disciplines are involved in studying of the peculiarities of the functioning of the system "city-nature". Consideration of problems in view of various aspects is determined by a number of factors: urban, functional, climatic, aesthetic, economic and informational. This allows to indicate the need of transformation of the existing coastal spaces in terms of established priorities in the interaction of architectural and natural components of the landscape. Ecological and urban planning estimation of the territory is a type of integrated assessment and is determined by the living conditions of the population in order to justify the design decisions to ensure regulatory environmental indicators. The assessment consists of various stages of designing the region, urban territories and major cities of Ukraine with suburban areas, village and industrial and other functional zones. Ecological and urban planning analysis consists of (Zadvoryanskaya, 2009):

- analysis of the state of the environment;
- identification of problems of engineering and environmental situation;
- prognosis of concrete measures to achieve normatively comfortable living conditions;
- working out of investment and urban development programs of these measures.

Vinnytsia is the administrative, economic and cultural center of Vinnytsia region, located on both banks of the middle stream of the Pivdennyj Buh (Southern Buh) River, 260 km from Kyiv, with a population of over 370 thousand people (http://www.vn.ukrstat.gov.ua/).

The city's development is closely linked to the river. The original castle was once built on the high left bank of the Pivdennyj Buh River. In order to fortify Vinnytsia better, a new fortress was built in 1558 on the Kempa (Camp) island between two riverbeds. After the construction of this fortress, "New Town" emerged on the right bank of the river and the name "Old Town" was affixed to the left bank area. Several bridges connect both parts of the city (Fig. 1).

The Pivdennyj Buh River (Southern Buh) flows through the entire territory of the region, from the northwest to the south and then southeast to the Black Sea. There are many barriers, bumps, rapids created by granite blocks in the river bed. In Vinnytsia region Pivdennyj Buh receives more than 30 tributaries, the largest of which are Zgar, Riv and Sob.

Fig.1 Historical views of the Pivdennyj Buh River in Vinnytsia (http://vinnytsia–museum.in.ua)

The industrialization era and the rules of functional zoning created difficulties in accessing the river and deformed the city's natural frame by subdividing and isolating the city's green spaces. However, the main obstacle to the balanced development of the Vinnytsia city and the modern use of the Pivdennyj Buh River with its tributaries that feed it, is pollution of them (lack of monitoring and observation posts). (Petruk et al., 2013). There are a number of unresolved issues in city water supply and sewerage as well. In 2019, the Concept of Integrated City 2030City Development named "Vinnytsia-2030" for the next decade was adopted **(**https://www.vmr.gov.ua/Lists**).** The vision "Ecological and green city over the Pivdennyj Buh River as a city of sustainable mobility" was worked out. The priority is to clean up the main city river and its tributaries, as well as to keep P. Buh River in good condition and in the future, development of the modern urban water supply networks and its complete reforming. It is also intended to create a concept of joint and several liability for the P. Buh River among all the cities and communities through which the river flows.

2. Material and Methods

In the planning structure of Vinnytsia, the bed of the P. Buh river and its tributaries mostly coincide with the landscaping frame of the city, which is a good tradition and needs development and improvement (Fig. 2).

The main problems of coastal river territories of the city of Vinnytsia were identified and further recommendations for their revitalization and urban development were formulated by the following architectural and urban planning methods.

Sociological surveys of 2016–2017 conducted by V. Polyans'ka helped to identify the milestones for the further development of the embankments of the Southern Bug River, taking into account the needs of the local population.

The analysis of the localization of public functions was carried out in order to identify the saturation of the flow of people in the central part of the city, and accordingly the need for quality and well-equipped public space.

Fig. 2. Hydrographic network of the city (https://www.vmr.gov.ua/ContentLibrary)

The landscape frame of the city analyzed by the authors revealed the existing problems and trends of its formation, as well as the percentage of landscaping in three areas of the city (Western, North-East, South-East). In addition, the landscaped areas have been divided into adapted for use and "wild" ones.

The analysis of the embankment communication system revealed different systems of planning and communication connections as:

- public transport systems of different types;
- pedestrian connections;
- basic approaches to the territory of design;
- connections between different territories;
- the main areas for car parking etc.

Examination and photo-fixations of the embankments in the city were carried out in order to find out the current state of improvement and their accessibility for visitors.

By means of comparative studies of embankments in large cities, the main planning and compositional elements and functional zones of embankments of large cities were identified, which will help to identify problems and elaborate the concept of embankments of Vinnytsia.

3. Results and Discussion

According to statistics, the majority of the citizens who regularly spends time in the city center is young people and adolescents. In Vinnytsia, more kindergartens are located in residential areas, while a significant part of schools, namely 32.2% are located in the center of the city, as well as the majority of higher education institutions and colleges (41.2%) (http://www.vn.ukrstat.gov.ua/). The city's plans confirm that the city is landscaped enough, but only in its outskirts. In the center, most areas are occupied by residential and public buildings. Also, the design area is limited by development, which directly affects the concentration of the city's population and the needs of residents. This is a common problem both for tourists and for residents of the city (for daily use and for different activities of different age groups).

The natural qualities of valleys and river shore line are the main natural assets structuring the landscape. This is a significant potential for identifying the city's structure and improving the quality of life in the surrounding areas. When such natural elements are programmed, designed and developed as recreational spaces, the city as a whole acquires a more sustainable environment for all residents. The city centre is surrounded by picturesque elements and consists of attractive urban spaces. However, at present, many important points of the city are not well defined and poorly integrated into the life of the city, and at the same time historical routes are developed only partially. Interview with residents in 2016–2017 (by V. Polyans'ka) highlighted several milestones for the development of the Pivdennyj Buh River embankments: the first – the creation of a representative image of the embankments; the second – the accessibility to them (integration into existing urban net) and setting of the existing coastal zones as places for development. It is also worth mentioning the improvement of the coastal zones for local recreation and tourism; formation of various public functions and attractive space for pedestrians and cyclists; paying attention to the ecological status and maintenance of vegetation.

An analysis of the localization of public functions in the city revealed that a significant part of major institutions, office centers and generally the most developed infrastructure is inherent in the central part of the city.

Accordingly, the needs of people in a well-executed and arranged space are much higher, since most of the day the citizens spend there. This is confirmed by the concentration of the streams of people, from the city center, and extending eastwards to the most urbanized residential areas of Vinnytsia like Podillia, Vyshenka and Barsk Highway (Fig. 3).

Fig. 3 The scheme of concentration of people in public spaces (by V. Polianska)

The analysis of the urban environment has been carefully accomplished for the "City Development Concept", which is the basis of the following analysis of the territory (Kompleksna stratehiya, 2015). On the basis of the above mentioned information and obtained data from the analysis of the territories, certain trends in the formation of the city landscape frame have been identified and a number of proposals have been formulated. The existing landscaped territories of the city are subdivided into three areas, depending upon the percentage of landscaping: 1 – the Western – the mostly landscaped area; 2 – the North-East – average concentration of landscaped areas; 3 – the South-East area is the district of the city with the smallest number of green areas, where private houses prevail, and public landscaped areas are almost absent. Thus, this area becomes "detached" from other landscaped areas which are situated mostly on opposite bank of the river. The Pivdennyj Buh River plays a role of barrier, fulfilling some function of natural obstacle in shaping of the green frame of the city.

The territory of design, which is located in the central part of the city, is surrounded by the main streets of the city and near the main transport nodes and roads leading to each district of the city. The transport accessibility to the coastal areas is quite simple. There is the Central Bus Station nearby and the embankment of the river trams "Pirogov" and "Lala Ratushna".

Taking into account the length of the city territory, it would be advisable to create additional approaches, especially from Kyivska street and from the neighbouring borders (from "The Roshen" waterfront and from "Khimik" public beach). Despite its good connection, the waterfronts are not the focus of the attraction, as the coastal areas in the central part of the city are neglected and are not a city attraction or places of recreational destination.

Fig. 4. The scheme of landscaping of the city and the existing state of the waterfront territories in Vinnytsia. The waterfront areas, which are adapted for the use are indicated with the red colour, "wild" spaces, which are not activated by the “City development Concept” yet, are indicated with the green colour (by V. Polianska)

Examination and photo-fixations of the embankments in the city revealed that they were defragmentated and in most cases inaccessible to visitors. At the site selected for the design, problems of degradation of nature were identified as:
– insufficient cleaning of the water reservoir and coastal area;
– insufficient illumination of pedestrian communications;
– lack of shoreline monitoring;
– unsatisfactory condition of the road surface and fencing of the embankment;
– the absence of small architectural forms, except for the existing rotunda, which is in unsatisfactory condition as well;
– morally outdated arrangement of the territory;
– neglected landscaping;
– non–functional approaches to the territory because of their neglect and lack of safety.

By means of comparative studies of embankments in major cities (based on the analysis of satellite images of the top embankments, such as: Waterfront in Oslo; Madrid–Rio in Madrid; Stockholm embankments system; Pontevedra (Spain); Lyon and Paris; Warsaw; embankments above Spree, Berlin), the main planning and compositional elements present in all embankments were identified:

– water body as a target object of the territory;
– coastline (which may have different arrangements);
– transit lane;
– central area;
– recreation area;
– the outer boundary of the embankment.

Functional zones, most characteristic for these territories, were also identified as such:

– recreational (for passive or active rest) zone;
– sports zone;
– exhibition or cultural zone;
– children's zone;
– parking area;
– retail zone;
– beach area;
– embankment area.

These zones can be grouped in a different way and complemented by other functions. In order to eliminate the existing problems of the territory, it is necessary to carry out the following measures:

– carrying out of sanitary and hygienic works (cleaning of the river bottom of the coastal zone, spreading and caring for vegetation and landscaping, etc.);
– restoration works of the embankments (complete replacement of the fence, road surface, improvement of the retaining walls, replacement of vertical communications: stairs and ramps);
– improvement of landscapes and landscaping facilities of the objects;
– restoration and streamlining of existing small architectural forms and illumination of the territory.

The main proposals for improving of the functioning of the coastal area are:

– the integration of the riverfront space into the urban environment;
– provision of the new pathways for both pedestrians and cyclists;
– including of the additional spaces to the waterfront area for mass entertainment events, or areas for outdoor activities, etc.;
– development of a project with new stylistic features of the coastal zone;
– arrangement of new functional zones and grounds for active rest with the necessary equipment;
– selection of the nessessary artifacts for these zones. In this way, the city has to create comfortable conditions for recreation and comfort of different age groups.

3.1. City landscape frame

It is proposed to integrate three districts (Western, North-East, South-East) by creating a single green urban space system by designing river-related communications. Thus, its function from a "barrier", would be transformed into the "attractive for citizens" area. It is also proposed to highlight the most promising green areas in the city center and revitalize them and adapt them for the use of citizens. This will create a landscaping in the center that connects the green corridors with landscaping (forests, forest parks, parks) within the sleeping areas (Fig. 5).

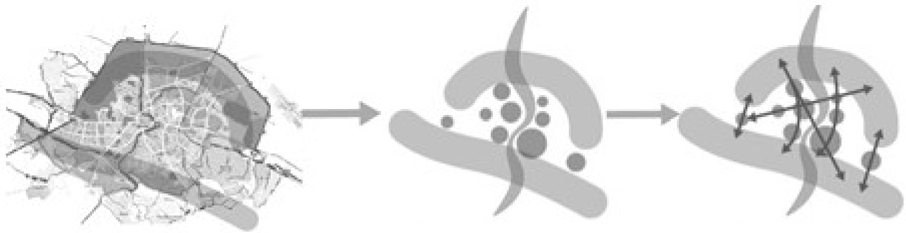

Fig. 5. The proposed scheme of formation of the green frame of the city: A– the existing state; B – augment of green areas in the cetral part of the city; C – the proposal to combine the green frame of the city with the river panorama (by V. Polianska)

3.2. System of embankments communications

In attempt to find an answer and a solution to the problem of embankments communications, the project proposal suggests creation of a comprehensive system of waterfront territories, which will be interconnected between themselves with functions, barrier-free bicycle and pedestrian connections from one territory to another. Thus, the person who comes to the seafront for a rest will not be limited by the space of 300–500 m, he will have free access to all parts of the coastal area as part of a single system. Depending on citizen needs, it was decided to create a specific zone in each area having a different function. In view of the localization of public activity, the concept of development of basic links is proposed having access to the coastal territories of the central part of the city (Fig. 6, Fig. 7).

Based on the previously discussed theories and ways of integration of the city landscaped frame, one of these options should be considered here in more details.

Taking into account the idea of the "City Development Strategy" (https://www.vmr.gov.ua/ContentLibrary) to integrate the South-West and North-East parts of the city, it was decided to create a green corridor from the North-East area, through the design territory, to the Panorama square, which is near Artynov stairs and then through existing landscaping near the Gorkyj Park. This proposal should be considered together with the idea of the pedestrian bridge that will lead from the green zone (Brigantine) to the other river bank, which is the beginning of the compositional axis of the city, leading straight to the heart of the city. Territories that may form a single waterfront system will be directly connected with the central part of the city and other major transport nodes leading to different parts of the city (including sleeping areas).

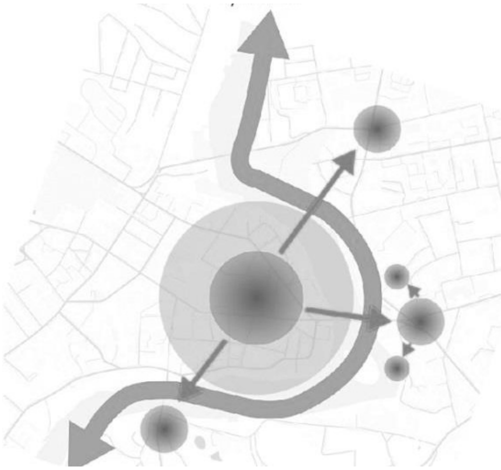

Fig. 6. The diagram of the basic connections of the central part of the city with the nearest public and communication nodes (by V. Polianska)

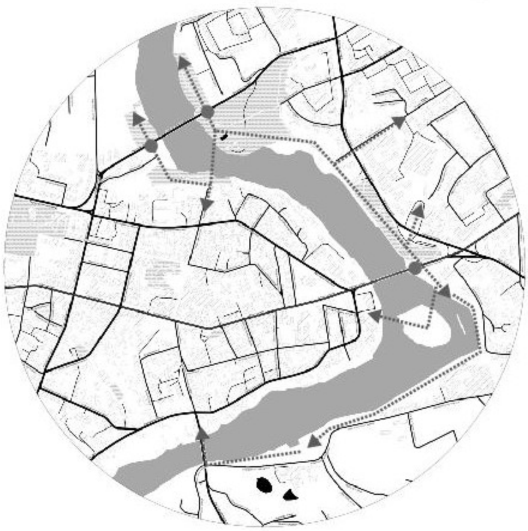

Fig. 7. Schema of basic connections and accessibility to the territories (by V. Polianska)

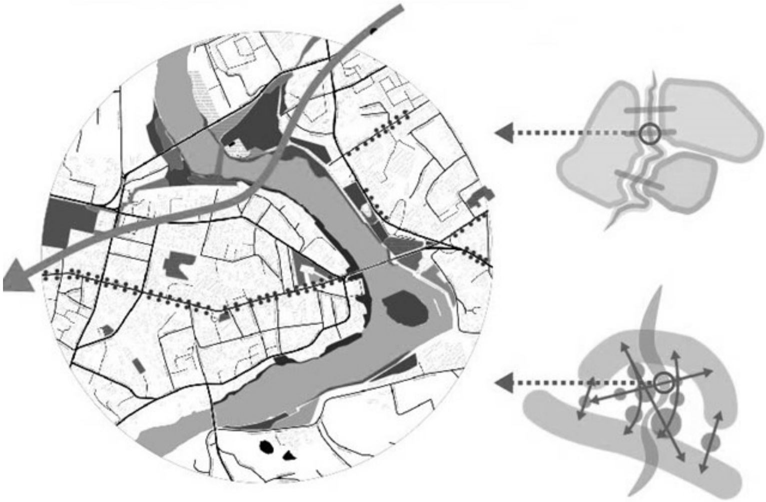

Fig. 8. Schema of the concept of landscaping of the central part of the city (by V. Polianska)

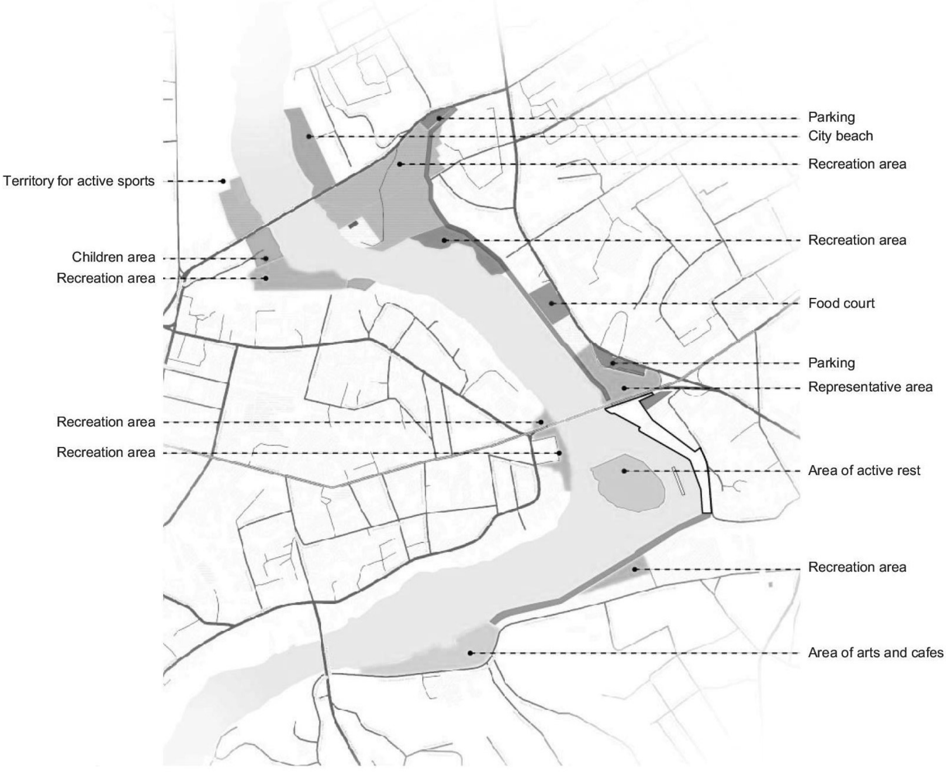

Fig. 9. Schema of the project proposal for zoning of the waterfront territories of the central part of the city (by V. Polianska)

According to the concept of organization of the embankment system in the central part of the city, specific functional zones of the city territory were identified. The description and filling of the components of the embankment system are shown in Fig. 9. Each territory is endowed with a function, depending upon the location, upon the adjacent territory, features of the site and topography, or the historical background of the city's development.

3.3. The territory of design

Based on the research of the territory, a basic scheme of zoning was created, which includes (from top to bottom) green areas of recreation for the citizens, coastal areas with free access to water in the form of cascading terraces and floating terraces made of wood and concrete. This third area is a representative one, because the first thing what the visitors of the city can see when leaving the central bus station is the embankment (Fig. 10).

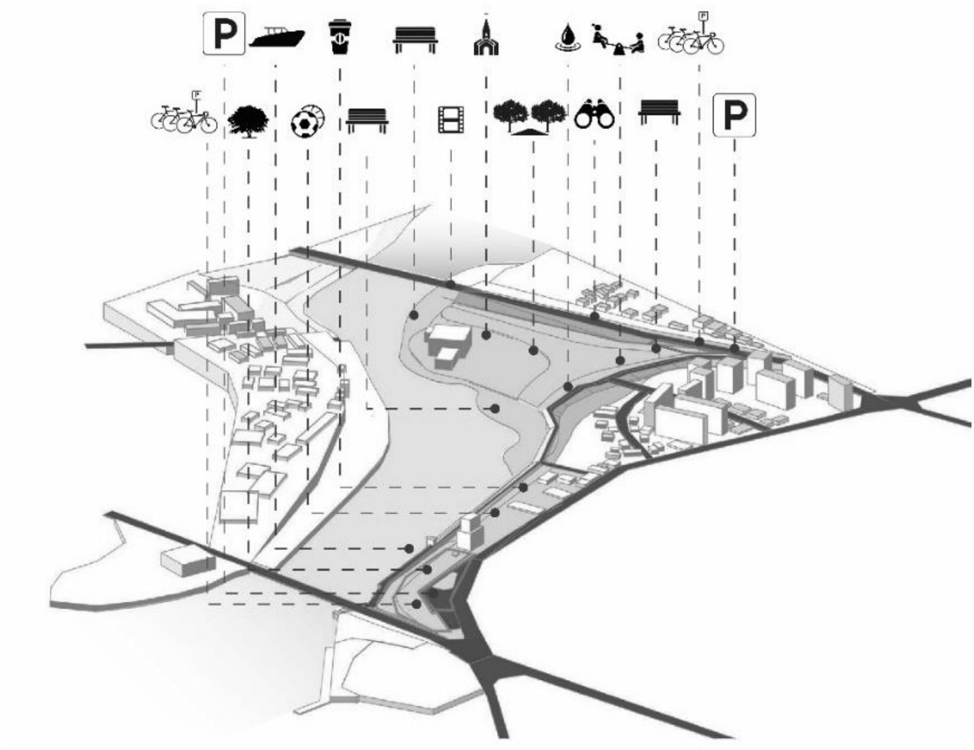

Fig. 10. Scheme of Zoning of the Territory (by V. Polianska)

After that, a compositional scheme of the territory was drawn up, which in the future would become the main component to which pedestrian and bicycle links would be "added". In addition, it was noticed during developing of the concept, that the territory is characterized by sharp diversity of the relief. Therefore, a scheme of high–altitude use of relief was applied. In view of the significant difference in relief (1–5 m), the concept of different levels of the embankment landscape has been proposed, the first one is on the ground and the second one is above the ground (Fig. 11–13).

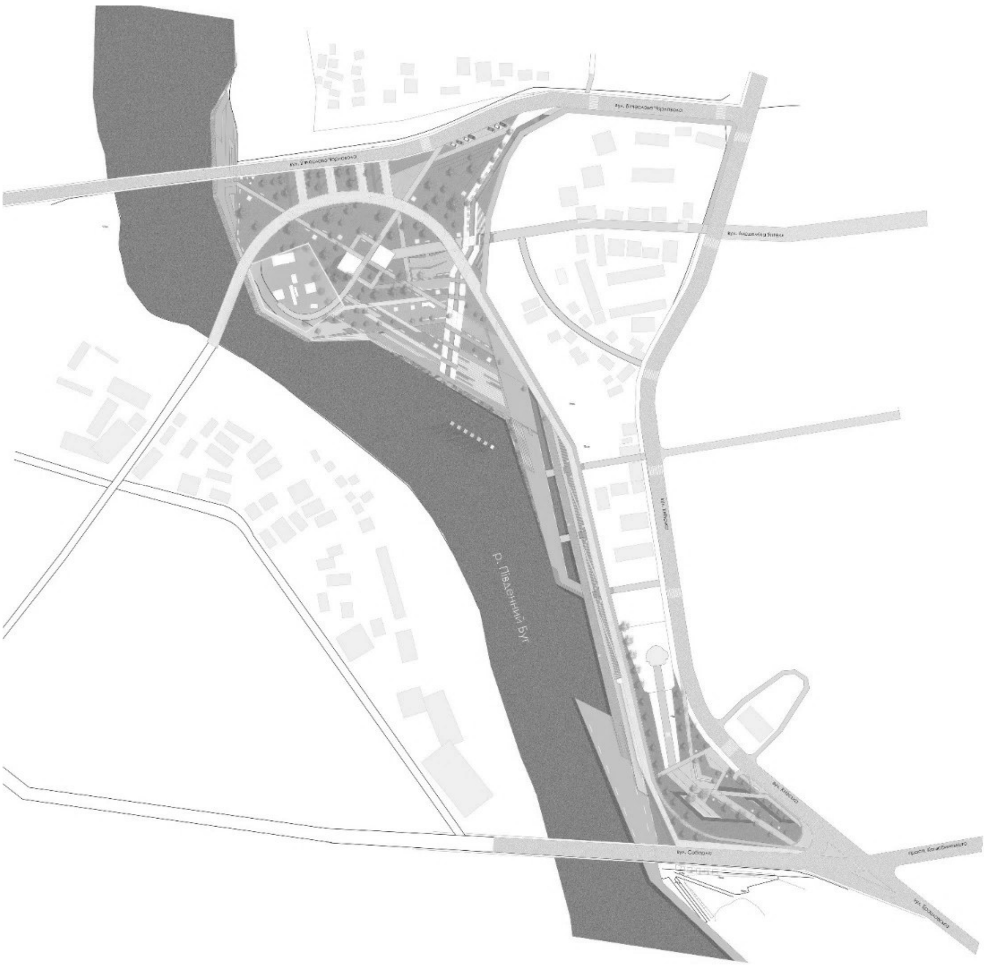

Fig. 11. Master Plan (by V. Polianska)

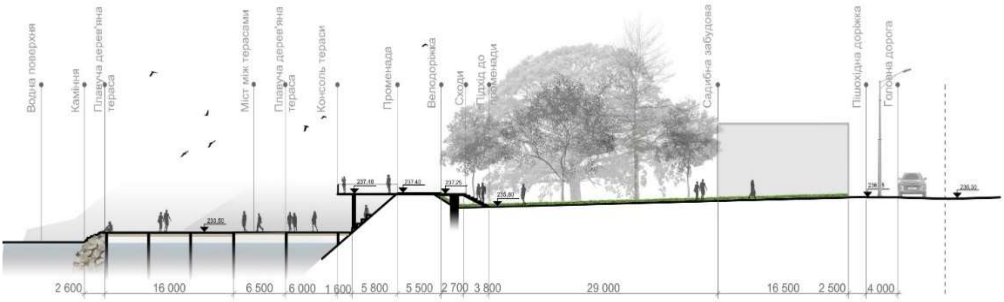

Fig. 12. Intersection of the territory (by V. Polianska)

Fig. 13. Project visualization (by V. Polianska)

4. Conclusions

The city of Vinnytsia needs balanced spatial development, which would include the creation of new recreational areas, the modernization of existing ones and their integration with a water–related system. This task is based on the research of the city development plans and the audit of all watery (wetland), green and neglected areas in the city and include them onto the “Water–green map of Vinnytsia” in order to allocate them later in the green frame of the city, designate them and assign the cadastre number. It is necessary to collaborate with and educate the radical-minded citizens and to involve them in the process of creating public orderly spaces as part of the city's water and landscaped frame. It is worth involving citizens and experts in the development of master plans of territories and implementation of projects as well as to find effective strategies and tactics for creating a water and green framework of the city. The main goal of the project is to develop the concept of green city framework, to monitor and mark the problems of the deterioration of the urban environment, to find the reasons of reduction of its quality and to create a modern urban trend for participation of citizens in landscaping and urban improvement.

The Pivdennyj Buh River influences many levels of planning and functional use of territories in the city of Vinnytsia. On the basis of progressive theoretical approaches, acquaintance with the world experience of urban development of embankments and on the basis of analysis of local plans, proposals, as well as analytical and field researches the several effective options of changing the perception and use of the Pivdennyjd Buh River in the city of Vinnitsa have been proposed, namely:

- macro level – a new arrangement of coastal areas can contribute to the sustainable development of the whole city i.e. enlargement and balancing of the frame of landscaped areas;
- mezzo level – the concept of continuous creation is proposed, which would include functionally diverse space for all age groups;
- microlevel – the project proposal was developed for the area near the bus station as the most commonly used one by the citizens of Vinnytsia.

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Application of modeling tools for monitoring the state of roadside territories and nearby surface waters

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Abstract

Environmental pollution is becoming more and more important issue. In the context of the influence on human health, as well as hydrosphere and pedosphere state, dispersion of the exhaust gases pollutants deserves particular attention. And thus, the monitoring of the pollution level of territories near potentially ecologically hazardous highways is an important task for environmental safety ensuring. It was found that the method proposed by M. E. Berland and supplemented by V. O. Kholodnov can be used in the context of monitoring traffic flows impact on the roadside areas and nearby waters. The implementation of this method was shown on the example of the Irpin River (Kyiv district) pollution, which is crossed by E40 motorway. It was found that in this case the most dangerous wind speed is 5 m/s; the most dangerous wind directions are northeast, east, southeast, southwest, west and northwest for particulate matter (PM), while east and northwest – for NO_x. The minimal distances at which a safe PM and NO_x concentrations can be achieved are 2.5 m and 9.5 m, while the maximum distances are 3.0 m and 36 m respectively. On the basis of mathematical modeling it was determined that the contamination of the urban waters located near the loaded motorways can be quite significant. The dispersion of the exhaust gases components potentially can lead to water quality worsening, harming aquatic organisms and human health. In particular, the acidity of the waters can increase, heavy metals and benzopyrene absorbed by small PM particles can contaminate them.

Keywords: environmental monitoring, mathematical modeling, traffic flow, exhaust gases, roadside territories, surface waters, particulate matter, nitrogen oxides, pollutant dispersion

1. Introduction

In recent years, in Europe more and more attention has been paid to the problems of ecology and environmental engineering solutions. Various measures are being taken to reduce pollutant emissions and prevent the negative impact of industrial activities on human health. At the same time, the emphasis in environmental protective measures is on the air quality, because atmospheric pollution affects hydrosphere and pedosphere. The study of statistical data shows that in Europe the air quality is gradually getting better. In particular, from 2011 a significant decrease in the percentage of the European urban population exposed to such air pollutants as particulate matter (PM) and nitrogen dioxide NO_2 can be observed (Fig. 1).

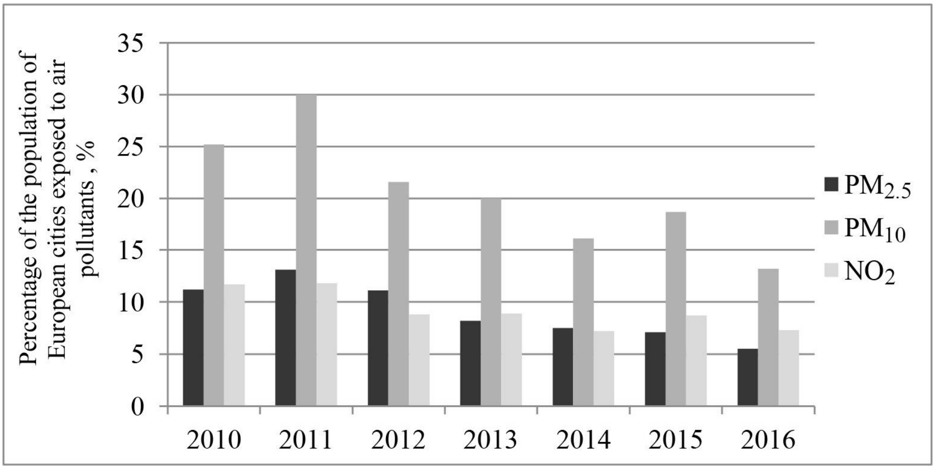

Fig. 1. Percentage of the population of European cities exposed to air pollutants $PM_{2.5}$, PM_{10} and NO_2 (created by the authors based on Statista data (www.statista.com))

However, in Ukraine a considerable part of the urban population still lives in conditions of the high levels of atmospheric pollution. Even Kyiv, the capital of Ukraine, almost every year is included in the list of cities with the highest levels of air pollution, and therefore it is also included in the list of cities with serious environmental problems, risks of increasing the sickness rate of the population, etc. (www.cgo-sreznevskyi.kiev.ua; Bondar et al., 2008). And road transport is one of the significant sources of such pollution.

In Ukraine and Kyiv city the level of motorization of the population is increasing every year. At the beginning of 2016, the level of Kyiv motorization exceeded the value of 350 cars per 1000 inhabitants, with the very high rate of automobile use − ~ 88% (www.autoconsulting.com.ua). In urban areas trunk lines occupy up to 30% of the length of the road network, while the high intensity of traffic flows on them (usually more than 2500–3000 cars per hour) causes an intense air pollution, which can be registered even at a great distances from the roads.

In Kyiv city the modern transport network is especially dense (www.mistosite.org.ua) and, according to the “World Bank” experts, the capital’s car park is quite outdated and does not meet Euro 5 standards in terms of the exhaust gases emission. Outdated infrastructure also causes an increase in emissions of pollutants because of the increased number of traffic jams and limiting the average speed of traffic flows (www.mistosite.org.ua).

By the chemical properties and the effect on humans, vehicle emissions are conventionally divided into non-toxic, which do not harm human health and the state of the biosphere (N_2, O_2, H_2O, H_2, etc.), and toxic. Among the harmful substances, the most dangerous are carbon monoxide CO, hydrocarbons C_xH_y (especially polyaromatic ones), nitrogen oxides NO_x, sulfur oxides (for example SO_2), hydrogen sulfide H_2S, aldehydes R−C(O)H, etc.

Waters are also affected by the motor transport exhaust gases components, because water contamination is directly connected with atmospheric local pollution and harmful substances dispersion. In particular, being emitted into the atmosphere, particulate matter can be carried over quite long distances by wind causing water contamination, making rivers and lakes acidic, damaging sensitive natural ecosystems (www.epa.gov). PM can also absorb other toxic substances on the surface, including heavy metals, benzopyrene, etc.

According to the data of the “United States Environmental Protection Agency” (www.epa.gov), small particles less than 10 μm in diameter are the most harmful for human health and environment. In 2016 in the European Union road transport was responsible for 10% of the PM_{10} and 11% of $PM_{2.5}$ emissions (www.statista.com). As can be seen from the Fig. 2, the overall PM_{10} and $PM_{2.5}$ emissions in the European Union in 2016 were less than in 2000 or even in 2010. But they are still significant and there were no positive dramatic changes in emission levels after 2010.

Nitrogen oxides NO_x also have a harmful effect on the human health and hydrosphere. The major part of the emissions of nitrogen oxides is NO and NO_2. But in the atmosphere, under the influence of oxidants, NO turns into NO_2. Nitrogen oxides, and especially NO_2, adversely affect myocardium, bronchi and mucous membranes of the nose, eyes and stomach, as well as the state of the human central nervous system and the photosynthetic apparatus of plants.

In addition, the presence of the unburned hydrocarbons in the exhaust gases significantly increases the toxicity of NO_x due to their combined synergistic action under the influence of solar radiation. The danger of nitrogen oxides is magnified by the fact that, when they react with the water vapour in the air, fine aerosols of acids (HNO_2 and HNO_3) are formed, which can cause acid rains and thus – worsen the environmental state of waters.

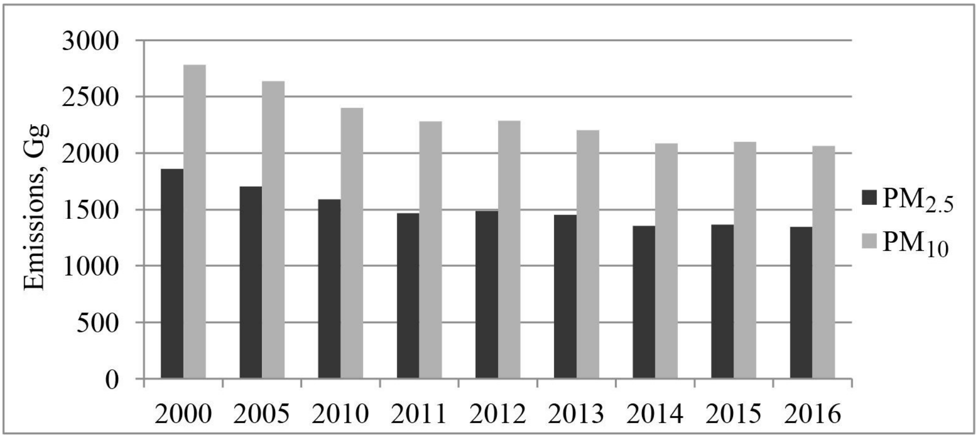

Fig. 2. Dynamics of the $PM_{2.5}$ and PM_{10} emissions in the European Union (created by the authors based on Statista data (www.statista.com))

Therefore, the study and monitoring of the pollution level of the territories near potentially ecologically hazardous highways is an important task for ensuring the environmental safety of ecosystems, waters, urban population in Ukraine and Europe. In addition, it is of a particular importance to investigate the short-term changes in the content of harmful substances in certain sections of the motorways, as well as at the specific distances from them in order to more accurately assess the ecotoxicological effects on human health and natural objects.

In most cases air quality in Ukrainian cities is evaluated by a complex integral indicator – the index of atmospheric pollution, calculated using the average annual or monthly concentrations of harmful substances. The most widely used abbreviation for the index of atmospheric pollution is IAP (transliterated from Ukrainian language). IAP takes into account the degree of harmful impact of the pollutants on the living beings.

As a rule, IAP is defined by the 5 most important for a certain city or district impurities (for example, CO, NO_2, PM, SO_2, and formaldehyde) as the sum of the average concentrations divided by the *MPC*. Partial IAP are used to characterize air pollution caused by individual pollutants. When IAP < 5, the level of contamination is considered as low, $IAP_5 = 5–7$ is considered as quite high level, $IAP_5 = 7–14$ – as high, while $IAP_5 > 14$ – as very high level (www.cgo-sreznevskyi.kiev.ua). Analysis of the statistical data has shown that the level of atmospheric air pollution in Kyiv city by IAP_5 is consistently high.

However, IAP calculation is not able to provide data on the levels of pollution in the areas where local concentration of pollutants is observed. Local pollution areas with maximum and minimum concentrations of certain pollutants are formed because of mixing of the exhaust components with each other and their interaction with objects of the natural environment. Such local pollution is peculiar for the highly loaded motorways; crossroads; parking lots near residential areas, offices and shops; car wash and service stations. Local pollution of the urban territories is generally associated with the influence of wind with a velocity of $u \leq 6$ m/s, since wind flows play a decisive role in the dispersion of pollutants in the surface air (Shevchenko, 2009).

There are two main factors that mostly affect dispersion of harmful impurities in the ambient air. The first one is hydrodynamic, caused by the formation of vortex flows near buildings, and the second is geometric, associated with the interaction of impurities with the obstacle surfaces, which, in turn, contributes to the additional dispersion of pollutants in the direction perpendicular to the average wind (Parashchuk et al., 2007).

In the previous studies by in situ experimentation and mathematical modeling we have found that in the roadway sections of motorways, as well as on sidewalks and roadside territories on the distance up to 15–20 m, the significant increase in the *MPC* of carbon and nitrogen oxides is observed. At the same time, according to (Eastwood, 2008), contamination with fine dust particles has an area of dispersion at a distance of 5–7 m from the road. This significantly increases the toxicity of the impurities due to such factors as their staying on the height of the human breath, the adsorption of other toxicants and the transfer over long distances with vehicles.

According to (Pryshchepov and Levytska, 2008), the pollutants dispersion characteristics along the highways depend on the height of the source of emissions above ground level, stratification of the atmosphere, wind speed, traffic conditions and characteristics of traffic flows, orography of the underlying surface, as well as the nature and density of the urban planning. In terms of the local pollution assessment it is expedient to model the transport highway as a linear source of emissions taking into account key factors which influence dispersion processes.

Significant contribution to the theory and practice of mathematical modeling of atmospheric air pollution was made by M. M. Belyaev, E. A. Zakarin and V. F. Kramar, F. V. Korshenko, V. G. Svinukhov, A. V. Starchenko, Ye. A. Samarska, A. G. Shapar, (Kvaterniuk et al., 2018) etc. An important method of studying the dispersion of gaseous impurities in the air by the modeling atmospheric diffusion processes in wind tunnels was proposed by M. Z. Zgurovsky and other scientists. Determination and modeling of pollution levels of roadside airspace was considered by N. V. Vnukova and G. M. Zhelnovach, V. M. Shmandiy, L. D. Platsuk,

V. S. Baharev, O. V. Stepanchuk and others. Significant contribution in the sphere of environmental water monitoring was made by Pohrebennyk and Romanyuk (2013), Korchenko et al. (2019), Mitryasova et al. (2016), Mitryasova and Pohrebennyk (2017), Pohrebennyk et al. (2019).

The method of calculation of urban air pollution “OND-86” and its modifications made in 1978, 1986 and 2017 are among the most widely used models in Ukraine. "OND-86" is usually used for short-term (from several hours to 2–3 days) forecasting of atmospheric air pollution levels. However, it requires special software and precision monitoring data, and because of its universality, this method can’t take into consideration local features of the contaminated areas (Shevchenko, 2009).

In turn, the “European Environment Agency” proposes the “COPERT 4” software package for the calculation and inventory of vehicle emissions, which is based on empirical data on specific emissions, as well as fuel consumption for certain types of vehicles, car park, its structure and age, lengths of roads of different categories, fuel type, environmental class and mileage of vehicles, characteristics of traffic flows, etc. “COPERT 4” software is used for submitting to the international organizations official data on the emissions of pollutants (including greenhouse gases) by vehicles, modeling the state and quality of atmospheric air in cities and suburbs, for the calculation of the local pollution of territories, etc.

“CALINE-4” (California Line Source Model), “HIWAY-2” (Highway air pollution model), “GFLSM” (General Finite Line Source Model), “OMG” (Osaka Municipal Government volume source model) and “GM” (General Line Model) are also widely used in European Union, USA and other countries. They are based on the normal Gauss distribution law (Anglia Polytechnic University, 2001; Taseiko et al., 2009). The models “Main Geophysical Observatory” and “ROADWAY” (Roadway air pollution model) which are based on the *K*-theory also can be used.

In turn, the “OSPM” (Operational Street Pollution Model) is used to determine the level of atmospheric air pollution in street canyons, which takes into account the characteristics of street canyons and urban planning, as well as meteorological conditions, street configuration, etc. (Berkowicz et al., 1997; Berkowicz, 2000). The dispersion of pollutants in the air is determined by the combination of “box and plume” models (Anglia Polytechnic University, 2001; Taseiko et al., 2009). There are also many methods of mathematical modeling of the state of the atmospheric air based on the GIS technologies (Mateichyk et al., 2013; Trofymchuk et al., 2015).

Of a particular attention are the models developed by M. E. Berland for the prediction of atmospheric air pollution based on the equation of turbulent diffusion, that implement numerical, statistical and synoptic approaches (Berlyand, 1975; 1985). These models are used to create dispersion fields of single maximum surface concentrations of harmful substances under the adverse meteorological conditions (wind speed reaches dangerous values and active turbulent exchange occurs in the surface layer of the atmosphere) and calculate the total pollution of the urban atmosphere.

2. Materials and Methods

In the study investigations of the road conditions (intensity, density and composition) of traffic flows on the highly loaded E40 highway of the Kyiv district were conducted with the purpose of modeling the fields of dispersion of pollutants from the exhaust gases. In particular, the part of the E40 motorway crossing the Irpin River (Fig. 3) was investigated.

Fig. 3. The object of the study (Irpin River, Kyiv district) crossed by highly loaded motorway E40 (created by the authors using Google Maps application)

The Irpin River is a strategically important river. It is the right tributary of Dnipro River (162 km long). It is located in Zhytomyr and Kyiv districts. In the last few years, the ecological status of the river has deteriorated – the water level decreased, the ecosystem is suffering (www.umoloda.kiev.ua). Such unfavourable conditions represent also a threat to the Dnipro River, which is one of the most important rivers of Ukraine and is actively used for water management purposes. Therefore, the assessment of the impact of motor transport pollution on the Irpin River as a part of the integrated environmental monitoring program is an urgent task.

It was found that in the context of monitoring traffic flows impact on the roadside areas and nearby waters, it is expedient to use mathematical modeling methods. So, for the development of mathematical models of dispersion of pollutants in the ground layer of the roadside space (including local pollution areas assessment) and the prediction of the ecological status of the investigated territories, the method of M. E. Berland (1975) was used in the interpretation of V. O. Kholodnov et al. (2007). This approach is relatively easy to apply and provides quite accurate results.

The idea of this method is that in the MathCad software a flare model is implemented. By this model the semi-empirical equation of the turbulent diffusion is solved in Cartesian coordinates for a linear source of pollution as a set of point sources of emissions based on the principle of superposition of the concentration fields of a particular impurity. The result of the determination of the surface concentrations of the pollutants is given as the multiplicity of excess of its maximum permissible concentration (*MPC*).

Thus, the utilized model, which is the solution of the semi-empirical equation of turbulent diffusion for a linear source of pollution as a set of point sources of emissions, was the following (Eq. (1)):

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

where: M – the power of the emission source (mass of the substance emitted by the pollution source per unit of time), n – the coefficient characterizing the stability of the atmosphere, u_1 – the parameter characterizing the wind speed, k_1 – the coefficient for the turbulent diffusion profile of the impurity in the atmosphere, φ_0 – the standard deviation for a pulsation of wind direction and H – the height of the emission source above the ground surface.

In the developed dispersion models, the coordinate system is oriented so that the OX axis coincides with the direction of the average wind; the OY axis coincides with the direction of the traffic flow and the OZ axis is perpendicular to the traffic flow. The concentration from a linear source is equal to the superposition from point sources in accordance with the formula (Eq. (2)):

$$Q_p = \int_{L_1}^{L_2} Q\cdot(a - L\cdot sin\beta, b - cos\beta)dL \tag{2}$$

where: a and b – the new coordinates in the redirected by the direction of the average wind system of coordinates that are related to the original coordinates by Eq. (3) and L – the length of the investigated highway segment.

$$a = x \cdot cos\beta + y \cdot sin\beta$$
$$b = -x \cdot sin\beta + y \cdot cos\beta \quad (3)$$

where: β – the angle between the direction of the average wind and the direction of the traffic flow on the motorway.

The final plots showing the dependency of the multiplicity of the *MPC* excess from the distance from the motorway were created using the Eq. (4).

$$Q' = \frac{Q_p}{MPC} \quad (4)$$

3. Results and Discussion

As a result of the modeling, it was established that the maximum exceedance of the *MPC* is observed in the center of the motorway and is 3.73 times (northeast direction) for PM and 49.41 times (east direction) for NO_x. Depending on the wind direction, the dispersion of harmful substances is not the same. As can be seen from the Fig. 4, the minimal distance at which a safe PM concentration can be achieved is 2.5 m at the north and south wind directions. For NO_x the minimal distance is 9.5 m at the north wind direction.

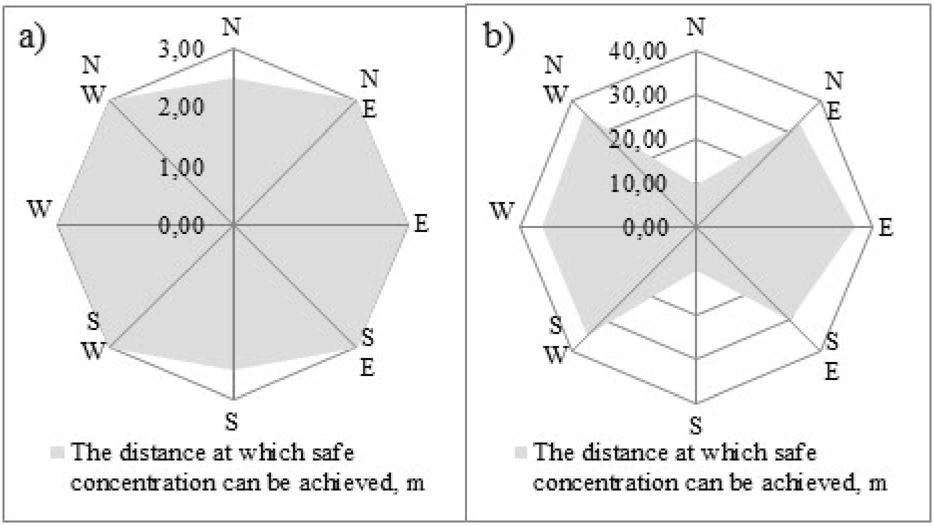

Fig. 4. The distance at which a safe PM (a) and NO_x (b) concentrations can be achieved at average wind speed of 5 m/s and different wind directions, m [created by the authors]

At the same time, the maximum distance at which a safe PM concentration can be achieved is 3.0 m at the northeast, east, southeast, southwest, west and northwest wind directions. For NO_x the maximum distance is 36 m at the east and northwest wind directions. According to the data of the "Climatic Inventory of Ukraine", during the year the west wind prevails in Kyiv city (Kosovets et al., 2013). Meteorological observations of the investigated section of the E40 highway also confirm the predominance of the west wind direction. Thus, the distance at which a safe concentration of harmful substances is achieved can be conditionally taken as 3.0 m for PM but 36 m for NO_x.

Thus, the dispersion of NO_x is much more dangerous compared to the PM, because in certain wind directions it reaches a distance of 36 m from the road immediately reaching the water surface of Irpin River. In Fig. 5–10 the examples of the developed PM and NO_x dispersion models at different directions and the most dangerous wind speed (5 m/s) are presented.

The developed models can be used as a component of an integrated environmental monitoring system for assessment of the state of waters in urban areas. The discrete-interpolation method developed by Yu. R. Holkovsky (2016) can be applied to obtain even more precise models on the pollutants dispersion in the atmospheric air. This method allows taking into account the geometric features of the motorways, the type of urban building and other additional factors. However, the amount of data and complexity of modeling will also increase.

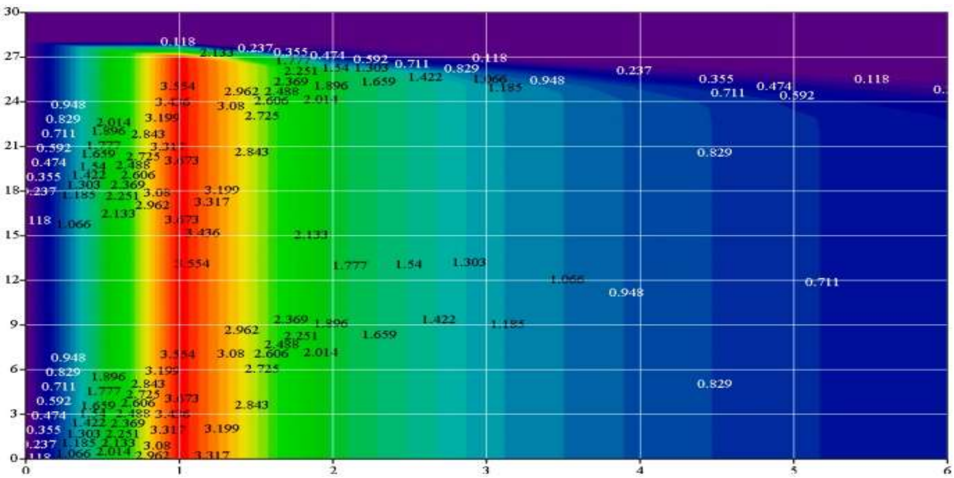

Fig. 5. Modeling results for the dispersion of particulate matter emissions (PM ≤ 10 μm in the diameter) at average wind speed of 5 m/s in the E40 motorway section crossing Irpin River in northeast direction (created by the authors)

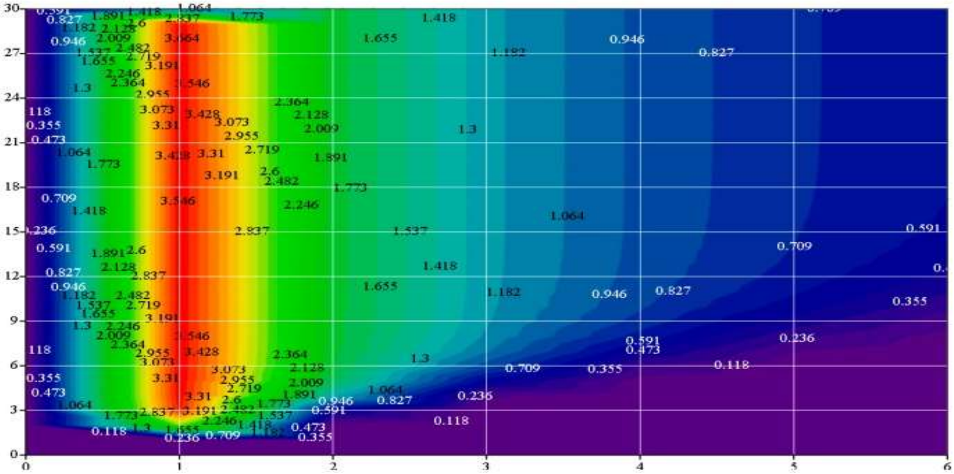

Fig. 6. Modeling results for the dispersion of particulate matter emissions (PM ≤ 10 μm in the diameter) at average wind speed of 5 m/s in the E40 motorway section crossing Irpin River in southeast direction (created by the authors)

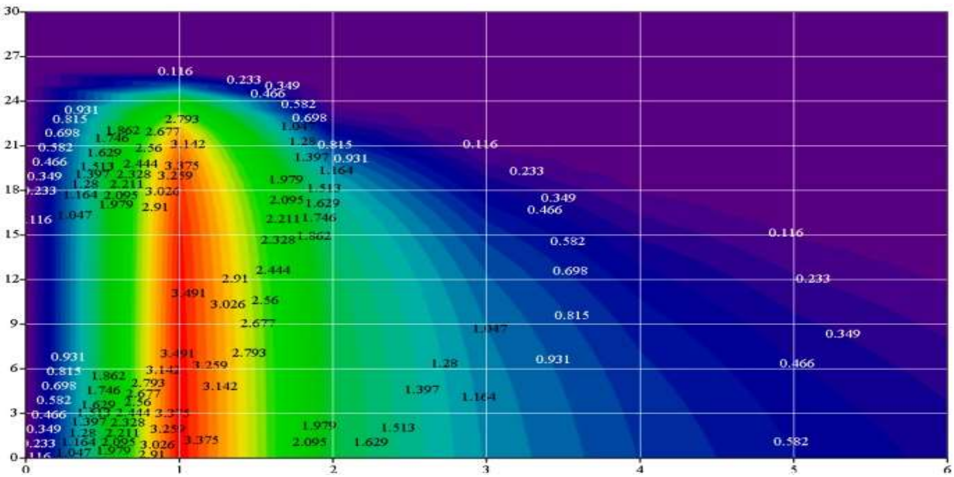

Fig. 7. Modeling results for the dispersion of particulate matter emissions (PM ≤ 10 μm in the diameter) at average wind speed of 5 m/s in the E40 motorway section crossing Irpin River in south directions (created by the authors)

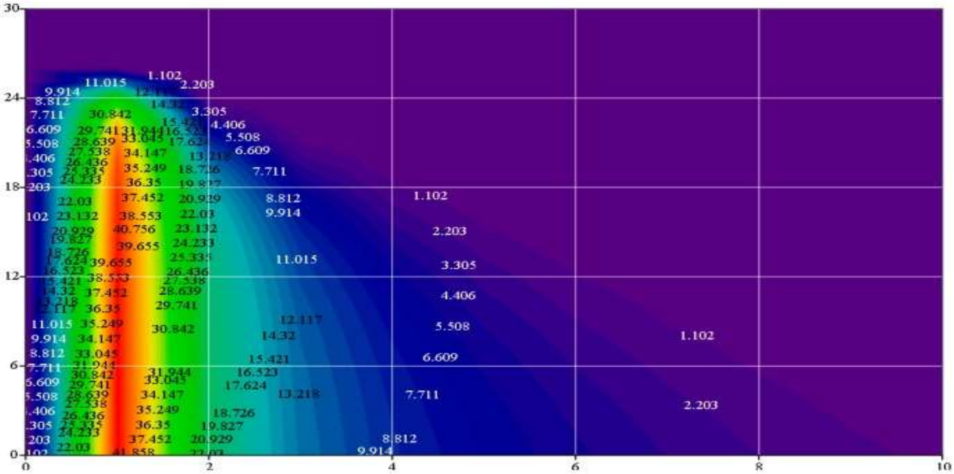

Fig. 8. Modeling results for the dispersion of NO_x emissions at average wind speed of 5 m/s in the E40 motorway section crossing Irpin River in north direction (created by the authors)

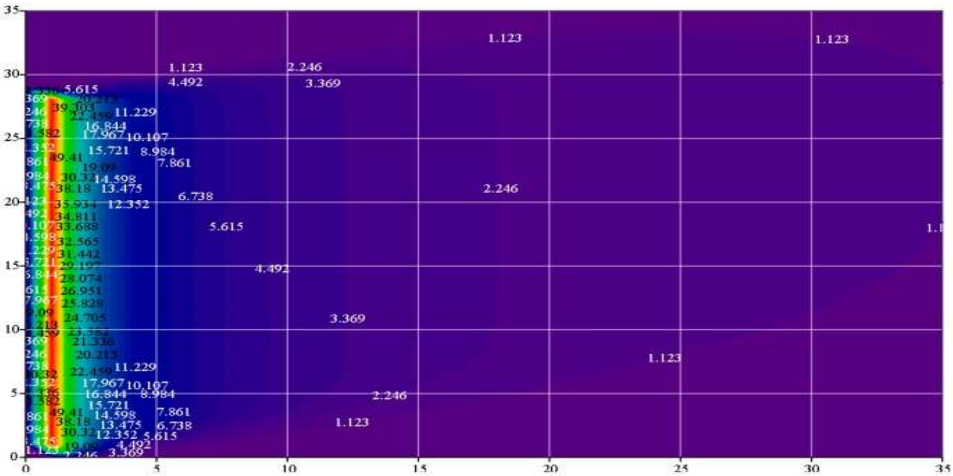

Fig. 9. Modeling results for the dispersion of NO_x emissions at average wind speed of 5 m/s in the E40 motorway section crossing Irpin River in east direction (created by the authors)

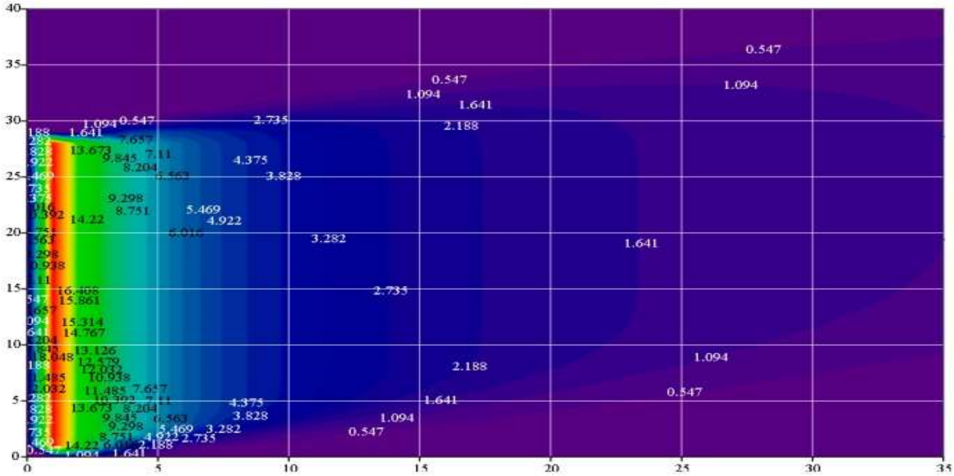

Fig. 10. Modeling results for the dispersion of NO_x emissions at average wind speed of 5 m/s in the E40 motorway section crossing Irpin River in northwest direction (created by the authors)

4. Summary and Conclusions

Ecosystems, including waters located at the urbanized territories of Ukraine and other European countries, are highly affected by industry and motor transport complex. In order to assess transport flows impact on the roadside airspace and nearby waters it was proposed to use the method of M. E. Berland in the interpretation of V. O. Kholodnov through the MathCad software. The implementation of this method was shown on the example of the Irpin River pollution (Kyiv district), which is crossed by E40 motorway. Irpin River was chosen because it is the object of potentially increased ecotoxicological load from the exhaust gases emissions.

With the help of a computational experiment, the directions of the wind and its speed, which are the most dangerous for the studied motorway section, were determined. The most dangerous speed is 5 m/s. The most dangerous wind directions are northeast, east, southeast, southwest, west and northwest for PM, east and northwest for NO_x. The minimal distances at which a safe PM and NO_x concentrations can be achieved are 2.5 m and 9.5 m respectively, while the maximum distances are 3.0 m and 36 m respectively.

So, the contamination of the urban waters located near the loaded motorways can be quite significant. The dispersion of the exhaust gases components (for example, PM and NO_x) potentially can lead to water quality worsening, harming aquatic organisms and human health. In particular, the acidity of the waters can increase, heavy metals and benzopyrene absorbed by small PM particles can contaminate them. Humans moving on the sidewalks are also affected by the exhaust gases emissions. Another negative factor is the impact on the health of drivers and cyclists, since the concentration of harmful substances in the center of the motorways can exceed *MPC* values significantly.

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Involving future biology teachers into researching the water quality of minor rivers in Ukraine (evidence from the Esman river in Hlukhiv, Sumy region)

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Abstract

The practice of public participation, in particular, of students of pedagogical universities, in the assessment of environmental quality on the example of the water resources in Hlukhiv, Sumy region (Ukraine) is considered in this article. The focus is on describing the results of such studies, in particular, the research on the dynamics of the phytotoxic properties of water along the riverbed of the Esman river within Hlukhiv urban ecosystem. It is also dedicated to developing the recommendations for improving the state of town's water resources. The involvement of the public in assessing the quality of the environment and establishing a two-way flow of environment-related information between the governing body and the community will increase the motivation to achieve sustainable development goals at the local level. This article also serves to prove that such involvement will advance a sustainable city development strategy and contribute to growing the research competence of future biology teachers.

Keywords: water quality research, phytotoxic effect, public participation in environmental quality assessment, future biology teachers

1. Introduction

The concept of sustainable development in modern world theory and practice is considered as a sole strategy to solve the problems of preserving and restoring the environment and ensuring a high standard of living for the global population. Sustainable development of every country determines the quality of human life and health, which depends on the state of the environment, the quality of food and drinking water (Karpinski et al., 2018; Kvaternyuk et al., 2017; Mitryasova et al., 2016; Petruk et al., 2016).

Natural resources undoubtedly act as a basic factor in the national economy of each country, including Ukraine.

However, quantitative assessment of natural resources, including water resources, in our country, as well as the assessment of their state and use, now require a considerable generalization and solid analysis; especially considering that these elements are the starting points in shaping the national sustainable development strategy.

The lack of a single national methodology for quantifying and evaluating natural resources and the absence of strategic planning in their use serve as additional proof of the statement above (Kushnir, 2013).

Water resources are strategic and vital elements of the system ensuring sustainable development. After all, water resources are the national wealth of each country.

International instruments adopted by the World Water Forum in the Hague in 2000, the International Conference on Freshwater in Bonn in 2001 and different UN documents recognize water quality as a key indicator of the sustainable development of society, its safety and the actual existence (Hvesik, 2005).

Particular attention was paid to ensuring the availability and rational use of water resources by the international community following the adoption of the United Nations Sustainable Development Goals (SDGs) in September 2015 (UN, 2015).

In September 2017, Ukraine presented the adapted indicators to meet the 17 Sustainable Development Goals. Among them the 6.3 task of Goal 6 for Ukraine is improving water quality and ensuring the rational use of water and sanitation for all (UN, 2017).

Although Ukraine has great water resource potential, it is extremely misused. The reason is the lack of a unified policy on the sustainable use of natural resources. Additional factors are outdated sewage water treatment technologies, the low level of ecological culture among the population of the country, the dominant idea of the inexhaustibility of water resources and their limitless capacity for restoration, which will allow our descendants to use these resources in the future.

Studies show that Ukraine is one of the least well-resourced countries in Europe in this regard. The water problem is one of the most acute issues nowadays. Considering that our rivers are the main sources of fresh water, their protection, rational use of water resources, prevention of pollution are urgent issues that require constant monitoring of the state of fresh water in the rivers.

The research on minor rivers of Ukraine (up to 100 km long) and their tributaries is of particular relevance. They form the water potential of the region, serve as a source of fields irrigation, animals watering, are used for technical purposes, and serve as unique recreational areas within towns and villages.

Most of them are not part of the state environmental monitoring network. Yet, reducing the runoff and increasing pollution levels in these rivers affects the conditions in Ukraine's large rivers to a great extent.

Researchers argue that public participation in decision-making on the conservation and management of natural resources is necessary. It reduces the distance between decision-makers and the community, promotes transparency of decision-making, impedes taking steps that threaten the region's sustainability (Scott and Ngoran, 2003).

Students have always been the most active population all around the world. That is why the involvement of students, in particular, future biology teachers, in the organization and conduct of environmental quality studies is relevant and important today in the context of developing sustainable development strategies for the region.

Students can help to intensify and accelerate the collection of scientifically proven information on the quality of the environment through the distribution of study areas.

In addition, such activities will achieve several goals: generalization and dissemination of information about the quality of the environment in the community. Moreover, it will enhance the formation of a number of professional competences (research, communication, etc.) among students.

Therefore, in this article we will outline the progress and results of such studies, conducted by future biology teachers while carrying out individual research works. The focus is on the study of phytotoxic properties of the water in the Esman river within Hlukhiv, Sumy region (Ukraine) and determining the features of the impact of the urban ecosystem on the river water.

2. Material and Methods

Biotesting was used to control the state of the Esman river ecosystem. Its essence is the determining of the effect (both inhibitory and stimulating) of substances in available water samples on specially selected test organisms under standard conditions. The registration of various morphometric parameters was conducted.

This method is widely used to control the quality of natural sewage water and toxicity of wastewater. It is applied during the environmental assessment of new technologies for wastewater treatment, to justify the standards of maximum permissible concentrations of contaminating components, etc. In addition, this method is one of the most accessible and visualizing ones. It allowed making a qualitative assessment of the tested water samples.

The plants were used as bioindicators as they are the most accessible indicators of environmental pollution, since they are the initial links of trophic chains. Plants also play a major role in the absorption of various pollutants. As a result, plants can enable accurate assessment of the environmental situation in the researched area.

To determine the presence or absence of phytotoxic properties in the studied water samples, a technique for assessing the toxicity of water sources was used using a growth test on floating disks (Horova et al., 2004). Winter wheat

(*Triticum aestivum L.*) plants were selected as biosystems. Their physiological functions closely correlate with the degree of toxicity in the water of the Esman river. The observation of the reaction of these test organisms gave us the data on the quality of water and allowed studying the established level of water quality in different river zones in town.

During the research on the phytotoxicity of water samples by applying the method of growth test, 250 ml of water samples were poured into laboratory glasses. Seeds of winter wheat (*Triticum aestivum L.*) (20–25 seeds in each) were germinated on special floating gauze-covered foam plastic rings.

Within two weeks, the parameters such as the time of emergence of tails and their number (each day) were noted. The length of aboveground seedlings and their growth (each day); the total number of sprouted seeds (at the end of the experiment); morphological features of plants (early yellowing, features of the development of the root system, etc.) were also observed. The study was conducted in three replicates. The control substrate for cultivation was boiled water from the artesian wells of the urban water supply

At the end of the study, measurements were made of the length of the root and stem parts of the plants, the dry mass of ten most typical sprouts of each study group was determined.

Mathematical processing was carried out according to the methodology chosen (Horova et al., 2004), which involved the calculation of the arithmetic mean of the length of the roots and the aboveground parts, the error rate, determination of the variance value and the reliability of the difference of the arithmetic mean values (according to the Student-Fisher test).

The phytotoxic effect was determined by such parameters as the length of the stem and root parts of the plants, the dry mass of the plants, as well the average value of the obtained parameters.

3. Results and Discussion

3.1. Review of the studies on researching rivers in Ukraine, in particular the Esman

Historical overview of the Esman river were found in the studies of local Hlukhiv region historians. In particular, the historical information about the anthropogenic impact on the river Esman regime of stream, the creation of dams and artificial reservoirs there were of the greatest interest and relevance for our study. Those aspects significantly influenced the overall state of the river in question.

Historian V. Belashov found that in 1893 the width of the river Esman within Hlukhiv reached 140 m, and it was navigable. During that time the Esman was barred in two places by solid dams. One was constructed near Bilopolivka village where Skoropadske pond was formed. The other dam was costructed opposite to the woodland Nova Hreblia, where Pavlivka pond was formed. There was already Chernecha Hreblia pond belonging to the Dormition Monastery.

The cascade of three ponds became an important factor in Hlukhiv town planning during the 19th century. In addition, there were many smaller lakes and bays (Malotecha (Vodotecha), Berezka) into suburbs quarters (Belashov, 1996).

3.2. Geographical setting of the study area

The town of Hlukhiv and the district are situated in the lowland Polissia region of Ukraine with its colorful diverse landscape, which has been formed for thousands of years in the basins of the large Desna and Seim rivers. There are many forests, swamps, animals and fish in the area.

Most of the settlements in the east and north of Hlukhiv district are “tied” to the right bank of the largest local Kleven river.

Its tributary, a minor river Esman, flows through the entire Hlukhiv district from the northeast to southwest. The upper part of the river is a swamp near the village of Luzhky. The length of the river corridor is 69 km, almost the whole river flows through the territory of Hlukhiv district and near the village of Rotivka, in Putyvl district. It flows into the largest river of our region – Kleven. However, in recent decades, there have been negative changes in the conditions of the Esman river, which is the main waterway Hlukhiv and the district.

Near the river, forests were destroyed, causing the disruption in the river’s hydrological regime. A few decades later, the meliorators drained the upper reaches – marshes near the village of Luzhky. Draining the upper part leads to the destroying of the river. Now, the riverhead area is overgrown, and the river level has fallen sharply. Its width within the town of Hlukhiv rarely exceeds 5–7 meters. Nevertheless, the Sumy region of Ukraine is considered to be well provided with water resources. According to the water resources department of the regional eco-resources’ authorities in Sumy region, the rivers belong to the Dnieper basin and can be classified as clean (as of 2007).

Therefore, the present state of minor rivers in Sumy region, in particular, the river Esman, has not become the object of detailed attention from scientists. That is why our study is devoted to the collection and analysis of primary data on the status of the river in question within the urban ecosystem of the town of Hlukhiv, in particular the level of phytotoxicity of water in different sections of the river in the urban area.

3.3. The results of the study of selected samples of river water

In the course of the study on the phytotoxicity of river water, seven water samples were taken by the students of the Faculty of Natural and Physical and Mathematical Education of Oleksandr Dovzhenko Hlukhiv National Pedagogical University at different distances within Hlukhiv.

- Sample # 1 was taken near Rodnychok cottage building cooperative – before the river flows through the town,
- Sample # 2 was taken near Rodionivske Lake pond – a small artificial reservoir in the town private sector near the farm;
- Sample # 3 was taken near Skopopadske Lake pond, which is located near the central part of the town and serves as a great recreational area for the local population during summer. It is located in close proximity to the highway of state importance;
- Sample # 4 was taken near the Crystal Bridge where the tributary Chernecha river flows into the Esman. Chernecha has many underground springs;
- Sample # 5 was taken near Verihinsky Bridge, a place of significant importance for the automobiles crossing it to get to the town,
- Sample # 6 was taken near Pavlivka Lake pond which is the largest water reservoir in town with a large recreational area located within the private sector,
- Sample # 7 was taken at the Goose Beach, which is actually located outside the city, where the water from the city's treatment facilities flows into the Esman river.

Air temperature was +18 C°. All samples were taken at one time during the same day. The veracity of the results was ensured by repeated experiments and the use of mathematical statistics methods to establish the reliability of the difference between obtained indicators from different samples.

The study was conducted in three replicates. Table 1 shows the average results of these repetitions and the empirical values of the *t*-test (reliability 95%). The number of test plants grown on each water sample was 20-25 seeds. The significance of the difference in the length of the aerial part, roots and dry weight of the test plants was established by means of a parametric method of comparison of the results of the study with the t-test criterion.

The results of the study showed that in the samples of water No 1, No 4, No 7 the phytotoxic effect was practically absent, and the quality of the tested water does not differ from the parameters of the control sample. In water samples No 2, No 3, No 6, the phytotoxic effect was observed, the water quality differs significantly from the control sample (see Tab. 1).

An increase in the level of phytotoxic effect of water was observed in the sampling sites of artificial reservoirs in town, namely Rodionivske, Skoropadske, and Pavlivske ponds.

Table 1. Phytotoxic effect values for different study parameters

Parameter	The % value for samples							
	Control	No 1	No 2	No 3	No 4	No 5	No 6	No 7
Phytotoxic effect (PE) (the plants' height)	0	15.0	2.82	57	22.5	28.2	39.0	2.82
PE (the roots' length)	0	0	33.6	77.9	0.56	3.38	48.0	2.82
PE (the dry mass)	0	15.0	7.0	28.9	34.0	13.0	15.0	21.0
PE (average)	0	10.0	15.0	54.6	18.8	14.7	34	8.8
The value of the t-test criterion	2.96	0.50	2.98	3.00	2.40	2.91	2.98	0.60

3.4. Discussion

The river is a source of drinking water, a reservoir of moisture, habitat for fish, waterfowl, some fur animals. It is a source of health and aesthetic pleasure. Unfortunately, Hlukhiv residents treat Esman differently. Wheels, bottles, iron, garbage, bricks, rags can be found in its waters.

Analyzing the data obtained by future biology teachers during their individual research, it can be concluded that the water in the Esman river has significant phytotoxic properties that are inherent in local ponds. Thus, the town of Hlukhiv exerts a considerable influence on the change of water quality towards its deterioration.

The runoff from private estates, mechanical contamination of water, agricultural cultivation of lands belonging to the water protection zone of the reservoir, the influence of motor transport, etc. all have the impact. A clear increase in the level of toxicity is observed in the sampling sites from the following ponds "Rodionivske Lake" (sample No 2), "Skoropadske Lake" (sample No 3), "Pavlivske Lake" (sample No 6) (Fig. 1).

The study found that the Esman River has a great capacity for self-purification in areas outside the local artificial reservoirs. The local ponds themselves are significant reservoirs of toxins that gather and cause deterioration of water quality and increased phytotoxicity.

Therefore, it is advisable to continue monitoring the seasonal changes in the toxic properties of water to prevent possible ecological catastrophe, to determine the qualitative composition of water pollutants. Such studies may provide information for the development of sustainable management of town's water resources.

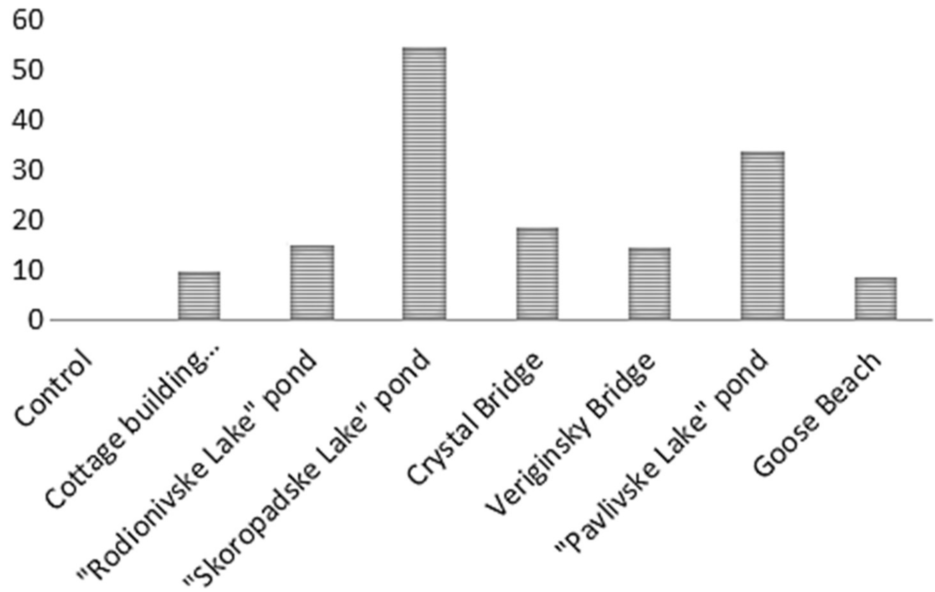

Fig. 1. The average phytotoxic effect of water in the study samples (in %)

The Esman River is one of the minor rivers in Ukraine, and it plays a significant role in the development of the social environment of Hlukhiv. Yet, excessive and irresponsible use of biological resources of the river and its water (water abstraction for irrigation and other household needs, use of water for washing vehicles, pollution of river runoff with wastewater, cutting off coastal plantations, etc.) have affected its natural state, hydrological regime, deteriorated water quality.

All of these have led to the depletion of the aquatic life of this water body. Esman grinds, mulches, the amount of bottom sediments in which heavy metals, pesticides and other harmful substances accumulates.

For the sustainable development of this town and the restoration and preservation of the wonderful recreational zone - the Esman River and the ponds nearby, students of the Faculty of Natural, Physical and Mathematical Education have prepared the recommendations for local authorities to protect the Esman River.

The measures should be the following:

– strict control and compliance with the environmental legislation with regard to the construction and agricultural use of coastal areas;
– carrying out sanitary monitoring of the river conditions and determining the factors of deterioration of its ecological state;

- on the basis of research, there should be the scientifically backed development of measures to remove / reduce the impact of the sources of environmental degradation of the river;
- implementation and use of the polluter-pays principle;
- reproduction of fish stocks on the basis of scientifically justified measures;
- prevention of anthropogenic, water and wind erosion in the river valley by planting woody vegetation (trees and shrubs) along the banks of the valley;
- search and preservation of reservoirs supply sources, their protection.

4. Summary and Conclusion

Thus, the public involvement in assessing the environmental quality, in particular, of future biology teachers within the framework of the organization of individual research tasks allowed:

- Firstly, to start developing an evidence base for local government decision-making based on monitoring studies of water quality in the minor river Esman, which is of great importance for Hlukhiv;
- Secondly, to establish partnerships and feedback provision between the authorities and the community of town and to develop recommendations that will improve the state of town’s water reservoirs.
- Thirdly, informing the population about the results of the study on the quality of surface waters. This will contribute to the development of environmental component of urban ecosystem sustainability. On the other hand, a wide public involvement in these activities will improve the social sustainability by engaging Hlukhiv citizens into addressing important socio-environmental issues of the community. This enables the formation of environmental responsibility for future generations and mastering sustainable environmental management skills;
- Fourthly, organizing and conducting such studies by students, covering the results of their own research in the media, have enhances the development of research and communication competences of future biology teachers.

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Mathematical model of dynamics of the process of simultaneous adsorption of copper and chromium ions

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Abstract

The process of joint adsorption of copper and chromium ions by natural zeolite of the structure of clinoptilolite from aqueous solutions in a column type apparatus was considered. The adsorption isotherms of separately taken copper and chromium ions on natural zeolite were presented and their satisfactory sorption capacities were shown.

It is noted that the heavy metals to which copper and chromium refer are toxic to the environment and the wastewater in which these elements are present is subject to mandatory cleaning. In sewage of industrial enterprises, in particular galvanic plants, not their individual components, but their mixtures may be present. The process of simultaneous absorption of copper and chromium ions in a columnar vertical apparatus filled with natural zeolite was investigated. The scheme of experimental installation was presented. The solution of salts of the two cations was fed into the column from top. A constant rate of filtration of water through the zeolite layer was established. At the exit of the apparatus water samples were taken for analysis of pollutants in them. According to the outcomes, the breakthrough adsorption curves were constructed. The breakthrough curves are presented separately for copper ions in the presence of chromium ions and chromium ions in the presence of copper ions for different layer heights. It is established that in the presence of copper and chromium ions, copper ions were absorbed and chromium ions were displaced. There was a chromatographic separation of the two components.

The breakthrough curves for the systems under study were mathematically described using the Thomas model, which provides a description of the breakthrough curve in a short layer with an exponential dependence that enables the determination of kinetic parameters. The transition to other heights was based on Laplace transforms.

Keywords: adsorption dynamics, heavy metals, wastewaters, mathematical model

1. Introduction

Technological wastewaters treatment processes on an industrial scale can be carried out either in machines with mechanical or pneumatic agitation (ideally these are ideal mixing devices) or in column type machines with a fixed adsorbent layer (ideal displacement devices). The development of new wastewater treatment technologies is necessary to ensure a proper environmental status. The low degree of pollution removal from wastewater containing heavy metals is a consequence of the low efficiency of existing wastewater treatment plants (Guo, et al., 2016). The need for stabilization of the precipitates formed requires additional costs. The need to develop new wastewater treatment technologies is also justified by the change in the nature and phase-dispersed state of heavy metal wastewater contaminants. Adsorption technologies are widely used in the wastewater treatment industry (Zhang et al., 2017). Adsorption processes consider the absorption of a component under static and dynamic conditions. The study of dynamics allows us to establish the distribution of the adsorbate in the liquid medium and the adsorbent in space and time. Based on the dynamics of sorption was determined when the phenomenon of "leakage", that is, the concentration of the substance at the outlet of the layer of adsorbent, which is unacceptable for discharge of wastewater into natural reservoirs. This is necessary to ensure the efficient operation of the equipment and to ensure the necessary degree of wastewater treatment.

Our technology of adsorption purification of wastewater containing heavy metals, using natural sorbent, allows solving the problems of reducing the aggressiveness of the environment, has low energy intensity and can be implemented in a wide range of changes in the composition of wastewater.

In previous studies, the adsorption properties of the zeolite of the Transcarpathian deposit, based on clinoptilolite to Cu (II) and Cr (VI) ions were studied (Sabadash et al., 2017). It was found that the adsorption isotherm is s-shaped and belongs to type II isotherms. It was found that after the formation of the monomolecular adsorption layer, the adsorption proceeds. This process continues to the forming of a bimolecular layer. The co-absorption of copper (II) and chromium (VI) ions in the anionic form on the natural zeolite was investigated and its adsorption capacity during their co-absorption was determined. A significant difference in its sorption capacity was found, which is significantly higher for copper cations than for the anionic form of chromium. The elemental composition of the sorbent surface after absorption of heavy metals from a two-component system containing Cu^{2+} and Cr^{3+} ions was studied by X-ray fluorescence method. The mechanism of copper and chromium ions sorption from bi-component solution was theoretically substantiated. We established that the selectivity of metal recovery depends to the radius of the element and the solubility of its hydroxides (Hyvlud et al., 2019). The conditions of the heavy metals hydroxides precipitation were calculated and a logarithmic diagram of the two-component system composition depending on the pH was constructed.

The adsorption dynamics provides for the determination of the adsorbate concentration at the out of the adsorbent layer during fluid motion (Futalan et al., 2019; Hu et al., 2019). The use of this method allows the wastewater to be cleaned of toxic pollutants with a high degree of adsorbent capture (Lü et al., 2019). Analytical models of adsorption dynamics obtained on the basis of the differential molecular diffusion equation for an individual adsorbent grain with initial and boundary conditions supplemented by the material balance equation for a fixed layer (Yan et al., 2019). The obtained analytical solutions of Rosen are characterized by complexity and cumbersome (Petrus et al., 1998; Yada et al., 2018; Gao et al., 2019). The most commonly used approximate solutions that determine the change in concentration over time depending on the height of the layer, which is represented in dimensionless form.

The proposed analytical solutions allow obtaining initial concentrations from the adsorbent layer of different heights. Solutions are made using dimensionless parameters (Naidu and Mathews, 2019). One of the parameters is the dimensionless length of the layer ω, which is obtained as a result of the theoretical solution of the system of differential equations of dynamics and is:

$$\omega = \frac{\sigma D^* z}{v R^2} \tag{1}$$

where: D^* – the effective diffusion coefficient in the adsorbent particle [m^2/s], z – the fixed layer height [m], v – the velocity of the fluid [m/s], R – the radius of the particles [m], σ – the porosity of the layer [m^3/m^3].

The dimensionless length of the layer is significantly influenced by the adsorption isotherm. Given that the concentration of harmful substances in wastewater is negligible, the adsorption isotherm can be represented by the Henry's equation:

$$C_a = \Gamma \cdot C \tag{2}$$

where: C_a – adsorption capacity [kg/m^3], C – concentration of adsorbent in liquids [kg/m^3], Γ – Henry's constant [m^3/m^3].

Taking into account the adsorption equation, the dimensionless length of the layer will be:

$$\omega^* = (1 + \Gamma) \cdot \omega \tag{3}$$

The approximate solutions given in the literature (Tyzhbir et al., 2009) for two cases $\omega^* \ll 1$ and $\omega^* \gg 1$ have the form:

a) for $\omega^* \ll 1$:
$$\frac{C_0 - C}{C_0 - C_K} = 1 - \omega^* \sum_{n=1}^{\infty} \frac{6Bi^2}{\mu_n^2 + Bi(Bi-1)} e^{-\mu_n^2 Fo} \tag{4}$$

b) for $\omega^* \gg 1$:
$$\frac{C_0 - C}{C_0 - C_K} = \frac{1}{2}\left(1 + erf\frac{Fo - \omega^*}{\sqrt{\frac{3}{4}\omega^*\left(\frac{1}{Bi} - \frac{1}{5}\right)}}\right) \tag{5}$$

where in equations (4) and (5): C_0 – initial concentration of the adsorbent in the liquid[kg / m^3], C – the current concentration of the adsorbent in the liquid at the outlet of the column apparatus [kg/m^3], C_K – the given final concentration of the adsorbent in the liquid [kg/m^3], $Bi = \beta \cdot R/D^*$ – Biot number; $Fo = D^* t/R^2$ – Fourier diffusion number, t – time [s].

As can be seen from equation (3), the dimensionless layer length is greatly influenced by the isotherm index in the region of low component concentrations in the liquid phase. According to the value of ω, approximate solutions were obtained for the quantities $\omega << 1$ and $\omega >> 1$, which is not always true for real layers. As shown below, we used the approximate Thomas model, which is based on the representation of the exponential change in concentrations for low layer heights, when the initial concentrations begin from the moment adsorption begins. For values $\omega << 1$ and $\omega << 1$, the description is exponential, which allows the use of this model. The following is a theoretical analysis of the Thomas model and its use.

We carried out a number of studies on the adsorption dynamics for various substances on the natural zeolite of the clinoptilolite structure. Breakthrough concentrations were theoretically and experimentally determined and their values were compared.

The dynamics of the sorption process of α-oxypropionic acid, copper, and a solution of a mixture of salts of copper (II) and chromium (iii) with natural zeolite were investigated in a column type apparatus. The results of experimental studies of the dynamics of sorption and ion exchange absorption of these substances by zeolite in a column-type apparatus depending on the height of the sorbent layer were presented, and the breakthrough curves were obtained.

The existing theoretical apparatus for describing adsorption processes was analyzed. Methods have been developed for identifying experimental data to theoretical models. The equilibrium adsorption layer was determined for which the initial concentration is numerically equal to the equilibrium concentration. This concentration is commensurate with the average adsorption in this layer. This allows us to simplify the solution of problems of obtaining the initial adsorption breakthrough curves under dynamic conditions, which can be easily obtained based on the data of adsorption isotherms.

To mathematically express the relationship between the concentration of the studied substances and the sorption time at a certain rate of transmission of the solution through the adsorption column, the Thomas model was used. The model relates the concentration at the outlet of the column to the transmission rate of the solution. The volumetric rate is not directly included in the linear dependence; it is implicitly included at any time of sorption, which is equal to the volume of the filtered solution divided by the volumetric rate. The model is used for the initial concentration range (0.08–0.93) · C_0 and fairly correctly describes the process of monomolecular adsorption, for which the Langmuir isotherm is valid.

The model also provides that the sorption process is controlled by mass transfer processes between solid and liquid phases. The amount of adsorbate that is retained in the column corresponds to the area under the breakthrough curve in *C-t* coordinates and was calculated by numerical integration.

Experimental data were identified by a theoretical model. According to the results of experimental studies, the coefficients of the dynamics of the adsorption process in the column type apparatus were determined (Jurtz et al., 2019).

During the study of the dynamics of adsorption, the change in the concentration of the adsorbent and adsorbate in time is determined ($C = f(\tau)$, $a = f(\tau)$). If the process is in the fixed-bed column, then these concentrations are not only functions of time, but also the height of the layer. The equations of external and internal diffusion were supplemented not only by boundary conditions, but also by the differential equation of material balance, which significantly complicates the obtained solutions. Analytically obtained solutions, for example, Rosen's solution (Petrus et al., 1998), because of their complexity it is not always can be used for practical calculations.

2. Materials and Methods

The processes of sorption dynamics were studied in a column type apparatus with a fixed sorbent layer by natural zeolite of the Sokirnytsa deposit, the main part of which (~85%) was clinoptilolite. The experiments were carried out at a temperature of 20°C. In all cases, the following amount of zeolite was loaded into an adsorption column with a diameter of 1.5 cm, depending on the required height of the sorbent layer: h = 2 cm to 4 g ,h = 5 cm to 10 g, h = 7 cm – 14 g, h = 20 cm to 40 g. Samples of the solution were taken at regular intervals (1 min, 3 min, 5 min, 7 min, 10 min and every 20 min until equilibrium was established). The concentrations of the studied solutions were determined by the photometric method.

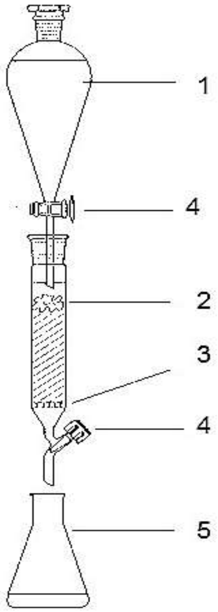

Fig. 1. The experimental setup: 1 – dividing funnel with eluent; 2 – zeolite; 3 – lattice, 4 – tap, 5 – receiver for collecting fractions

The studies were carried out on an installation (Fig. 1), which works according to the following scheme. The model solution is supplied from the separating funnel 1 into an adsorption column with zeolite backfill 2. The sorbent is poured onto the grid 3 with low-density sandpaper (black tape). The filtering speed is regulated by tap 4 in the dividing funnel 1. The tap of the machine column must be fully open. The filtrate was collected in the tank 5 at the established time intervals and analyzed by potentiometric method on the ion meter IM-160M.

3. Results and Discussion

3.1. Mathematical model of adsorption dynamics of wastewater components

The mathematical analysis of adsorption dynamics bases on a system of differential equations. The obteined solutions are only possible with considerable simplifications (Futalan et al., 2019), (Hu et al., 2019).

For the mathematical expression of the relationship between the concentration of α-oxypropionic acid and the time of sorption at a certain speed of passing the solution through the column, we used the Thomas model, which is the simplest and most convenient. Breakthrough curve in this model begins from the beginning of adsorption. The breakthrough curve for the short layer describes by the following expression:

$$\frac{C}{C_0} = 1 - ae^{-\lambda Fo} \tag{6}$$

where: λ – the model constant, a – proportionality factor.

The values of C/C_0 for other lengths of layer Z are obtained on the basis of the Laplace transforms, according to which certain function N dependent to the concentration, changes depending on:

$$N''_n = \frac{1}{p}(pN^1)^n$$

$$N' = \frac{\lambda}{p(\lambda + 1)} \tag{7}$$

$$N'' = \frac{\lambda''}{p(\lambda + 1)^n}$$

where: p – Laplace parameter.

The transition to the original function bases on the transition tables from the image to the original. The original approximate solution has the form:

$$\left(\frac{C}{C_0}\right)_n = 1 - \left[\lambda Fo + \frac{(\lambda Fo)^2}{2!} + \cdots + \frac{(\lambda Fo)^{n-1}}{(n-1)!}\right] e^{-\lambda Fo} \tag{8}$$

where: n – the integer length of the layer $n = 2, 3, \ldots, Z_2 = n \cdot Z_1$.

The model binds the concentration at the outlet of the column to the solution flow rate. And although the linear velocity was not directly included in the linear dependence, it implicitly enters at any time the sorption, which was equal to the volume of the filtered solution divided by the volume velocity. The model was applied to the range of initial concentrations (0.08–0.93) · C_0 and sufficiently correctly describes the monomolecular adsorption process for which the isotherm holds. The model also assumes that the sorption process was controlled by mass-exchange processes between the solid and liquid phases. We have tested the application of this model on the absorption of a one-component solution of α-oxypropionic acid by natural zeolite in the adsorbent layer $Z = 2$ cm.

The amount of α-oxypropionic acid, which is retained in the column, corresponds to the area under the breakthrough curve in the $C - t$ coordinates and is calculated by numerically integrating the breakthrough curves.

To determine the coefficients λ and a take the logarithm of the equation (6):

$$ln\left(1-\frac{C}{C_0}\right)=ln(a)-\lambda Fo \tag{9}$$

The transition to other lengths of the adsorbent layer can be performed based on the following approximate solution:

$$\left(\frac{C}{C_0}\right)_n=1-\left[1+\lambda Fo+\frac{(\lambda Fo)^2}{2!}+\cdots+\frac{(\lambda Fo)^{n-1}}{(n-1)!}\right] \tag{10}$$

where: n – the multiplied of the layer height.

To determine the coefficients λ and a we construct the logarithmic dependence for the experimental results according to (9).

From Fig. 2 we determine $ln(a) = -3 \cdot 10^{-16}$, $a = 1$, $\lambda = 24868$.

A curve describing adsorption in a 2 cm layer will look like this:

$$\frac{C}{C_0}=1-1.0e^{-24868Fo} \tag{11}$$

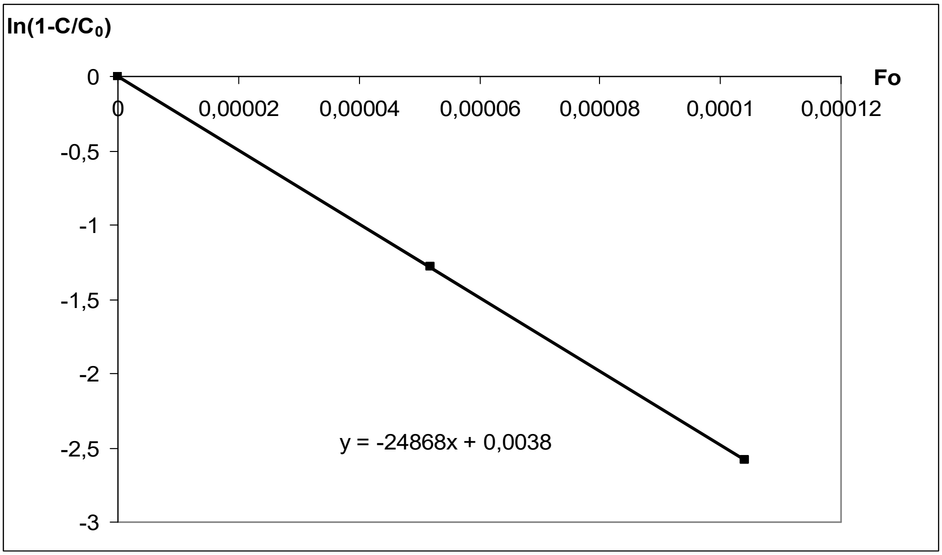

Fig. 2. Breackthrough curve of α-oxypropionic acid sorption in a fixed-bed column-type apparatus with height of zeolite layer $Z = 2$ cm in logarithmic coordinates

The approximate solution of the equation (6) at the layer length z = 6 cm, which lies between the heights 5 and 7 cm was verified. Let us represent the dependence (6) at real intervals of time, expressed in minutes, as in Fig. 3.

Since the value of the breakthrough curve obtained for the layer of 2 cm high, the height 6 cm will be a multiple of 3. Accordingly, the equation for the layer height $z = 2$ cm, in which we enter the real time in minutes, will be determined by:

$$\frac{C}{C_0} = 1 - \left[1 - \lambda_1 \cdot \tau + \frac{(\lambda_1 \cdot \tau)^2}{2!} + \cdots + \frac{(\lambda_1 \cdot \tau)^3}{3!}\right] \tag{12}$$

Determined according to (12) the value of the parameter $\lambda_1 = 0.012$ 1/min. The calculation of the breakthrough curve according to (9) was shown in Fig. 3.

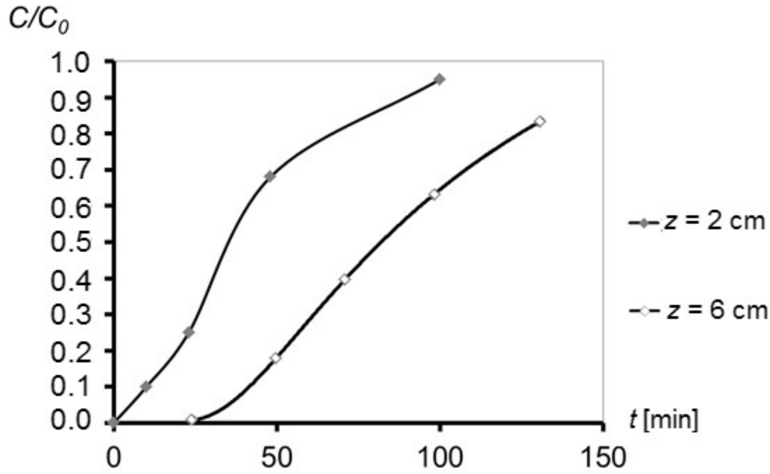

Fig. 3. The breackthrough curve calculated according to (12) for a layer heights of $z = 2$ cm and $z = 6$ cm

The values in Fig. 3 allows an approximate calculation of the initial curve by using outcomes of previously set experiment on a low-altitude layer and obtaining an breakthrough curve that can be approximated by an exponential dependence.

3.2. Experimental

Investigation of the process of sorption of cuprum and chromium ions by natural zeolite under dynamic conditions was carried out in a column type apparatus. The solution was fed from the top of the column, passed through a layer of adsorbent of different heights and collected in the receiver of purified water. Liquid volume measurements were made at specific intervals. The selected samples were analyzed for the content of copper and chromium ions. The initial curves for different heights of the zeolite layer were shown in Fig. 4 and Fig. 5.

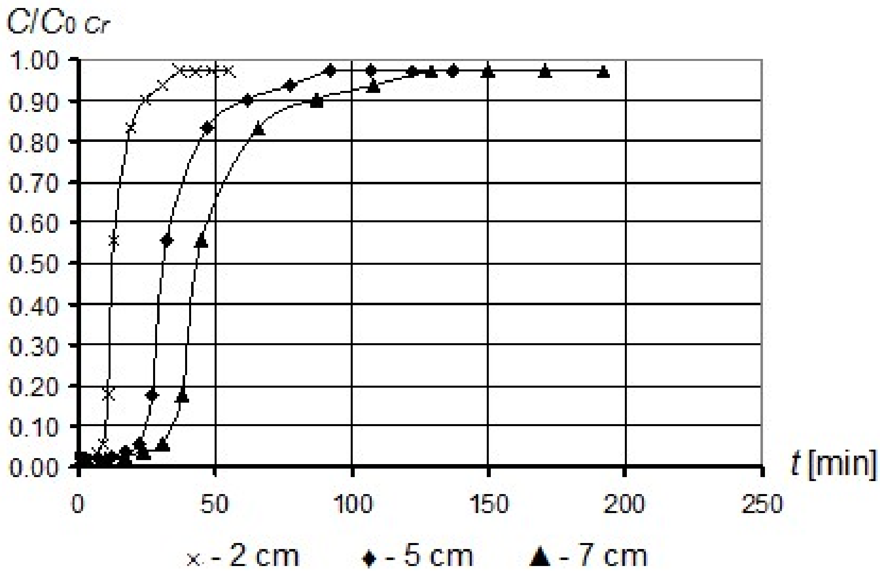

Fig. 4. The breakthrough curve of Cr^{3+} sorption from the bi-component solution depending on the height of the sorbent layer

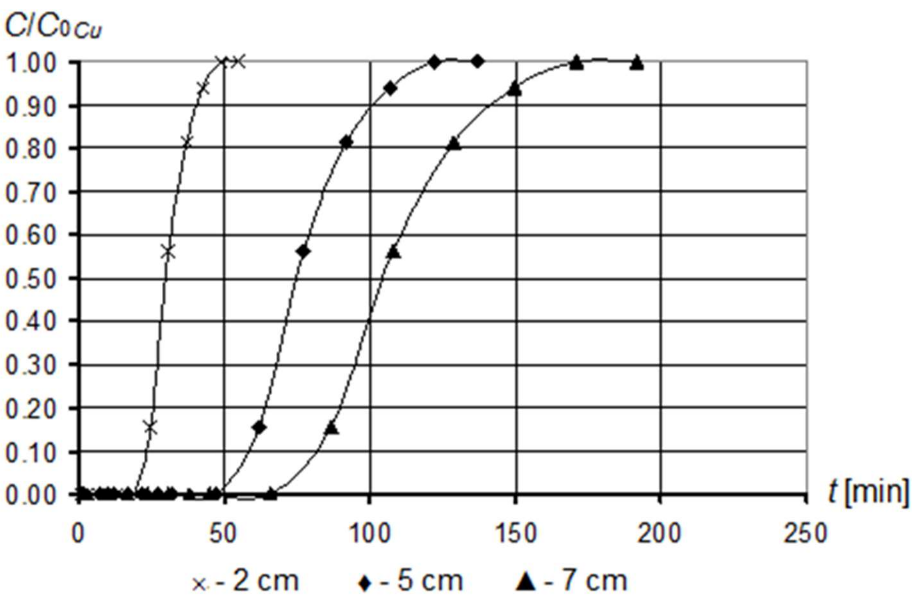

Fig. 5. The breakthrough curve of Cu^{2+} sorption from the bi-component solution depending on the height of the sorbent layer

From the above data it is clear that under the conditions of the hydrodynamic regime of the process of adsorption of copper and chromium ions on the zeolite there is a mixed diffusion mechanism of adsorption. With insufficient height of the sorbent layer, even if the solution flow rate is 3 ml/min, a small amount of contaminant penetrates from the first minutes of the experiment. Therefore, the minimum height of the sorbent layer should be at least 5 cm.

The breakthrough curves shown in Fig. 4 and 5 relate to the adsorption of a two-component system when copper and chromium cations are present in the wastewater. In Fig. 4 shows the breakthrough sorption curves of Cr^{3+} ions on a fixed adsorbent layer in the presence of Cu^{2+} ions. If we compare the breakthrough curves for Cr^{3+} ions (Fig. 5) with the original curves for Cu^{2+} ions, we see that for the same time, the breakthrough occurs much later for the breakthrough of chromium ions. This indicates the displacement of chromium ions by copper ions. Chromatographic separation of ions occurs. The Cu^{2+} ion remains on the zeolite, the Cr^{3+} ion leaks out of the apparatus.

As the analysis of the adsorption isotherms of Cu^{2+} ions (Fig. 6) and Cr^{3+} (Fig. 7) shows, the static activity of these components is quite high and is approximately at the same levels. Thus, the obtained data of the dynamics of sorption of the two components indicate the presence of chromatographic separation of these components.

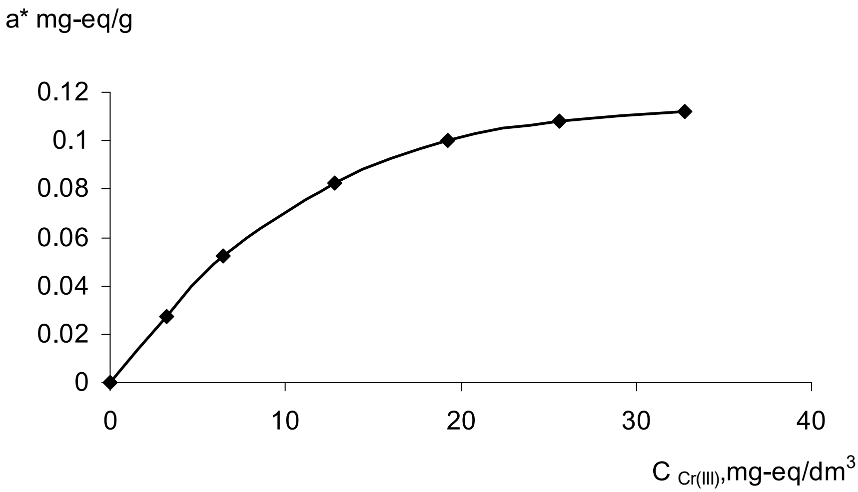

Fig. 6. Adsorption isotherm of chromium (III) cations by natural zeolite

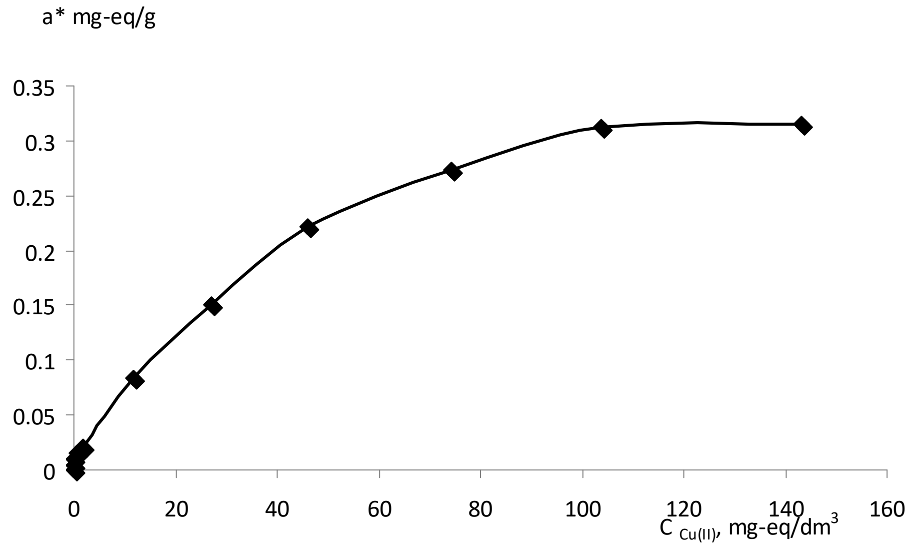

Fig. 7. Adsorption isotherm of copper (II) cations by natural zeolite

Mathematical analysis of adsorption dynamics was based on a system of differential equations, the solution of which is possible only with considerable simplifications.

For the mathematical expression of the relationship between the copper and chromium ions concentration and the time of sorption at a certain rate of passing the solution through the column, we used the Thomas model, which is the simplest and most convenient. The equation of the breackthrough curve for the certain layer describes by model (3)–(5). This model relates the concentration at the outlet of the column to the solution throughput rate. And although the linear velocity was not directly included in the linear dependence, it implicitly enters at any time of the sorption, which is equal to the volume of the filtered solution divided by the volume velocity. The model was applied to the range of initial concentrations (0.08–0.93) $\cdot$ C_0 and sufficiently correctly describes the monomolecular adsorption process for which the Langmuir isotherm equation. The model also assumes that the sorption process was controlled by mass transfer processes on the boundary of solid and liquid phases. The amount of copper and chromium ions retained in the column corresponds to the area under the breakthrough curve in the $C - t$ coordinates and was calculated by numerical integration. At an initial concentration of copper and chromium ions of 0.015 kg/m^3, an initial curve of adsorption of copper and chromium ions under dynamic conditions was constructed on the adsorbent layer with a height of Z = 2 cm (Fig. 6, Fig. 7).

To determine the coefficients λ and a, we took the logarithm of Eq. (6):

$$ln\left(1-\frac{C}{C_0}\right) = ln(a) - \lambda Fo \tag{13}$$

From the graph (Fig. 8) we determine $ln(a) = 3.5365$, $a = 34.34$, $\lambda = 3.899$.

The breakthrough curve equation for the certain layer of zeolite at the adsorption of copper ions will look like:

$$\frac{C}{C_0} = 1 - 3.5365e^{-3.889Fo} \tag{14}$$

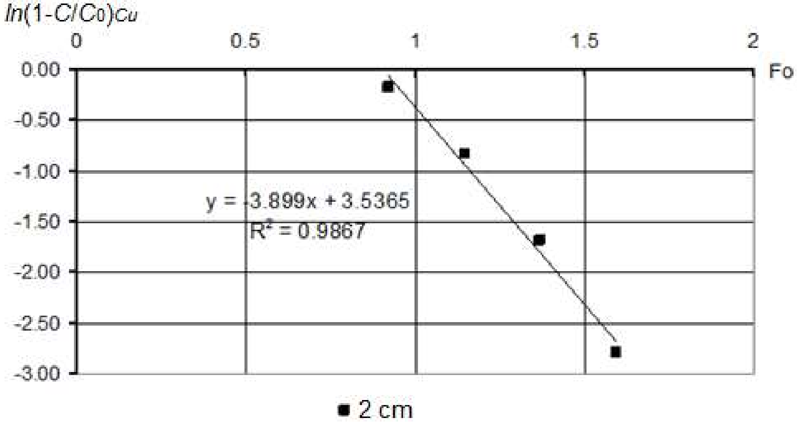

Fig. 6. Breakthrough curve of copper ions sorption at Z = 2 cm in linear coordinates

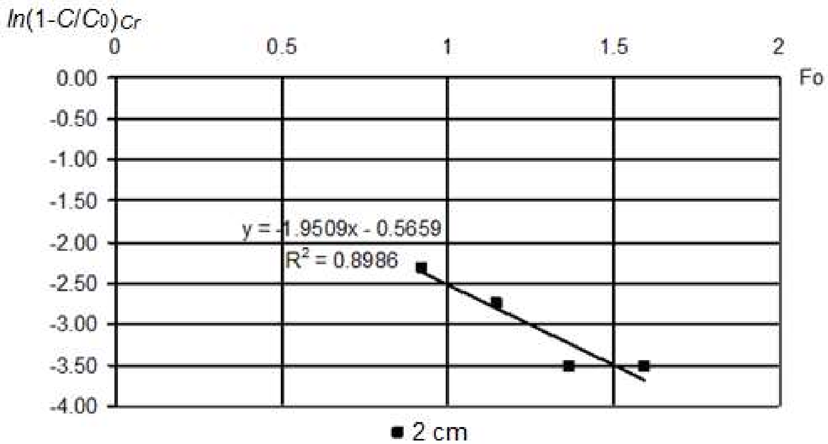

Fig. 7. Breakthrough curve of chromium ions sorption at Z = 2 sm in linear coordinates

From the graph (Fig. 9) we determine $ln(a) = 0.5659$, $a = 0.5678$, $\lambda = 1.9509$. The breakthrough curve equation for the certain layer of zeolite at the adsorption of chromium ions will look like:

$$\frac{C}{C_0} = 1 - 0.5659e^{-1.9509Fo} \tag{15}$$

The transition to other lengths of the adsorbent layer can be performed based on the following approximate solution:

$$\left(\frac{C}{C_0}\right)_n = 1 - \left[1 + \lambda Fo + \frac{(\lambda Fo)^2}{2!} + \cdots + \frac{(\lambda Fo)^{n-1}}{(n-1)!}\right] \tag{16}$$

where: n – a multiple layer height.

The results of experimental studies allow us to determine the coefficients of the sorption process of copper and chromium ions in a column type apparatus.

4. Summary and Conclusions

The results of experimental studies and theoretical calculations of the adsorption efficiency of copper and chromium ions depending on the height of the zeolite layer in the column-type apparatus were presented. The breakthrough curves of the adsorption dynamics of copper and chromium ions of zeolite in a column-type apparatus were constructed. The protective action time and the slip time for the different sorbent height were set. The experimental data on the dynamics of adsorption of copper and chromium ions by zeolite in a column type apparatus were presented.

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Iron ions removal from wastewater by aquatic plant 'Lemna minor'

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Abstract

Food production enterprises wastewater could have significant concentrations of total iron that must be treated. Aquatic macrophytes, for example *lemna* genera, have high potential for iron ions removal, but kinetics and treatment parameters should be qualified.

The aim of the work is to increase in the efficiency of removal of iron ions from wastewater in the process of biological wastewater treatment using '*Lemna minor*' and to determine rational parameters of the treatment (biomass, process duration, hydraulic load).

The kinetics of the removal of iron ions from water was studied in the batch mode of a biological reactor operation under various biomass quantities. Verification of the obtained rational parameters of the process was carried out under continuous mode conditions. The results obtained from the kinetics of the periodic mode the bioreactor operation process indicate an increase in the degree of removal of ferrous ions from wastewater from 61.0% to 91.7% with an increase in the plant biomass concentration from 8 mg/L to 25 mg/L during the wastewater treatment process of 24 hours.

The rational parameters of removal of iron ions from wastewater in the batch mode of the bioreactor operation are determined: biomass of duckweed is 25 mg/L; the treatment process duration is 8 hours; the hydraulic load is 0.126 L/(h·L). The purification effect was 89.8%.

Keywords: wastewater, waste, duckweed, iron ions, purification, biomass, hydraulic loading

1. Introduction

At industrial enterprises, large volumes of hazardous waste that are in need of processing are formed. The introduction of new production technologies, the change in the range of products produced, leads to the formation of a new composition of waste components that require recycling. For example, highly concentrated wastewater is characterized by a significant content of organic substances, compounds of nitrogen and phosphorus, heavy metal ions, and others. Today, physicochemical methods are used to provide highly effective treatment of wastewater contaminated by heavy metal ions (Qasim and Mane, 2013; Melnyk et al., 2015) . The use of coagulants and flocculants is associated with the constant consumption of reagents and the formation of large volumes of sediments. Ion-exchange materials are expensive and require the use of chemical reagents for their regeneration. Biological methods of water treatment, for example, using higher aquatic plants (duckweeds) that do not require complex equipment and the addition of chemical reagents, can be attributed to promising methods.

Wastewater from industrial enterprises can contain significant concentrations of heavy metal ions, in particular, iron up to 14 mg/L (Qasim and Mane, 2013).

A number of scientists studied the heavy metal ions removal from the water of various origin by duckweed '*Lemna minor*' (Miretzky et al., 2004; Teixeira et al., 2014; Bokhari et al., 2016; Petrakova and Anischenko, 2016). At the wastewater treatment, a high degree of ion ferrous removal was obtained in 4–5 days, which was 80 ± 5% (Miretzky et al., 2004). To date, no information has been found on the effect of duckweed planting density on the kinetics of the process and on the degree of removal of iron ions from water. *L. minor* has a high potential for removal a wide range of pollutants such as phosphorus, nitrogen, fluorine, copper, manganese, arsenic, cadmium, chromium, nickel, and ferrous from wastewater (Hozhina et al., 2001; 5 Miretzky et al., 2004; Hou et al., 2007; Teixeira et al., 2014). It is known that *L. minor* grows well and is stable in an environment with organic contamination and doubles its mass for 5–6 days (Konontsev et al., 2018).

The iron in wastewater may be presented in the form of Fe (II), Fe (III), and ferrous organic compounds (Kvartenko, 2017). Fe (II) accumulates in the form of an oxidized film Fe (III) on the fronds and roots of plants due to oxygen release from the roots (Teixeira et al., 2014). The formation of such a film promotes the adsorption of phosphorus compounds from water (Yang et al., 2011). The mechanism of Fe (III) uptake into the duckweeds cell occurs due to the preliminary reduction of Fe (II) by ferric-chelate reductase at the surface of the cell membrane and subsequent transfer of Fe (II) into the cell by transport protein (Marschner and Römheld, 1994). A chelating agent is required for the process (Brüggemann, 1993; Nikolic and Römheld, 1999).

In the presence of heavy metals ions in the environment of higher plants, phytochelatins are produced in the form of peptide tails constructed from γ-glutamylcysteine on the cell wall (Grill et al., 1987). The mechanism is well studied in the model organism *Arabidopsis thaliana* and is characteristic of most plants, except herbs (Kim et al., 2007). The partial absorption of Fe (III) ions by the cell wall is possible, however, according to the results of studies (Olsen and

Miller, 1986), the iron ions is subsequently transported to the plant by the above mechanism. Further, the Fe (II) accumulates in cells of the leaf's mesophyll and serve as a catalyst in the synthesis of chlorophyll at the stage of formation of aminolevulinic acid and the synthesis of protoporphyrin. Iron is required in the synthesis of cytochromes (Schimdt, 2002).

The aim of the work is to increase in the efficiency of removal of iron ions in the biological wastewater treatment process using '*Lemna minor*' and to determine rational parameters of the treatment process (biomass, process duration, hydraulic load).

To achieve the aim the following objectives were investigated:

- to study the effect of the biomass concentration of duckweed from 8 to 25 g/L on the kinetics of removal of iron ions in the process of biological wastewater treatment in the contact conditions of the bioreactor for 24 hours at a concentration of iron ions in wastewater of 2 mg/L;
- to determine rational technological parameters of the bioreactor: the duration of treatment, hydraulic load, the biomass concentration of duckweed, the effect of removing of iron ions from the wastewater;
- to apply the obtained values of the parameters in continuous mode of the bioreactor operation and determine the rational biomass concentration and the duration of the process of removal of iron ions from water.

2. Materials and Methods

The '*Lemna minor*' was picked from a cultivator and grown in non-sterile conditions on a modified Steinberg medium, the composition of which is given in Tab. 1. The cultivation temperature was 26 ± 1 °C. One third of water volume was replaced once a week. The illumination was provided by a fluorescent lamp (illumination of 3000 lux, light day 12 hours).

The selected duckweed was placed on a filter net with 0.5 mm holes and washed with distilled water, after which it was left for 5 minutes to separate excess water. Then duckweed, necessary for the experiment, was weighed. Weighing samples of duckweed was performed using OHAUS Scout Pro SPU123 weights.

Table 1. The composition of the modified Steinberg medium

Name	Concentration, mg/L	Name	Concentration, mg/L
KNO_3	350.00	$ZnSO_4 \cdot 7H_2O$	0.18
$Ca(NO_3)_2 \cdot 4H_20$	295.00	$Na_2MoO_4 \cdot 2H_2O$	0.04
KH_2PO_4	90.00	$MnCl_2 \cdot 4H_2O$	0.18
K_2HPO_4	12.60	$NH_4Fe(SO_4)_2 \cdot 12H_2O$	1.33
$MgSO_4 \cdot 7H_2O$	100.00	Disodium EDTA	1.5
H_3BO_3	0.12		

A model solution simulating biologically treated wastewater was used (Yang et al., 2011). The composition of the solution is as follows: BOD_{20} – 20.0 mg/L; NO_3 concentration – 20.0 mg /L; PO_4^{3-} – 4.0 mg/L; Fe^{3+} – 2.00 mg/L. The pH of the model solution is 6.5. For the formation of organic complexes of Fe (III) disodium EDTA (1.5 mg/L) was added in the model solution. To prepare the model solution, reagents were used in the concentrations given in Tab. 2.

Table 2. Concentrations of reagents for preparing a model solution

Name	Concentration, mg/L	Name	Concentration, mg/L
KNO_3	17.50	$ZnSO_4{\cdot}7H_2O$	0.18
$Ca(NO_3)_2{\cdot}4H_20$	15.00	$Na_2MoO_4{\cdot}2H_2O$	0.044
KH_2PO_4	4.50	$MnCl_2{\cdot}4H_2O$	0.18
K_2HPO_4	0.50	$NH_4Fe(SO_4)_2{\cdot}12H_2O$	17.670
$MgSO_4{\cdot}7H_2O$	5.00	Disodium EDTA	1.5
H_3BO_3	0.12	Saccharose	41.00

The work was carried out on an experimental setup, which is depicted in Fig. 1. To feed the model solution the following elements were used: tank for solution 1; peristaltic pump 2 with a power of 7.5 W; intermediate tank 3 with a constant level of water; overflow pipe 4. Tanks 1 and 3 are made from polyethylene terephthalate. The flow rate was set by the Exadrop flow regulator 5 from 10 to 250 L/hour. Bioreactor 6 with a volume of 2.4 L with dimensions 220 × 310 × 47 mm, has a design depicted in Fig. 2. The volume of the bioreactor is divided into cells with holes in diameter of 5 mm, alternating in height. Water is drained through pipe 8 of 8 mm in diameter. All tubes are made from polyvinyl chloride. Water feeding was performed by a peristaltic pump. Lighting was provided by a fluorescent lamp 7.

The setup works as follows (Fig. 1). The model solution is fed from the tank 1 by pump 2 to the intermediate tank 3. The excess water returns to the tank 1 through the overflow pipe 4, thus providing a constant level of water in the intermediate tank. From the tank 3, water through the flow regulator 5 enters the bioreactor 6 with a given flow rate. In the bioreactor 6, wastewater gradually passes through the cells, contacting the duckweed in the surface layer. The water purification takes place. The illumination of the surface of a water mirror with the duckweed in the bioreactor was provided with a fluorescent lamp 7. The treated water was drained self-flowing through the pipeline 8.

The setup provided an illumination of 3000 lux with a working period of 12 hours. The water temperature in the bioreactor was within the range of 18–22°C, pH 7.0 ± 0.2. The temperature and pH were measured by a portable pH meter PH-035 (KL-035).

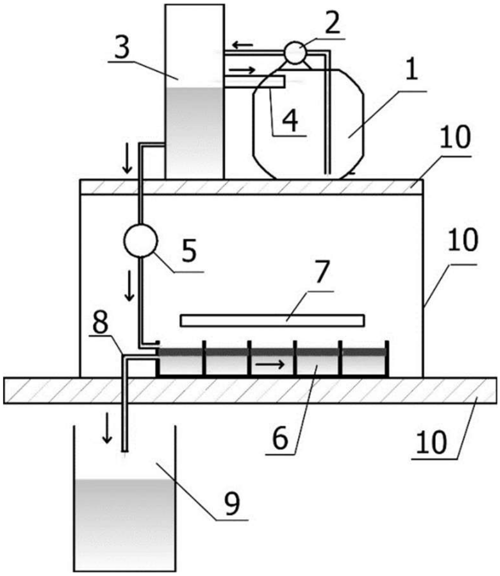

Fig.1. Scheme of the experimental setup: 1 – tank for solution, 2 – peristaltic pump, 3 – intermediate tank, 4 – overflow tube, 5 – flow regulator, 6 – bioreactor, 7 – fluorescent lamp, 8 – the drainage pipeline of treated water, 9 – water collector, 10 – support

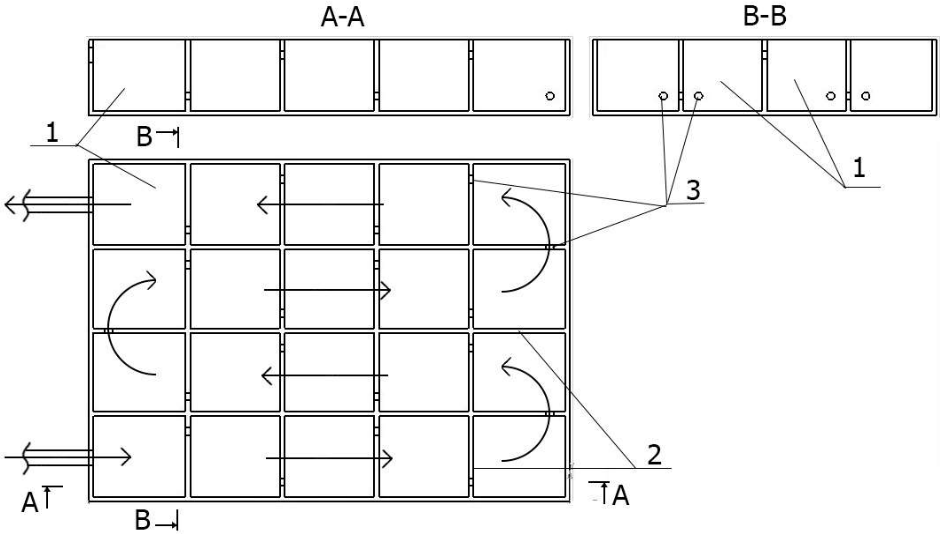

Fig. 2. Scheme of the design of a bioreactor: 1 – cells, 2 – partitions, 3 – holes

To determine the kinetics of the water treatment process, investigations were carried out in a batch mode with sampling during the day at biomass concentration of 8, 13, 17 and 25 g per 1 L of water. Total volume of model solution was 2.4 L. Sampling in the contact mode was performed with glass pipette from the last cell of the bioreactor at 0.5, 1, 2, 3, 4, 5, 6 and 24 hours. Volume of samples were 20 ml each. Batch mode investigations were carried out in duplicates.

Later, investigations were carried out in a continuous mode to check obtained results in batch mode and determine rational operational parameters. The setup operation cycle was $T = 7$ days, with the hydraulic residence time τ in the setup – 24 hours with biomass concentrations 25 and 17 g/L. The water flow was $Q = 0.1$ L/h; load on the bioreactor $q = 0.042$ L/(h·L). The load on the bioreactor is determined by the equation:

$$q = \frac{Q}{V} \tag{1}$$

where: Q – water flow rate [L/h], V – volume of bioreactor [L].

In addition, hydraulic residence time $t = 8$ h were checked – $Q = 0.3$ L/h; $q = 0.126$ L/ (h·L). Biomass concentration – 25 g/L. Sampling was performed at the outlet of the bioreactor with 50 ml volume of each sample.

All sampling were carried out in triplicates. Batch mode experiments were performed two times. Continuous mode experiments were performed two times.

The content of total iron ions was determined by spectrophotometric method with ammonium thiocyanate using a spectrophotometer ULAB 102 (wavelength error is 0.5 nm; Transmittance error is 0.5%). The purification effect was determined by the equation:

$$E = \frac{C_{in} \cdot C_{ef}}{C_{in}} \cdot 100, \% \tag{2}$$

where: C_{in} – iron ions concentration at the inlet of the bioreactor [mg/L], C_{ef} – iron ions concentration at the outlet of the bioreactor [mg/L].

3. Results and Discussion

The results obtained in batch mode (Fig. 1) show the dynamics of the water treatment process during 24 hours, which allows estimating the decrease in the concentration of iron ions at different biomass concentration. As is evident from the figure, the increasing of the process duration leads to a slowdown in the removal of iron ions. Slowdown can be explained by the processes of sorption on the surface of the roots and leaves of duckweed, on the one hand, and the decrease of the diffusion efficiency with a decrease in the difference in osmotic pressure between the aqueous medium and plant cells (Olsen and Miller, 1986; Brüggemann, 1993; Nikolic and Römheld, 1999).

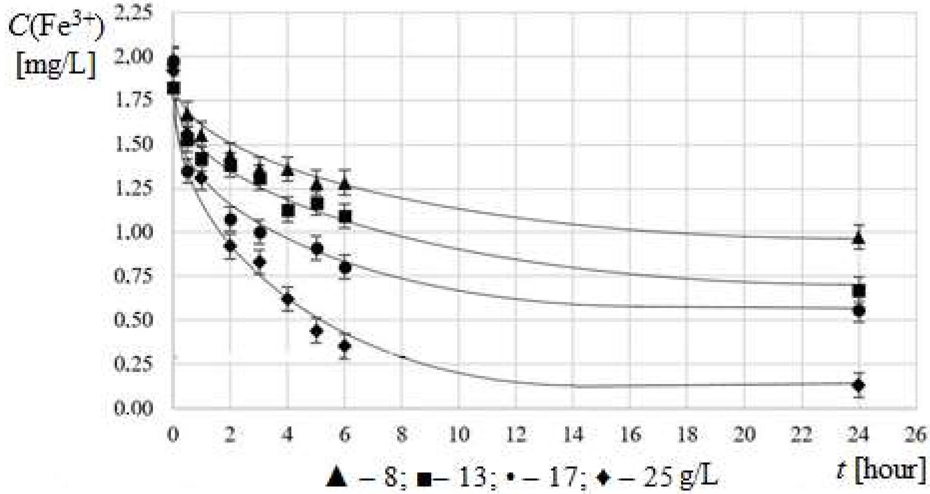

Fig. 1. Kinetics of Fe (III) ions removal from water vs hydraulic retention time *t* with specific biomass concentration in a batch mode

An increase of a biomass concentration from 8 to 25 g/L improves the treatment process – lower concentrations of iron ions in treated water are achieved. The results obtained at concentrations of 8 and 13 g/L and the removal rate of 61 ± 1.5% and 71 ± 1.5% (Fig. 2), respectively, are confirmed by data from (Hou et al., 2007), in which the removal effect of iron ions is 60% with a biomass concentration of 10 g/L. Concentration of iron ions is most rapidly reduced during 2 hours of the treatment process. The removal rate reaches 52.1% at a biomass concentration of 25 mg/L. With treatment duration of 2–8 hours, the removal of iron ions occurs more slowly, the concentration of iron ions reaches 0.26 mg/L, the removal effect is 87.8%. In the further research, with treatment duration of up to 24 hours, the iron ions concentration is 0.16 mg/L, the removal rate is 91.7%. At the same time, the change in the concentration of iron ions is little, so the process duration is not rational. Consequently, the preliminary rational process duration is 8 hours.

Studies in continuous mode were performed to verify the removal effect of iron ions in batch mode during the period of the bioreactor operation for 7 days.

The results obtained (Fig. 3) for the duckweed biomass concentration of 17 g/L show an insignificant fluctuations of total iron concentration in treated water with an average value of 0.72 ± 0.3 mg/L and the removal effect of 63.1 ± 1.5%. Obtained iron concentrations are higher in continious mode, than in batch mode with same hydraulic retention time 24 h and biomass concentration 17 g/L. This could correspond to temperature fluctuations in 18–22°C range.

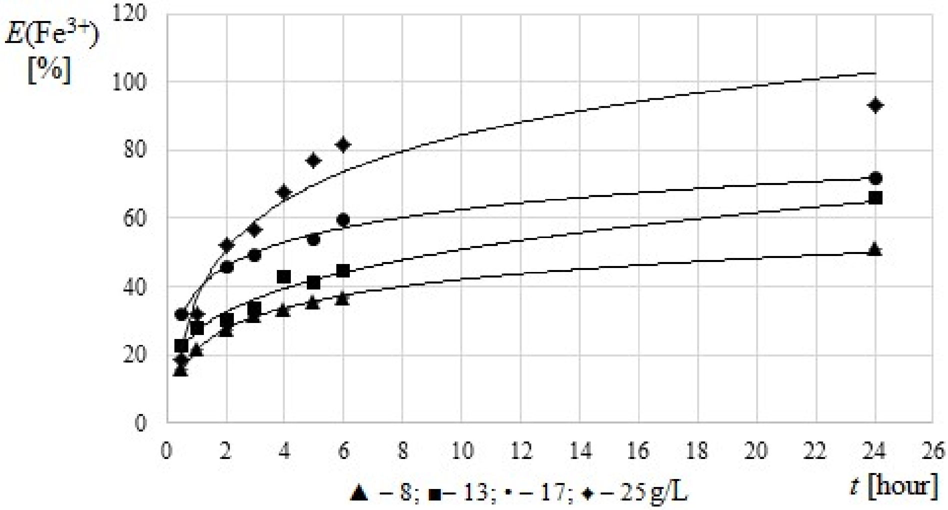

Fig. 2. Removal rate of Fe (III) vs hydraulic retention time *t* with specific biomass concentration in a batch mode

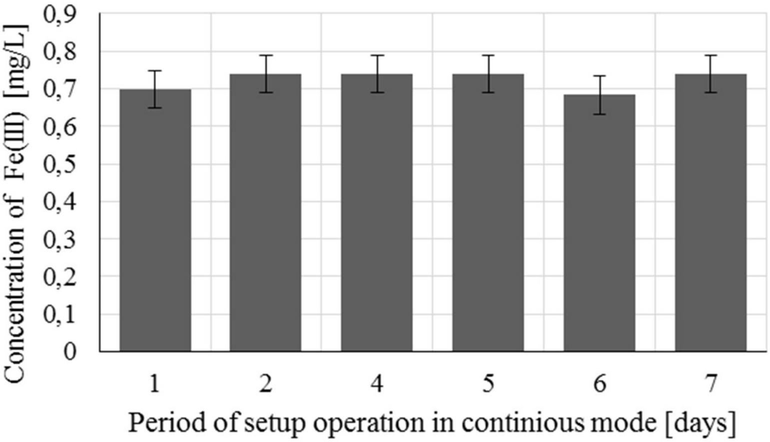

Fig. 3. Changes in the iron ions concentration in treated water with gydraulic retention time of 24 hours and the biomass concentration of 17 g/L in a continious mode

With a biomass concentration of 25 g/L (Fig. 4 and 5), the average total iron concentration in treated water is 0.16 ± 0.2 mg/L, the average removal effect is 91.7 ± 0.8% (error ± 0.05 mg/L). Therefore, the removal effect can be considered stable. Obtained iron concentrations in continious mode comparable with concentrations in batch mode with same hydraulic retention time 24 h and biomass concentration 25 g/L.

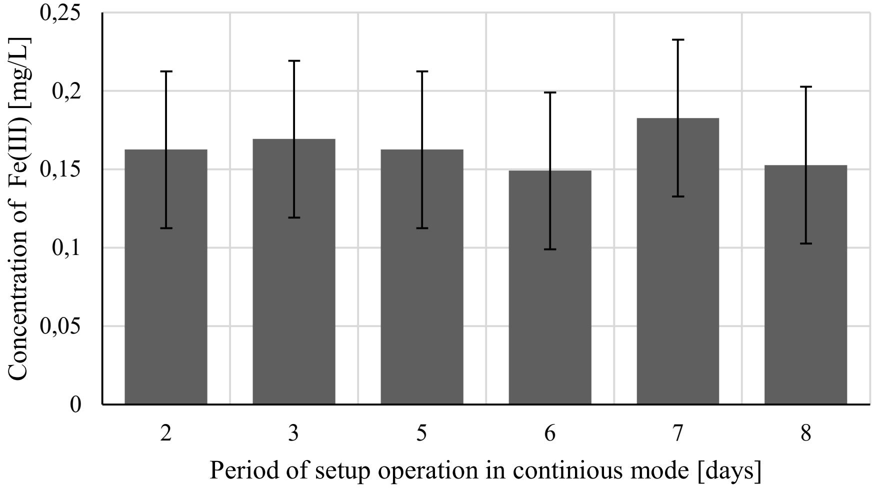

Fig. 4. Changes in the iron ions concentration in treated water with gydraulic retention time of 24 hours and the biomass concentration of 25 g/L in a continious mode

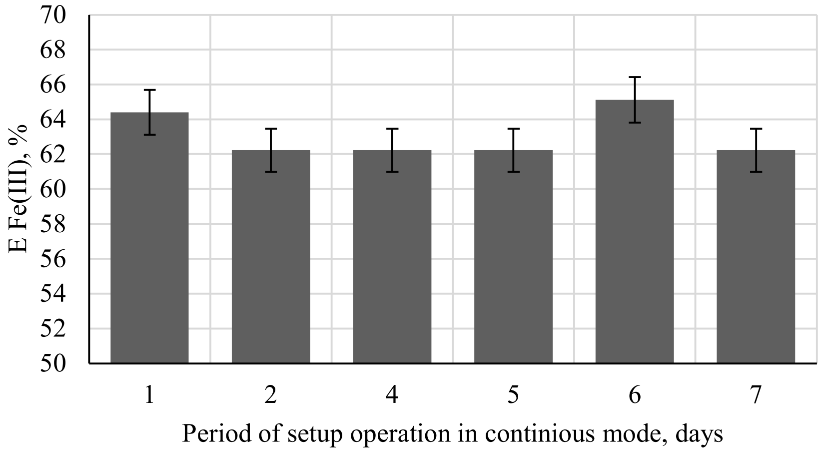

Fig. 5. Removal rate of iron ions in treated water with gydraulic retention time of 24 hours and the biomass concentration of 25 g/L in a continious mode

The results of iron ion concentrations in treated water obtained during in the batch mode with hydraulic residence time of 8 hours (as preliminary rational one) were checked in the continuous mode (Fig. 6 and Fig. 7). The period of the setup work was 7 days. The average concentration of iron ions in water was 0.24 ± 0.05 mg/L, the removal effect was 89.8 ± 2.5%. Fluctuations of the values of the concentration of iron ions in treated water were within the measurement error ± 0.05 mg/L. Obtained iron concentrations in continious mode comparable with concentrations in batch mode.

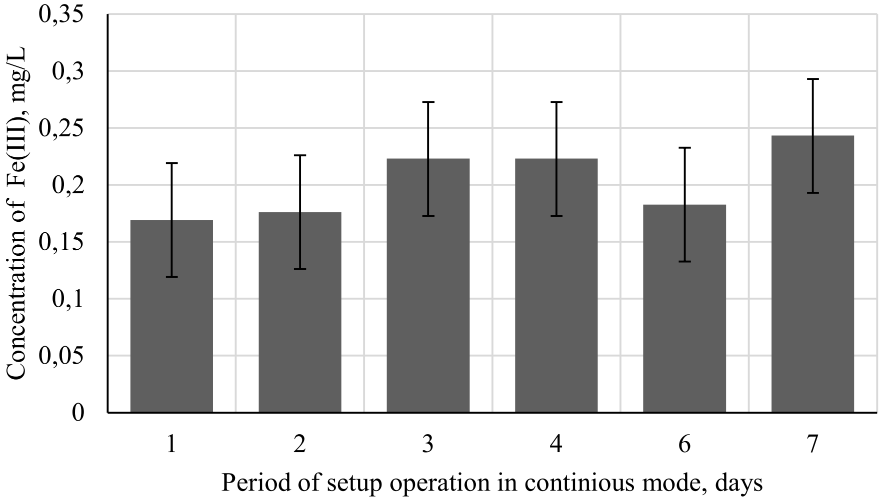

Fig. 6. Changes in the iron ions concentration in treated water with gydraulic retention time of 8 hours and the biomass concentration of 25 g/L in a continious mode

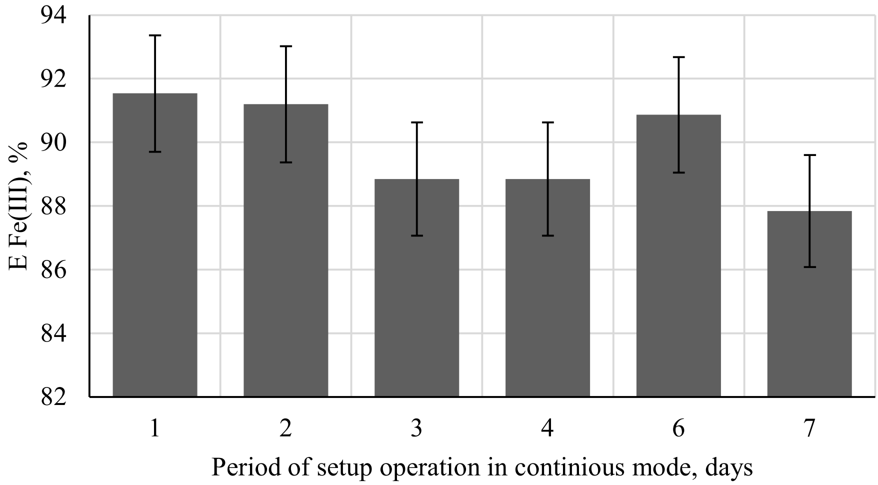

Fig. 7. Removal rate of iron ions in treated water with gydraulic retention time of 8 hours and the biomass concentration of 25 g/L in a continious mode

In the continuous mode during the 7-day operation of the setup, duckweed biomass concentration of 8–25 mg/L, and the duration of biological water treatment for 8–24 hours, no increase in the iron ions concentration in treated water was observed. Due to this fact, duckweed depletion time was not found, and supposed to be longer than setup work time.

4. Conclusions

The obtained results from the kinetics of the process in the batch mode of the bioreactor operation with duckweed show an increase in the degree of removal of iron ions from wastewater from 61.0% to 91.7% when the biomass concentration of duckweed change from 8 mg/L to 25 mg/L at the duration of biological treatment of 24 hours.

The results obtained from the kinetics of the batch mode of the bioreactor operation process showed that duckweed increased the rate of removal of iron ions from wastewater from 61.0% to 91.7% when the biomass concentration of duckweed change from 8 mg/L to 25 mg/L at the duration of biological treatment of 24 hours.

The rational parameters of removal of iron ions from wastewater of the continuous mode of bioreactor operation process are determined: biomass of duckweed is 25 mg/L; the duration of the process is 8 hours; hydraulic load is 0,126 L/(h·L). The removal effect is 89.8%.

Further studies may be aimed at determining the time of the duckweed depletion as a biological agent, since the plant may supersaturate with iron ions, which can provoke their release back into water, and determine the period of effective operation of the setup without replacing the biomass.

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Economic, reliability and technological analysis of selected variants of underground parking lot fire protection

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Abstract

This paper presents the multivariate analysis of four designed systems of fire protection for multi-space underground car parking lot. The designed systems for 3563 m2 of parking covered: the standard fire hydrants, sprinklers (wet and dry) and nozzles. The proposed fire protection was assessed due to its cost-efficiency, reliability and technology. The financial assessment was based on dynamic generation costs (*DGC*), net present value (*NPV*) and benefit-cost ratio (*BCR*) determined after assessment of the investment as well as operation and maintenance costs. The reliability analysis was based on calculated readiness indicator while technological aspects were assessed according to i.e. speed of action, required volume of water, sensitivity to low temperatures, degree of automation and facilitation of fire-fighting action. Finally, all the developed indicators were applied to weight sum model method, allowing to select the most appropriate design in relation to its cost-efficiency, reliability and technology.

Keywords: fire protection, hydrants, sprinklers, nozzles, multivariate analysis

1. Introduction

According to actually binding law in Poland (Dz. U.2010.109.719; Dz. U.1991.81.351) the requirements level of fire protection and applied firefighting equipment depends to the category of the protected building. The buildings qualified to category of possible human life threat should be equipped in external hydrants of hydrant valves. Additionally, the rules imply obligatory installation of fire signaling and audio warning systems or automatic firefighting water equipment in commercial buildings, high-rise public and living buildings.

The detailed rules of particular fire protection devices (warning or firefighting) spatial distribution are dependent to area and location of fire zone. The size of fire zone depends to zone type and its location in the underground part of the construction, number of floors in the building, presence of automatic firefighting and smoke extraction devices, initialized by smoke detection systems, occurrence of spaces endangered by explosion or density of fire load (Q).

In case of buildings the fire zone covers the building itself, or its part, separated from the remaining parts by elements of fire separation (walls and ceilings constructed of incombustible materials of specified fire resistance) (Dz. U. 2019.75.690).

The acceptable area of fire zone in the building qualified to human threat category should not exceed, for categories ZLI, ZLIII-ZLV, according to Polish regulations (Dz. U. 2019.75.690), in low multi-storey buildings 8000 m^2, medium-high 5000 m^2 and high as well as high rise buildings 2500 m^2. In case of Polish ZLII category (Dz. U. 2019.75.690) these values are lower and equal 5000 m^2 (low buildings), 3500 m^2 (medium-high) and 2000 m^2 (high as well as high rise). In case of underground part of the construction, the acceptable area of fire zone should not exceed 50% of allowed fire zone area of the same category of human threat determined to the first overground storey of the building. It is possible to enlarge the fire zones by 100%, except zones in high and high rise buildings, providing the permanent water firefighting devices as well as automatic smoke detection and extraction devices. In case of simultaneous application of both above mentioned installations, the fire zone size may be extended by 200%.

Taking into account the biding law, actual national standards, engineering state of art and available modern technologies it is possible, from the technological point of view, to ensure the required fire protection of public buildings, including underground lots, by application of several available various firefighting system. However, the available technical means of fire protection may significantly differ, not only in the aspect of investment or operation and maintenance (O&M) costs but also in complexity of the system, required volume of water, participation of people, degree of automation, sensitivity to environmental conditions etc. Thus, the selection of a most suitable and efficient system of fire protection, already at the level of design, should be supported by the sound multivariate analysis utilizing selected technical and financial indicators of sustainability e.g. capital costs, operation and maintenance costs, cost-efficiency, reliability, durability, resources and energy use (Ellis et al., 2004; Palme et al., 2005; Palme and Tillman, 2008; Peter and Nkambule, 2012; Widomski et al., 2015). Then, after selection of the sound indicators, the proper multivariate sustainability assessment should be based on the further multicriteria analyses utilizing e.g. weighed sum model (Ellis et al., 2004; Palme et al., 2005; Benzerra et al., 2012).

This paper presents the multivariate analysis of four various proposed designs of fire protection systems, in agreement with biding law, actual standards and utilizing modern technologies, for multi-space underground car parking lot. The performed analysis included several indicators of cost-efficiency of investment, reliability and technological durability and resources use.

2. Materials and Methods

The presented multivariate analyses, including cost-efficiency, reliability and technology aspects was performed for underground multi-space parking of area 3563 m^2 located in municipal public services building in Poland. The studied parking is the only fire zone in the municipal building, according to Polish biding law (Dz. U. 2019.75.690). The fire load for the tested parking lot was assumed as 500 MJ/m^2, like for production or warehouse building, containing rooms for simultaneous stay of 50 people, not permanent residents of this building.

Four variants of actual and inline with the biding law fire projection were tested. Variant I, standard hydrant installation, in agreement with Dz. U. Nr 109, poz. 719, utilized 5 HP 33 hydrants of range 30 m and minimal water flow rate 1.5 dm^3/s, installed close to pathways and stairways on the parking space (see Fig. 1).

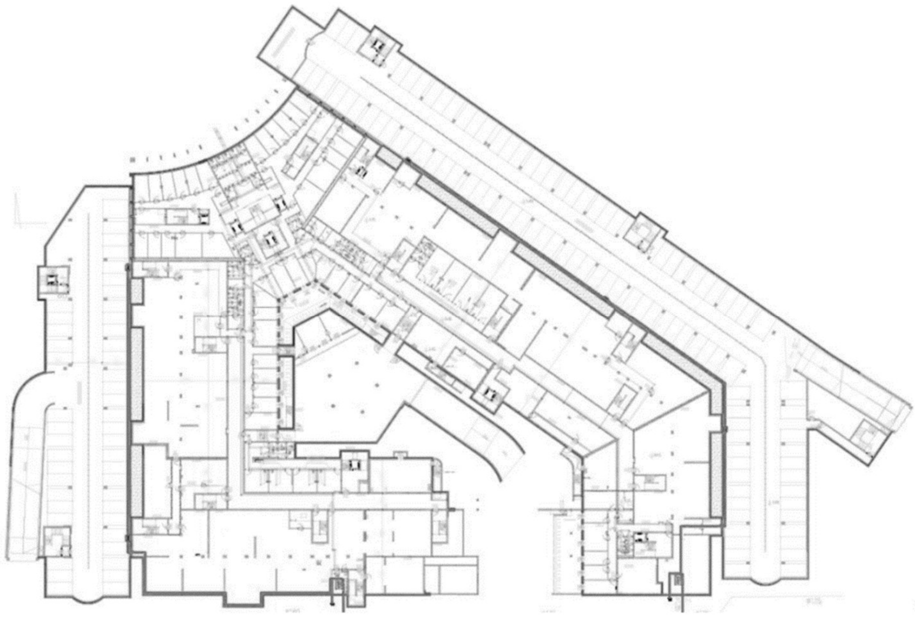

Fig. 1. Proposed Variant I, standard hydrants installation

The second and the third options, Variant II and III (Fig. 2), were based on wet and dry sprinklers installation, respectively designed in agreement with EN 12845:2015. Variant II utilized 308 TYCO TY 3131 FRB wet sprinklers, 2 alarm check valves J-1 by Viking while Variant III consisted of 308 TYCO TY 3131 FRB dry sprinklers. The last assumed variant, Variant IV (Fig. 3), nozzles installation, in line with requirements of NFPA 15 standard, was based on 365 nozzles and alarm-control valve Tyco model DV-5.

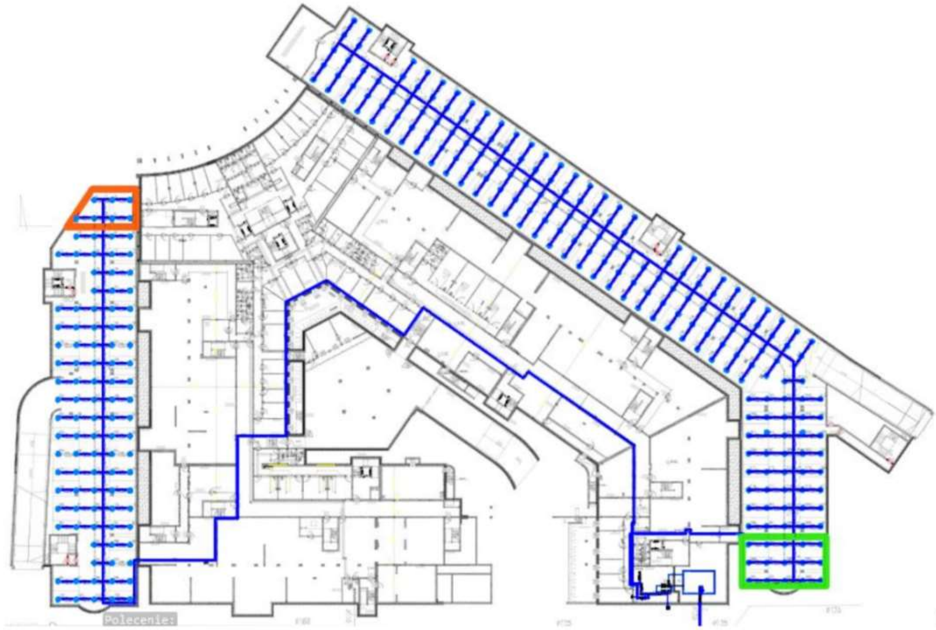

Fig. 2. Proposed Variant II and III, sprinklers installation

Fig. 3. Proposed Variant IV, nozzles installation

All pipelines in presented variants of parking fire protection were designed as galvanized steel pipes of diameters 50–80 mm with brass fittings. Water supply to designed variants of fire protection installation will be delivered by municipal water supply system.

The required investment costs and annual financial load necessary for operation and maintenance of designed were calculated according to performed preliminary cost-estimation and available commercial prices of materials, services and repairs. The performed financial analyses were based on the following assumptions: i) assumed time duration 30 years, ii) no fire during assumed time duration, iii) discount rate equal 6%.

The financial assessment was based on Dynamic Generation Costs (*DGC*), Net Present Value (*NPV*) and benefic-cost ratio (*BCR*) determined after assessment of the investment as well as operation and maintenance costs. The *DGC* shows the financial load required allowing to obtain the discounted revenues equal to discounted costs. So, *DGC* value may be understand as the price of unit effect of the investment, e.g. 1 m^3 volume of delivered tap water and treated sanitary sewage, or, like in our case, 1 m^2 of parking area protected against fire. Its application is very easy, the lowest indicator value the highest cost-efficiency of the design. The *DGC* may be calculated using the formula (e.g. Rączka, 2002):

$$DGC = p_{EE} = \frac{\sum_0^{t=n} \frac{IC_t - EC_t}{(1+i)^t}}{\sum_0^{t=n} \frac{EE_t}{(1+i)^t}} \tag{1}$$

where: IC_t – annual investment costs in given year [Euro], EC_t – annual exploitation (operation and maintenance) costs in given year [Euro], t – year of investment time duration, from 0 to n, where n is the last assessed year of investment activity [year], i – discount rate [%], p_{EE} – price of the ecological unit effect of the investment [Euro m^{-3}], EE_t– annual ecological unit in given year [m^3].

Net Present Value indicator presents sum of discounted cash flows, benefits and costs, reduced by the investment capital costs (Berry et al., 2007). The *NPV* for a positively assesses design should fit NPV≥0. NPV, presented in monetary units, for time duration of investment (n) may be calculated as follows (e.g. Miłaszewski, 2003):

$$NPV = \sum_{t=0}^{n} \frac{R_t}{(1+i)^t} \tag{2}$$

where: R_t – net cash flow for a i year of investment operation [Euro], i – discount rate [%], t – year.

The net cash flow, R_t, covers sum of all financial effects, including investment and exploitation costs, for a given year.

Benefit-Cost Rate is a dimensionless relation benefits of investment to its costs (investment and O&M) in studied year. The value of BCR indicator for profitable investment should be $BCR \geq 1$.

BCR may be calculated using the below formula:

$$BCR = \frac{PV_b}{PV_c} \tag{3}$$

where: PV_b – present value of benefits [Euro], PV_c – present value of costs [Euro].

Table 1. Inestment and O&M costs of studied fire protection variants

Variant	Investment costs (Euro)	Annual operation and maintenance costs (Euro)
I	11270	258/297 (5y)
II	74547	1422/2895 (3 and 10y)
III	72889	1422/2895 (3 and 10y)
IV	264859	1641/3269 (3 and 10y)

The reliability analysis was based on calculated readiness indicator while technological aspects were assessed according to i.e. speed of action, required volume of water, sensitivity to low temperatures, degree of automation and facilitation of fire-fighting action.

The direct comparison of all studied variants of fire protection for tested parking, including financial sustainability, reliability and technological aspects the weighed sum model (WSM) was applied (Benzerra et al., 2012; Lewicka et al., 2016):

$$PC_j = \sum_{i=1}^{n} PI_{ji} w_{ji} \tag{4}$$

where: PC_j – performance value of j criterion; n – number of indicators included in the criterion; PI_{ji} – performance value of indicator in the criterion, w_{ij} – weight factor of the indicator in the criterion.

The assumed weights factors for studied variants of fire protection are presented in Tab. 2.

Table 2. Assumed percentage weight factors for all criteria

Criterion	Weight factor (%)
Economic	10
Reliability	50
Technological	40

3. Results and Discussion

Table 3 presents determined values of cost-efficiency indicators for all four tested variants of fire protection installation. As it is visible the lowest unite cost of the required fire protection effect, reflected by *DGC* indicator, was determined for Variant I, in which the standard hydrant installation was proposed. On the other hand, the highest *DGC* value was determined for Variant IV, nozzles installation as it was characterized by the highest investment and O&M costs. The calculated values of *NPV* and *BCR* cost-efficiency indicators show that none type of fire protection installation, included in tested variants, brings profits to the investors. The financial loads presented by discounted cash flow in *NPV* indicator are the lowest for the simplest Variant I, the standard hydrants installation.

Table 3. Determined cost-efficiency indicators

Indicator	Variant			
	I	II	III	IV
DGC (Euro/m^2)	0.29	1.96	1.93	5.66
NPV (Euro)	–15745	–103252	–101595	–297755
BCR (-)	0	0	0	0

Table 4 presents results of technological assessment performed for all four tested variants of fire protection installations for the underground parking according to the assumed point system in six categories. The lowest sum of pints characterizing the technological aspect of fire protection installation was determined for Variant I, standard hydrants installation, which showed the slowest speed and none facilitation of fire-fighting action as well as null degree of automation. This system also requires the highest volume of water available for fire-fighting action. On the other hand, the highest sum of points were determined for two similar Variants, II and III, representing wet and dry sprinklers installation. These variants obtained the highest possible value of points in case of analyzed number of devices included and facilitation of fire-fighting action as well highly developed degree of automation. There were also some differences underlined between these two types of sprinklers installation. The dry sprinkler system presents lower speed of fire-fighting action initialization due to the manner of water delivery to the sprinklers. However, the wet sprinklers installation shows significant sensitivity to low temperatures because of permanent water storage inside the piping.

Table 4. Results of technological analyses of proposed variants of fire protection. Explanation to points system: 0 – unsatisfactory, 1 – acceptable, 2 – good, 3 – very good

Criterion	Variant			
	I	II	III	IV
Speed of action	0	3	1	2
Number of devices included in fire fighting	2	3	3	0
Required volume of water	3	2	2	0
Facilitation of fire-fighting action	0	3	3	2
Sensitivity to low temperatures, below 4 C deg.	2	0	3	2
Degree of automation	0	3	3	3
Sum	7	14	15	9

The results of reliability assessment for all tested variants of fire protection of underground parking are presented in Tab. 5. Generally, it may be stated, that all proposed variants showed high values of readiness factor, from range 0.9776–0.9984. The highest value was determined for the simplest standard hydrants system, while the lowest value of readiness factor was obtained for the nozzles installation.

Table 5. Obtained values of dimensionless readiness factor

Variant	Readiness indicator
I	0.9984
II	0.9980
III	0.9980
IV	0.9776

Table 6 shows assigned performance values required to calculations of weighed sum model (WSM) for each tested variant of fire protection in three criteria: financial, reliability and technological. The results of performed calculations are presented in Fig. 4. The highest value of WSM, i.e. 3.3, was determined for Variant III, dry sprinklers installation, thus this variant should be stated as most suitable according to the assumed method of financial, reliability and technological assessment. The lowest value of WSM were determined for Variant IV, the nozzles installation, which showed very low financial attractiveness, due to significant investment and O&M costs as well as some technological requirements, i.e. required volume of water and Number of devices included in firefighting. The obtained results of multivariate analyses are subjective, they are highly affected by assumed criteria of assessment and values of weight factors for weight sum model. In this case, the reliability and technological aspects were underlined in the assessment by weight factors higher than for the financial aspects.

Table 6. Performance values of each variant (4 – the best, 1 – the weakest)

Variant	Criterion		
	Financial	Reliability	Technological
I	4	4	1
II	3	3	3
III	2	3	4
IV	1	2	2

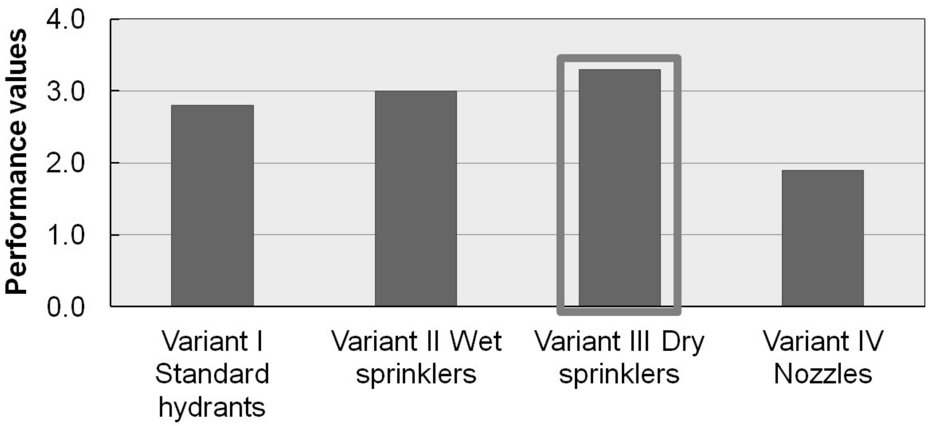

Fig. 4. Results of weighted sum model applied to analysis of four installations of fire protection

4. Summary and Conclusions

Fire protection of multi-space underground car parking lot is a crucial issue in case of public buildings, due to high risk for human health and welfare. According to actual state of knowledge and biding law and standards several possible technical solutions are acceptable, including standard fire hydrants, sprinklers (wet and dry) and nozzles, which were tested in this paper. However, all these systems may significantly differ in many aspects, starting from investment and O&M costs, through reliability to various technologic aspects e.g. speed of action, sensitivity to low temperatures, required amount of water and participation of people in firefighting. Thus, the proper method of assessment, allowing to include several important factors, should be introduced to decision making at the designing stage.

Our studies allowed to draw the following conclusions:

– The performed analysis of four designed systems of fire protection for multi-space underground car parking lot based on financial, reliability and technical

assessment, after assumption of weight factors and WSM application allowed to select the optimal variant, according to assumed criteria of assessment.
- The observed financial or cost efficiency of proposed variants was inversely proportional to their degree of technological development, required services and maintenance.
- Various technological aspects of studied fire protection installations influence results of the performed assessment due to the possible effects on the real firefighting action.
- All the proposed variants of fire protection installation presented similar value of reliability indicator.
- The final results of SWM assessment are directly affected by the assumed values of percentage weight factors, which, in each separated case should be selected individually, in relation to the local conditions and investors policies.

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Calibrating water distribution system model with hydrant tests

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Abstract

The calibration process is an inherent but also the most challenging part of a proper assembling of water distribution system (WDS) hydraulic model. During its endless continuance, if necessary, the data describing the WDS model is adjusted until model-predicted results reasonably agree with the measured system performance. To ensure its compatibility over a wide range of operating conditions, the calibration process should include not only typical residual flows but also peak demand periods. To obtain data necessary for simulation of high flow conditions, fire hydrant flow tests are commonly used. The additional application of fire-hydrant tests is the possibility of pipe roughness calculation. Among many parameters possible for adjustment (water demands, pump characteristics, etc.), the pipes' roughness fine-tuning may lead to the satisfactory level of model and system convergence.

The aim of this paper is to present the case study of calibrating distribution pipes' roughness in a highly complex WDS in Poland. The pipe's roughness calibration was based on two-gage head loss tests, conducted for 5 different pipe segments. The roughness coefficients were calculated in accordance to Prandtl-Kármán and Colebrook-White formulas. The second part of pipe's roughness calibration was based on simulations in Bentley WaterGEMS using Darwin Calibrator with implemented genetic algorithm (GA). In the following case, the individual adjustment of roughness coefficients was performed for each pressure zone of the WDS, within each the pipes were divided into 5 material groups. The additional hydrant tests were performed in each pressure zone to cause a significant high flow in a zone. As a result, the adjusted roughness coefficients lead to a better convergence between model and WDS, decreasing fitness parameter from 16.75 to 4.23.

Keywords: roughness, head loss, fire hydrant test, Darwin Calibrator, Bentley WaterGEMS

1. Introduction

The calibration process is an inherent but also the most challenging part of a proper assembling of water distribution system (WDS) hydraulic model. During its endless continuance, if necessary, the data describing the WDS model is adjusted until model-predicted results reasonably agree with the measured system performance (Walski, 1983). There are many general tips to successfully calibrate the WDS hydraulic model (Khedr et al., 2015), but it should be clearly emphasized that the WDS model cannot be fully and completely calibrated. As every WDS has an individual character due to its location, geometrical structure and operating schedule, there are no global standards which can work in any water distribution model (Walski, 2019).

During the calibration process, there are several parameters that can be adjusted to guarantee the acceptable level of compatibility between simulated results and measured data. The model development requires proper elevation data, pump characteristics, demand values as well as operating tank levels (Walski, 2017). Later, the model can be tuned by demands and roughness modifications. To ensure model compatibility over a wide range of operating conditions, the calibration process should include not only typical residual flows but also peak demand periods (Grayman et al., 2006). If the calibration is performed only for residual flows with low velocity values, the pipe roughness is negligible because it does not cause a significant pressure head loss (Hirrel, 2008). In such case, the water distribution model may not be reliable during the fire flow or emergency conditions. Therefore, to obtain data necessary for simulation of high flow conditions, fire hydrant flow tests are commonly used (Wu and Song, 2014). Among many parameters possible for adjustment, the pipes' roughness fine-tuning may lead to the satisfactory level of model and system convergence. To estimate the pipe roughness, a straight section of a pipe with a minimum of three fire hydrants is needed. There are two main hydrant head loss tests for estimating pipe roughness: the two-gauge and the parallel hose test (Cooper, 2017). In both methods, the first step is to determine the length and pipe diameter. Next, the pipe is isolated by closing several valves and the pressure drop and flow are measured by using pressure gauge or loggers. Further, the pipe roughness can be approximated by direct application of a mathematical formulas. The most common equations to calculate friction head losses are: Colebrook-White (Colebrook and White, 1937), Prandtl-Kármán (Finnemore and Franzini, 2002), Altshul (Finnemore and Franzini, 2002) or Nikuradse (Nikuradse, 1932).

Due to the fact that fire hydrant head loss tests have very local character, their results may be misleading during extrapolating roughness coefficients to remaining parts of the network. Every WDS consists of pipes of different material and operation age. The pipe roughness may also differ due to physical-chemical properties of the distributed water and different hydraulic conditions in WDS. The aim of this paper is to present the case study of calibrating distribution pipes' roughness in a highly complex WDS in Poland. The calibration process was based on field hydrant tests and was further complemented by the application of a metaheuristic approach.

2. Materials and Methods

The fire-hydrant flow tests and model calibration was conducted for a highly complex WDS located in mountainous area, with significant elevation difference. The urban, branched-looped WDS consists of 260 km pipe lines in 24 pressure zones and delivers water to approx. 30 000 inhabitants, including both household and industrial customers, which demand water in significant amounts at the random time of the day. The total daily water consumption is approx. 3 850 m^3/day. The geometrical structure of the analysed WDS, with size-scaled diameters and elevation contours is presented in Fig. 1.

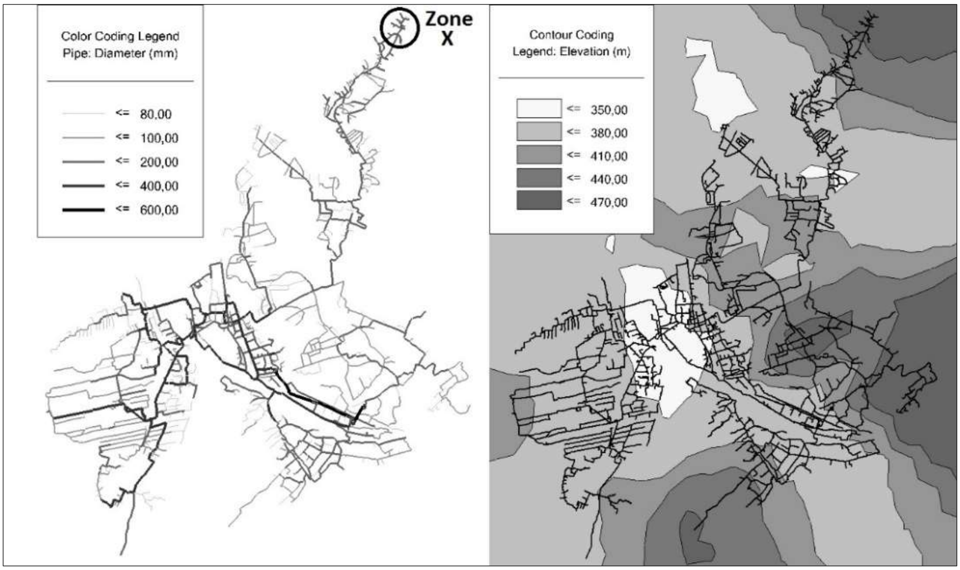

Fig. 1. Geometrical structure of the WDS with pipe diameters and elevation contours and marked zone X

The WDS characterizes by great water losses, varying from 7% up to 43% between zones (averagely: 38%). The material structure of a water supply network includes asbestos cement, ductile iron and steel pipes in the oldest city district, and PE and PVC pipes prevailing in newer districts. The diameters ranges from DN32 for household connections to DN600 for distribution mains.

Due to the wide territorial range and significant elevation difference, WDS includes 14 pump stations, 7 tanks but only one surface water intake. The population density in the majority of 24 pressure zones is low or medium, which usually results in long breakage detection time – the water outflow to the surface can be notices in a few to several days.

The developed hydraulic model of the analysed WDS consisted of approx. 11 000 pipes and junctions. The model of a basic character (including all pipes excluding household connections, total length: approx. 221 km) was built in Bentley WaterGEMS software. The extended period simulation (EPS) model was developed in accordance to the GIS database, with calculation time step equal to 20 minutes and total duration time 168 hours (7 days). The hydraulic simulation results of the water velocity revealed that the WDS operates in the condition of a significant pipe diameter over-sizing. The maximum flow velocity in the peak demand time step was 0.6 m/s in the main pipes, while the majority of the network operated with the flow velocity in the range of 0.1÷0.2 m/s.

The detailed results of an automatic roughness calibration process will be presented for an exemplary zone in the analysed WDS – zone X. This end-located zone characterizes with small velocity values during normal residual flows. Zone X consist only of plastic (PE and PVC) pipes, which operational age is between 5 and 10 years. The geometrical structure of a zone X is presented in Fig. 2. The zone is supplied with water by pump station (*PS* in Fig. 2) and is equipped with 1 pressure monitoring point (*P* in Fig. 2). *H* in Fig. 2 symbolizes an open hydrant during the calibration field campaign.

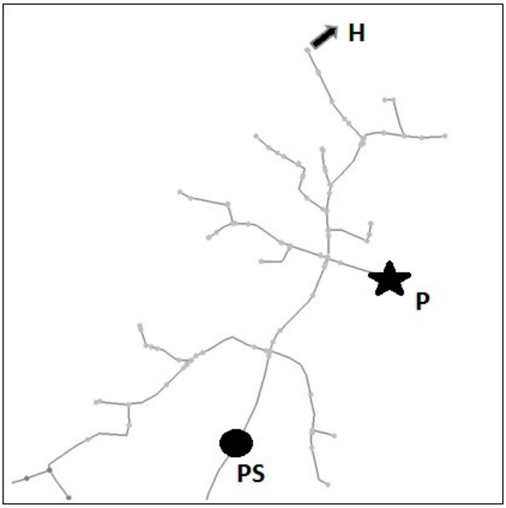

Fig. 2. Geometrical structure of an exemplary zone X (*PS* – pump station, P – pressure monitoring point, H – open fire hydrant)

The pipe's roughness calibration was based on two-gage head loss tests, in accordance do AWWA methodology (Panguluri et al., 2005). Due to the high complexity of a geometrical structure of the network, only 5 different pipe segments, with three in-line fire hydrants, could be selected for the calibration field campaign. Segments included 1 cast iron (DN/ID 150), 3 PE (DN/OD 110) and 1 PVC (DN/OD 160) pipes. The cast iron segment was located in the oldest part of the WDS (old town districts) where the pipes operational age was over 70 years in this zone. The plastic pipe segments (PE and PVC) were in the newer part of the municipality (operational age: 5÷15 years). Pressure head at fire hydrants was measured by 2 pressure loggers SEBAKMT Sebalog P3. Pressure measurements frequency was equalled to 5 s. The head loss was further calculated as difference between measured values by pressure loggers. The distance L between pressure loggers equalled to: 143.8 m for a cast iron pipe, 117.8, 132.2 and 122.1 for PE segments pipes and 104.8 for PVC segment. The water outflow at the open fire hydrant was measured by ultrasonic flow meter (Microsonics Portaflow 300). The scheme of a field tests setup is presented in Fig. 3. The roughness coefficients were calculated in accordance to Darcy-Weisbach (Eq. 1), Prandtl-Kármán (Eq. 2) and Colebrook-White (Eq. 3) formulas.

$$H = \lambda \frac{l}{d} \frac{v^2}{2g} \tag{1}$$

$$\frac{1}{\sqrt{\lambda}} = 2\, lg \frac{3.71}{\frac{k}{d}} \tag{2}$$

$$\frac{1}{\sqrt{\lambda}} = -2\, lg \left(\frac{2.51}{Re\sqrt{\lambda}} + \frac{k}{3.71d} \right) \tag{3}$$

where: ΔH – head loss [m], λ – friction factor loss [-], l – length [m], d - pipe internal diameter [mm], v – flow velocity [m/s], g – standard gravity [m/s^2], k – absolute roughness [mm], Re – Reynolds number [-].

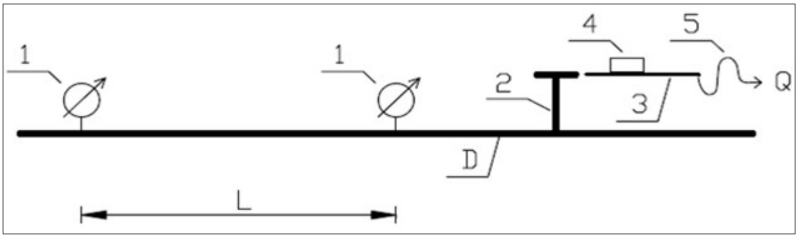

Fig. 3. Scheme of two-gauge head loss test: L – distance between pressure loggers, D – pipe internal diameter, Q – water outflow, 1 – pressure loggers SEBAKMT Sebalog P3, 2 – open fire hydrant, 3 – 2,5" steel pipe, 4 – flow meter Microsonics Portaflow 300, 5 – fire hose

Calculated roughness values, on the basis of hydrant tests, should be interpreted as equivalent roughness, not the absolute roughness. The equivalent roughness includes not only the internal wall smoothness of a pipe but also existing minor losses caused by pipe connections, fittings and sediments inside the pipe. The application of the equivalent roughness is recommended by modelling software producers, as it meaningly simplifies the numerical calculations and shortens the simulation calculation time. However, due to the fact that fire hydrant head loss tests have very local character, their results may be misleading during extrapolating roughness coefficients to remaining parts of the network. Therefore, the second part of pipe’s roughness calibration was based on simulations in Bentley WaterGEMS using Darwin Calibrator with implemented genetic algorithm (GA). The main idea of Darwin Calibrator is to compare model and system performances and search for the most corresponding solution by adjusting demands or pipe’s roughness, basing on the principles of natural evolution and genetic reproduction. The Darwin Calibrator can be used not only to support the process of a calibration but also can be used for leakage detection and identification of a closed valves (Walski et al, 2007).

In the following case, the individual adjustment of roughness coefficients was performed for each pressure zone of the WDS (19 calibration processes), within each the pipes were divided into 4 material groups (asbestocement *AC*, cast iron *CI*, steel *St* and plastic pipes *PE+PVC*). The additional 19 hydrant were opened, one per each WDS zone to cause a significant high flow in a zone. During the calibration, no demands were adjusted. The automatic calibration process was performed for the defaults genetic algorithm settings: fitness tolerance: 0.001, maximum trials: 10 000, non-improvement generations: 100, maximum era number: 6, era generation number: 150, population size: 50, cut probability: 2%, splice probability: 90%, mutation probability: 1.0%, random seed: 0.5, roughness min/max/increment: 0.5/1.5/0.1. The results of the calibration were verified by the *Fitness F* parameter (Eq. 4). The *Fitness F* parameter is a relative number, which should be converging to zero but its value depends on size of the system, number of monitoring points and quality of monitoring data. Therefore, there are no standards for interpreting the *Fitness F* number, the only rule says, that the lower *Fitness F* parameter the better. *Fitness F* can be calculated by Minimize Difference Squares, Minimize Difference Absolute Values or Minimize Maximum Difference methods (Walski et al, 2007).

$$F = \frac{1}{W_H}\sum(H_{mod} - H_{obs})^2 + \frac{1}{W_Q}\sum(Q_{mod} - Q_{obs})^2 \qquad (4)$$

where: F – fitness parameter [-], W_H – weighting factor for observed hydraulic grades, H_{mod} – model simulated hydraulic grade [m], H_{obs} – observed hydraulic grade [m], W_Q – weighting factor for observed flow, Q_{mod} – model simulated flow [m^3/h], Q_{obs} – observed flow [m^3/h].

3. Results and Discussion

The equivalent roughness parameters values, calculated on a basis of conducted fire hydrants tests, are presented in Tab. 1. Roughness values, both calculated by Colebrook-White and Prandtl-Kármán formulas, were similar. However, all testes pipe segments characterizes with higher roughness values, in comparison to producers reference values, as well as in comparison to reference values given by the technical regulation Polish Norm (PN-M-34034:1976). Segment 1 (cast iron pipe) has an equivalent roughness equalled do 77.3% of an internal diameter of the pipe. Such situations occur quite often in old parts of a operated water distribution networks and are caused mainly by sediments decreasing the internal pipe diameter (Musz et al., 2011). Higher equivalent roughness values in plastic pipes (PE, PVC), in accordance to reference standard values given by producers and PN-76-M34034, are caused primarily by pipe connections and fittings.

Table 1. Fire hydrant equivalent roughness test results

Segment	Material	Field data				Roughness			
						Equivalent		Reference	
		DN/ID	L	Q	ΔH	Prandtl-Karman	Colebrook-White	Producers	PN-M-34034:1976
		mm	m	m^3/s	m H_2O	mm	mm	mm	mm
1	CI	150.0	143.8	0.0051	2.22	115.6	116.0	-	1.4-4.0
2	PE	97.0	117.8	0.0099	8.5	5.2	5.4	0.01	-
3	PE	97.0	132.2	0.0071	4.3	4.5	4.3		-
4	PE	97.0	122.1	0.0113	7.1	1.8	1.8		-
5	PVC	141.0	104.8	0.0287	7.24	4.1	4.1	0.01	-
Avg PE/PVC:						3.9			

Presented in Tab. 1 equivalent roughness results apply only to 5 segments of a analysed WDS, as there were the only pipe segments which fulfilled the AWWA requirements for fire hydrant tests. Therefore, these values were initially implemented into the model and later modified during the automatic calibration in Darwin Calibrator. In accordance to the presented methodology, the calibration process was performed for all 19 pressure zones separately. In all zones, the peak flow was artificially generated by opening of a fire hydrant. The results of the adjusted roughness values are presented in Tab. 2. Presented values are averagely adjusted for the whole material groups, individually in each zone. There is only one zone (I) in which all four material groups appear. The mark "-" in the Tab. 2. means that specified pipe material does not appear in the specific zone.

Table 2. Roughness coefficients [m] in selected material groups after automatic calibration

Zone	Roughness (mm) after Darwin Calibration			
	AC	CI	St	PE/PVC
I	12.0	80.0	12.0	1.9
II	-	60.0	9.0	1.9
III	-	50.0	-	1.9
IV	-	50.0	7.5	1.6
V	-	60.0	9.0	1.6
VI	-	-	7.5	1.6
VII	-	-	-	1.6
VIII	-	-	-	1.6
IX	-	-	-	1.6
X	-	-	-	1.6
XI	-	60.0	9.0	1.9
XII	-	-	9.0	1.6
XIII	-	-	-	1.6
XIV	-	-	-	1.9
XV	-	-	-	1.6
XVI	-	70.0	10.5	1.9
XVII	-	-	-	1.6
XVIII	-	-	-	1.6
XIX	-	-	-	1.6

Automatic calculations in Darwin Calibrator lead to decreasing the equivalent roughness values in the numerical model of the analysed WDS. The values were decreased differently in accordance to separate zones. Calculated values are equal to 52÷68% of the measured roughness values for CI pipes, 30÷89% for PE pipes and 39% for PVC pipes. The equivalent roughness decrease confirms that there is a high need of verification of the fire hydrant test results, performed only for local locations. Moreover, there is also a possibility of existing of unknown minor losses (e.g. semi-closed isolation valve) in the analysed pipe segments, not appearing in the rest of the WDS. Additionally, it is worth to mention, that in all calculated values the equivalent roughness values are significantly higher than the values given by pipe producers.

The exemplary results of automatic calibration in zone X are presented in Tab. 3. The calculated *Fitness F* parameter for measured and simulated pressure head values (in pump station and at the monitoring point) was equal to 16.75. After the automatic calibration, the *Fitness F* parameter decreased almost 4 times, to the value 4.23. It lead to the better convergence between simulated and observed values: the pressure head difference at the monitoring point decreased from –2.15 to –1.07 m H_2O.

Table 3. Roughness automatic calibration results for zone X

<table>
<tr><td colspan="3" rowspan="2">FITNESS</td><td colspan="3">Base fitness</td><td colspan="3">Automatic Calibration</td></tr>
<tr><td colspan="3">16.75</td><td colspan="3">4.23</td></tr>
<tr><td colspan="3">Zone X</td><td>Model</td><td>SCADA</td><td>Difference</td><td>Model</td><td>SCADA</td><td>Difference</td></tr>
<tr><td>Pump station</td><td>Hydraulic grade</td><td>m</td><td>519.88</td><td>520.03</td><td>0.15</td><td>519.88</td><td>520.03</td><td>0.15</td></tr>
<tr><td>Pressure monitoring point</td><td>Hydraulic grade</td><td>m</td><td>517.47</td><td>515.32</td><td>-2.15</td><td>517.47</td><td>516.40</td><td>-1.07</td></tr>
<tr><td>Equivalent roughness</td><td>PVC/PE</td><td>mm</td><td colspan="3">3.9</td><td colspan="3">1.6</td></tr>
</table>

4. Summary and Conclusions

Roughness coefficients estimations are an inherent part of creating digital models of water distribution networks. Roughness coefficients can vary significantly within the same WDS and meaningly differ from literature reference values.

In all analysed cases, roughness coefficients calculated on a basis of hydrant tests were significantly higher than manufacturer's properties of pipes. Possible reasons: minor losses at pipe connections or sediments. In one case (cast iron pipe), the absolute roughness coefficient was distinctly high due to the pipe age or possible semi-closed undetected valve. This section was farther recommended for mechanical cleaning or replacement.

Performing head loss hydrant tests for every water pipe is unenforceable. Due to the fact that fire hydrant head loss tests have very local character, their results may be misleading during extrapolating roughness coefficients to remaining parts of the network. The calibration of the model by pipe roughness adjustment can be completed by optimization calculations. Roughness coefficients calculated in Darwin Calibrator proved to be smaller than obtained in hydrant tests but still higher than manufacturer's values.

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Assessment of Solotvyno agglomeration mines flooding impact on water resources with GIS

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Abstract

Solotvyno rock salt mine is located in the Tyachivsky district of the Transcarpathian region of Ukraine, which is a section of the right-bank water catchment of the transboundary Tisza River. During the active exploitation of the Solotvyno salt deposit within the salt stock, up to 9 mines have been built and decommissioned due to flooding mainly as result of the imperfect mining technology. The mine fields of the deposit are located within the first above floodplain terraces, which contribute to the development of aquifers and the development of flood processes that makes the mining-geological and environmental-geological conditions of excavation, development and decommissioning of mines more complicated.

In this paper, we investigated the subsidence deformation field, and its influence on changing the environmental status of the Tisza River. Using the technology of space monitoring (interferometry), field magnetic-electric survey and GIS modelling, the authors have investigated and analysed the spatial-temporal structure and the balance of precipitation of the surface. To determine the rate of sinkhole formation in the area of the abandoned mine workings, where the ground is considered too unstable for detailed ground work, the use of the radar data is considered to be essential from the authors perspective.

An active increase in the inflow of fresh groundwater and the associated intensive development of man-made karst caused the formation of destructive subsidence deformations of the surface and the rocks of the foundations of residential and industrial buildings, roads, water supply and sewerage networks of the Solotvyno settlement.

Keywords: GIS, interferometric analysis, deformation, subsidence of the daylight area, karst-suffusion processes, shear deformations

1. Introduction

General characteristics of mining and geological conditions

Solotvyno rock salt mine is located in the Tyachiv district of the Transcarpathian region, which is a part of the right-bank catchment area of the transboundary Tisza River. In a geomorphological sense, the Solotvyno deposit is characterized by a hill topography with absolute marks of 200–600 m.

The mine fields of the deposit are located within the first above floodplain terraces, which contribute to the development of aquifers and the development of flood processes that makes the mining-geological and environmental-geological conditions of excavation, development and decommissioning of mines more complicated. The Tisza River, its hydrologically connected local watercourses (springs Izvor, Glod, Mlyn) and protective drainage galleries create a leading drainage system for surface and underground runoff, which over the past decades has been significantly slowed down within areas of influence of karst-sinkholes and territories of the subsidence daylight area over the mine workings of the flooded mines (Fig. 1).

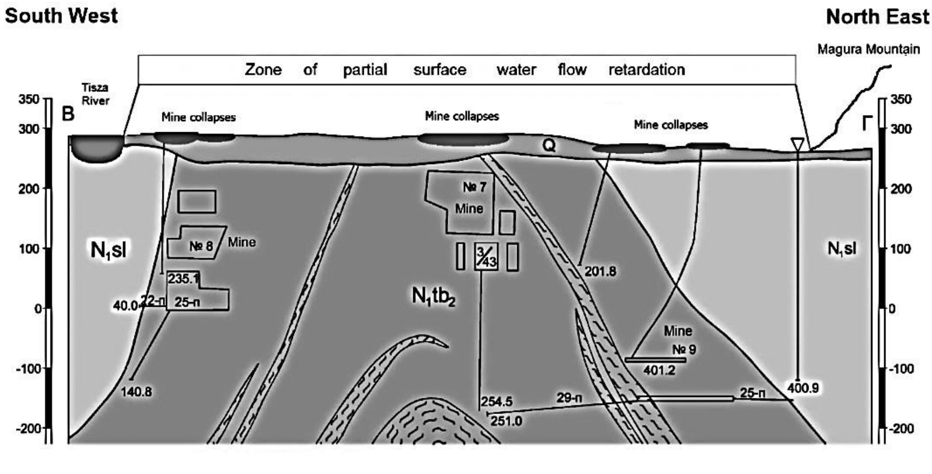

Fig. 1. Zone of partial water flow retardation: Q – Quaternary, alluvium; N_1sl – Miocene, Teresvynska suite of alternating: clay, siltstone, sandstone, and tuff; N_1tb_2 – Miocene, Tereblynska suite of alternating: rock salt with clays

According to the estimations of the majority of researchers, the Solotvyno salt deposit in the structural and geological terms is approaching to a diapir of salt pillar or dome type. The characteristic features of this structure which actively influence the technogenic transformations of the ecological state of the geological environment (GE) after mines decommissioning are tectonic grinding of host rocks with their upward rotation and the occurrence of clay rocks on the surface of the salt body in contact with loose water-saturated sediments. Clay deposits, which function as a filtration (protective) barrier in the development of deposits, are regarded by the majority of authors as residual products of physical and chemical weathering of salts (Fig. 2).

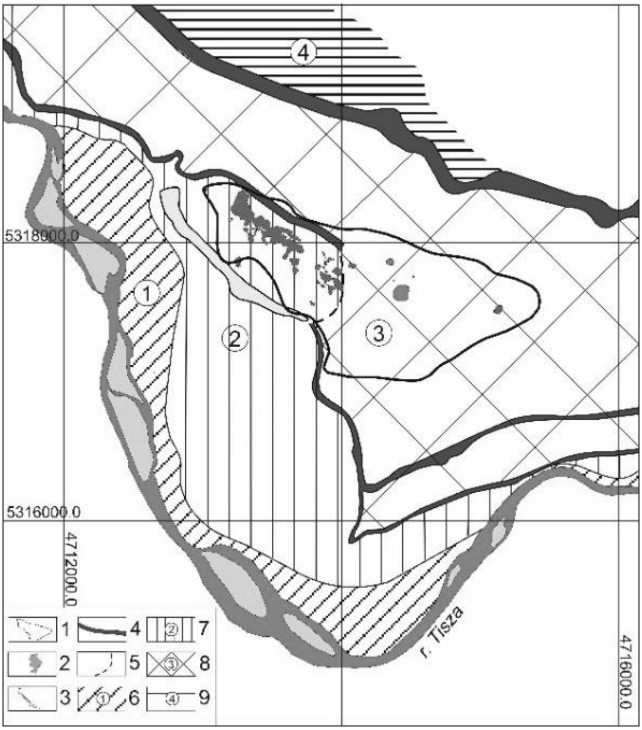

Fig. 2. Geomorphological scheme (Trofymchuk et al., 2014): 1 – outline of the salt dome in absolute mark "0", 2 – salt lake, 3 – dam, 4 – terraces, 5 – outline terraces cut mining operations, 6 – the first flood-plain bench, 7 – second flood-plain bench, 8 – the first terrace rising above the floodplain, 9 – the second terrace rising above the floodplain.

During the historical period of geological exploration of the Solotvyno deposit up to 2000 wells were drilled, a large complex of geological-surveying, geophysical, geochemical, engineering-hydrogeological and other researches was performed (Shekhunova et al., 2015). However, significant differences in the geodynamic (stress-strain) state of the individual sections of the salt rock mass and its spatio-temporal stability which were developed in the course of the operation, proved that the mines were decommissioned. The latter, as recent studies have shown, the deterioration of environmental and geological factors of life safety of the Solotvyno industrial-urban agglomeration have been significantly affected once the mines have been decommissioned and the post-mining phase has been formed. Such phase is characterized by auto-rehabilitation flooding of mines under the influence of the historical boundary parameters of the hydro-geofiltration system "watershed-main stream". At the same time there is a significant change in the stress-deformed state of the salt rock mass and the active development of karst-collapse forms and subsidence of the daylight area (Risk Assessment Report of Advisory Mission to Ukraine "Solotvyno salt mine area", 2016; Shekhunova et al., 2015; Yakovlev et al., 2016).

In our opinion, the main factor which complicates the mine-geological and ecological-geological conditions since the period of mines removal from the exploitation at the Solotvyno deposit is the discrepancy of persistence parameters of the simplified structural-geological model of the salt-rock mass of the rod structure complex of the challenging technogenic changes of hydrogeological and the geotechnical conditions, primarily the increase of the moisture under the condition of the density and the reduced strength, as well as the activation of karst-suffusion processes.

2. Materials and Methods

The dynamics of the hazardous processes activation were investigated by the data from the space images (Fig. 3–5), hosted by the Wayback resource (https://livingatlas.arcgis.com/wayback/, 2019). Wayback is a digital archive that gives the users access to various versions of World Imagery created over the time. Each layer in the archive is a snapshot of the entire map of the World Images as it existed at the date of its publication. Wayback has been providing access to all published versions of World Imagery since February 20, 2014. For each version of ArcGIS Online, there is an ArcGIS Online item that can be accessed directly from this application or through the Wayback Imagery group.

The deepest mine No. 9 was built in 1975 and is located in the northern part of the salt rod, in 2008, with a total volume of mine working space 9.4 million m^3 was flooded due to a water break with more than 500 m^3/year.

Fig. 3. Space survey data of the Solotvyno deposit territory as of September 13, 2017 (https://livingatlas.arcgis.com/wayback/, 2019)

Fig. 4. Space survey data of the Solotvyno deposit territory as of September 26, 2018 (https://livingatlas.arcgis.com/wayback/, 2019)

Fig. 5. Space survey data of the Solotvyno deposit territory as of August 07, 2019 (https://livingatlas.arcgis.com/wayback/, 2019)

Now, according to GIS analysis, interferometric studies of the dynamics of mine field gypsometry, there is a development of a local gradient contour of sediments of the daylight area, which has a long-term character in the conditions of increasing deformations and moistening of the salt body (Fig. 6).

Its formation at the foot of the southern slope of Magura, which is now being actively built up, according to interferometry data 2016 (Risk Assessment Report of Advisory Mission to Ukraine "Solotvyno salt mine area", 2016; Yakovlev et al., 2016), is in a phase of the increased disturbance of the stress-strain equilibrium state and the danger of forming a block mega-shift. This conclusion is partially confirmed by the continuation of the field of subsidence of the daylight area in the north direction beyond the generalized outer contour of the mine No. 9 mine workings.

In the southern part of the mining area there is an unmanaged flooding of the mine workings of mine No. 8 (built in 1804), whose operation was completed in 2010 with the total volume of extracted mineral mass (making of waste workings cavities) to 10.0 million. m^3, reaching 45% of the total volume of mining space of the XX-XXI centuries. In this regard, it should be noted that the flooding of mine No. 8 could be significantly accelerated by the partial flow of water from gypsometrically above located flooded mine workings of fields No. 7 and No. 9.

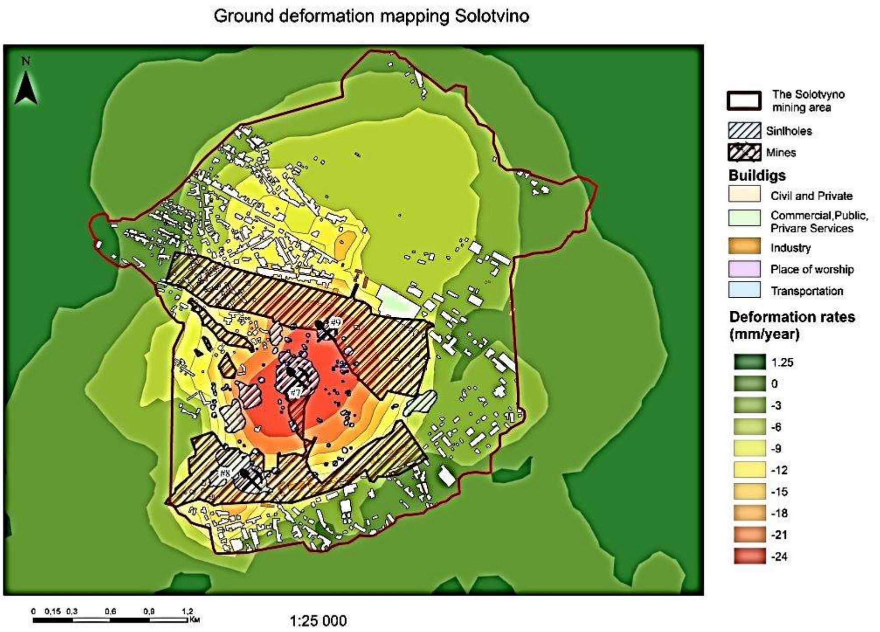

Fig. 6. Map of the Solotvyno agglomeration surface deformation

At the same time, taking into account the complicated structure and dense network of the tectonic disturbances of the salt rock mass of the mine of the Solotvyno deposit, they are included in the “List of especially dangerous enterprises”, whose long-term operation and termination of activity requires special measures to prevent harm to life and health of the community and the negative changes of the environment. In this case, the additional factors of complication of the ecological-geological situation in the area of salt mine’s impact is the increased region seismicity (up to 6–7 points of the MSK-64 scale or the threat of transient longitudinal waves with acceleration to 0.15–0.20 g) and the significant water saturation of the overlapping loose rocks. In our opinion, the analysis of remote sensing data or other sources (interferometry, change of relief, hydrographic network, etc.) can be considered as the leading factor of the development of the salt rock mass and daylight area deformations outside the summarized estimated contour of deformation influence of the mine workings No.7, 8, 9 (Trofymchuk et al., 2014; Dovgyi et al., 2019).

The large-scale floods of 1995–1996, 2001, 2010 and the associated additional rise of groundwater level increased their hydro-geodynamic pressure on the upper zone of the disturbed rocks of the salt mine, which, according to the authors' studies, have significant structural-geological, lithological and hydro-geodeformation fragmentation. The latter contributed to the activation of wetting and plasticization of the salt mass, karst collapse deformation and subsidence of the daylight area.

3.Results and Discussion

Taking into account the structural-geological and engineering-geodynamic inhomogeneity of the salt rock mass of the Solotvyno structure (Yakovlev et al., 2016), the authors constructed a map with the separation of the main zones of geological structures (Fig. 7) and calculated in percentage terms the areas of development affected by the geodynamic influence. (Fig. 8 and Fig. 9).

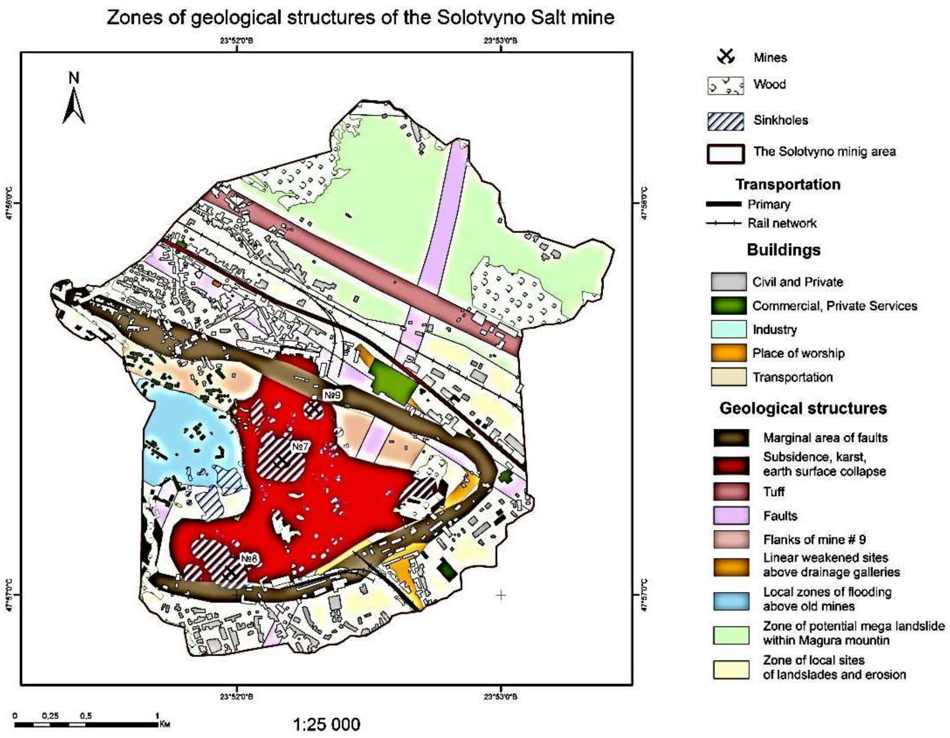

Fig. 7. Zones of geological structures of Solotvyno salt mine

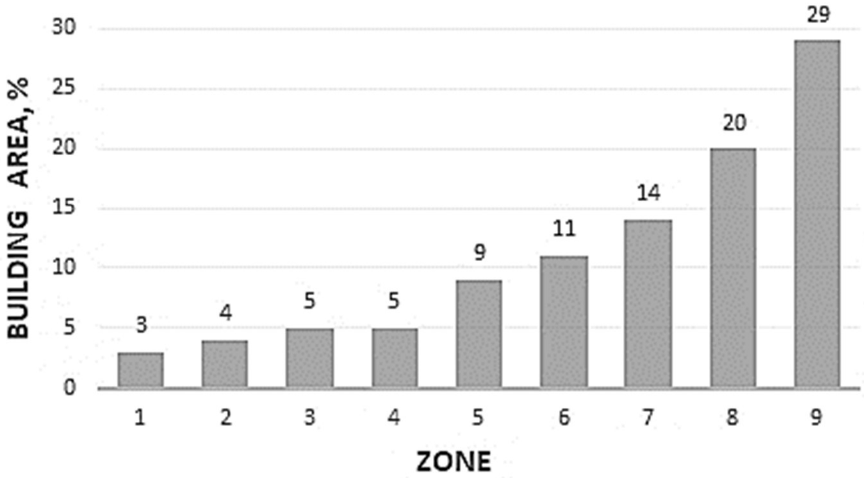

Fig. 8. Geodynamic influence of the salt mine on the construction of the Solotvyno agglomeration: 1 – zone of potential mega-landslide of Magura, 2 – zone of volcanic tuffs development, 3 – zone of karst-collapse impact, 4 – zones of flooding above historical (old) mines (XIX c.), 5 – flanks of the mine field No. 9, 6 – boundary zone of rifts, 7– zones of rifts, 8 – zones of development of local landslide and erosion processes, 9 – linear weakened zones above drainage galleries

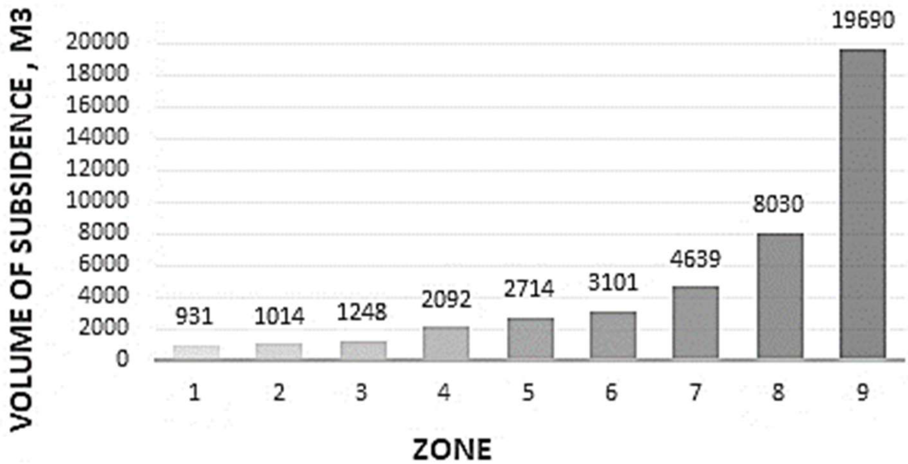

Fig. 9. Volume of subsidence of the surface of geological structures zones: 1 – linear weakened zones above drainage galleries, 2 – zone of volcanic tuffs development, 3 – zones of flooding over historical (old) mines (XIX c.), 4 – flanks of the mine No.9 field, 5 – boundary zone of rifts, 6 – zones of rifts, 7 – zone of karst–collapse impact, 8 – zone of potential mega–landslide of Magura, 9 – zones of local landslides and erosion processes

In general, the active development of the destructive deformations of the daylight surface and the upper zone of the GE in the zone of mining and extraction works on the salt-rock massive has a negative influence on the engineering and geotechnical stability of the bases of a significant number of residential and industrial buildings, roads, water supply and other critical infrastructure objects in Solotvyno.

As of January 1, 2019, more than 300 dwellings with more than 1.5 thousand persons, two secondary schools, kindergartens, a local hospital and a clinic, water utilities, power lines, gas pipelines and road sections were found in the area of geodynamic influence of the salt mine in terms of landslide, subsidence and karst collapse processes development.

It should be noted that the situation on the territory of the SE “Solotvyno Salt Mine” mining works influence has been significantly worsened in the recent period. Extremely limited realization of the protective measures has led to a steady spatio-temporal increase of areas and volumes of karst collapses and sinkholes at the deposit (Fig. 10 and Fig. 11).

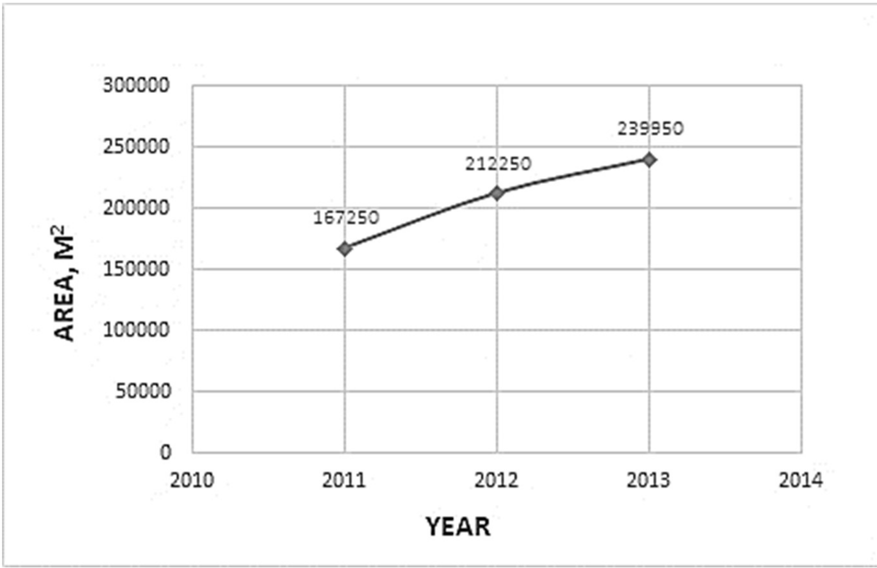

Fig. 10. Increase of karst collapses volume on the territory of the Solotvyno Salt Mine during 2011–2013

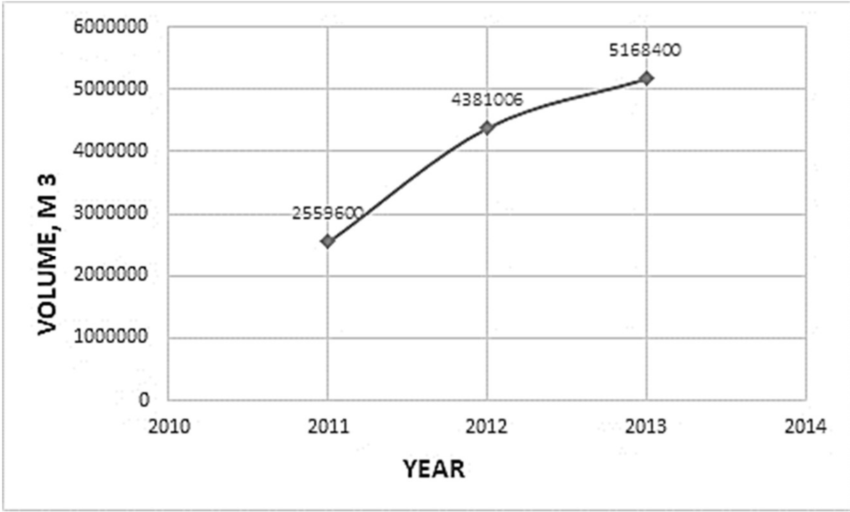

Fig. 11. Increase of karst collapses volume on the territory of the Solotvyno Salt Mine during 2011–2013

The authors have investigated the deformation field of the local catchment area and established its effect on the change of ecological – resource status of the transboundary sections of the Tisza River basin, the preliminary changes of its surface and underground water balance and chemical composition were estimated.

Using the space monitoring (interferometry) technologies, the field magnetic-electric survey and GIS modeling, the authors investigated and analyzed the space-time structure and the balance of the daylight surface subsidence.

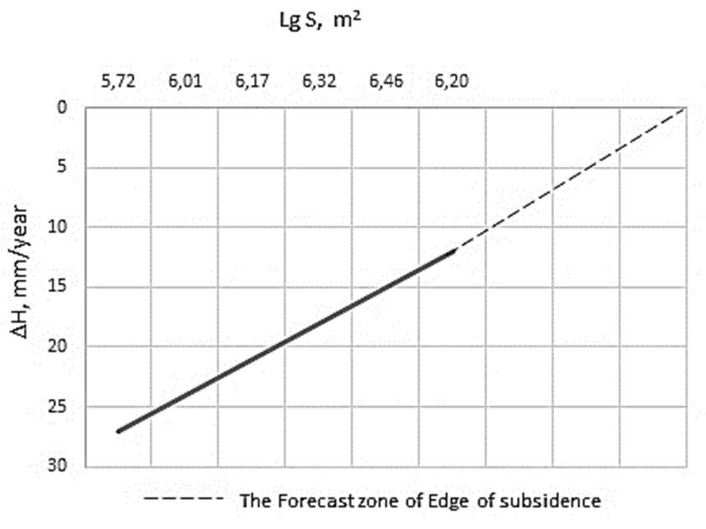

Fig. 12. Flat-radial development of karst deformation of the daylight surface of the mine No.7 field influence zone

The first time calculations show the dynamics of the increase in the generalizing karst-subsidence sinkhole, which goes on in the structure of the plane-radial field of the development of elastic-plastic and plastic-fluid deformations of the salt rod central part and the upper loose sedimentary rocks, which are associated with the largest karst collapse and a section of the subsoil imbalance of the mine No.7 field (Fig.12).

According to the results of the geological-statistical modeling, a regular dependence was obtained, having a radial-linear character and demonstrating a stable regular radial relationship between the parameters of vertical (subsidence) and horizontal (area of subsidence interval) deformations of the daylight surface of the mine field.

The above mentioned results of our analysis of modern hydrogeodynamics of changes in the parameters of karst-subsidence deformations of the surface on the mine fields of the Solotvyno Salt Mine allow us to conclude that their volumes increased up to 2.5 times and the area – only (approximately) 2 times for the period 2011–2016. In our opinion, this may be an indication that the karst destruction of both upper and deep flooded horizons is currently taking place, mainly in mines No.8 and No.9, where fresh water from the overlying layers of loose water-saturated rocks may flow. Besides, according to the results of interferometry data complex analysis, electro-magnetometric survey (Shekhunova et al., 2015; Yakovlev et al., 2016), the dynamics of gypsometric relief changes, it is possible to conclude that the general territorial field of elastic-plastic deformations of the salt-rock mass and the daylight surface can be formed inside both modern mines No 7, 8, 9 zones impact and adjacent mines flooded in the early of the XX century (Kunigunda, Ludwig, etc.). This conclusion is consistent with the development of the modern radial-spatial deformations of the daylight surface beyond the estimated boundary of forecast subsidence for distances up to 250–350 m with a large number of buildings and critical infrastructure facilities.

4. Summary and Conclusions

In our opinion, the simultaneous increase in the depth of karst formation and plasticization of the salt-rock mass in the contour of mining work close to Solotvyno settlement mine No.8 will lead to the activation of the dangerous deformations of the daylight surface, additional destruction of a number of residential and industrial buildings, engineering and the significantly increased threat to the life of the population.

1. On the territory of the Solotvyno industrial-urban agglomeration there is a threatening tendency to decrease the level of ecological safety due to the progressive destruction of the salt rock mass of the mine. At the same time,

recent data indicates that there is an increased risk of transboundary emergencies of engineering-geodynamic and aquatic-ecological origin on the territory of the Solotvyno Salt Mine due to the spread of karst processes towards Solotvyno settlement and the Tisza River Valley.

2. Large-scale threats associated with the complex impact of the hazardous geological processes on the territory of Solotvyno settlement (subsidence and deformation of the daylight surface, karst collapses, landslides etc.) and the activation possibility of the highly mineralized waters migration cause the urgent need to create and develop preventive measures to prevent transboundary emergency.

3. Until now, there is an absence of the separate state program for overcoming ecological consequences inside the Solotvyno agglomeration and the presence of increased threats of a water-ecological emergency in the transboundary basin of the Tisza River determine the necessity of works complex justification for the salt mine influence area transformation into the safety ecology-technogenic state.

4. Practical absence of the systematic monitoring of the spread of karst collapses, subsidence deformations of the daylight surface and the flow of mineralized groundwater in the Tisza River Valley poses a serious threat with possible negative consequences for the population life safety and the transboundary level environment.

Acknowledgments

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Assessment of the impact of anthropogenic activities on aquatic ecosystems

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Abstract

The article presents methodological approaches to improving the environmental monitoring system, improving its objectivity and visual aspects of presenting data using Earth Remote Sensing (ERS) methods and geoinformation technologies (GIS) for assessing and analyzing the risks of water bodies contamination with solid waste during floods and submergence. At the same time, direct and inverse relationships were identified; self-regulation phenomena were analyzed; integrity, order and centralization of information indicators of flood zones potential ecological hazard formation were assessed. It is suggested to use information-analytical data processing technologies for studies of changes dynamics in the condition of the studied territories. ArcGis tools are used to collect, accumulate, process, formalize, and present data on ecosystem impact factors and conditions. The above tools provide interpretation of the analysis results in graphical form on electronic maps and implementation of mathematical methods for estimating the intensity of anthropogenic impact and modeling its effects on the environment. Synthesized interactive mapping materials are created using state-of-the-art geodatabase information technology, have high visibility and can be updated with continued use by conservation agencies.

In addition to imaging, the developed ecological and mapping models are the basis for assessing the environmental status of the study area and compiling a set of digital thematic maps within GIS environment. In order to assess and analyze the risks of water bodies contamination with municipal solid waste, to ensure environmental safety and to prevent hazardous impacts, it is necessary to thoroughly and systematically analyze the status of water bodies using GIS technologies.

Keywords: aquatic ecosystems, landfills, anthropogenic impact, geoinformation systems, spatial modeling, data base, Earth Remote Sensing methods

1. Introduction

Investigation of aquatic ecosystems status is necessary for studying of the patterns of water resources functioning under stable anthropogenic load. Measures as for water bodies environmental status improving should be based on research findings in the field of anthropogenic load modeling.

Hazard phenomena such as rising groundwater levels causing floods have become very common. Settlements, farmland are being flooded, the conditions of functioning of economic objects are deteriorating, the fertility of land is being reduced, architectural and historical monuments are being damaged, etc. A significant factor of water bodies environmental safety impact is the surface runoff from agricultural land, urban areas. Impact of solid waste sites can be distinguished separately. During periods of snowfall, heavy rainfall and torrential flow, the generated stream transports soil erosion products and waste decay products to the hydrographic network, as well as radioactive and toxic substances that are deposited on the catchment areas not only as a result of accidental emissions, but also during normal operation.

Waste is a threat to the health of the population living near the landfill, causing epidemiological danger and biological contamination. Particularly negative impact of pollution processes is on biota, soil cover, surface and groundwater sources. The organic matter contained in the solid household waste forms a filtrate that is complex in chemical composition. Penetration of the filtrate into groundwater leads to contamination, which extends over considerable distances from the landfill.

2. Materials and Methods

The paper proposes the use of Earth Remote Sensing methods and geoinformation technologies to assess and analyze the risks of water bodies contamination with solid household wastes during floods and submergences (Dovhyi et al., 2001). At the same time, direct and inverse relationships were identified, self-regulation phenomena were analyzed, integrity, order and centralization of information indicators of the formation of potential environmental hazard of flood zones were evaluated.

The authors propose the following algorithm for the study of anthropogenic impact on aquatic ecosystems by remote sensing (ERS) methods:

- collection of ERS data, cartographic materials and descriptive information;
- creation of a detailed digital map of the study area;
- determining the seasonal variability of the ecosystem using multiple images;
- classification of the adjacent territory;

- identification of sources of anthropogenic load, namely identification of topogeodetic parameters of the landfill;
- classification of aquatic vegetation;
- determination of the temperature regime of the water body using the time ERS data (thermal channel);
- conducting ground (surface) measurements, selection of test sites;
- comparison and calibration of the obtained results with the help of ERS data processing with ground measurements;
- creation of geodatabase of the study area.

Given the significant environmental impact of man-made objects, there is a need to investigate the area of migration of toxic migratory substances. Therefore, in the study of the main ways of toxic hazardous substances being generated, it was necessary to identify and investigate the migratory flow of pollutants. Since direct measurement is impossible due to the extremely complex mechanism of contaminant migration into the array, it has been proposed to involve ERS methods to identify the source of impact and survey the terrain, while taking into account direct decryption features that characterize the properties of the object and display object properties and contain direct reflection on the images (Novokhatska, 2014). These are such features as geometric (shape, shadow, size), brightness (photon, brightness level, color, spectral image), structural (texture, structure). Since spectral brightness often depends on the influence of external factors, it is suggested to use algorithms that use structural features in addition to algorithms based on the transformation of spectral brightness when deciphering space images and finding changes in terrain. As bright features of objects that include a number of image elements, the study suggested use of characteristics that describe the shape of the brightness histogram – average brightness, variance, asymmetry coefficient, kurtosis, defined by the following expressions:

$$m = \frac{1}{n-1}\sum_{i,j} I_{i,j} \tag{1}$$

$$D = \frac{\sum_{i,j}\left(I_{i,j} - m\right)^2}{n-1} \tag{2}$$

$$S = \frac{\sum_{i,j}\left(I_{i,j} - m\right)^3}{(n-1)D^{3/2}} \tag{3}$$

$$Kr = \frac{\sum_{i,j}\left(I_{i,j} - m\right)^4}{(n-1)D^4} \tag{4}$$

where: m – the average value of the pixels in the scan window, I – the pixel brightness value, i, j – the coordinates of the pixels in the scan window, n – the number of pixels in the scan window, D – dispersion of brightness values, S – bias (asymmetry), Kr – kurtosis.

For a comprehensive analysis, it is proposed to study the local area on its model, performing the identification of topogeodetic parameters of the landfill in order to determine their dynamics to a certain depth of the retrospective, as well as determining the directions of migration of products of destruction of accumulated waste with the waters of the first aquifer. Geosystem model is used as the scientific basis for nature management (Sokolovskaya et al., 2015). This model is used for forecasting as well as for nature management purposes. The presented technology combines traditional database operations with full visualization and geographical (spatial) analysis provided by the map.

3. Results and Discussion

The main purpose of the forecast is to evaluate the possible reaction of the environment on direct or indirect anthropogenic impact, to address the issues of rational use of nature in accordance with the expected state of the environment.

In the period of increasing anthropogenic load, hazardous processes of flood phenomena are increasingly activated. Every year, the issue of new territories groundwater flooding becomes more sensitive, which leads to deterioration of sanitary and epidemiological conditions, change of groundwater and soils chemical composition (Timchenko, 2006), increase of their corrosion activity in relation to the bases of engineering structures and communications, activation of hazardous geological phenomena, etc.

Flood prevention requires continuous areas monitoring with data assessment and analysis. Therefore, the study proposes to analyze the features of landfill location by means of spatial modeling with respect to the natural protection of underground aquifers (Korchenko et al., 2019). A well-known schematic map of Ukraine's natural groundwater protection (geographical atlas of Ukraine), which was scanned and spatially linked to ArcGIS, was used to construct such a mapping model. Mapping model of the of Kyiv region groundwater natural protection was developed by highlighting and appropriate processing in the GIS environment of the indicated map of the Kyiv region (as an example), which is presented in Fig. 1.

As a result of combining of two layers: the natural groundwater protection of the Kyiv region and the Kyiv region landfill, which was constructed according to the register of disposal sites, they obtained a cartographic model of landfills in Kyiv region location with respect to the natural groundwater protection. This model shows the spatial location of landfills, their impact on underground aquifers used for water supply to the population. Thus, we see the critical hazardous locations of solid waste landfills that need to be addressed first and foremost, namely sanitation, reclamation and taking appropriate measures to prevent the formation of natural landfills in these stress areas.

In order to determine the degree of danger of flooded areas, it is necessary to assess the potential risk of shallow groundwater. Creation of new and improvement of existing methods of construction of geomodels of probable flood zones is possible only on the basis of complex use of aerospace and contact measurements data taking into account the variety of hydrogeological conditions and specificity of the analyzed area.

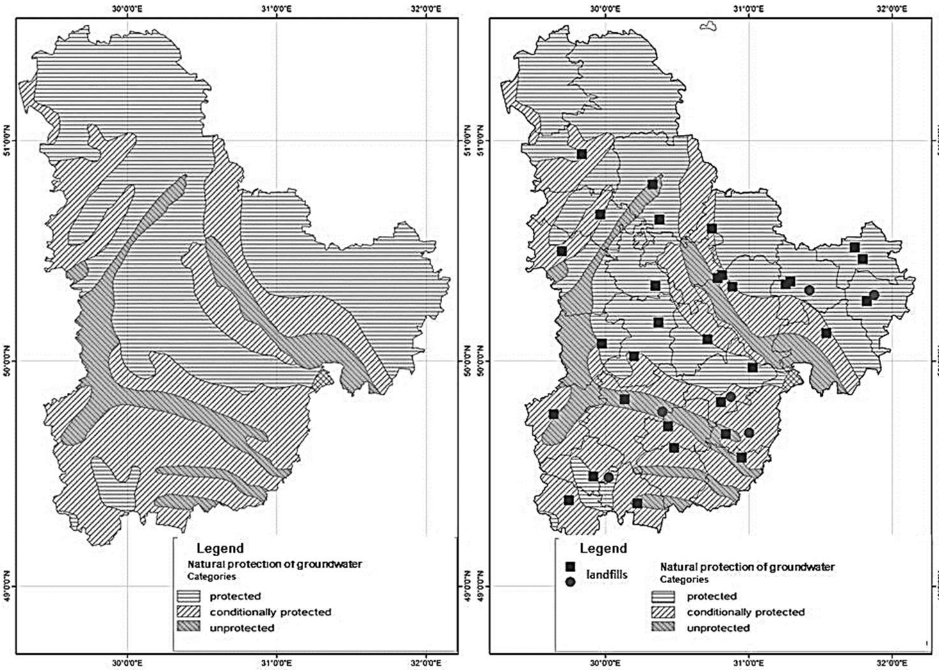

Fig. 1. Mapping model of landfills and solid domestic waste disposal sites in relation to groundwater nature protection location

To highlight the location of a solid domestic waste landfill, histograms of the ranges of pixels belonging to the landfill were calculated. The study used a multi-zone image of the satellite QuickBird with a spatial resolution of 0.61 m (Fig. 2).

While working with space images, measurements of the plane characteristics of the found dumps were made and the total area of the stored waste was calculated. Influence on the landscape of the natural-technogenic system containing the landfill is analyzed (Sheviakina et al., 2019). So, on space images we can see the presence of runoff from the landfill, their direction and source of impact, damage to the grass cover and other vegetation around the landfill, as well as burning (smoke plume) of waste.

To visualize the object of study, it is proposed to use ArcINFO / ArcGIS tools with Spatial Analyst and ArcScene / 3Danalyst modules, which involves the construction of a spatial terrain model based on geodetic measurements and a space snapshot with coordinate anchors. With this aim, additional ground surveys were conducted and a track was constructed using a GPS receiver (Magelan Triton 400) directly into the landfill site. Also, a topographic raster map (1: 10,000 scale) is digitized, linked to layers in ArcMap, and vectorized. The attribution data in the table and text forms of the study object, specified in the passport of the waste disposal site, are taken into account (Fig. 3). In addition to rendering the image, this model allows us to predict possible contamination and to outline the area of impact of the landfill.

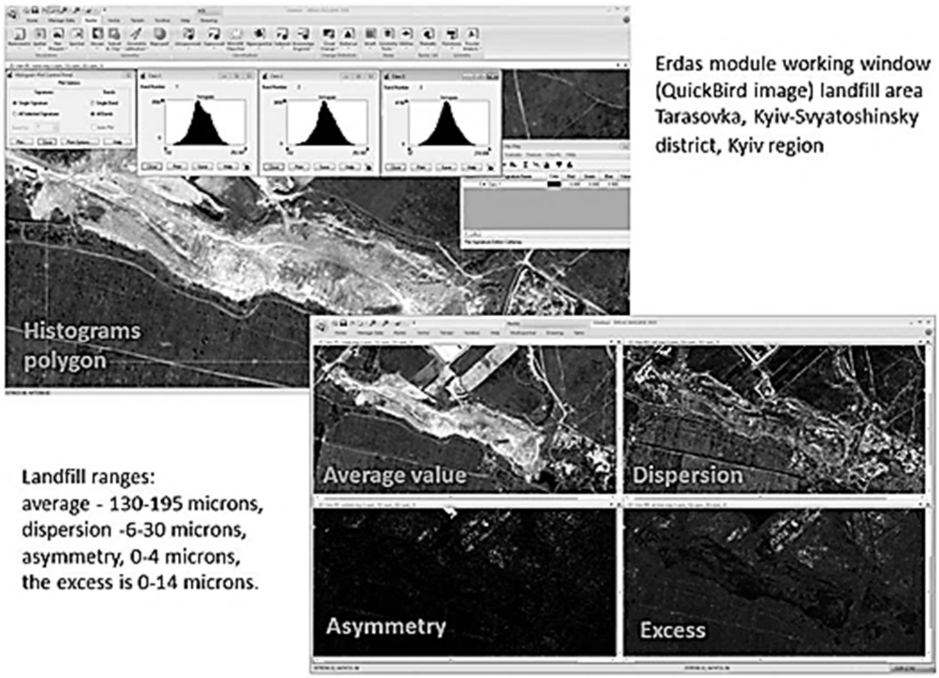

Fig. 2. Landfill site assessment

Such an approach provides an online mode of obtaining reliable and accurate data on the spatial and temporal distributions of environmental status parameters of certain flooding areas with high levels of anthropogenic pollution, including solid domestic waste (Trofymchuk et al., 2014). Therefore, the use of space imagery allows us to analyze the individual features of landfills location in relation to water bodies, settlements and natural-technogenic systems. These features determine the conditions under which waste is stored and their interaction with the environment, namely the conditions for the migration of pollutants formed during the operation of landfills.

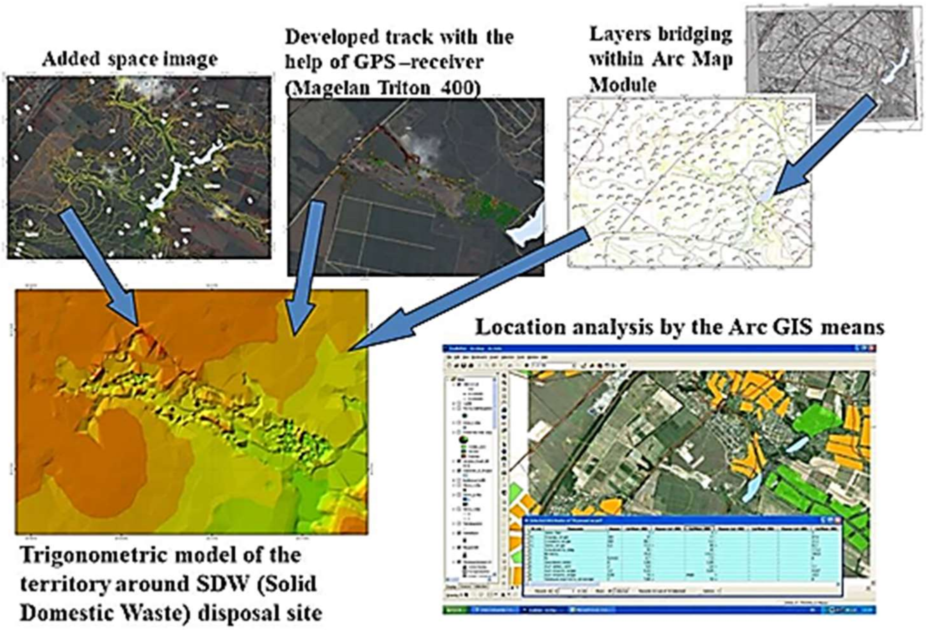

Fig. 3. Cartographic model of spatial modeling of landfills

4. Summary and Conclusions

The study concluded that for more detailed analysis and assessment of water bodies contamination by solid domestic waste, and the establishment of direct and feedback relationships, it is advisable to use ERS methods and GIS technologies.

The authors have proposed an algorithm for the study of anthropogenic impact on aquatic ecosystems by ERS methods, which evaluated and analyzed the location of landfills for groundwater protection. Most of the landfills found are in close proximity to a critical area where groundwater is not naturally protected. A cartographic model of the zone of critical impact of solid waste landfills on surface water sources and groundwater has been developed. As a result, a list of landfills in need of reclamation has been established in order to effectively sanitize the area from unauthorized natural landfills.

The spatial cartographic model of landfill location was synthesized by means of geoinformation systems, by processing and analysis of information obtained by space monitoring methods and hydrogeological data. ArcGIS provides a triangulation model of the area around the landfill. Using the available information, it is concluded that it is expedient to supplement the database on natural-geological conditions by adding spatial hydrogeological and hydrological schemes with information on the geometric and quantitative characteristics of surface and underground runoff, surface and underground watersheds, reservoirs and reservoirs in the area of influence as well as the indicative contours and area of the surface, groundwater and groundwater aquifers contamination indicating their depth of occurrence and power. This will allow detailed and clear use of minimal financial, time and human costs to predict the development of negative phenomena and processes, develop a set of actions, as well as make timely decisions on reducing the impact on environmental components to significantly improve the level of environmental safety at regional and national levels.

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Application of cavitation in technologies for purification of industrial wastewater from aromatic compounds

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Abstract

The genesis of wastewater containing aromatic compounds and their influence on the composition of natural waters in Ukraine are analyzed. The methods of wastewater treatment from aromatic compounds are analyzed. In particular, biological and reagent methods of wastewater treatment from aromatic compounds are discussed. One of the most promising methods of wastewater treatment, namely cavitation, which can be implemented both without reagents and with their use, is considered. Schemes of laboratory cavitation units, in particular using an ultrasonic emitter and hydrodynamic cavitator, for the study of purification of aqueous mediums from aromatic compounds, namely, benzene, toluene and phenol, as well as methods of analysis of reaction mediums are given. The results of cavitation oxidative destruction of benzene and toluene under anaerobic and aerobic conditions are presented. The effect of temperature on the transformation of aromatic compounds under the action of cavitation was established and an explanation of this phenomenon was given. The peculiarities of the transformation of phenol in the cavitation field and their dependence on the presence of some oxidants in the medium are described. Acoustic analysis confirmed the positive role of benzene as a component of the waste species on the occurrence of the cavitation phenomenon. The concept of industrial process realization for wastewater treatment of various industries from aromatic compounds was developed.

Keywords: wastewater, aromatic compounds, gasoline, toluene, phenol, cavitation, destruction

1. Introduction

Organic compounds are typical components of wastewater generated by chemical, petrochemical (Israel et al., 2008) and coke-chemical industries. Aromatic compounds are used to obtain dyes and drugs, synthetic fibers, phenol, nitrobenzene, explosives, and the like. Aromatic compounds, most of which are poorly biodegradable, pose a significant threat to natural ecological systems. For example, in 2015, the concentration of phenol exceeded the maximum permissible concentration in almost all major rivers of Ukraine and their basins. The greatest excess of phenol concentration was found: up to 10 times in tributaries of the Danube and the Dnieper; tributaries of Seversky Donets – up to 8; tributaries of the Southern Bug, Siversky Donets River, Kremenchuk Reservoir – up to 5–6 times; up to 4 in the Danube, Dnister, Southern Bug, Dnieper and Kakhovka reservoirs; in the Poltva River, the Dniester tributaries, the rivers between the Danube, the Dniester and the Southern Bug, the Kyiv and Kakhovka reservoirs – up to 3 (Bodnar et al, 2017). In general, the level of pollution of natural reservoirs with phenol was the same as in previous years. This indicates the constant contamination of natural reservoirs with aromatic compounds.

Improving the quality of water in natural reservoirs certainly requires a system of integrated measures. An important component of this complex is the organization of local treatment plants at the enterprises where pollutants are formed. The traditional method of treating wastewater from certain aromatic compounds is biological (Vogt, 2011). However, it requires the provision in the wastewater of a certain molar ratio between the biogenic elements, in particular, C(COD) : N : P = 100 : 5 : 1. According to the rules for receiving wastewater into wastewater networks, there are restrictions on the content of a number of compounds in wastewater, in particular, aromatic. In addition, according to these rules, factories producing organic compounds, in particular benzene and toluene, as representatives of a homologous series of aromatic hydrocarbons, must be equipped with local treatment facilities. Various substances having oxidizing properties, such as Fenton reagent (Deng et al., 2006), sodium hypochlorite (Znak et al, 2012), etc., are used as oxidizing agents in the treatment of wastewater from organic compounds. Cavitation processes are promising in wastewater treatment technologies for inorganic and organic compounds (Zin et al., 2016), in particular, aromatic (Kang at al., 2001). Cavitation processes for wastewater treatment are proposed to be carried out both without the use of reagents (Rajendrasinh, al., 2015) and with the use of oxidants (Gogate, 2015), in particular, the Fenton reagent (Bagal at al., 2014; Chakinala et al., 2009). It is very interesting to use a modified cavitation process in an electric field (Junga et al., 2014).

Higher efficiency in introducing energy into the aquatic medium that results in cavitation compared to the ultrasonic cavitator is achieved in a hydrodynamic jet solid-type cavitator (Yavorskiy et al., 2016; Znak et al., 2016).

Consequently, the analysis of the sources of information shows that the cavitation method of purification of wastewater from aromatic compounds is quite effective. It is advisable to use hydrodynamic cavitator for the treatment of wastewater generated by enterprises. Unlike ultrasonic cavitator, they are characterized by much higher performance. However, the optimal or rational parameters for such a process have not yet been fully established.

2. Materials and Methods

2.1. Laboratory study of cavitation wastewater purification from aromatic compounds

For the research, installations were used in which cavitation was excited in different ways: by ultrasonic vibrations and the use of kinetic energy of fluid jets. For decomposition of aromatic compounds, which simulate the stage of wastewater treatment, in the first case used an ultrasonic generator "Ultrasonic disintegrator UD-20" (Fig. 1), in the second – a hydrodynamic jet cavitation generator (Fig. 2).

The radiation frequency of the ultrasonic emitter was 20 kHz and the power was from 8.2 to 12.5 W. Research with the ultrasound cavitation generator were performed under isothermal conditions, which were created using a thermostat.

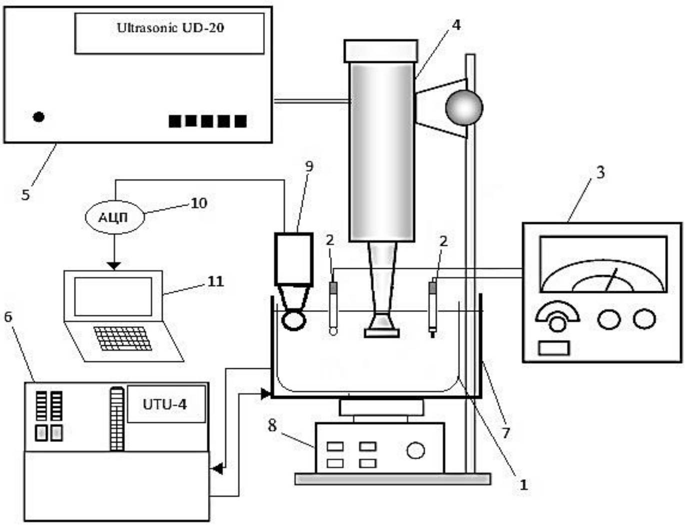

Fig. 1. Scheme of installation for the research of cavitation decomposition of aromatic compounds by ultrasonic radiation: 1 – reaction flask, 2 – electrodes, 3 – pH meter, 4 – magnetostrictive emitter UD–20, 5 – power supply, 6 – ultra thermostat, 7 – thermostatic bath, 8 – magnetic stirrer, 9 – hydrophone, 10 – analog–to–digital converter (ADC), 11 – laptop computer

The nominal power of the pump of the hydrodynamic cavitator was 1.1 kW. The pressure at the inlet of the cavitator was 0.3–0.6 MPa. The number of nozzles in the hydrodynamic cavitator was 3, the angle between the axes of the nozzles is 160–170 degrees.

For anaerobic studies, the reaction flask was isolated from the air with an elastic membrane.

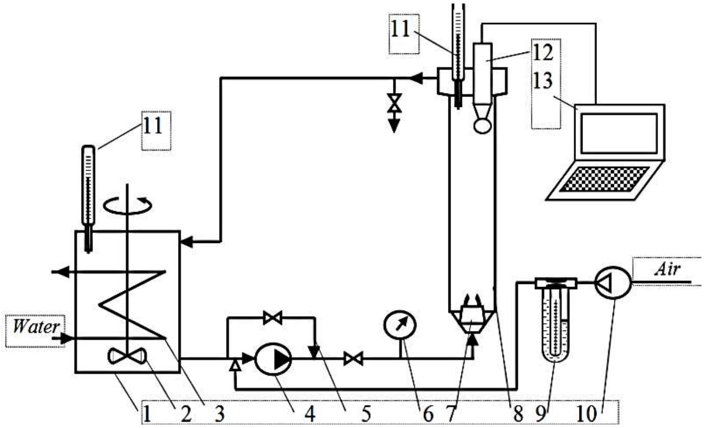

Fig. 2. Scheme of installation with hydrodynamic jet cavitator for research of aromatic compounds destruction: 1 – circulation capacity, 2 – stirrer, 3 – cooling circuit, 4 – the pump, 5 – bypass, 6 – pressure gauge, 7 – working body (cavitation element), 8 – the cavitation generator, 9 – pressure gauge, 10 – compressor, 11 – control thermometer, 12 – hydrophone, 13 – PC

Analysis of the reaction medium for the content of aromatic compounds was carried out by UV/Viz spectroscopy on a double-beam Carl Zeiss JENA SPECORD M40 (UV-VIS) spectrophotometer using a 10 mm quartz cell in the wavelength range 200–900 nm (comparison medium – distilled water): the amount of chemical oxygen demand (COD) determined by ISO 6060: 2003.

The energy characteristics of the cavitators were determined by the calorimetry method. The development of cavitation fields was analyzed by method of sonochemical analysis using a spherical hydrophone of type 8105 (frequency range – from 0.1 Hz to 160 kHz; sensitivity – 205 dB at 1V/μPa; directional characteristics: at 100 kHz, the directivity is not less than 270 degrees in axial plane and 360 degrees in radial). Hydrophone was commuted with a PC via an analog-to-digital converter. The waveforms and spectra of the received signals were analyzed and interpreted using a standard specialized program for recording and editing audio files "Adobe Audition 1.5".

2.2. Laboratory modeling of the process of wastewater imitation purification by cavitation method

For research, was used synthetic wastewater obtained from intensive mixing of distilled water with a specific aromatic compound (benzene, toluene, phenol), which was taken in excess of its maximum solubility at 293 K. After stirring for 30 minutes. the resulting medium was kept to separate the aqueous-organic and organic phases. Thus, the maximum content of the aromatic compound in the aqueous medium was reached. The concentration of organic substance was monitored spectrophotometrically and the determination of the COD values of the water-organic medium.

The results that are shown in Fig. 5–7 was performed in two parallel experiments. Based on the data obtained, the average concentration of the aromatic compound at a certain point in time was calculated. For all dependences of the concentration of the aromatic compound (benzene or toluene) on time, the value of the approximation reliability ($R2$) was calculated. These values are indicated in the boxes 5–7. The smallest value of the value of the $R2$ approximation is 0.959. This indicates the high reliability of the results obtained.

Samples of the reaction medium for analysis on the content of the aromatic compound were taken every 5 minutes. The time from the moment of sampling to the beginning of its analysis by spectrophotometric method in all cases was one minute.

Experiments on cavitation degradation of aromatic compounds were carried out to achieve a concentration of benzene or toluene of 0.01–0.002 mol/m^3.

3. Results and Discussion

Analysis of the results of cavitation treatment of wastewater simulations containing individual aromatic compounds revealed the peculiarities of the transformation of benzene, toluene and phenol. It was found that, in the absence of oxidizing agent in the reaction medium, the conversion of these compounds practically does not occur. In the presence of gaseous oxygen in the reaction system, there is a rather intense transformation of both benzene and toluene. At the same time, the intensity changes of the UV spectra of these compounds were observed (Fig. 3 and Fig. 4).

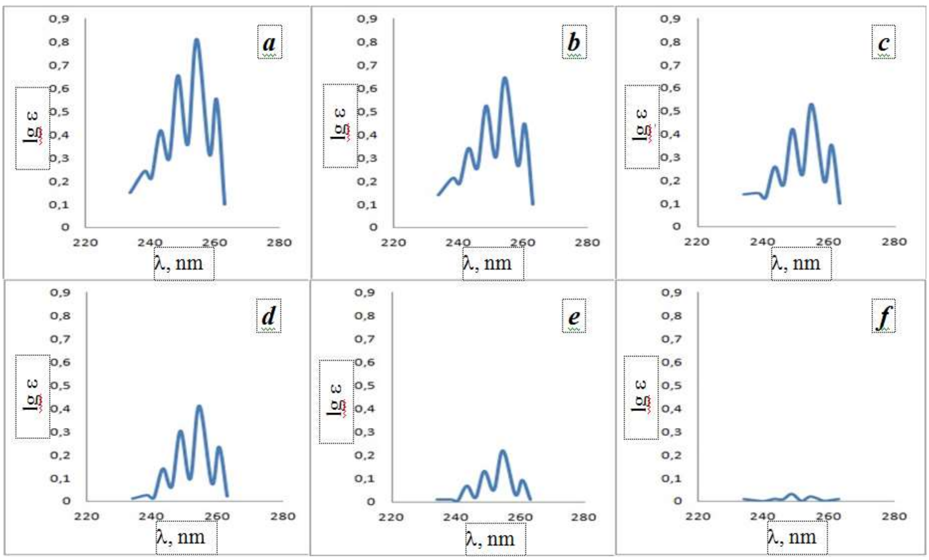

Fig. 3. Changing the intensity of the benzene UV spectrum during its cavitation decomposition; the duration of the process [min]: a – 0, b – 10, c – 15, d – 30, e – 45, f – 60

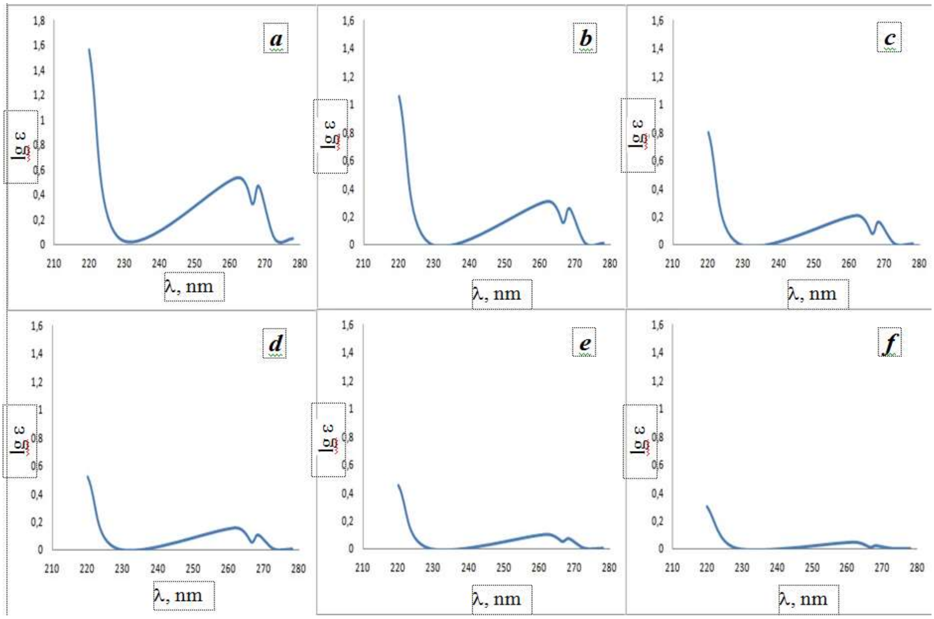

Fig. 4. Changing the intensity of the toluene UV spectrum during its cavitation decomposition; the duration of the process [min]: a – 0, b – 10, c – 15, d – 30, e – 45, f – 60

However, the structure of the spectra of benzene and toluene did not change, and no other spectra were detected in the 200–900 nm range. This means that benzene and toluene are mineralized, ie oxidized to such end products as CO_2 and H_2O. This conclusion is confirmed by the fact that the magnitude of the COD decreases in time almost in proportion to the change in the intensity of the spectra and, consequently, the concentrations of benzene (Fig. 5) and toluene (Fig. 6) in the reaction media.

In both cases, at anaerobic conditions in the initial stages of the process showed a decrease in the concentration of benzene and toluene. Once the conversion rate of 20–25% is reached, further decomposition of these compounds is virtually stopped. This can be explained by the fact that benzene and toluene are characterized by high partial pressure values. Such substances are known to contribute to the phenomenon of cavitation. As a result of the transformation in the cavitation field, the content of benzene and toluene in the reaction medium decreases. Therefore, the conditions for cavitation in the absence of other components with high partial pressure, such as air, oxygen or other gases that are well soluble in water, are deteriorating. The following this conclusion will be confirmed by the acoustic analysis of the cavitation process under different conditions.

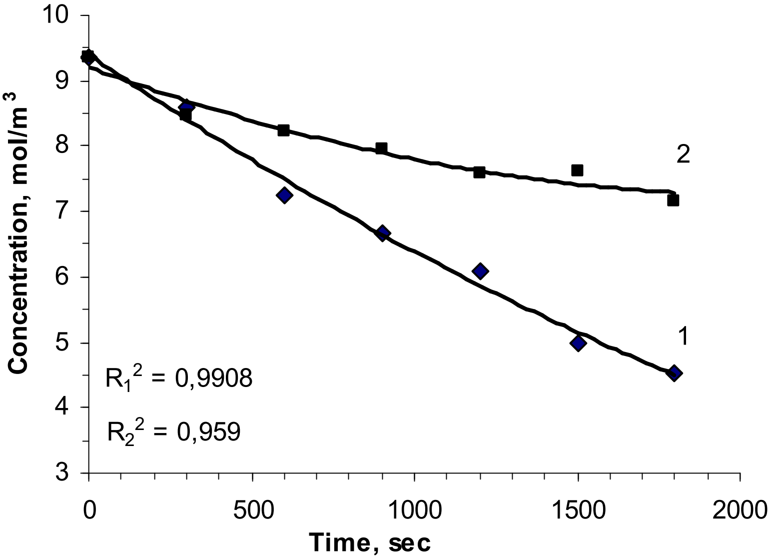

Fig. 5. The dependence of the concentration of benzene under the action of ultrasonic cavitation: 1 – anaerobic conditions, 2 – aerobic conditions

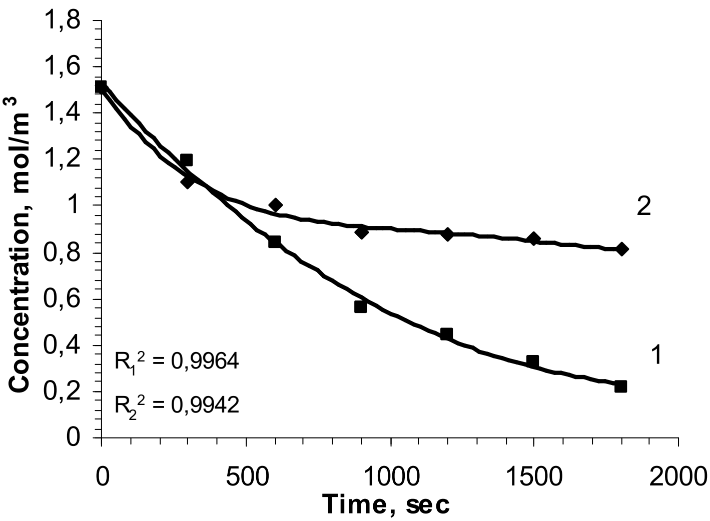

Fig. 6. The dependence of the concentration of toluene under the action of ultrasonic cavitation: 1 – anaerobic conditions, 2 – aerobic conditions

It is established that in the temperature range of 293–323 K, the lowest conversion rate of benzene and toluene is in the region of 313 K (Fig. 7).

This phenomenon is caused by the formation in the cavitation field at temperatures of about 313 K stable microbubbles, which are quite resistant to collapse (Bunkin at al, 2009).

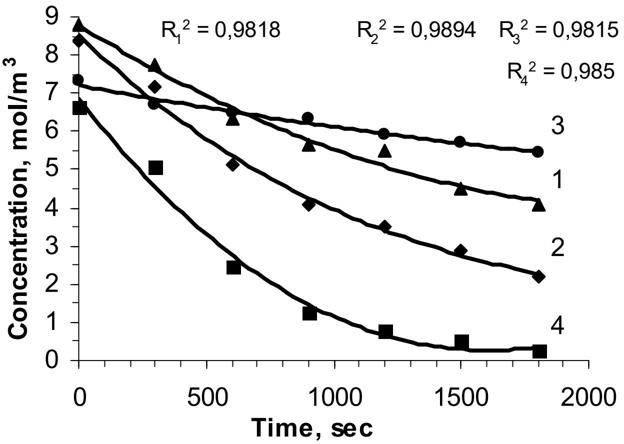

Fig. 7. The dependence of the concentration of benzene on time at temperature [K]: 1 – 289; 2 – 303; 3 – 313; 4 – 323

Their collapse is limited, so the energy released during this process is relatively small. Therefore, the degree of conversion of benzene and toluene is negligible. For example, at temperatures of 293, 303, 313, and 323 K, the rate constant of cavitation decomposition of benzene in steady state cavitation was equal to (sec^{-1}): $1.26\cdot10^{-4}$, $7.94\cdot10^{-4}$, $0.28\cdot10^{-4}$ and $6.76\cdot10^{-4}$, benzene – $5.07\cdot10^{-4}$, $8.25\cdot10^{-4}$, $2.10\cdot10^{-4}$ and $13.60\cdot10^{-4}$.

The higher rate of cavitation oxidation of toluene compared to gasoline is explained by the presence of a methyl substituent in the benzene ring.

Previous studies have shown the high efficiency of cavitation processes in a jet-jet hydrodynamic cavitator (Yavors'kyi at al, 2017). Increasing the pressure at the inlet of the hydrodynamic cavitator provides higher velocity and higher kinetic energy of fluid jets. This causes a greater amount of energy released during the collision of the jets, that is, promotes cavitation. Indeed, with increasing pressure at the inlet of the cavitator of only from 0.29 to 0.57 MPa, the decomposition time of benzene at 293 K was reduced by at least three times.

Increasing the temperature increases the speed and degree of conversion of benzene. As in the ultrasonic cavitator, the rate of conversion of benzene in the hydrodynamic cavitator at a temperature of 303 K was greater than at a temperature of 313 K. However, this difference was much smaller than in the ultrasonic cavitator. Thus, at temperatures of 303 and 313 K, the initial decomposition rate of benzene was $5.33 \cdot 10^{-3}$ and $4.23 \cdot 10^{-3}$ mol/sec·m^3. That is, at a temperature of 303 K, the process speed was only 1.25 times higher than at a temperature of 313 K. The degree of transformation of benzene after 1800 s at temperatures of 303 and 313 K was 73 and 63%, respectively. The total duration of the cavitation decomposition of benzene at these temperatures was 57 and 73 min. (for ultrasound emitters, the process duration for 303 and 313 K was 46 and 118 minutes, respectively). The specific power of the hydrodynamic cavitator was 51.9 kW/m^3, and the ultrasonic emitter – 83.3 kW/m^3, which is 60% more than at hydrodynamic cavitator.

As the pressure at the inlet of the hydrodynamic cavitator increases from 0.39 to 0.57 MPa, the specific energy consumption for cavitation transformation of benzene decreases from 25600 to 22500 kJ / mol (approximately 14%). It can be assumed that by increasing the kinetic energy of the jets, the energy released is more fully utilized to cause cavitation and decomposition of benzene, respectively.

On the basis of the comparison of the acoustic waveforms of the acoustic signals of the cavitation fields, the conclusion is drawn that benzene contributes to their development (Fig. 7a, Fig. 7b). Thus, the magnitude of the acoustic signal in the imitation is 4 dB greater than in pure water, and the sound pressure in the presence of benzene is 1.6 times higher.

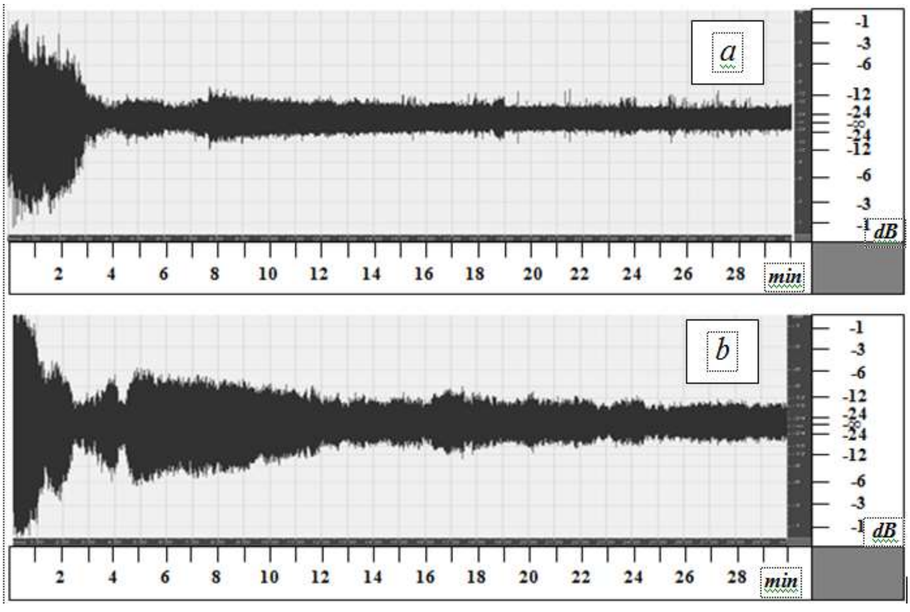

Fig. 8. Waveforms of the acoustic signal of cavitation fields in: a – water; b – simulated wastewater containing benzene

The positive effect of the influence of benzene on the emergence and development of cavitation can be explained by the higher partial pressure of benzene than water. Is known, that presence of the vapor phase in the reaction system to promote the appearance of cavitation.

From the obtained results we can conclude that as a result of excitation of cavitation in the water-benzene medium radical processes occurring by a chain mechanism are initiated. The high oxidation rate of benzene is also achieved when used as an oxidizer of the NaClO solution. The NaClO solution is alkaline, in which this compound decomposes under the action of cavitation by an oxygen mechanism - with the formation of atomic oxygen. A high degree of conversion (at least 95%) is achieved by a molar ratio of C_6H_6: NaClO = 4.5–5.5. According to the stoichiometry of the reaction

$$C_6H_6 + 15NaClO = 6CO_2 + 3H_2O + 15NaCl \quad (1)$$

15 moles of sodium hypochlorite are required to oxidize one mole of benzene. This result can be explained by the fact that during the decomposition of sodium hypochlorite, atomic oxygen is generated, which leads to the emergence and further development of radical processes.

During cavitation, a considerable amount of energy is released and the temperature of the medium is increased. Therefore, it is promising to carry out the process of cavitation neutralization of aromatic compounds under adiabatic conditions. Therefore, it is promising to carry out the process of cavitation neutralization of aromatic compounds under adiabatic conditions.

Phenol, in contradistinction to benzene and toluene, is not degraded in the presence of oxygen in the system. The substituents (OH^- and CH_3^-) in the aromatic ring belong to one species. When a stronger oxidizing agent is used, in particular sodium hypochlorite, there is also a deep oxidation of phenol to CO_2 and H_2O. However, in contradistinction to benzene and toluene, there is an induction period during the decomposition of phenol. During this time, cavitational decomposition of sodium hypochlorite occurs, resulting in the accumulation of secondary products in the reaction medium, which have oxidizing properties, such as atomic oxide, ozone, hydrogen peroxide. Changing the concentration of benzene is observed only after that (Fig. 9). However, the speed of the process is less than in the presence of oxygen in the reaction medium with benzene or toluene. This can be explained by the deactivation of the oxidant compounds due to various processes such as recombination of atomic oxygen, peroxide hydrogen degradation etc. This conclusion is confirmed by the fact that as the content of NaClO increases, the rate of oxidation of benzene decreases. It is obvious that studies on the reagent purification of water from phenol, in particular using sodium hypochlorite, need further investigation.

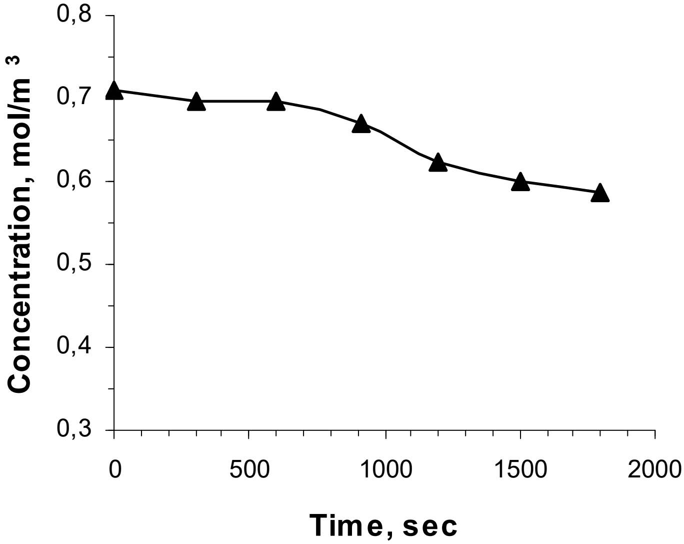

Fig. 9. Dependence of phenol concentration on time in the presence of sodium hypochlorite

For example, it is advisable to study the process of batch addition of sodium hypochlorite solution to wastewater, the effect of temperature, hydrodynamic conditions in the cavitation emitter etc. The use of sodium hypochlorite solution as an oxidizing agent is advantageous because it is a waste of chlorine and caustic soda production.

Based on the obtained results, technological concepts of the cavitation process of wastewater treatment from aromatic compounds are formulated. Among them are:

– the use of energy released during cavitation;
– oxidation of aromatic compounds contained in wastewater by wastewater from other production (for example, non-standard low-concentrated hypochlorite solution).

4. Summary and Conclusions

Wastewaters containing aromatic compounds have a significant threat to natural aquatic ecosystems. The rules for receiving wastewater into municipal wastewater facilities require pre-treatment of wastewater containing aromatic compounds. Reagent methods do not provide the proper treatment rate for such wastewater. The use of the cavitation phenomenon in the presence of oxidants in the reaction system leads to deep oxidation of aromatic compounds with the formation of CO_2 and H_2O. Rapid oxidation of benzene and toluene is achieved even in the presence of oxygen in the reaction medium. The oxidation efficiency of these aromatic compounds in the hydrodynamic cavitator is higher than under the action of ultrasonic radiation. The highest conversion rate of benzene and toluene is observed at temperatures in the region of 303±2 and 323±2 K. The minimum rate of oxidation is at temperatures of 313±2 K. At this temperature, microbubble-resistant collapses are formed. Phenol in the presence of oxygen under the action of cavitation is almost not transformed. Noticeable oxidation of phenol is achieved by the use of a stronger oxidant, such as sodium hypochlorite.

Acknowledgments

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