

Досліджено комбінаторику фізико-біохімічних методів очищення підземних слабокислих вод, які містять залізоорганічні комплекси, сірководень, аміак. Визначено вплив процесів попереднього підлучення та гідродинамічної кавітації на ефективність очищення. Розроблені технологія та обладнання можуть бути використаними для очищення води в системах водопостачання населених пунктів продуктивністю до 500 м³/добу із наступними показниками якості: концентрацією загального заліза до 8 мг/дм³, азоту амонійного до 3,0 мг/дм³, сірководню до 2 мг/дм³, вільного диоксиду вуглецю до 70 мг/дм³, рН 6,0–6,5, перманганатної окисності до 6,0 мгО/дм³, лужності до 4,0 мг-екв/дм³

Ключові слова: залізоорганічні комплекси, азот амонійний, залізобактерії, гідродинамічна кавітація

Исследована комбинаторика физико-биохимических методов очистки подземных слабокислых вод, содержащих железоорганические комплексы, сероводород и аммиак. Определено влияние процессов предварительного подщелачивания и гидродинамической кавитации на эффективность очистки. Разработанные технология и оборудование могут использоваться для очистки воды в системах водоснабжения населенных пунктов производительностью до 500 м³/сутки, содержащей концентрации общего железа до 8 мг/дм³, азот амонийного до 3,0 мг/дм³, сероводорода до 2,0 мг/дм³, свободного диоксида углерода до 70 мг/дм³, рН 6,0–6,5, перманганатной окисляемости до 6,0 мгО/дм³, щелочности до 4,0 мг-екв/дм³

Ключевые слова: железоорганические комплексы, азот аммонийный, железобактерии, гидродинамическая кавитация

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TECHNOLOGY OF DE-IRONING OF WEAKLY ACIDIC LOW ALKALINE UNDERGROUND WATER CONTAINING AMMONIUM NITROGEN

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1. Introduction

Modern ecological situation in many regions of the world is characterized by extremely high technogenic load on the sources of their water supply. Based on insufficient protection of areas of their underground horizons, the factor of significance of wastewater treatment facilities in the supply of good quality water to population increases dramatically [1]. The majority of those existing today de-ironing stations were built in the mid 70-ies of XXth century by one of the two most common methods of iron removal: a simplified aeration – filtration, deep aeration – filtration [1–3]. The existing de-ironing plants do not provide for the water purification processes from anthropogenic pollution, carrying out stabilizing treatment, which significantly reduces reliability of their performance under present conditions and requires modernization [4].

According to the conducted monitoring of parameters of water quality in 86 localities of Rivne, Volyn, Lviv, Khmelnytsky, Zhytomyr regions of Ukraine, it was found that in 22 % of them, the water supply systems are based on underground waters with bicarbonate alkalinity lower than 2 mg-eqv/dm³,

in 10 % – with bicarbonate alkalinity 2.1–2.5 mg-eqv/dm³. As is known, the use of reagentless methods of de-ironing is ineffective for such waters [3].

In addition, in most cases underground waters are partially fed by wild rivers and lakes that are rich in water soluble organic compounds that form, with ions of iron, hard oxidative compounds, which can be removed from water only by reagent methods [2–4].

That is why the development, research, implementation of new technologies and equipment for conditioning aggressive, iron-containing, slightly acid underground waters with low alkaline reserve in the presence of anthropogenic pollution is a relevant problem. Solving which will improve environmental and social issues of supplying the population with water of drinking quality.

2. Literature review and problem statement

Modern publications cover a large number of methods of separate extraction of ammonium nitrogen and iron com-

pounds from underground water. Thus paper [5] proposed the method of electro-pulse treatment in the layer of iron granules for removal of iron organic complexes from water. The water quality parameters were set: permanganate oxidizability (PO) 6.0 mgO/dm³, Fe²⁺=4.0 mg/dm³, pH=6.5. The studies were carried out under static conditions in the reactor of volume of 1.5 dm³, equipped with electrodes. There were 300 g of iron granules between the electrodes. The optimal time of treating granules with pulse discharge was 10 seconds, the time of contact of the water with active products of the iron erosion – 1 hour. The shortcomings of the considered scheme include: conducting the experiments under static conditions, low values of efficiency of de-ironing in the first 10 and 30 minutes of contact with active loading that amounted to 38 and 67 %, respectively, and complexity of the technology. Article [6] examined the technology of comprehensive purification of groundwater with a chromaticity of 50 degrees; Fe_{total}=9.55 mg/dm³; by iron bound with humic substances 1.8 mg/dm³; PO=5.7 mgO/dm³; pH=6.5. The set-up of technological scheme included the following processes: ozonization (30 mg/dm³) – electrocoagulation (30 mg/dm³) – sedimentation – filtration. The efficiency of removing iron compounds is 96 %. As the drawbacks we may highlight the need for a special energy-intensive equipment (ozonizers and electrolyzers), which requires qualified personnel during its operation, the lack of research results regarding the removal of NH₄⁺. The most promising from the point of view of intensification of the work of existing de-ironing stations is the use of the biochemical method of oxidation [7, 8]. In addition to biological removal of iron and manganese, biological removal of NH₃ is observed in the bioreactors [9]. One of the main anthropogenic pollutants of natural waters are the ions of ammonium nitrogen, for the removal of which they use sorption, ion-exchange processes, oxidation, biofiltration, reverse osmosis. Paper [10] presents the results of research into purification of underground water from the compounds of ammonium nitrogen by the biological method, which is implemented by bacteria: *Nitrosomonas* and *Nitrospira*, which convert the NH₄⁺ ions to nitrates. The parameters of quality of underground water in the town of Palo Iowa were: Fe²⁺=0.82 mg/dm³, P=0.07 mg PO₄/dm³, NH₄⁺=3.3 mg N/dm³, pH=7.4. The water-purifying station, brought to operation in January 2014, consisted of: two cylindrical tanks of D=3.2 m and H=3.05 m, for aeration and biological oxidation of ammonium nitrogen fixed on the granules of crushed anthracite (H=114 cm, δ=10 mm) by biocenose, three pressure filters D=198 cm, H=152 cm with a two-layer sand-anthracite loading, block of reagent system, three air blowers with power of each N=5.6 kW, block of pumps for pumping the fluid through the pressure filters. The reagent block consisted of consumption tanks of pumps of dozers of three types for preparation and dosing: phosphates (0.03 mgPO₄/dm³), NaOH solution, to maintain the medium's pH, necessary for development of microorganisms, the NaClO disinfectant solution. The level of concentration of 0.8 mg/dm³ by ammonium nitrogen in the filtrate was achieved only in 138 days from the beginning of operation of the station. The technological scheme is complicated to operate, energy-consuming; it increases biogenicity of drinking water. To speed up the processes of water purification, a number of authors suggest using in technological schemes the processes of coagulation, chemical oxidation, blocks of sorption purification [11]. Article [12] demonstrates the results of research into using biofiltration for additional groundwater

purification from organic impurities. The quality parameters of original water were: Fe²⁺=14–44 g/m³; NH₄⁺=1.2–1.98 g/m³; PO=11–16 gO₂/m³; pH=6.4–7.0. The technological scheme included the processes of aeration – chemical oxidation – coagulation – sedimentation – filtration on two-layer filters with sand and anthracite loading – additional purification on the biofilter with activated carbon, on the surface of which a biofilm formed over time. Due to the processes that took place in the biofilm, the magnitudes of soluble carbon and permanganate oxidizability were significantly reduced in water. The research was conducted at a pilot installation of diameter 55 mm, height of 112 cm, filtration rate reached 2–3 m/h. The drawback of the scheme is the use of biofiltration process at the output of the technological scheme, where it is difficult to control the output of agglomerates of cells of the biofilm in a reservoir with drinking water. The chemical method of ammonium removal, with the use of active chlorine, is based on complete oxidation of ammonium ions to nitrogen [13]. In this case, there is a possibility of formation of unsafe for human health chlororganic compounds, which practically eliminates its use at large and medium-sized water treatment stations. In paper [14], the authors examined and recommended for implementation a technology based on applying combinatorics of physical and chemical methods of removal from water the ions of iron, manganese, ammonium nitrogen [14]. The research was carried out on the underground waters with concentrations: Fe²⁺=14.6 mg/dm³, Mn²⁺=2.2 mg/dm³, NH₄⁺=3.2 mg/dm³, PO=10.4 mgO₂/dm³, H₂S=4.5 mg/dm³, pH=6.6. The technological scheme included: pre-filter – aeration column (pressurized tank D=550 mm, H=1920 mm) – the NaOH alkalization unit – swap pumps – the dispensing NaClO solution unit – contact chamber of high pressure – filter (D=370 mm, H=1650 mm) – RCW. The filler of filter is the mixture of catalytic materials “Sorbent AS+MS”. The speed of filtration was 5 m/h. Reduction in the concentration of ions of Fe²⁺ and Mn²⁺ to permissible values was observed only at a dose of NaClO of 160 mg/dm³ and at increasing pH up to 9.0. Although this method allows for complex purification but it is energy- and resource-intensive, difficult to operate; the use of high concentrations of NaClO may lead to formation of chlororganic compounds at high permanganate oxidizability of the original water.

3. Aims and objectives of the research

The aim of the work is to develop energy-saving, ecological technology and equipment for purification of aggressive slightly acid iron-containing underground waters with low alkaline reserve in the presence of ammonium nitrogen.

To achieve the set aim, the following tasks were to be solved:

- research into efficiency of applying combinatorics of physical and biochemical methods of purification from iron organic and ammonium nitrogen compounds;
- examining the dependency of efficiency of the process of purification on different types and concentrations of chemical reagents;
- exploration of destruction of complex iron organic complexes and ammonia by using the method of hydrodynamic cavitation;
- study of the change in parameters of water quality during filtration cycles.

4. Materials and methods of research

4.1. Materials and equipment used in the experiment

As a carrier of catalytic and biological films we used foamed polystyrene of the PSV type, with size of fractions 0.8–2.0 mm, thickness of the filtering layer of 1.5 m. The catalytic loading was received by treatment of 40 dm³ of the polystyrene by 35 dm³ of solution of modifying reagent – 0.6 % of MnCl₂. The period of treatment was 30 minutes. As the studied medium we used artesian water, on which the water supply system in the village of Balashivka, Ukraine is based. The research was carried out in several stages from 2004 to 2014, due to gradual deterioration of quality of the underground waters (Table 1). Measurements were carried out during commissioning works at each stage of the scheme’s modification; control measurements – once a month. During the rest of the periods, the quality control was managed by the local state sanitary station.

Characteristic of parameters of quality of artesian water in the village of Balashivka

Research stage	Parameters of quality of water					
	pH	Fe, mg/dm ³	Alkalinity, mg-eqv/dm ³	H ₂ S, mg/dm ³	NH ₄ ⁺ , mg/dm ³	PO, mgO/dm ³
I–II	6,4	4,0...4,8	1,28...1,4	not determined	0,55	3,5
III	6,45	5,4...6,0	1,45...1,5	0,8...1,3	0,55...0,64	3,55
IV	6,40	4,8...5,5	1,45...1,5	not determined	0,9...1,2	4,7
V	6,25	8,7...10,6	1,30...1,40	1,4	1,45...1,8	5,65

We used as reagents: the 8 % solution of soda ash (GOST 5100-85), the 1 % solution of aluminium chlorohydrate POLVAK P-68 (TU U 19155069.001-1999), the 0.1 % solution of nonionic flocculant of brand HENGFLOC 70010, solution of sodium hypochlorite as disinfectant.

For the dosing of reagents, we used dosing pumps of the brand DLX-MA/A (Italy). For decontamination, we used electrolyzer installation “Polumya-2” (Ukraine). The main equipment was a production installation with a capacity of 2.5 m³/h. The installation included the following equipment: aeration block (ejector or hydrodynamic cavitator), mounted on the bypass line from the well, contact column of diameter 420 mm, height 4000 mm with foampolystyrene loading h=500 mm, two lighting filters of diameter 720 mm, height of 3300 mm. The filters were equipped with a hydro automated system for flushing.

The magnitude of alkalinity, pH–Eh of medium were determined by the potentiometric method. Concentrations of the ions of ammonium and iron – by the photocolometric method. The value of permanganate oxidization – by the tetrametric method (by the Winkler method). Exploring the structure of sediment, its quantitative and qualitative composition – by using spectral analysis at the raster electronic microscope Philips, series XL-30 (The Netherlands).

4.2. The method of experiment

The study of the process of water purification from easily oxidative organic compounds, Fe²⁺, NH₄⁺ was carried out under dynamic conditions. The source water passed through a node of aeration, presented, depending on configuration of

the examined technological scheme, by various equipment (nozzle, ejector, hydrodynamic cavitator), reached on a tangent the unit of air separator – mixer (Fig. 1, a), to which the solution of chemical reagents was supplied – coagulant and flocculant (Fig. 1, b). Then, along the system of bypass pipelines, the treated water passed to the lower part of the contact column in which the processes took place of oxidation of pollutants and formation of flakes in the water upward flow (Fig. 1, c). From the contact column, the water by the systems of pipelines passed to the bottom part of foam polystyrene filters. The filtering was performed in the upward flow at velocities of 3, 5, 6 m/h. Clean water is collected over the filtering space and is sent to RCW.

The sampling took place both before and after the aeration device, at the outlet from the contact column and filters. The flushing of the filter loading was carried out under hydro automated mode with the help of the system of hydraulic robots at intensity of 12 l/cm², for 80 seconds.

Table 1

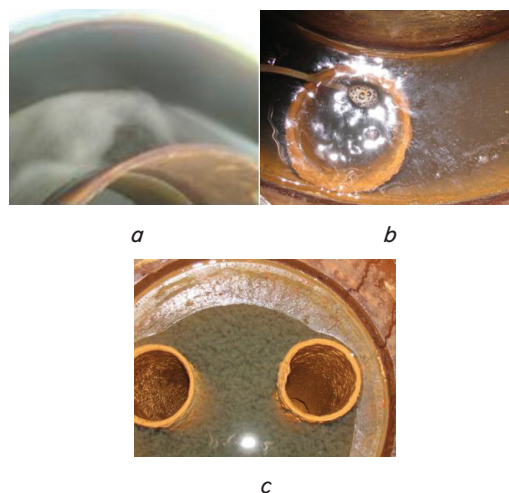


Fig. 1. Photographs of the stages of water treatment in the unit of equipment of contact columns: a – jet of water after leaving the nozzle of ejector (cavitator); b – introduction of flocculant to bypass pipe after air separator before the contact column; c – formation of flakes in the contact column

5. Results of research into technology and equipment of de-ironing of weakly acidic groundwater with low alkaline reserve, which contains ammonium ions

At the first stage of research, the set-up of technological scheme included simplified aeration – filtering through the foam polystyrene loading. The installation worked for several months by this scheme but the efficiency of purification from the compounds of iron was 12...15 % only. The catalytic film from iron oxides formed very slowly on the granules of loading.

To speed up the processes of oxidation of iron compounds, at the second stage of the research, part loading of filters was modified by putting a layer of active film from the manganese oxides MnO₂, Mn₂O₇ on the surface of granules of foam polystyrene. The installation worked two weeks at the velocity of filtration of 5–6 m/h under this mode. De-ironing efficiency increased to 60...70 %. The analysis of sediment samples from the contact column revealed a biofilm formation with domination in natural association of

unicellular iron bacteria *Gallionella* and filamentous forms of *Leptothrix*.

At the third stage of research, to enhance the oxidative capacity of equipment, technological scheme was added with an ejecting device. The water-cleaning equipment worked by the following technological scheme: ejecting – jet aeration-contact column – filtering through the modified loading. The air-water ratio on the ejector changed from 1:1 to 1:5. The velocity of filtration was maintained within 5 m/h. In this scheme we applied combinatorics of oxidizers: oxygen of air – active oxidizing film of manganese oxides – and hydrogen peroxide, formed as a result of vital activity of iron bacteria, immobilized on the surface of the granules of filtration loading. The research results of a typical filtering cycle under this scheme are given in Fig. 2.

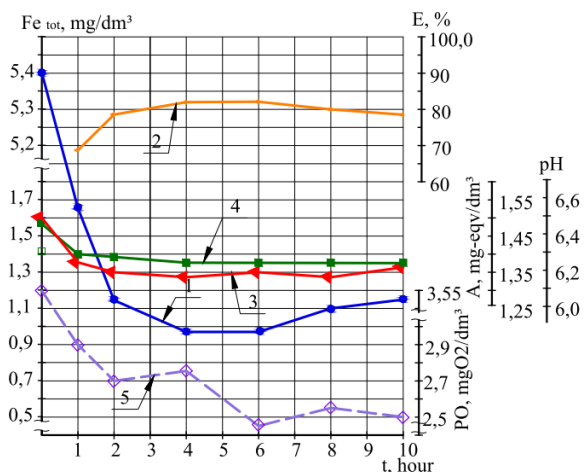


Fig. 2. Change in the concentration of iron (1), the magnitudes of bicarbonate alkalinity (3), pH (4), permanganate oxidation (5), the degree of removal of iron (2) in a filtering cycle ($t_{k, \text{hour}}$), during purification of underground water at initial concentrations: $\text{Fe}^{2+}= 5.4 \text{ mg/dm}^3$, $\text{A}=1.5 \text{ mg-eqv/dm}^3$, $\text{PO}=3.55 \text{ mgO/dm}^3$, $\text{pH}=6.45$

The duration of filtration cycles on average amounted to 10–12 hours. The concentration of total iron in the filtrate, depending on its concentration in the original water, was from 0.4 to 0.95 mg/dm³, in this case the percentage of not oxidized ions of Fe²⁺ reached 18–20 %, the rest of the iron was represented in the form of Fe³⁺, which was either in the associated state with organic acids or in the stable colloidal state. The filtrate is clear, of cream shade with a chromaticity of 80 degrees PCS. The efficiency of the de-ironing process reached 78–82 %. Throughout the filtering cycle we observed a gradual reduction in the magnitudes of alkalinity (to 1.35 mg-eqv/dm³) and acidity of the filtrate (to pH 6.2). One should note a gradual step decrease in the concentrations of soluble organic substances, the removal efficiency of which reached 33 %.

At the fourth stage of the studies, the water-cleaning equipment worked by the following technological scheme: alkalinization by the solution of soda ash – ejecting-jet aeration – introduction of the solution of coagulant – contact column – filtration through the polystyrene loading. The concentration of soda was 16–18 mg/dm³. Mixing the original water with the solution of soda ash and coagulant (dose of 10–15 mg/dm³) occurred in a turbulent flow (Fig. 1, a). This enabled us to actively carry out, on one hand, the processes of desorption of aggressive dioxide of carbon and hy-

drogen, and on the other hand, the processes of mass transfer between water and reagents. The contact time of water with the dissolved oxygen of air was 1.5–2 minutes; the air-water ratio was 1:2. The treated water's period in the contact chamber ranged from 25 to 33 minutes, the station's performance decreased to 1.5 m³/h. The results of the change in parameters of water quality for half of one of the filtration cycles are shown in Fig. 3.

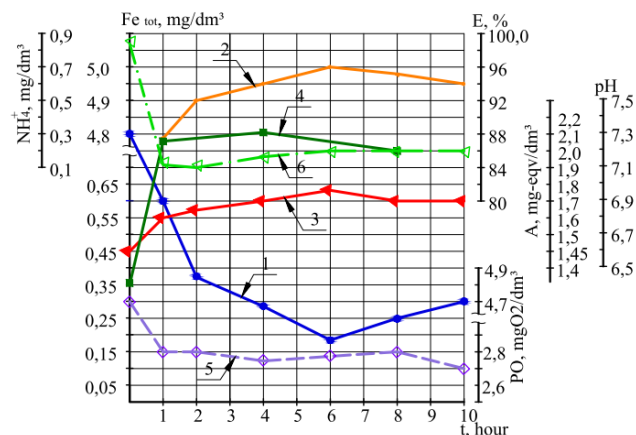


Fig. 3. Change in the concentration of iron (1), the magnitudes of bicarbonate alkalinity (3), pH (4), permanganate oxidation (5), ammonium nitrogen (6), during purification of underground water with the original concentrations: $\text{Fe}^{2+}=4.8 \text{ mg/dm}^3$, $\text{CA}=1.45 \text{ mg-eqv/dm}^3$, $\text{PO}=4.7 \text{ mgO/dm}^3$, $\text{NH}_4^+=0.9 \text{ mg/dm}^3$, $\text{pH}=6.4$

As a result of water treatment by the solution of soda ash, in the early filtering cycle we observed gradual increase, up to 1.8 mg-eqv/dm³, in alkalinity of the filtrate with finally entering the plateau of 1.7 mg-eqv/dm³, and its acidity to pH 7.2–7.3. It should be noted that the quality of water by the content of ions Fe²⁺ within 60 minutes after the end of the mode of flushing the filtering load reached the magnitudes of 0.5–0.6 mg-eqv/dm³, as well as its average concentration over the entire filtering cycle was 0.32 mg/dm³. At the same time, there occurred a decline of ammonium nitrogen to 0.2 mg/dm³ and of permanganate oxidation to 2 units of magnitude, which testified to the reduction by almost twice of the concentration of dissolved organic substances in the filtrate. The duration of the filtering cycle increased to 24 hours.

At the fifth stage, the studies were conducted to examine the change in efficiency of technological scheme under conditions of seasonal deterioration of the quality of underground waters (Table 1). To enhance oxidative capacity of the scheme, the existing ejecting device was modified to a hydro cavitation device. Dosages of reagents were: soda ash 35–45 mg/dm³, coagulant 15–20 mg/dm³, flocculant 1.0–1.5 mg/dm³. This made it possible to increase alkalinity of the filtrate up to 2.0–2.2 mg-eqv/dm³, and acidity to neutral medium. The research results are shown in Fig. 4. The average concentrations of iron and ammonium nitrogen within a filtration cycle were 0.3 mg/dm³ and 0.25–0.4 mg/dm³, respectively, which corresponded to the 96 % and 76–85 % effects of purification.

The magnitude of the permanganate oxidation decreased to 2.3–2.65 mgO₂/dm³. The presence of hydrogen sulfide in the filtrate was not determined. The optimal dura-

tion of filtration cycle at a concentration of iron in the original water up to 8.7 mg/dm³ amounted to, on average, 12 hours, followed by the increase in iron compounds in the filtrate (Fig. 4). At a repeated seasonal deterioration of water quality, we recommend applying the filter of additional cleaning with sorption loading and carrying out further research.

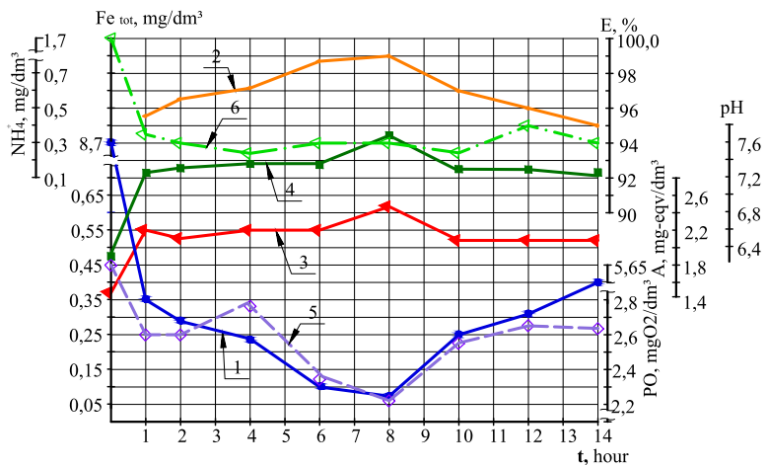
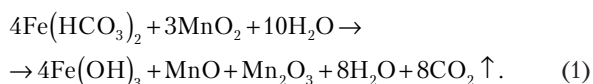


Fig. 4. Change in the concentration of iron (1), the magnitudes of bicarbonate alkalinity (3), pH (4), permanganate oxidation (5), the degree of removal of iron (2) in a filtering cycle (t_k , hour), during purification of underground water the original concentrations: $Fe^{2+}=8.7 \text{ mg/dm}^3$, $CA=1.40 \text{ mg-eqv/dm}^3$, $NH_4^+=1,7 \text{ mg/dm}^3$, $PO=5.65 \text{ mgO/dm}^3$, $pH=6.25$

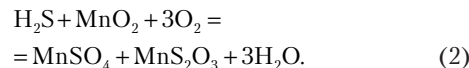
6. Discussion of results of the research into groundwater de-ironing technology with low alkaline reserve containing ammonium nitrogen

At each stage of the conducted studies, we considered the effect of total oxidative capacity of the system and various related factors on the efficiency of removal of compounds of iron and ammonium nitrogen. Low efficiency of the process of oxidation of iron compounds at the first stage may be explained by presence of the following inhibiting factors: low alkaline reserve – to 1.4 mg-eqv/dm³, presence of aggressive carbon dioxide – up to 50 mg/dm³ and soluble humic acids. It is known [3] that soluble carbon dioxide is one of the important factors that keep the iron in the dissolved state. However, as can be seen from the Allopo-Dubin diagram [3], removing aggressive carbon dioxide by the method of aeration depends in turn on the bicarbonate alkalinity of water and is possible only at its magnitude larger than 2.0 mg-eqv/dm³. Another factor that keeps the iron in the dissolved state is humic acids, which form hard oxidative iron organic complexes with two-valent iron. At the second stage of research, when filtering water through a modified filtering loading, there occurred the processes of oxidation of iron compounds by the higher manganese oxides with their subsequent restoration to lower oxidation states:

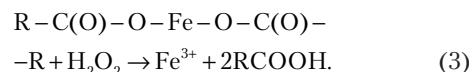


The catalytic action of the higher oxides of manganese enabled to reach the 70 % de-ironing effect at increasing the velocity of filtering up to 6 m/h. But over time, in the composition of the catalytic film, the decrease of manganese dioxide content occurred with simultaneous increase in the

compounds of its oxide, which led to gradual reduction of its oxidative ability. In addition, the reduction in the oxidative capacity of this film and, as a result, the achievement of modest effect of purification were affected by the blocking of its active centers by adsorbed compounds of iron, soluble humic complexes and oxidation of hydrogen sulfide:

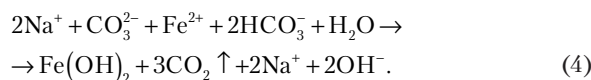


The need for potassium permanganate for regeneration, and the fact that it is a precursor led to the rejection of its application. During the period of pilot filtration cycles, the process of formation of a biofilm from the consortium of iron bacteria occurred on the surface of the active catalytic film. The formation of a catalytic biofilm made it possible to set the work of the installation from the mode of using only physical and chemical methods, into the comprehensive bio physical chemical purification method, which allowed applying the nature of formation of hydrogen peroxide, as a result of inter-cellular metabolism of iron bacteria, for oxidizing various forms of iron, including the iron organic complexes:

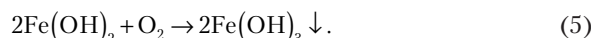


The process took place in capsules, mucous secretions, on the surface of the cell wall [7]. This fact, along with the use of ejector for aeration, allowed us at the third stage of research to significantly increase the oxidative capacity of the system (Fig. 2). Chromaticity of the filtrate decreased from 180 degrees PCS in the original water to 50–80 degrees PCS in the filtrate.

At the fourth stage of the research we used the combinatorics of biochemical and physical-chemical methods of water purification. Introduction of the solution of soda ash, needed to neutralize aggressive dioxide of carbon and to increase alkalinity of water to the boundaries of activities of iron bacteria [9], enabled us to increase the efficiency of de-ironing up to 94 % and the removal of soluble organic compounds to 44–50 % (Fig. 3). Chromaticity of the filtrate decreased to 15–20 degrees PCS. The mechanism of effect of soda ash on the process can be described by the following equations:



Since as a result of hydrolysis the ions H^+ and OH^- , are present simultaneously in water, the process occurs in parallel of forming the little-dissociated substance – water: $2H^+ + 2OH^- \rightarrow 2H_2O$, which removes the products of hydrolysis from the reaction zone and contributes to a more complete course of the process by its oxidation with the air oxygen:



Carbon dioxide, released as a result of the reaction, may be used by the iron bacteria of the *Gallionella* type as an additional source of carbon for constructing the cell biomass and

accelerating biochemical reactions. The results of analysis of the formed biooxides of iron (Fig. 5), which was achieved due to the diffraction of x-rays, of scanning electronic microscopy (SEM), indicate the presence of iron, carbon, phosphorus, silicon and aluminum on their surface.

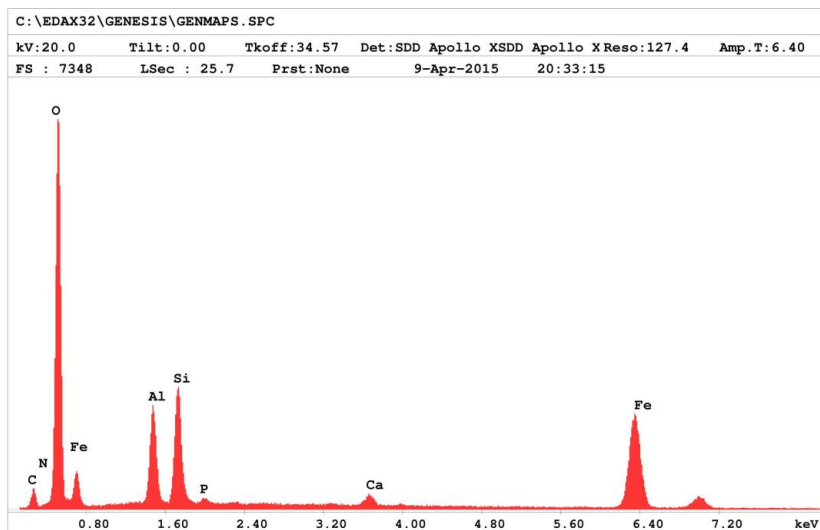
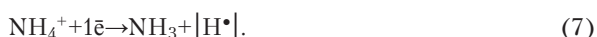


Fig. 5. X-ray microanalysis of sediment of the cover surface of the bacteria *Leptothrix ochracea* after the water treatment with aluminum oxychloride

The presence of adsorbed aluminum characterizes biominerals as a reliable ecological barrier in the thickness of the filter loading before RCW.

At the fifth stage of the research, to increase the oxidative ability of this system, we used the most powerful of all known oxidizers – hydroxide radicals that formed during the passage of water through the hydrodynamic cavitator [15]:



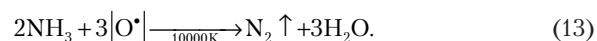
Further, there is a recombination of intermediates with formation of molecular compounds:



In the middle of bubbles, under the influence of high pressure (the order of 10000 atm.) and temperature (the order of 1000–2000 °C), H₂O₂ dissociates by the radical mechanism



Then NH₃ oxidizes:



There also occurs the destruction of the iron-humic complexes and oxidation of the iron associated with them:



A colloidal system is created, which is easily removed when using coagulants on the filters. By comparing the obtained research results to the research results [5–8, 10–14], one may draw the following conclusions. First, the most of the considered papers do not explore comprehensive purification of groundwater from iron compounds, organic complexes and ammonium nitrogen. Second, in contrast to other articles where the sequence of using certain methods of purification in most cases is caused by the necessity of removal at the appropriate stage of technological scheme of the corresponding contaminant, we used the principle of synergistic effect of purification in the examined scheme. In paper [12], the authors present the research results of the use of biofiltration as the final stage in removing organic impurities from water, after preliminary six-stage chemical-physical purification when the water biogenicity is minimal. Whereas in the conducted

research, this method is part of a complex of physical and biochemical processes that occur in the contact column and filter. In addition, when using a hydrodynamic cavitator, ammonium nitrogen oxidation occurs before it proceeds to the filter, thus reducing the load by polluting ingredients. Article [14] considered the technology, which is based on the use of high concentrations of reagents with the danger of formation of chlororganic compounds, in contrast to which, in the proposed technology, the concentration of reagents is 4–5 times lower.

According to the proposed technological scheme (Fig. 6), water from the well is mixed with a solution of soda ash, neutralizing aggressive carbon dioxide, increasing pH, is saturated with air oxygen.

When passing through the hydrodynamic cavitator, the highly active hydroxides radicals form, due to which the destruction of iron organic complexes occurs, as well as oxidation of ammonia and formation of colloidal particles. In the contact column, due to the hovering layer of active sediment, additional oxidation of iron organic complexes occurs, of easily oxidizing organic compounds, of ammonia. At the same time, the process of coagulation of colloidal particles occurs, as a result of their interaction with the FeOOH biominerals, formed as a result of the activity and the solution of aluminum oxychloride introduced from the outside. The final division of the phases and additional oxidation of the iron compounds takes place in the thickness of the filtering loading of the foampolystyrene filter. Before entering the RCW, the filtrate undergoes stabilizing treatment and decontamination by the solution of sodium hypochlorite.

The recommended technological scheme may be used to purify water in water supply systems of settlements with a capacity up to 500 m³/day with the following quality parameters: concentration of total iron to 8 mg/dm³, of ammonium nitrogen to 3.0 mg/dm³, of hydrogen sulfide to 2.0 mg/dm³,

of free carbon dioxide to 70 mg/dm^3 , of permanganate oxidation to 6 mgO/dm^3 , of alkalinity to $1.0\text{--}4.0 \text{ mg-eqv/dm}^3$, pH $6.0\text{--}6.5$. The industrial verification of the technology, equipment and facilities was carried out from 2004 to 2014 in the water supply system of the school-collegium and pool in the village of Balashivka (Fig. 7).

The results of the research were implemented in working designs of de-ironing stations for schools in the villages of Balashivka (2004), Stare Selo (2010) and the town of Korets (2012), Ukraine, developed by the State Enterprise "Firma – Octan", Rivne.

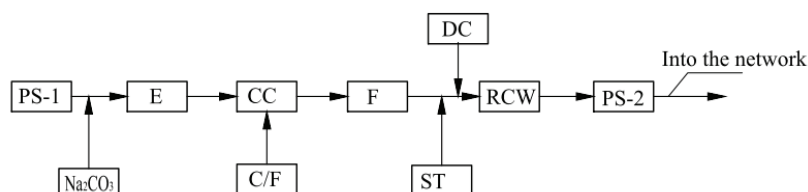


Fig. 6. Schematic technological scheme and equipment for de-ironing of underground water with low alkaline reserve, containing ammonium nitrogen compounds: PS-1 – pumps of the first lifting; E – ejector (hydrodynamic cavitator); CC – contact column; F – two-stage filter; ST, DC – equipment for stabilizing treatment and decontamination; Na_2CO_3 , C/F – equipment for introduction of soda ash, coagulant and flocculant; RCW – reservoir of clean water; NS-2 – pumping station of the second lifting

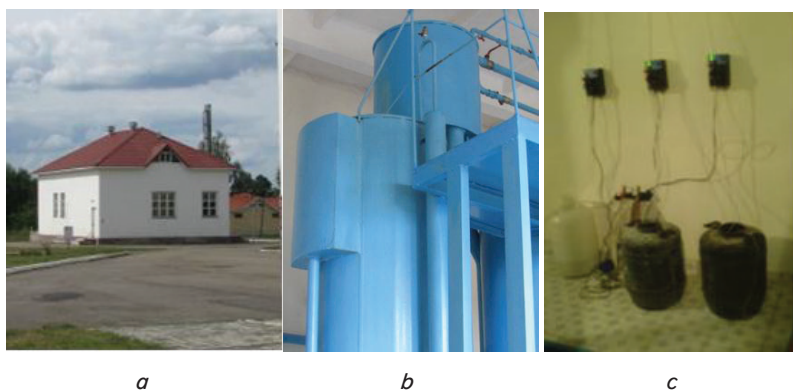


Fig. 7. De-ironing station in the village of Balashivka: *a* – general view of the facility; *b* – general view of the block of water purification equipment; *c* – block of reagent system with consumption tanks and pumps dozers

7. Conclusions

1. As a result of the conducted studies we received results that indicate the need for comprehensive purification of underground weakly acidic waters with low alkaline reserve for simultaneous oxidation of ammonium nitrogen and iron organic compounds.

2. It was found that the preliminary alkalization provides for the 98 % of the extraction of iron organic compounds from water as a result of intensification of the processes of biochemical oxidation and coagulation. We determined the optimal concentrations of reagents: soda ash $35\text{--}45 \text{ mg/dm}^3$, coagulant $15\text{--}20 \text{ mg/dm}^3$, flocculant $1\text{--}1.5 \text{ mg/dm}^3$, which are 4–5 times lower than in the known technologies.

3. We designed and implemented the technology and equipment, which are based on the consistent use of physical and biochemical methods of purification of multi-component groundwater. The effect is achieved by the stage-to-stage destruction of complex iron organic complexes, ammonium nitrogen through the processes of hydrodynamic cavitation, biochemical additional oxidation of the formed compounds by the consortia of iron bacteria, coagulation of colloids and the ultimate separation of phases in the volume of filtering loading.

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Наведено результати багаторічних досліджень різноманітних способів і методів збору і переробки синьо-зелених водоростей, що викликають «цвітіння» дніпровських водосховищ. Обґрунтовано можливість і доцільність переробки біомаси синьо-зелених водоростей на біогаз шляхом метаногенезу. Експериментально встановлено динаміку утворення біогазу, його якісний склад і кількісні характеристики. Проведено біотестування відпрацьованого субстрату на визначення його токсичності задля подальшого застосування як біодобрива у сільському господарстві

Ключові слова: синьо-зелені водорості, метаногенез, екологічна біотехнологія, біопаливо, біогаз, біодобрива

Приведены результаты многолетних исследований различных способов и методов сбора и переработки сине-зеленых водорослей, вызывающих «цветение» днепровских водохранилищ (Украина). Обоснована возможность и целесообразность переработки биомассы сине-зеленых водорослей в биогаз путем метаногенеза. Экспериментально установлена динамика образования биогаза, его качественный состав и количественные характеристики. Проведено биотестирование отработанного субстрата на установление его токсичности для дальнейшего использования в качестве биоудобрения в сельском хозяйстве

Ключевые слова: сине-зелёные водоросли, метаногенез, экологическая биотехнология, биотопливо, биогаз, биоудобрения

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THE BIOTECHNOLOGICAL WAYS OF BLUE-GREEN ALGAE COMPLEX PROCESSING

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1. Introduction

Financial instability of the world economy as a result of an energy crisis brings into focus the search for new non-conventional (alternative) energy sources. Among others, these include solar energy, accumulated in the biomass of photosynthetic (autotrophic) plants (so-called solar energy bioconservation).

It should be noted that to date a certain portion of the energy potential of land-based plant biomass is already utilized by mankind. A sixth of the energy consumed is produced from

agricultural and other phytomass. This is equivalent to the daily use of more than 4 million tons of oil. However, the biomass of aquatic microorganisms and phytoplankton (algae) is not in demand at all [1].

Plants utilize on average about 0.1 % of the total amount of solar radiation annually reaching the Earth's surface. This value is almost 10 times greater than world energy consumption. Therefore, there is an idea of using the biogas – the fuel produced from organic matter by means of bioconversion – biomethanogenesis, or methane “fermentation” [2].