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 mg/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 chromatgraphicity of 50 degrees; Fe⁺total=9.55 mg/dm³; by iron bound with humic substances 1.8 mg/dm³; PO=5.7 mg/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 NH₄ 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 dozens of three types for preparation and dosing phosphates (0.03 mg PO₄/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 biogeneity 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 chlororganoc 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 chlororganoc 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 changes 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 dm$^3$ of the polystyrene by 35 dm$^3$ of solution of modifying reagent – 0.6% of MnCl$_2$. 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.

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 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 m$^3$/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 420 mm, thickness of the filtering layer of 1.5 m. 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 photocolorimetric 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, Fe$^{2+}$, NH$_4^+$ 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/cm$^2$, for 80 seconds.

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 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 m$^3$/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 420 mm, thickness of the filtering layer of 1.5 m. 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 photocolorimetric 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).

![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](image)

Table 1

| Research stage | Parameters of quality of water |
|----------------|-------------------------------|
|                | pH | Fe$^{2+}$, mg/dm$^3$ | Alkalinity, mg-equiv/dm$^3$ | H$_2$S, mg/dm$^3$ | NH$_4^+$, mg/dm$^3$ | PO$_4$, 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             | 6.4 | 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 |
unicellular iron bacteria *Galtonella* 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 3 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 oxidization (5), the degree of removal of iron (2) in a filtering cycle (t<sub>filtration</sub>), during purification of underground water at initial concentrations: Fe<sup>2+</sup>= 5.4 mg/dm<sup>3</sup>, A=1.5 mg-eqv/dm<sup>3</sup>, PO=3.55 mgO/dm<sup>3</sup>, pH=6.45.](image)

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/dm<sup>3</sup>, in this case the percentage of not oxidized ions of Fe<sup>2+</sup> reached 18–20 %, the rest of the iron was represented in the form of Fe<sup>3+</sup>, 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 chroma 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/dm<sup>3</sup>) 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/dm<sup>3</sup>. Mixing the original water with the solution of soda ash and coagulant (dose of 10–15 mg/dm<sup>3</sup>) 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 hydrogen, 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 m<sup>3</sup>/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 oxidization (5), ammonium nitrogen (6), the degree of removal of iron (2) in a filtering cycle (t<sub>filtration</sub>), during purification of underground water with the original concentrations: Fe<sup>2+</sup>=4.8 mg/dm<sup>3</sup>, CA=1.45 mg-eqv/dm<sup>3</sup>, PO=4.7 mgO/dm<sup>3</sup>, NH<sub>4</sub><sup>+</sup>=0.9 mg/dm<sup>3</sup>, pH=6.4.](image)

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/dm<sup>3</sup>, in alkalinity of the filtrate with finally entering the plateau of 1.7 mg-eqv/dm<sup>3</sup>, and its acidity to pH 7.2–7.3. It should be noted that the quality of water by the content of ions Fe<sup>2+</sup> within 60 minutes after the end of the mode of flushing the filtering load reached the magnitudes of 0.5–0.6 mg-eqv/dm<sup>3</sup>, as well as its average concentration over the entire filtering cycle was 0.32 mg/dm<sup>3</sup>. At the same time, there occurred a decline of ammonium nitrogen to 0.2 mg/dm<sup>3</sup> and of permanganate oxidization 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/dm<sup>3</sup>, coagulant 15–20 mg/dm<sup>3</sup>, floculant 1.0–1.5 mg/dm<sup>3</sup>. This made it possible to increase alkalinity of the filtrate up to 2.0–2.2 mg-eqv/dm<sup>3</sup>, 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/dm<sup>3</sup> and 0.25–0.4 mg/dm<sup>3</sup>, respectively, which corresponded to the 96 % and 76–85 % effects of purification.

The magnitude of the permanganate oxidization decreased to 2.3–2.65 mgO<sub>2</sub>/dm<sup>3</sup>. 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/dm$^3$ 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.

At the second stage of research, when filtering water through hard oxidative iron organic complexes with two-valent iron. 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-eq/v/dm$^3$, presence of aggressive carbon dioxide – up to 50 mg/dm$^3$ 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-eq/dm$^3$. 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:

$$4\text{Fe}({\text{HCO}}_3)_2 + 3\text{MnO}_2 + 10\text{H}_2\text{O} \rightarrow$$
$$\rightarrow 4\text{Fe(OH)}_2 + \text{MnO} + \text{Mn}_2\text{O}_3 + 8\text{H}_2\text{O} + 8\text{CO}_2 \uparrow.$$ (1)

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:

$$\text{H}_2\text{S} + \text{MnO}_3 + 3\text{O}_2 =$$
$$\rightarrow \text{MnSO}_4 + \text{Mn}_2\text{SO}_4 + 3\text{H}_2\text{O}.$$ (2)

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 combinatories 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 18–20% (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:

$$2\text{Na}^+ + \text{CO}_3^{2-} + \text{Fe}^{2+} + 2\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow$$
$$\rightarrow \text{Fe(OH)}_2 + 3\text{CO}_2 \uparrow + 2\text{Na}^+ + 2\text{OH}^-.$$ (4)

Since as a result of hydrolysis the ions $\text{H}^+$ and $\text{OH}^-$, are present simultaneously in water, the process occurs in parallel of forming the little-dissociated substance – water: $2\text{H}^+ + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O}$, 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:

$$2\text{Fe(OH)}_2 + \text{O}_2 \rightarrow 2\text{Fe(OH)}_3.$$ (5)

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

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

At the fourth stage of the research we used the combinatories 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 18–20% (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:

$$2\text{Na}^+ + \text{CO}_3^{2-} + \text{Fe}^{2+} + 2\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow$$
$$\rightarrow \text{Fe(OH)}_2 + 3\text{CO}_2 \uparrow + 2\text{Na}^+ + 2\text{OH}^-.$$ (4)

Since as a result of hydrolysis the ions $\text{H}^+$ and $\text{OH}^-$, are present simultaneously in water, the process occurs in parallel of forming the little-dissociated substance – water: $2\text{H}^+ + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O}$, 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:

$$2\text{Fe(OH)}_2 + \text{O}_2 \rightarrow 2\text{Fe(OH)}_3.$$ (5)

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.

$$\text{(RCOO)}_2\text{Fe}^{2+} + 1\text{O}_4^+ + \text{H}^+ \rightarrow \text{RCOOH} \rightarrow \text{(RCOO)}_3\text{Fe}^{3+} + \text{H}_2\text{O}.$$  \hspace{1cm} (14)

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 bio-minerals, 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 m$^3$/day with the following quality parameters: concentration of total iron to 8 mg/dm$^3$, of ammonium nitrogen to 3.0 mg/dm$^3$, of hydrogen sulfide to 2.0 mg/dm$^3$. 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]:

$$\text{OH}^– + \text{e}^- \rightarrow [\text{OH}^*],$$  \hspace{1cm} (6)

$$\text{NH}_4^+ + \text{e}^- \rightarrow \text{NH}_3 + \text{[H}^*].$$  \hspace{1cm} (7)

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

$$2\text{OH}^* \rightarrow \text{H}_2\text{O}_2,$$  \hspace{1cm} (8)

$$2\text{[H}^*] \rightarrow \text{H}_2\text{[H}^*],$$  \hspace{1cm} (9)

$$\text{[H}^*] + \text{[OH}^*] \rightarrow \text{H}_2\text{O}.$$  \hspace{1cm} (10)

In the middle of bubbles, under the influence of high pressure (the order of 10000 atm.) and temperature (the order of 1000–2000 °C), hydrogen sulfide to 2.0 mg/dm$^3$, of ammonium nitrogen to 3.0 mg/dm$^3$, of hydrogen sulfide to 2.0 mg/dm$^3$. The presence of adsorbed aluminum characterizes biominerals as a reliable ecological barrier in the thickness of the filter loading before RCW.
of free carbon dioxide to 70 mg/dm³, of permanganate oxidation to 6 mgO/dm³, of alkalinity to 1.0–4.0 mg-eqv/dm³, pH 6.0–6.5. 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.

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 35–45 mg/dm³, coagulant 15–20 mg/dm³, flocculant 1–1.5 mg/dm³, 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.

References

1. Girol’, M. M. Nacional’na dopovid’ pro jakist’ pytnoi’ vody ta stan pytynogo vodopostachannja v Ukraini u 2003 roci [Text] / M. M. Girol’, S. B. Procenko, V. S. Kravchenko. – Rivne printing. 2005. – 143 p.

2. Orlov, V. O. Znezalіznennya pіdzemnix vod sproshhenoyu aeracіeyu ta fіltruvannyam [Text] / V. O. Orlov. – National University of Water Industry and Nature Management, 2008. – 158 p.

3. Nikoladze, G. I. Uluchshenija kachestva podzemnyh vod [Text] / G. I. Nikoladze. – Strojizdat, 1987. – 240 p.

4. Kvartenko, A. N. Practical stabilization methods of groundwater in north-western region of Ukraine [Text] / A. N. Kvartenko // Water Supply and Wastewater Removal. – 2014. – P. 103–116.

5. Lobanova, G. L. Electropulse treatment of water solution of humic substances in a layer iron granules in process of water treatment [Text] / G. L. Lobanova,T. A. Yurmazova, L. N. Shiyano, K. I. Machechina // IOP Conference Series: Materials Science and Engineering. – 2016. – Vol. 110. – P. 012098. doi: 10.1088/1757-899x/110/1/012098

6. Tropina, E. A. Apparaturno-technologicheskaja sistema poluchenija pit’evoj vody iz podzemnyh istochnikov zapadno-sibirskogo regiona [Text] / E. A. Tropina. – Tomsk Politechnic University, 2007. – 20 p.

7. Zhurba, M. G. Studies and experience of introducing innovative technologies of ground water conditioning [Text] / M. G. Zhurba, O. B. Govorov, Zh. M. Govorova., A. N. Kvartenko. // Vodosnabzhenje i Sanitarnia Tekhnika. – 2014. – Vol. 9. – P. 38–49.

8. Du Toit, G. Biological filtration for sustainable treatment of groundwater with high iron content – a case study [Text] / G. du Toit, H. Blijmaut, B. Theunissen, J. Briggs. – Water SA, 2014.

9. Kvartenko, O. M. Doslidzhennja metodiv ochysjenja pidzemnix zalizomistnyh vod vid amonijnyh spoluk ta amiaku [Text] / O. M. Kvartenko, L. A. Sabli // Water and water purification technologies. Scientific and technical news. – 2016. – Vol. 1, Issue 18. – P. 39–49.

10. Lytle, D. A. Biological Treatment Process for the Removal of Ammonia from a Small Drinking Water System in Iowa: Pilot to Full-Scale [Text] / D. A. Lytle, D. Williams, Ch. Muhlen, M. Pham, K. Kelty // Water Supply and Water Resources Division. – 2014. – P. 1–53.

11. Kaleta, J. Removal of humic substances from aqueous solution by the coagulation process [Text] / J. Kaleta, M. Elektorowicz // Environmental Technology. – 2009. – Vol. 30, Issue 2. – P. 119–127. doi: 10.1080/09593330802421482
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 biocorversion – biomethanogenesis, or methane “fermentation” [2].