Nature-similarity water treatment technology: EMERALD-UNIVERSAL

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Annotation:

The article experimentally substantiates the technological methods of water purification from microorganisms and xenobiotics, which simulate natural processes of water purification in an artificial electrochemical system by reactions of oxidation and reduction that are separated in time and space by filtration processes. The use of the latest advances in the design of the flow-through electrochemical reactors allowed the creation of a universal technology for removing ions of heavy metals, iron, manganese, dissolved organic compounds of natural and artificial origin, microflora and microbial toxins from water. The universality of the technology consists in the possibility of its application not only for fresh water, but also for water with any degree of mineralization. Based on the obtained experimental data, a compact high-performance device for purifying of natural fresh water is created.

Keywords:

Electrochemical activation, water, solutions, anolyte, catholyte, metastability, electrochemical reactor, chlorine, ozone, oxygen, hydrogen peroxide, hypochlorous acid, phagocytes, hydroxides, coagulation, EMERALD, AQUATRON, diaphragm, electrodes, redox potential, ion activity, ion concentration, oxidation, reduction, filtration, iron, manganese, biofilms, microorganisms, resistance, hypochlorite, chloramine.

Phenomenological analysis of the problem.

Before becoming potable, natural fresh water must be decontaminated from microorganisms and xenobiotics, as well as from excessive amounts of dissolved or suspended chemical compounds that impair its biological, organoleptic or physico-chemical properties. A great number of scientific publications is devoted to water purification and conditioning, however, the problem continues to be relevant. Moreover, it becomes more and more complicated, and might be better to be studied from the standpoint of the Unified Theory of All Interactions in a Matter, created by theoretical physicist I.L. Gerlovin [1]. In accordance with the theory, the speed of the evolutionary development of the Universe is much higher than the speed of human cognition of the surrounding world. Therefore, a human being will always lag behind in assessing and responding to any changes in the world in general and the world of water in particular. I.L. Gerlovin used, as an epigraph to one of the chapters, Einstein's remarkable words that perfectly characterize the current situation in water treatment: “Who would have thought that we would know so much more and understand so much less”. Today’s practice of water purification by addition of an equimolar or excess amount of chemical reagents in comparison to the amount of pollutants is obviously irrational, it has a negative impact on the environment and does not allow effective water purification and conditioning. The first statement is easy to explain: in order to add chemicals into the water, they need to be produced, which requires additional consumption of raw material, energy, labor, time. Chemical reagents addition for water purification in the process of drinking water preparation inevitably leads to the enrichment of water with other, often no less harmful effects. For example, the introduction of a disinfecting solution of sodium hypochlorite into water at municipal water treatment plants is inevitably accompanied by the introduction of ballast substances in the form of alkali and salt, which increases the rate of corrosion and sedimentation. Insufficient antimicrobial activity of hypochlorite, which does not provide residual chlorine in remote areas of the water distribution system, forces to water ammoniation by introducing ammonia or ammonium sulphate, which leads to the formation of even less active antimicrobial agent, chloramine, in the form of inorganic and organic chlorine. Chloramine allows to extend the existence of residual chlorine, but in fact is a xenobiotic, a substance that is alien to life, from the Greek: ξένος is alien and βίος is life. The general pattern of xenobiotic action is an increased frequency of allergic reactions, lethal effect on live organisms, a change in inherited traits, a decrease in immunity, a metabolic disorder, a disturbance in the processes in natural ecosystems up to the scale of the biosphere as a whole.

The second statement is based on the chemical law of mass action, discovered in 1867 by the Norwegian scientists C. Guldberg (Cato Maximilian Guldberg) and P. Waage (Peter Waage). One of the consequences of this law states that the lower the concentration of interacting substances in a solution, the slower the reaction of interaction between them. In this case, it means: the lower the concentration of dissolved substances, the more time is required for reactions of their neutralization by equimolar amount of chemical reagents. Often this time is much longer than time of water treatment and conditioning at existing water treatment plants. This is one of the reasons for the emergence in drinking water of new types of pollutants such as antibiotics, hormonal drugs (used by people for their own needs, for growing poultry, fish, farm animals), antidepressants, contraceptives and many other pharmaceutical formulations.

The main disadvantage of the traditional method of water disinfection with chemical reagents, such as hypochlorite and chloramines, is in development of microbial resistance to low-active oxidizing and disinfecting agents.

When opening a faucet in their city apartment, people sometimes notice a small dark strip that flashes away within the water stream, which is a biofilm, that comes off the inner wall of the water pipe. The biofilm usually covers the entire internal surface of the water distribution pipes, especially if disinfection is performed with sodium hypochlorite in combination with ammonization. Microorganisms that form the biofilm, feed on among other things the organic part of chloramines. At the end of the biological lifecycle, the biofilm is detached from the pipe surface in some areas that are by that time have been covered with new biofilms. Microorganisms continuously build up and improve their protective structure - the biofilm, which provides them comfortable environment.

It’s true: the living nature always defeats the dead. Alive, cultivating and adapting to the changing environment microorganisms will always find a way to protect themselves from toxic to their lives substance with stable chemical properties. However, they will be unable develop resistivity against a metastable mixture of interacting compounds that is diverse in the constantly changing reactivity, by orders of magnitude. Microorganisms have long learned how to adopt to ineffective or disinfecting agents that have lost their activity, they successfully live at a constant temperature of 400 °C (black smokers' chemotrophs), but for millions of years they have not been able to adapt to the effects of direct sunlight, wood fire (300 °C) or contact with the mixture of oxidants (hypochlorous acid and hydrogen peroxide) produced by phagocytes in a living organism. For the last two centuries they have not been able to adapt to x-ray and gamma radiation, non-burning flame of boric acid diethyl ester (40 °C), glowing electrical discharge; however, they develop resistance to new disinfectants generously introduced into medicine and food industry within a few weeks. The fact is the activity of ions in metastable chemical compounds formed during various kinds of non-equilibrium effects is higher than the activity of life-supporting ions in living microorganisms. That is why the complex effect of unpleasant for microorganisms components of the environment, having excessive chemical activity, causes their damage and death. The concept of ion activity was introduced by the American scientist G. Lewis (Gilbert Newton Lewis) in 1907. He called the activity of the apparent concentration of a substance, the use of which in the equation of the law of mass action makes it valid for any solutions at any concentrations. The activity rate, which combines the real (mass) and apparent (effective, chemically realized in the reactions) concentration of the solute takes into account the deviations of the real solution from the ideal, which are caused by electrical interactions between ions in the solution.

The activity rate of ions in dilute solutions, including drinking water, is close to one, that is, the activity is approximately equal to the concentration. This statement does not apply to living systems represented by microorganisms. Life is always associated with the excess electrical activity of the structures that represent it. Being in close interaction with sources of electric fields in microorganisms, the ions acquire increased activity that does not correspond to the concentration. Excess energy as a rule manifests itself in the self-organization of structural elements containing this energy. It is the abundance of the internal potential energy of living systems that determines their ability to transform and adapt to environmental conditions, ultimately to develop and improve. A model of self-organizing inanimate structures with excess energy is Benard cells - the appearance of order in the form of convective cells in the form of cylindrical shafts or regular hexagonal structures in a layer of viscous fluid (oil) with a vertical temperature gradient, that is, uniformly heated from the bottom.

In living systems, the activity of ions is not equal to their concentration, and the life supporting processes in aqueous conditions, activate the ions. Therefore, natural fresh water is similar to

living systems by some properties. This fact was noted not only by scientists, but also by observant and thinking people: Leonardo da Vinci (“The water was given a magical power to become the juice of life on Earth”), Albert Szent-Györgyi (“Water is life’s matter and matrix, mother and medium. There is no life without water"), Antoine de Saint Exupéry ("Water, thou hast no taste, no color, no odor; canst not be defined, art relished while ever mysterious. Not necessary to life, but rather life itself, thou fillest us with a gratification that exceeds the delight of the senses").

Study of the process of electrochemical regulation of redox and acid-base properties of fresh water.

The results of the process of changing the activity of bidistilled water, with a very low content of impurity electrolyte ions, under the action of an electric field [2] showed the possibility of attaining electron activity measured by a platinum electrode relative to a silver chloride reference electrode, values of electromotive force, somewhat simplerly called redox potential exceeding the limits of thermodynamic stability of water. These deviations are guaranteed to cause the death of all known forms of life due to the impossibility of living structures to compensate the influence of the activated medium. These studies were continued in 2018 in the AQUATRON-15–50L device equipped with an RPE-14 reactor of the MB-11T-01 flow-through modular electrochemical elements [3], each of which is in fact an independent compact diaphragm-type electrochemical reactor. The aim of the research was to study the range of electron activity values in the electrochemical treatment of fresh drinking water with a total mineralization of less than 0.3 g/l. Along with biological experiments based on the use of electrochemically activated substances and envisaged by the program of work on the grant of RSF, studies have been carried out on the synthesis of anolyte and catholyte of ordinary tap drinking water in various flow regimes through narrow annular gaps between the electrode (anode, cathode) and the ceramic ultrafiltration diaphragm from aluminum oxide in alpha form. Electrochemically activated water and solutions are very actively studied by representatives of the scientific community all over the world. During the period from 1995 to 2015, more than 300,000 scientific papers in this field were published. Researchers pay attention to the processes of using electrochemically activated solutions in various technological processes, but an endlessly small amount of work is devoted to the study of electrochemical systems for the synthesis of electrochemically activated water and solutions. The authors of the article repeatedly had to see in the laboratories of reputable universities, whose employees published the most interesting articles about the results of using electrochemically activated water in various processes, primitive devices in which researchers obtained the main component of their research - electrochemically activated solution or water. Virtually all electrochemical devices — industrial, laboratory, household, manufactured by unauthorized manufacturers — allow only small or trace quantitative and qualitative effects due to the metastable state of the near-electrode layer to be obtained. Given the imperfection of the equipment on which most of the research was conducted, it is safe to say that the prospects for using electrochemical activation technology are much broader than described in scientific publications.

Since the Russian group of scientists and specialists is leading in the world in the field of designing technical systems for the synthesis of electrochemically activated water and solutions, in these studies we have additionally focused on the study of the homogeneity of the physicochemical properties of various ceramic ultrafiltration diaphragms from aluminum oxide in alpha form. The new diaphragms are manufactured by extrusion molding technology, in contrast to the slip casting method, which produced zirconium oxide diaphragms for many years. Such diaphragms were used in many hundreds of thousands of FEM and MB electrochemical elements produced from 1990 to 2015. Dispersion of the physicochemical parameters of the zirconium oxide diaphragms required an individual selection for the assembly of reactors consisting of a large number of FEM or MB elements.

Studies of the parameters of water subjected to a cathode or anode treatment were previously carried out mainly on single electrochemical reactors or reactors assembled from individually selected several FEM and MB elements [4-10]. As a result, it was found that the pH and the redox potential of anolyte and catholyte of fresh water acquire abnormal properties in compare to values calculated on the basis of laws of equilibrium thermodynamics, as well as the values obtained by modeling the acid-base properties of anolyte and catholyte by introducing into the original water acid and alkali.

The additional research task was solved through the main one by changing the design of the reactor assembled from fourteen electrochemical elements connected hydraulically in parallel without individual selection by characteristics of diaphragm.

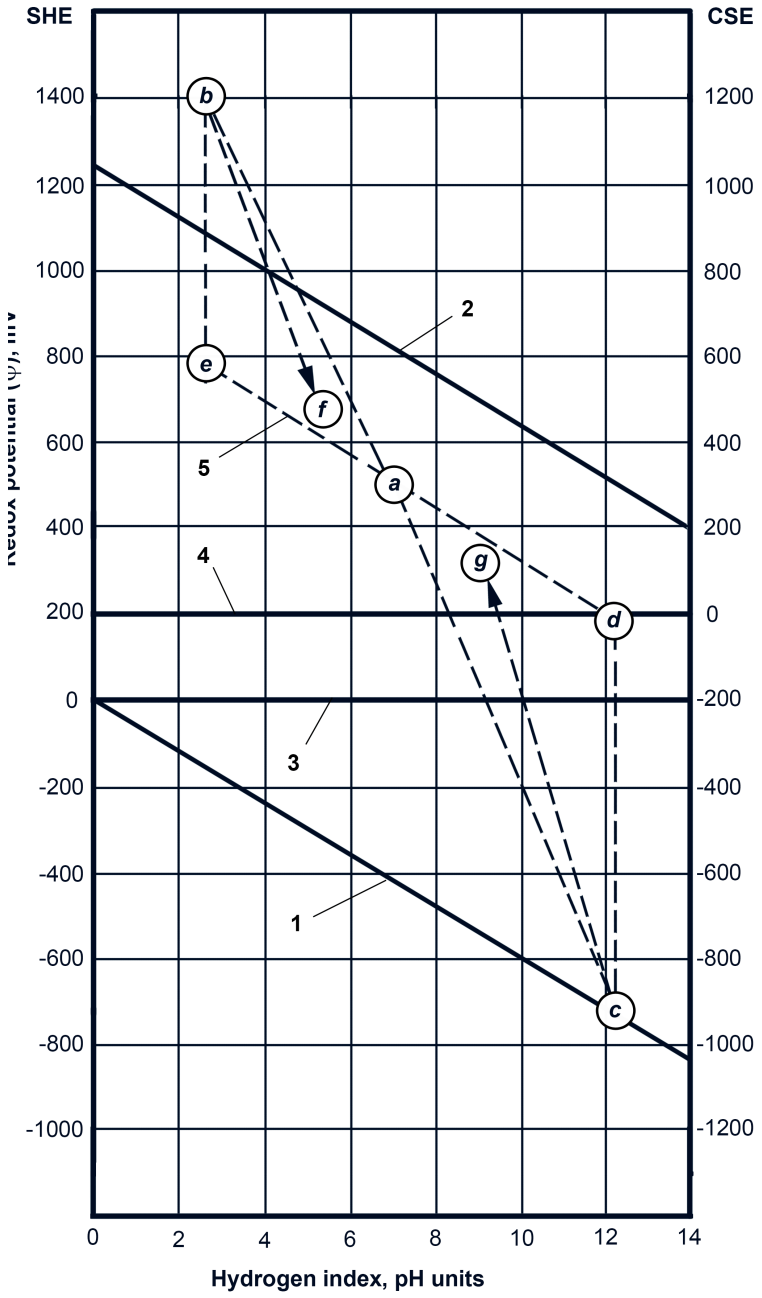

Fig. 1. The ratio of pH and ORP in the electrochemical and chemical regulation of the parameters of fresh water. Legend: 1 and 2 - potentials of water reduction at an inert cathode (φ_1 = - 0,0592 pH) and oxidation at an inert anode (φ_2 = 1,23 - 0,0592 pH), respectively; 3 and 4 - the zero lines of the scales of hydrogen (SHE) and silver chloride (CSE) reference electrodes; 5 - the direction of change in pH and ORP during chemical regulation of water parameters; a - initial values of fresh water parameters: pH = 7.0; ORP = + 320 mV (CSE); b and c are the parameters of anolyte and catholyte, respectively: pH = 2.7; ORP = + 1200 mV (CSE), pH = 12.3; ORP = – 920 mV (CSE); d and e — parameters of chemical models of catholyte and anolyte, respectively: pH = 12.3; ORP = 0 mV (CSE), pH = 2.7; ORP = + 780 mV (CSE); f and g are the parameters of anolyte and catholyte after the end of relaxation, respectively: pH = 5.7; ORP = + 400 mV (CSE), pH = 9.0; ORP = + 120 mV (CSE).

The result of the research was the experimental confirmation of previously obtained data on the change in pH and redox potential of fresh water, subjected to electrochemical effects at surface of positive and negative electrodes of electrochemical system, obtained with less power consumption. The novelty of the results obtained in 2018 is that due to the operation of the reactors of the electrochemical system in the mode of self-organizing structures, energy and mass transfer required approximately 2.5 times less energy to achieve the maximum parameters of pH and ORP deviation from the equilibrium state. In fig. 1 the results of experiments on the study of the parameters of electrochemically activated fresh water obtained using the AQUATRON-15-50L device is shown. In all the experiments tap water from the northwestern region of Moscow was used as the initial one with the following parameters: total salinity - 0.21 g/l; hardness - 3.6 mEq/l; pH - 7.1-7.2; redox potential, measured with a platinum electrode relative to a silver chloride reference electrode, is from +250 to + 290 mV; electrical conductivity - an average of 0.00031 S/cm.

The pH and ORP were measured with a pH meter FE20 (METTLER-TOLEDO), and the specific conductivity of the water was measured with a FP-30 conductometer - STANDARD (METTLER-TOLEDO).

In AQUATRON-15-50L device, in contrast to the known electrochemical systems for producing anolyte and catholyte of fresh water [11], a reactor of fourteen flow-through electrochemical modular elements MB-11T-01 (Fig. 2) was used, whose ultrafiltration diaphragms are made of chemically pure alumina in alpha form. The uniformity of the structure and physicochemical properties of diaphragms made it possible to

ensure the almost complete separation of ions into cations and anions with the formation of the corresponding electrochemically activated products of anodic and cathodic reactions.

The cooled electrodes of the MB-11T-01 elements ensured the constancy of the temperature of the water flowing through the electrode chambers within 22 plus or minus 1 °C. The current was maintained in the range of 9.1 - 9.2 A at a voltage of 10 - 12 volts. The specific amount of electricity expended on the electrical treatment of water in cathode or anode chambers of MB element ranged from 300 to 400 coulomb per liter (C/L).

Measurements of pH, ORP and electrical conductivity were made within 2 to 3 minutes after the termination of the process of electrochemical treatment. The time of each measurement did not exceed 5 minutes.

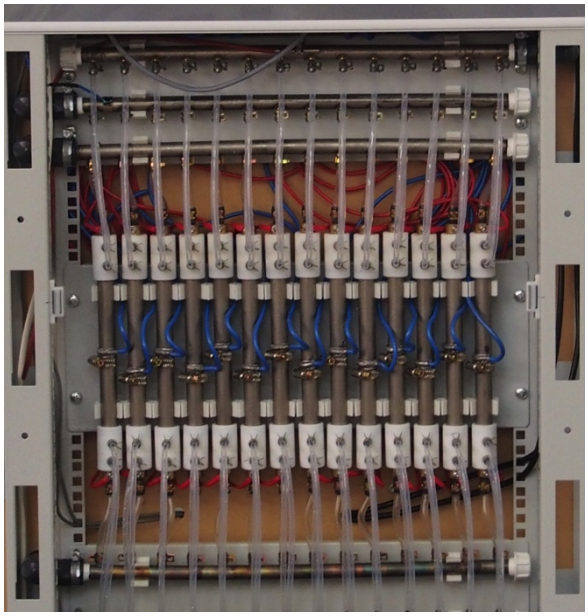

Fig. 2. RPE-14 electrochemical reactor of the AQUATRON-15-50L device

The research results are reflected in fig. 1, where both the initial values of these parameters and the resulting cathode and anode treatments are shown in coordinates of pH - ORP. The parameters of anolyte and catholyte after the end of the relaxation period are also shown (about 72 hours in closed vessels). The letters “e” and “d” mark the areas of chemical modeling of the pH of freshly obtained catholyte and anolyte, respectively.

The catholyte was simulated by dosing of microvolumes of sodium hydroxide into the original water. To simulate the anolyte microvolumes of hydrochloric acid were dosed. Replacing hydrochloric acid with sulfuric acid did not lead to significant difference.

Compared with research data on bidistilled water [2], an increase in the concentration of electrolyte ions in the source fresh water from several tens to several hundred milligrams per liter many times increased the “activation” component of the reactivity of anolyte and catholyte due to variation in the activity rate within, close to unity, and, accordingly, increases the role and technological value of activated water.

Analysis of experiment confirmed that **electrochemical non-equilibrium effect can change the reactivity (activity) of ions in solutions tens of times without changing their concentration.**

The pH values reached during the electrochemical treatment correspond to equilibrium concentrations of alkali and acid, many times higher than the salt content in water, from which these alkali and acid could be produced. The values of the ORP are beyond the scope of chemical modeling with a given electrical conductivity and therefore are unique.

Findings:

1. Electrochemical reagent-free regulation of the properties and parameters of water allows the oxidation or reduction of virtually any substance contained in water.

2. The most economical method of electrochemical control of the properties and parameters of fresh water is to use flow-through electrochemical modular elements MB with diaphragms based on aluminum oxide in alpha form.

Electricity and water: the search for the best combination.

Fresh water is a poor conductor of electricity, which is due to the low concentration of charged particles - ions that are formed when various salts dissolved, which represent the mineral content of water. Fig. 3 shows dependence of the electrical conductivity of water on the concentration of dissolved electrolytes, including not only various salts, but also the corresponding acids and bases. Fresh drinking water in most cases has a specific electrical conductivity in the range of 0.0001 - 0.001 S/cm, that is, about a thousand times less than electrolyte solutions in traditional electrochemical processes. That is why until the end of the 1980-s it was assumed that the electrolysis of fresh, and especially distilled water, is impossible.

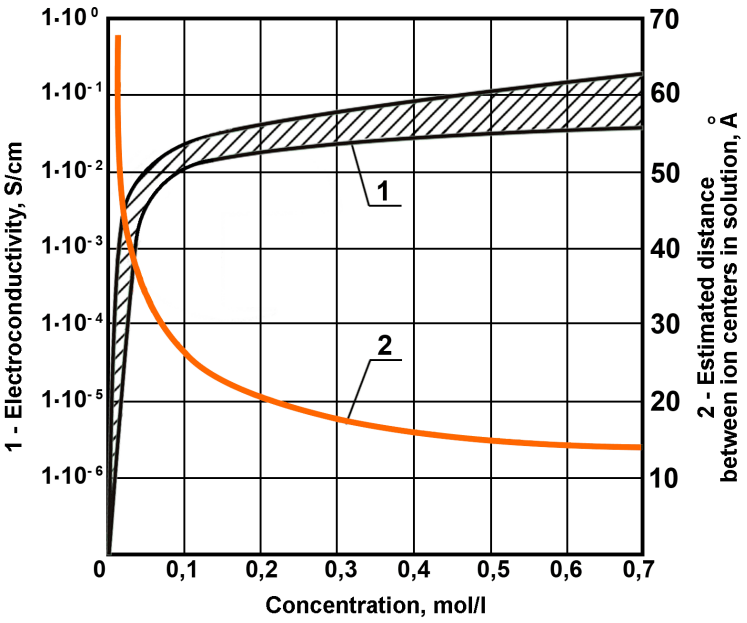

Fig. 3. Dependence of electrical conductivity of aqueous solutions of inorganic electrolytes (acids, bases, salts) on the concentration

Another factor hindering the development of electrochemical technologies for fresh and brackish waters is the complexity of the instrumentation of the process. During operation of any electrochemical system in a dilute solution of a mixture of various electrolytes with a spontaneously changing chemical composition, constant and often unpredictable changes occur in the conditions of electrochemical exposure associated with the formation of precipitates, the release of corrosive gases that damage structural elements, chemically active electrolysis products that react with the starting materials with the formation of solid particles and non-conductive films. Blocking of electrodes and diaphragm with hardly soluble inorganic and organic products of physicochemical reactions in electrode chambers is often observed. Traditionally, these comlications are eliminated either by using initial solutions with a strictly defined chemical composition free from interfering impurities (hydrogen, oxygen, chlorine and alkali production, electroplating), or by creating coarse, massive and undemanding maintenance structures (refining non-ferrous and noble metals, production of non-ferrous metals from ores). In both cases, water is used, but either as an extremely purified concentrated electrolyte solution of a strictly constant composition, or an unpurified, but also concentrated electrolyte solution.

Obviously, the very first creator of the electrochemical purification of water of varying degrees of mineralization - from fresh rainwater to salty sea and ocean, is Nature.

The mechanism of water purification processes in Nature is represented by two main processes: redox reactions and filtration. Other processes - sorption, ion exchange, coagulation, flocculation, coalescence, sedimentation are additional and usually take place during filtration of the purified water through the soil layers, sedimentary and rock masses.

In Nature, the processes of oxidation and reduction of substances dissolved in water proceed separately in time and space. For example, oxidation of dissolved chemical compounds with oxygen in the air occurs when ripples form in water or waves with lambs of foam from gusts of wind, and recovery occurs when water contacts oxidized natural minerals or soil substrates during filtration.

The processes of reception and transmission of electrons in Nature proceed slowly, under conditions not very distant from the state of thermodynamic equilibrium, in accordance with the law of mass action. Mainly the area of purification of fresh and slightly saline water in the natural environment is in the concentration range of 0.0015 - 0.03 mol/l. The distances between the ions of the salts in water are very large; figuratively speaking, the ions practically do not “see” each other (curve 2 in Fig. 2). It is possible in principle to accelerate artificially oxidation or reduction processes in diaphragm electrolyzers, where the anode and cathode spaces are separated by a porous partition that prevents the mixing of liquids, which, regardless of chemical composition, are called catholyte or anolyte, if subjected to electric current in the cathode or anode chambers, accordingly, of the diaphragm electrolyzer. But it must be borne in mind that ions in water even under the action of an electric field move very slowly, just a few millimeters per hour. In any partition, through which the ions move under the action of only electromigration mass transfer, their speed decreases. An especially large delay in the rate of transfer of ions is characteristic of polymer ion-selective membranes, where the rate of movement of ions decreases thousands of times in comparison with the speed of their movement in a free solution. The nature of the flow of fluid in the electrode chambers of the electrolyzer (electrochemical reactor) also plays a big role. Conventionally, the surface of the electrode acts as an active reagent in electrochemical reactions. Therefore, the task of increasing the efficiency of interaction processes with this reagent under conditions

dictated by the law of mass action is not to increase the concentration of active reagents, as is usually done in chemical and traditional electrochemical technologies, but to ensure the contact of interacting substances. In other words, each microvolume of fluid flowing through the electrode chamber should be in contact with the surface of the corresponding electrode, where in the diffuse part of the double electrical layer (DEL) the electric field strength ranges from several thousand to several hundred thousand volts per centimeter and where ion mobility does not depend on the viscosity of their environment, but only on the intensity of the electric field. The task is very difficult and requires special electrochemical reactors for the implementation of electrochemical activation processes, since traditional electrolyzers, both lab scale and industrial, designed for the optimal implementation of traditional technological processes of applied electrochemistry, are not suitable for treatment of fresh water or dilute aqueous solutions. DEL has a very small thickness: in dilute solutions and fresh water - about 0.1 microns, in concentrated - much less. In order to better understand the level of complexity to ensure the contact of each micro-volumes of water surrounding an electrode with its surface, let us imaging that a metal rod electrode with a diameter of a pencil is immersed in a glass of water. If we also assume that the region of high electric intencity around the electrode (the zone influence of DEL) suddenly increased and reached 1 mm, then, to preserve the proportions of the system, the diameter of the glass should increase from 7 centimeters to 700 meters. It is clear that it is impossible to ensure the processing of all the water of this "lake" at the surface of the electrode - a pencil, without resorting to special techniques.

With the development of flow-through electrochemical modular FEM elements in 1989 [12-19], it became possible to conduct water purification process in flow-through mode, with low energy consumption, by direct only oxidation process in the anode chamber or only reduction process in the cathode chamber, separated in time and space. The minimum power consumption was provided by a thousand-fold increased rate of ion transfer through the ceramic diaphragm of FEM elements. The increase in the rate of ion transfer through the ceramic porous diaphragm of FEM elements was caused by an artificially induced ion-selectivity of the diaphragm due to the pressure drop between the anode and cathode chambers and the formation of a filtration flow saturated with ions of the same sign due to separation in an electric field. This process was subsequently called as ion-selective electrolysis with a diaphragm [10].

The appearance of EMERALD devices in 1991 actually opened up a new direction in water purification technology, since it allowed to implement complex purification processes, usually consisting of oxidation stages in the anode chamber, reduction stages in the cathode chamber, with intermediate stages implementing the results of physicochemical processes after active (electrochemical) stages of exposure. Such stages were flotation, sorption, induced by abnormal values of ORP electrocatalysis, oxidative removal of chlorine oxygen oxidants on activated carbone.

In total, from 1991 to 2016, more than 300,000 original EMERALD devices for drinking water purification were produced and sold to consumers.

Most of all EMERALD devices were manufactured using FEM-3 and MB-11 elements [11] equipped with 11 mm diameter zirconia diaphragms. The water treatment rate was in the range of 40 to 60 liters per hour. When the flow rate decreased, the degree of conversion of hardly oxidizable elements in water, such as organic iron, organic manganese, increased with a decrease in flow rate only if the flow rate was less than 10 liters per hour and at twice the current strength. With increasing flow rate, the removal efficiency of organic iron decreased. These results were adopted for many years as characteristics of EMERALD units, since the main method of removing suspended or turned into insoluble particles was flotation in a pressurized flotation reactor. Flotation removal of impurities made it possible, with small dimensions of the device, to remove more than sixty percent of substances that have undergone changes in the state of aggregation in the electrode chambers of FEM or MB elements. Contaminants did not accumulate in the cleaning system and this saved the consumer from the need to periodically replace any elements of the device. Periodic and more and more frequently repeated requests from consumers about the need for large capacity EMERALD to install have stimulated research in this direction, carried out jointly with scientists from Institute of Theoretical and Experimental Biophysics. It turned out that based on the results of experimental biophysical research, the desire to inspire a person with the benefit of constant water consumption with a certain value of the redox potential is incorrect. Water with high oxidation or reduction potential produced in certified electrochemical devices can only be used for medicinal purposes and only as prescribed by a physician. Water produced in existing EMERALD devices is not subject to storage due to the absence of agents protecting it from microflora. Under conditions of long-term preservation of water with a negative value of the ORP in

closed systems (tanks, pipelines without ducts), it is infected with sulphate-reducing bacteria, which receive energy through the oxidation of hydrogen dissolved in cathode treated water.

Findings:

1. Flotation in EMERALD devices does not allow to remove colloid-dispersed particles.

2. EMERALD devices should be equipped with filtering elements to remove all colloid-dispersed particles formed as a result of oxidative or reducing electrochemical effects, which will also reduce water loss by eliminating drainage discharges from flotation reactors.

Research on water purification technology: oxidation, reduction, filtration.

The creation in 2016 of a new generation of MB-11T and MB-26T electrochemical reactors (Fig. 4) with ceramic ultrafiltration diaphragms made of aluminum oxide in alpha form and pore sizes from 0.01 to 01 microns made it possible to intensify the processes of electrochemical exposure to diluted electrolyte solutions due to the stable physicochemical and physicomechanical properties of diaphragms and the steady ability to create self-organizing vortex flow structures in a working electrochemical reactor at high speeds of liquid flow.

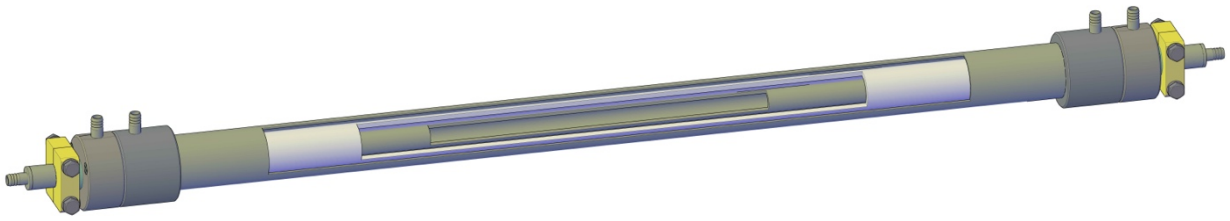

Fig. 4. Flow-through electrochemical modular element MB, model 2016. Extended annular gaps between the coaxially placed electrodes separated with the ceramic ultrafiltration diaphragm made of aluminum oxide in alpha form provide MB element simultaneously with the properties of an ideal mixing reactor and an ideal displacement reactor.

The practical way out is the new constructive and technological solutions found in the creation of high-performance EMERALD-UNIVERSAL devices.

Based on the above research results, the design of water purification devices with MB-26 type elements with a diaphragm of 29 mm in diameter was carried out on the basis of the similarity law: if the current through the MB-11 element is 1 ampere, and the flow rate is 50 liters per hour, then with the current strength through the MB-26 element equal to 5 amps the flow rate should be 250 liters per hour. But with such parameters, the degree of water purification in the MB-26 elements was much worse than in the MB-11 elements. A rapid method for assessing the quality of water treatment by observing the rate at which the filter color changes, through which water that initially contains iron and/or manganese ions flows at a constant rate, passes through such practical assessments of the effectiveness of water purification. The faster the filter color changes, the better the cleaning, other things being equal, that is, the more efficient the electrochemical conversion in a liquid. Typically, the filter color change time occurs within 30 to 40 minutes, even when working on ordinary tap water. Control measurements of the efficiency of water purification from iron were carried out by the colorimetric method with sulfosalicylic acid according to GOST 4011-72. It was previously established that when processing fresh water in the anode chamber of an MB element with an amount of electricity of 30-40 C/l, all microorganisms are guaranteed to be destroyed, including in the form of a biofilm and microbial toxins are destroyed. Therefore, studies of the efficiency of extracting iron and manganese from water were carried out at obviously large values of the specific amount of electricity expended on water treatment.

A schematic diagram of a flow-through electrochemical system, shown in Fig. 5, allowed to consider the following important points of cleaning technology. At the beginning of the cleaning process, it is necessary to destroy the entire microflora so that in the future all filter elements work “clean”, that is, they would be completely free of biofilms, which are common in almost all filter systems where water is not preliminarily disinfected with introduced substances which protects the water from microflora. Then, after separating the coagulated particles on the filter, the removal of metal ions with a low pH of hydrate formation should be ensured. This category includes almost all heavy metals, iron, copper, zinc, magnesium and some others. Then, after removing the hydroxides on the filter, it is necessary to protect the water again by synthesizing oxidants in it. All electrochemical conversions — cathodic and anodic —

must be symmetrical in the specific amount of electricity to keep the pH of the purified water at the same level.

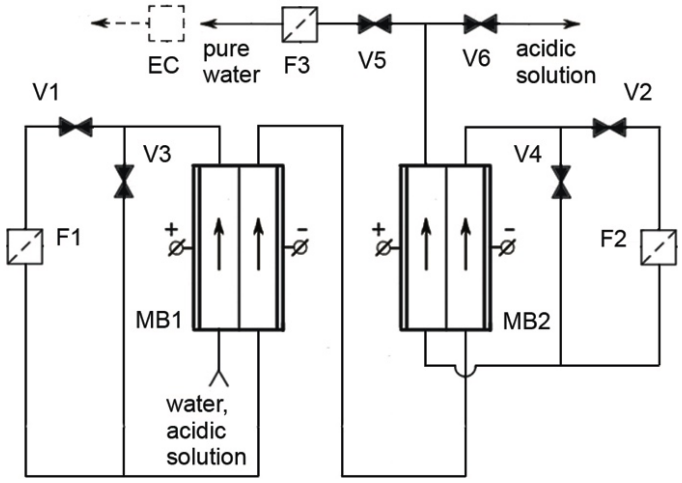

Fig. 5. Principal hydraulic scheme of the process of water purification in EMERALD-UNIVERSAL device

Studies have shown that with a relatively small change in consumed electrical power, cleaning efficiency has maxima and minima, depending on the flow rate, water temperature and iron concentration. Since the specific energy consumption before, during and after the extremum of the cleaning efficiency curve changes in proportion to the water consumption, the detected effect was associated with the formation of a resonant self-organizing flow structure in the electrode chambers under the superposition of various fields: electrostatic forces between the electrode and the diaphragm surface vector velocity field flux, the electric field between the electrodes, the field of bulk current density, the field of electrophoretic movement is highly charged products of electrochemical reactions. In other words, it was found that the MB-26T elements with a larger diaphragm (29 mm) have the same law of minima and maxima of electrical conductivity as in the MB-11T elements, with a smaller diaphragm (12 mm). One of the highs for the MB-26T elements lies in the range of 300 - 500 liters per hour. Some changes in the design of the inlet and outlet chambers of the MB-26T element made it possible to provide a flow of 500 liters per hour through the MB-26T element with a current of 5 amps and hourly removal of 2100 mg of iron from the flowing water. Previously, at the same current strength and flow rate of 250 l/h, it was possible to extract only 1300 mg of iron per hour. This means that in accordance with the law of mass action, the probability of mutual contact of reacting particles in the flow of water between themselves and with the electrode surface has sharply increased. Therefore, the reaction rate of interaction has increased without changing the concentration of interacting substances. The law of the masses in most traditional water purification technologies is used only for one component of controlling the speed of interaction reactions - the concentration of interacting substances, which is due to the design of the equipment used. However, in this case, in the MB elements operating in the mode of self-organizing flow microstructures, another component plays the main role, also controlling the reaction rate — the frequency of contacts of interacting particles at a given concentration. Elements of MB, in contrast to all electrolyzers known in the world, are electrochemical reactors of ideal mixing and at the same time are reactors of ideal displacement. All other known electrochemical systems do not meet these criteria.

The discovered effect confirmed the correctness of choosing a new concept of EMERALD devices, which was enriched by the requirement of mandatory thorough removal of colloid-dispersed anodic oxidation products and cathode reduction from water by filtering before starting the next active (electrochemical) stage of water treatment. The processes of removal of the colloid-dispersed phase from water may be different in nature. Filtering is the simplest and most accessible technique. In accordance with the new concept, production of compact units for deep water treatment in cottages has been organized. The first batches of these devices arrived to consumers. The schematic diagram of the device, made in accordance with the developed concept and corresponds to that is shown in Fig. 5. The first tests of model and prototypes on fresh water and saline water solutions fully confirmed the validity of the new concept and allowed to determine the name of this technological scheme, as well as the family of devices for implementing this scheme as EMERALD-UNIVERSAL.

In the EMERALD-UNIVERSAL device, the following processes are carried out sequentially: water treatment in the anode chamber of the first electrochemical reactor followed by filtration, water treatment that has passed the first filter successively in two cathode chambers (in the first and second electrochemical reactors), followed by filtration, water treatment that has passed the second filter in the anode chamber of the second reactor, followed by filtration. Analysis of sediment from each of the three filters (Fig. 6) of the experimental EMERALD-UNIVERSAL device allowed us to construct an

approximate chemical scheme of the processes that occur in the device with four active and three passive stages of purification.

The water first enters the anode chamber of a flow-through diaphragm electrochemical reactor, represented by an MB electrochemical modular element or a group of these elements (indicated on MB1 diagram, Fig.5). The pressure in the anode chamber of MB1 element is greater than in the cathode chamber. Under the action of an electric current, electromigration of a part of metal cations from water through the ultrafiltration diaphragm into the cathode chamber occurs.

The first active stage of water purification is the primary anodic electrochemical treatment:

$2H_2O - 4e \rightarrow 4H^+ + O_2$; $O_2 + H_2O - 2e \rightarrow O_3 + 2H^+$; $2H_2O - 2e \rightarrow 2H^+ + H_2O_2$;

$3H_2O - 6e \rightarrow O_3 + 6H^+$; $H_2O - 2e \rightarrow 2H^+ + O^{\bullet}$; $H_2O - e \rightarrow H^+ + OH^{\bullet}$;

$Cl^- + H_2O - 2e \rightarrow HClO + H^+$; $Cl^- + 2H_2O - 5e \rightarrow ClO_2 + 4H^+$; $2SO_4^{2-} - 2e \rightarrow S_2O_8^{2-}$;

$2FeSO_4 + H_2SO_4 - 2e \rightarrow Fe_2(SO_4)_3 + 2H^+$; $Fe^{2+} - e \rightarrow Fe^{3+}$.

Carbonic acid and its salts are almost always present in natural fresh water. Most of the carbon dioxide is in the form of free molecularly dissolved gas CO_2 and bicarbonate ions HCO_3^-. When treating water in the anode chamber, the water is enriched with free carbon dioxide as a result of the reactions:

$Ca(HCO_3)_2 + 2H^+ + 2SO_4^{2-} - 2e \rightarrow CaSO_4 + 2H_2O + 2CO_2$;

$Ca(HCO_3)_2 + 2H^+ + 2Cl^- - 2e \rightarrow CaCl_2 + 2H_2O + 2CO_2$;

$Mg(HCO_3)_2 + 2H^+ + 2SO_4^{2-} - 2e \rightarrow MgSO_4 + 2H_2O + 2CO_2$;

$Mg(HCO_3)_2 + 2H^+ + 2Cl^- - 2e \rightarrow MgCl_2 + 2H_2O + 2CO_2$.

Fig. 6. Appearance of ten micron filters of the experimental EMERALD-UNIVERSAL-500 device after 4 hours of operation on fresh artesian water with the content of ferrous ions about 4 mg / l.

With traditional methods of removing ions of bivalent iron and manganese, aeration (oxidation by air bubbling) is most often used, and chlorine, ozone, and potassium permanganate are used as oxidizing agents in the process of mechanical filtration of water on sandy or anthracite loads. However, the effectiveness of these technologies is low, since the process of oxidation and the formation of flakes is quite long.

In the anode chamber of MB elements the oxidation process proceeds almost instantaneously due to its combined properties of a reactor of ideal mixing and ideal displacement. Also, the microbial microflora of all types and forms (bacteria, mycobacteria, viruses, fungi, spores), microbial toxins, other organic compounds, including herbicides, pesticides, hormones, antibiotics, antidepressants are destroyed in the anode chamber. The destruction of living and inanimate organic matter occurs as a result of oxidation by products of anodic electrochemical reactions, as well as due to direct oxidation in the double electric layer (DEL) at the anode surface. The process of direct oxidative destruction of organic compounds captures a significant part of the volume of flowing water due to the special nature of the flow of water in the gap between the coaxially arranged cylindrical electrode (anode) and the diaphragm. The superposition of hydrodynamic and electrostatic interactions in a moving flow core between an electrically charged surface of an electrode that generates microbubbles of gases (ozone, oxygen) and an electrically charged surface of a ceramic ultrafiltration diaphragm forms a flow structure

in the form of a set of microtoroidal jets interacting with the main flow core and progressively moving in an annular gap in the electrode chamber.

Thus, in the operating element MB, with the flow of electric current and the corresponding flow rate of water (collectively referred to as anolyte), the anode chamber turns into a double-acting reactor: perfect mixing and, at the same time, perfect displacement. Similar processes of transformation of the electrode chamber into the reactor of ideal mixing and ideal displacement also take place in the cathode chamber of the MB element when current flows with evolution of electrolysis gases (mainly hydrogen) on the cathode surface and the corresponding flow rate, also collectively referred to as catholyte.

Compounds of divalent manganese are converted to tetravalent, divalent iron - into ferric ones.

If the pH of the source water was around 7, then after the first stage of anodic treatment the pH of the water decreases by approximately 1.0 pH units.

All insoluble compounds - coagulated organic matter, iron, manganese - are retained by filter F1, which performs the function of the first passive stage of water purification.

The second active stage of water purification is the primary cathodic electrochemical treatment.

$2H_2O + 2e \rightarrow H_2 + 2OH^-$; $O_2 + e \rightarrow O_2^-$; $O_2 + H_2O + 2e \rightarrow HO_2^- + OH^-$;

$Fe(OH)_2 + 2H^+ + 2e \rightarrow Fe + 2H_2O$; $Fe(OH)_2 + 2e \rightarrow Fe + 2OH^-$;

$FeCO_3 + 2e \rightarrow Fe + CO_3^{2-}$;

As a result of the cathode treatment of water in the first element MB, the pH of the water at the outlet reaches 7.5–8.2.

The third active stage of water purification is secondary cathodic electrochemical treatment.

$e_{cathode} + H_2O \rightarrow e_{aq}$; $H^+ + e_{aq} \rightarrow H^\bullet$; $H_2O + e_{aq} \rightarrow H^\bullet + OH^-$;

$HO_2^- + H_2O + e \rightarrow HO^\bullet + 2OH^-$; $O_2 + 2H^+ + 2e \rightarrow H_2O_2$; $Fe^{2+} + 2e \rightarrow Fe$;

After leaving the cathode chamber of the second MB element, the water acquires a pH in the range of about 9.

Ions of heavy metals, iron, copper, zinc are converted into insoluble hydroxides and are separated on an F2 filter (second passive stage of water purification). Water is saturated with hydrogen and becomes suitable for the introduction of the last portion of oxidants in the anode chamber of element MB2.

The fourth active stage of water purification is secondary anodic electrochemical treatment.

$OH^- - e \rightarrow HO^\bullet$; $O_2 + 2OH^- - 3e \rightarrow O_3 + H_2O$; $3OH^- - 2e \rightarrow HO_2^- + H_2O$;

$H_2O_2 - e \rightarrow HO_2^\bullet + H^+$; $H_2O - e \rightarrow HO^\bullet + H^+$; $H_2O_2 - e \rightarrow HO_2^\bullet + H^+$;

$Cl^- + 4OH^- - 5e \rightarrow ClO_2 + 2H_2O$;

Organic Manganese and Iron:

$Fe(OH)_2 + OH^- - e \rightarrow Fe(OH)_3$; $2Fe(OH)_2 - 2e \rightarrow Fe_2O_3 + H_2O + H^+$;

$Mn^{2+} + 3H_2O - 2e \rightarrow Mn_2O_3 + 6H^+$; $Fe(OH)_2 + H_2O - e \rightarrow Fe(OH)_3 + H^+$;

$Mn^{2+} + 2H_2O - 2e \rightarrow MnO_2 + 4H^+$.

In the anode chamber of MB2 element organic bivalent iron and manganese is oxidized, additional oxidation occurs with simultaneous coarsening of the particles of all those impurities that have passed the previous steps. All coagulated particles are separated on an F3 filter, which is the third passive stage of water purification.

The use of filters with automatic cleaning process, for example, by backwashing, will eliminate the need to buy replaceable cartridges and eliminate the manual replacement of cartridges. Cleaning the device will be reduced down to periodic automatic removal of sediments from the filters and periodic washing, as well as automatic (in Moscow water - once a year) of all the chambers of electrochemical elements with citric or weak hydrochloric acid. To prevent the acid accumulation on the filters during electrochemical cells descaling cycles, bypasses are provided with a manual (as in the diagram) or an automatic (using electromagnetic valves) switching the hydraulic circuit from the water purification operating mode to the descaling mode of the electrode chambers and back to water purification mode.

This system with a similar technological cleaning scheme has great potential for development. In particular, it can be used for the treatment of sea water. The product will actually be Anolyte ANK SUPER with a very low concentration of oxidants, in seawater decontaminated from microorganisms, organic and inorganic harmful impurities. That type of water is preferred for the cultivation of young shrimp and other aquaculture. The same technological process can be used when cleaning the initial concentrated solutions of natural rock salt for the preparation of brines in the food industry, as well as

initial solutions for feeding various electrochemical installations, for example, producing sodium hypochlorite, chlorine, sodium hydroxide. Another area of use of such electrochemical water purification systems is for sea and fresh water for swimming pools treatment and disinfection, as well as the constant purification and conditioning of water in the circulating system of swimming pools. Large capacity systems with the same technological processes can be used for water conditioning and purification in the cooling towers systems of power plants, where they provide effective biofilm control and prevention of scale formation and accumulation.

Such electrochemical systems can be easily and quickly installed in any place where centralized purification for water bottling will be performed. As an additional final stage in water bottling process could be the use a carbon filter of any design. In case of the higher residual oxidants content required for water decontaminated, for example, for biofilm elimination during the initial stage of systems installation in the old distribution pipelines, it can be achieved by either higher current applied through the second (by the movement of water) electrochemical reactor or through the use of an additional reactor (electrochemical element), providing only anodic water treatment. EMERALD-UNIVERSAL systems can be recommended for use in some European countries, as well as countries in the Middle East, Southeast Asia, Africa, Latin America.

Fig. 7. EMERALD-UNIVERSAL-500 device as the main universal device for cleaning and conditioning water in the cottage. When a low-level sensor of purified water is triggered in a storage tank, water from a well with a constant flow rate of 500 liters per hour enters the storage tank, having previously passed all cleaning steps in EMERALD-UNIVERSAL-500 device. When reaching the top level in the storage tank, the EMERALD-UNIVERSAL device is turned off. A pressure booster station connected to a storage tank and connected to an in-house water distribution system provides the entire cottage with clean water at any time and in any required quantity.

EMERALD-UNIVERSAL system is presented on Fig.7, that system is installed for treatment of up to 500 liters per hour of water in the private home. It provides turbidity and color control, as well as water decontamination from iron, manganese, hydrogen sulfide, organic impurities (herbicides, pesticides, surfactants, phenols, antibiotics, hormones, antidepressants, anabolic steroids), heavy metal ions, microorganisms of all kinds (bacteria, bacteria, viruses, fungi, spores), microbial toxins. It has capacity from 250 to 500 liters per hour (adjustable) and works in automatic mode: it turns on when the level in a storage tank connected to the booster station is low. Filters cartridges replacement conducted manually once every two months in case of water consumption of about 15 cubic meters per month.

Comparative analysis of water quality from a well with a depth of 120 meters in the Istrinsky district of the Moscow region are presented in the Table 1. Water with a total mineralization of 0.3 g/l of hydrocarbonate-sulphate-calcium-magnesium from coal deposits of the Paleocene was subjected to electrochemical purification in EMERALD-UNIVERSAL-500 system. The water consumption was 420 l/h, the pressure at the inlet to the device was 1.6 bar, the amperage was 5.7 amps, and the voltage was 95 volts.

Table 1.

Comparative analysis of well water purified by the EMERALD-UNIVERSAL-500 system.

Indicator	Measurement result		Normative value	Units of measurement	Ratio of elimination, %
	Initial water	Purified water			

Organoleptic characteristics					
Turbidity	1,6	1,2	2,6	FTU	25
Chromaticity	15	10	20	degree	33
Smell	1	0	2	number	100
Metals and metalloids					
Barium	0,095	0,001	0,1	mg/l	98,9
Iron	3,102	0,001	0,3	mg/l	99,9
Strontium	7,112	0,001	7	mg/l	99,9
Copper	0,011	0,002	1	mg/l	81,8
Zink	0,087	0,003	5	mg/l	96,5
Silica	7,321	1,315	10	mg/l	82,0
Boron	0,270	0,005	0,5	mg/l	98,1
Generalized indicators					
Hardness	4,8	2,1	7	mg-eq/l	56,2
Chemical Oxygen Demand	3,3	0,8	5	mg/l	75,7
Residual Combined Chlorine	0	0	1,2	mg/l	--

Residual Free Chlorine	0	0,01	0,5	mg/l	--
Solid Residue	321	279	1000	mg/l	13,1
Microbiological indicators					
Total Microbial Count	247	0	50	CFU / ml	100

Analysis of water parameters before and after treatment by Emerald – Universal System, demonstrated high effectiveness of the technological process and electrochemical system, and its advantages for well water treatment.

Conclusion. Saint Seraphim of Sarov, one of the most renowned Russian saints in the Eastern Ortodox Church, said: “Drink where the horse drinks. Horse will never drink bad water." In the absence of a horse, the water purification technology was tested on cats. In all cases, cats preferred water purified by the EMERALD-UNIVERSAL system to untreated well water, tap water, bottled water (Evian), or ordinary natural water, which used as control for comparison.

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