Non-reagent electrochemical water purification technology for the needs of agriculture

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Abstract. The paper experimentally investigates and theoretically substantiates a reagent-free electrochemical technology for fresh natural water purification, which simulates oxidative, reduction and filtration processes of water purification for the needs of agriculture. The use of the latest advances in the design of flow-through electrochemical diaphragm reactors has made it possible to develop a universal technology for removing heavy metal, iron, manganese ions, dissolved organic compounds of natural and artificial origin, microorganisms of all types and forms, as well as microbial toxins and pharmaceuticals from water. The versatility of the technology lies 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 unit for purifying natural fresh water to obtain high quality drinking water has been created.

1. Introduction

Natural fresh water, before becoming potable, must be free from microorganisms and xenobiotic substances, as well as from excessive amounts of dissolved or suspended chemical compounds that impair its biological, organoleptic or physicochemical properties. The addition of chemical reagents to water in order to remove undesirable substances inevitably leads to the enrichment of water with other, often no less harmful substances.

The desire to improve the efficiency of water purification systems from pollution, while taking into account the need to create environmentally friendly technologies, inevitably leads to the development and practical use of electrochemical methods for water purification [1].

As a physicochemical process, electrochemical activation is a minimal-heat-release set of electrochemical and electrophysical effects on a liquid (mainly water) with ions and molecules of dissolved substances contained in it in the space charge region at the electrode surface (either anode or cathode) of an electrochemical system with nonequilibrium charge transfer across the electrode-electrolyte interface by electrons.

As a result of electrochemical activation, water transforms into a metastable (activated) state, while exhibiting increased reactivity in various physicochemical processes for several tens of hours. Water activated at the cathode (catholyte) has an increased activity of electrons and possesses pronounced properties of a reducing agent [7]. Accordingly, water activated at the anode (anolyte) is characterized by a reduced activity of electrons and exhibits the properties of an oxidizing agent.

The main distinguishing features of FEM and MB elements are the combination in one element of the properties of a plug-flow reactor and a perfect-mixing reactor, as well as the ability to effectively...
control the process of electrochemical treatment of water and electrolyte solutions by regulating the artificially induced ion-selective conductivity of a ceramic ultrafiltration diaphragm over a wide range.

2. Materials and methods
The study of the possibility of implementing a continuous technological process for purifying natural fresh water from organic compounds, microorganisms, ions of heavy metals and iron in one flow-through pressure electrochemical system was carried out in original AQUATRON devices equipped with electrochemical reactors of MB elements, developed in 2016-2018 as part of work on grants of the Russian Science Foundation (projects No. 16-16-0020 and No. 17-76-20014).

The activity coefficient of ions in dilute solutions, to which drinking water can be attributed, is close to one, that is, the activity practically corresponds to the concentration. The results of the study of the process of changing the activity of bidistilled water with a very low content of electrolyte ions of impurities under the action of an electric field showed the possibility of achieving the activity of electrons, measured by means of a platinum electrode relative to a silver chloride reference electrode, the values of the electromotive force, somewhat simplistically called the redox potential (ORP) exceeding the limits of thermodynamic stability of water [3]. These deviations are guaranteed to cause the death of all known life forms due to the impossibility of living structures to compensate for the influence of an activated medium. Those studies were continued in 2020 at the AQUATRON-15-800L device [2] equipped with an RPE-14 reactor made of flow-through modular MB electrochemical cells, each of which is actually an independent compact diaphragm electrochemical reactor. The purpose of the research was to study the range of values of electron activity during electrochemical processing of fresh drinking water with a total mineralization of less than 0.3 g/l in an electrochemical reactor. Along with biological experiments based on the use of electrochemically activated substances and provided for by the program of work under the grant from the Russian Science Foundation, studies of the synthesis of anolyte and catholyte of ordinary tap fresh water were carried out in various flow modes through narrow annular long gaps between the electrode (anode, cathode) and a ceramic ultrafiltration diaphragm made of aluminum oxide in alpha form. Researchers pay attention to the processes of using electrochemically activated solutions in various technological processes, but a vanishingly small number of works are devoted to the study of electrochemical systems proper for the synthesis of electrochemically activated water and solutions.

An additional research task was to determine the efficiency of the parallel operation of a group of new generation MB elements with ceramic ultrafiltration diaphragms made of aluminum oxide in the alpha form and pore sizes from 0.01 to 0.1 μm. It was necessary to obtain quantitative estimates of the degree of intensification of the processes of electrochemical action on dilute electrolyte solutions due to the stable physicochemical and physico-mechanical properties of diaphragms and the possibility of the formation of self-organizing vortex flow structures in an operating electrochemical reactor at relatively high rates of liquid movement in each of its elements [5].

This problem was solved by using an electrochemical reactor of fourteen hydraulically connected in parallel electrochemical cells.

3. Results
The result of the research was the achievement of previously obtained experimental data on the change in the pH and redox potential of fresh water subjected to electrochemical action at the surface of the positive and negative electrodes of a single MB cell, with more than half the power consumption. As a starting point in all experiments, we used drinking water from the north-western region of Moscow with the following parameters: total mineralization - 0.25 g/l; hardness - 3.6 mg-eq/l; pH - 7.1 ÷ 7.2; redox potential measured with a platinum electrode relative to a silver chloride reference electrode - from +250 to + 350 mV; specific electrical conductivity - on average 0.00031 S/cm.

The pH and ORP were measured with a PH FE20 pH meter (METTLER-TOLEDO), the specific electrical conductivity of water - with a conductometer FP-30 – STANDARD (METTLER-TOLEDO).
The cooled electrodes of the MB elements ensured the constancy of the temperature of the water flowing through the electrode chambers within 15 plus or minus 1°C with a flow rate of 800 to 850 l/h. The current strength was maintained in the range from 20 to 25 A at a voltage of 24 to 36 volts. The specific amount of electricity consumed for the electrical treatment of water in the cathode or anode chambers of the MB elements averaged 100 C/L [6].

**Table 1.** Comparative results of the quality analysis of natural fresh well water purification in an EMERALD-UNIVERSAL-500 device

| Index                        | Units       | Measurement result | Normative value |
|------------------------------|-------------|--------------------|-----------------|
|                              |             |Starting water | Purified water |                  |
| **Organoletic indicators**   |             |                |                |                 |
| Turbidity                    | FTU         | 1.6            | 0              | 2.6             |
| Chromaticity                 | degree      | 4.6            | 0              | 20              |
| Smell                        | score       | 2              | 0              | 2               |
| **General indicators**       |             |                |                |                 |
| General hardness             | meq/l       | 6.38           | 5.92           | 7               |
| Permanganate                 | mg/l        | 1.3            | 0.9            | 5               |
| Chlorine total               | mg/l        | 0.0            | 0.6            | 1.2             |
| Residual free chlorine       | mg/l        | 0.0            | 0.5            | 0.5             |
| Dry residue                  | mg/l        | 321            | 295            | 1000            |
| Specific electrical conductivity | μS/cm | 630          | 650            | -               |
| Total alkalinity             | mmol-eq/l   | 6.1            | 6.2            | -               |
| Free alkalinity              | mmol-eq/l   | 0.0            | -              | -               |
| **Cations**                  |             |                |                |                 |
| Iron                         | mg/l        | 3.1            | 0              | 0.3             |
| Strontium                    | mg/l        | 0.8            | 0              | 7               |
| Manganese                    | mg/l        | 0.04           | 0              | 1               |
| Calcium                      | mg/l        | 92.0           | 90.8           | 25 - 130        |
| Magnesium                    | mg/l        | 25.6           | 22.5           | 5 - 65          |
| Silicon                      | mg/l        | 6.5            | 6.4            | 10              |
| **Anions**                   |             |                |                |                 |
| Hydrocarbonates              | mg/l        | 370            | 380            | -               |
| Carbonates                   | mg/l        | 5.0            | 6.0            | -               |
| Fluorides                    | mg/l        | 0.4            | 0.5            | 1.5             |
| Chlorides                    | mg/l        | 2.0            | 3.0            | 350             |
| Nitrates                     | mg/l        | 4.3            | 4.5            | 45              |
| Sulphates                    | mg/l        | 10.1           | 11.2           | 500             |
| **Microbiological indicators** | CFU/ml | 450            | 0              | 50              |
| Total microbial count (TMC)  | CFU/ml      | 450            | 0              | 50              |
| Total coliform bacteria (CGB coliforms) | The number of bacteria per 100 cm³ | Found | Not found | 0 |
| Thermotolerant coliform bacteria | The number of bacteria per 100 cm³ | Found | Not found | 0 |

Measurements of pH, ORP and electrical conductivity were carried out within 2 or 3 minutes after the termination of the electrochemical treatment process. The time of each measurement did not exceed 5 minutes.
Analysis of the results of the practical experiment has confirmed that electrochemical nonequilibrium effect is capable of changing the reactivity (activity) of ions in solutions by tens of times without changing their concentration.

The pH values reached in the course of electrochemical action correspond to equilibrium concentrations of alkali and acid, many times higher than the content of salts in water, from which these alkalis and acids could be obtained. The ORP values go beyond the capabilities of chemical modeling for a given electrical conductivity and are therefore unique [4].

Based on the results of the first stage of the study, the following conclusions were made:

1. Electrochemical reagent-free regulation of the properties and parameters of water allows for the oxidation or reduction of almost any substance contained in water.
2. The most economical method of electrochemical regulation of the properties and parameters of fresh water is using flow-through electrochemical modular MB elements with diaphragms based on aluminum oxide in the alpha form.

The second stage of the study consisted in determining the principle of constructing an electrochemical system for the purification of natural fresh water in obtaining purified water at the outlet and its comparative analysis according to the main chemical and microbiological indicators.

Therefore, studies of the efficiency of extraction of iron and manganese from water were carried out at obviously high values of the specific amount of electricity consumed for water treatment. It was taken into account that there are practically no chlorides in the water to be treated. Table 1 shows the results of chemical and microbiological analyses of water before and after the installation of EMERALD-UNIVERSAL-500.

**4. Discussion and analysis of results**

With traditional methods of removing ferrous iron and manganese ions, aeration (oxidation by bubbling with air) is most often used; chlorine, ozone, and potassium permanganate are also used as oxidants 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 formation of flakes is quite long.

In the anode chamber of the MB elements (Fig. 1), the oxidation process occurs almost instantaneously due to its combined properties of a perfect-mixing reactor and a plug-flow reactor. Also, the anode chamber destroys microbial microflora of all types and forms, microbial toxins, other organic compounds, including herbicides, pesticides, pharmaceuticals.

![Figure 1. Flow-through electrochemical MB modular cell, 2016 model](image)

The destruction of living and nonliving organic matter occurs as a result of oxidation by the 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 located cylindrical electrode (anode) and the diaphragm. The superposition of hydrodynamic and electrostatic interactions in the moving core of the flow between the electrically charged electrode surface generating microbubbles of gases (ozone, oxygen) and the electrically charged surface of the ceramic ultrafiltration diaphragm (due to the adsorption layer of electrically active particles formed as a result of processes on the electrode) forms the flow structure in the form of a set of microtoroidal jets interacting with the main flow core and translationally moving in the annular gap in the electrode chamber.

Thus, in the working MB element, with the flow of an electric current and a corresponding flow rate of water, which during its stay in the anode chamber and after leaving it is generally called...
anolyte, the anode chamber turns into a double-acting reactor: perfect mixing and, at the same time, plug-flow reactor. Similar processes of transformation of the electrode chamber into a perfect mixing and a plug-flow reactor take place in the cathode chamber of each of the MB elements when the current flows with the release of hydrogen on the cathode surface and the corresponding water flow rate, also generally referred to as catholyte.

In the anode chamber of the MB2 element, there is oxidation of organic ferrous iron and manganese, and additional oxidation with simultaneous enlargement of particles of all the impurities that have passed the previous stages. The coagulated particles are separated on the F3 filter, which is the third passive stage of water purification. Comparison of the parameters of initial and purified water obtained during test studies (Table 1), which are benchmarks for assessing the effectiveness of the process and technical system, indicates the viability and high efficiency of water purification technology in the EMERALD-UNIVERSAL type electrochemical systems. Fig. 2 shows the generalized dependence of the electrical conductivity of water depending on the concentration of dissolved electrolytes, including not only various salts, but also the corresponding acids and bases.

![Figure 2. Dependence of the electrical conductivity of aqueous solutions of inorganic electrolytes (acids, bases, salts) on the concentration](image)

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 that of electrolyte solutions in traditional electrochemical production. That is why, until the end of the eighties, it was believed that electrolysis of fresh, let alone distilled water, was impossible.

The advent of flow-through electrochemical modular elements FEM (MB), made it possible to carry out water purification processes in a flow-through mode, at low power consumption, by direct only oxidizing processes in the anode chamber or only reducing processes in the cathode chamber, which, moreover, can be separated in time and space. For example, a portion of water subjected to anode electrochemical treatment in a diaphragm electrochemical reactor can be sent to a pressure flotation reactor to remove particles adhering to oxygen bubbles, then to a pressure filter to remove the residual amount of coagulated oxidized organic compounds particles, after which this portion of water can be subjected to cathode treatment in the same reactor with subsequent treatments in auxiliary elements of the system. Thus, each portion of water in a continuous flow in the system from pressure diaphragm electrochemical reactors (active elements of the system) and intermediate auxiliary passive elements (flotation and catalytic reactors, filters) turns out at different times in the same active element (electrochemical reactor), but in another electrode chamber with directly opposite direction of energy and mass transfer.
The use of filters with automatic cleaning, for example, by backwashing, will relieve the user from buying replacement cartridges and eliminate the need for manual cartridge replacement. Cleaning of the device will be limited just to periodic automatic removal of sediment from filters and periodic flushing, also automatic, of all chambers of electrochemical cells with citric or weak hydrochloric acid.

5. Conclusions
This device with this kind of treatment flow chart has great development potential. In particular, it can be used to treat sea water. with the seawater will being purified from microorganisms, organic compounds and heavy metals. It is this kind of water that is necessary for growing juvenile shrimp and other marine life. The same flow chart can be used for the purification of the starting concentrated solutions of natural rock salt for making brines in the food industry, including for the regeneration of ion-exchange filters of water softening systems at food enterprises, as well as starting solutions for powering various electrochemical plants, for example, producing sodium hypochlorite. Using the "mild" and effective antimicrobial activity of water and its increased washing ability, such electrochemical devices are advisable to be used in agricultural livestock and poultry complexes, in a pond system, in slaughterhouses of poultry farms, factories for the primary washing of wool, in the cultivation of silkworms and other areas. The use of electrochemically purified water with specified properties will prevent the growth of biofilms on the inner surfaces of food processing equipment and improve the quality of agricultural products.

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