

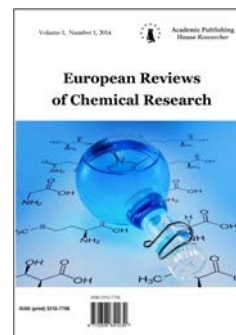
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Published in the Russian Federation
European Reviews of Chemical Research
Has been issued since 2014.
ISSN: 2312-7708
Vol. 4, Is. 2, pp. 72-86, 2015

DOI: 10.13187/ercr.2015.4.72

www.ejournal14.com



UDC 631.531.027: 635.63

The Evaluation of the Mathematical Model of Interaction of Electrochemically Activated Water Solutions (Anolyte and Catholyte) with Water

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Abstract

This paper deals with the evaluation of the basis of the mathematical model of interaction of electrochemically activated water solutions (catholyte/anolyte), obtained in the diaphragm electrolysis cell, with water and sodium chloride and the basic physical-chemical processes underlying the electrolysis of water as well. In order to provide additional data about the distribution of H₂O molecules according to the energies of hydrogen bonds in the electrochemically activated water solutions of the catholyte and the anolyte, the non-equilibrium energy spectrum

(NES) and differential non-equilibrium energy spectrum (DNES) of the anolyte and the catholyte were measured as a result of which were established the basis for evaluation of the mathematical model explaining the behavior of the anolyte and the catholyte regarding the distribution of H₂O molecules to the energies of hydrogen bonds. The local maximum for catholyte in the NES-spectrum was at -0,1285 eV, for anolyte – at -0,1227 eV and for the control sample of deionized water – at -0,1245 eV. The calculations of $\Delta E_{H..O}$ for catholyte with using the DNES method compiles (-0,004±0,0011 eV) and for anolyte (+1,8±0,0011 eV). The average energy of hydrogen bonds between H₂O molecules was measured by the DNES method to be compiled at -0,1067±0,0011 eV.

Keywords: electrochemical treatment of water, electrolysis, anolyte, catholyte, NES, DNES.

Introduction

The phenomenon of electrochemical activation of water (EAW) is a set of electrochemical and electrical processes occur in water in the electric double layer (EDL) type of electrodes (anode and cathode) with non-equilibrium electric charge transfer through EDL by electrons under the intensive dispersion in water the gaseous products of electrochemical reactions [1]. In 1985 EAW was officially recognized as a new class of physical and chemical phenomena.

As a result of the treatment of water by a constant electric current at electric potentials equal to or greater than the decomposition potential of water (1,25 V), water goes into a metastable state, accompanied by electrochemical processes and characterized by the abnormal activity levels of electrons, the redox potential, and other physical-chemical parameters (pH, E_h, ORP) [2].

During the EAW occur four main processes:

- 1) Electrolytical decomposition of water by electrolysis on account of redox reactions on the electrodes due to the external electric field;
- 2) Electrophoresis – the movement in the electric field of a positively charged particles and ions toward the cathode and negatively charged particles and ions toward the anode;
- 3) Electroflotation – the gas formation and flocculation of aggregates consisting of fine-dispersed gas bubbles (H₂ at the cathode and O₂ at the anode) and suspended solids in water;
- 4) Electrocoagulation – the formation of colloidal aggregates of particles of deposited disperse phase through a process of anode dissolution of the metal and the formation of metal cations Al³⁺, Fe²⁺, Fe³⁺ under the influence of electric field.

The electrochemical processes, which occur at the passage of the direct electric current through the water volume, are accompanied as a result of redox reactions leading to coagulation of colloids, flocculation of suspended solids and subsequent flotation. The advantages of electrochemical water treatment is that it allows to correct the pH value and redox potential E_h, on which depends the possibility of occurrence of various chemical processes in water; increases the enzymatic activity of activated sludge in aeration tanks; reduces the resistivity and improves coagulation and sedimentation of organic sediments from water.

The purpose of this research was the evaluation of the basis of the mathematical model of interaction of electrochemically activated water solutions – the anolyte and catholyte.

Material and Methods

The experiments were conducted with the diaphragm electrolysis apparatus “Wasserionisierer Hybrid PWI 2100” (Drink In Clear Co., Germany), equipped with four titanium plate electrodes coated with platinum.

Technical data: dimensions – 380×230×230 mm; weight – 3,8 kg; the voltage of the electric power supply – 220 V, the frequency of the electric current – 50 Hz, the power of the electric current 0,2–0,7 A; the power consumption – 200 Watts; pH range – 3,5 - 10,5; inlet water temperature 5–30 °C; the time of electro processing – 30–40 min. The volumes of the electrochemically activated water solutions: anolyte – 0,3 l; catholyte – 0,9 l.

The elementary electrolysis cell was formed by two electrodes – a positively charged anode and a negatively charged cathode connected to different poles to a DC source. Interelectrode space was filled with water, which is an electrolyte capable of conducting the electrical current, or with 0,3% solution of chemically pure NaCl in distilled H₂O, as schematically shown in Figure 1 below.

The anolyte had pH = 3,2 and ORP = +1070 mV; the active components – HClO, Cl₂, HCl, HO₂*;

The catholyte had pH = 9,0 and ORP = -300...-500 mV); the active components – O₂, HO₂⁻, HO₂^{*}, H₂O₂, H⁺, OH⁻.

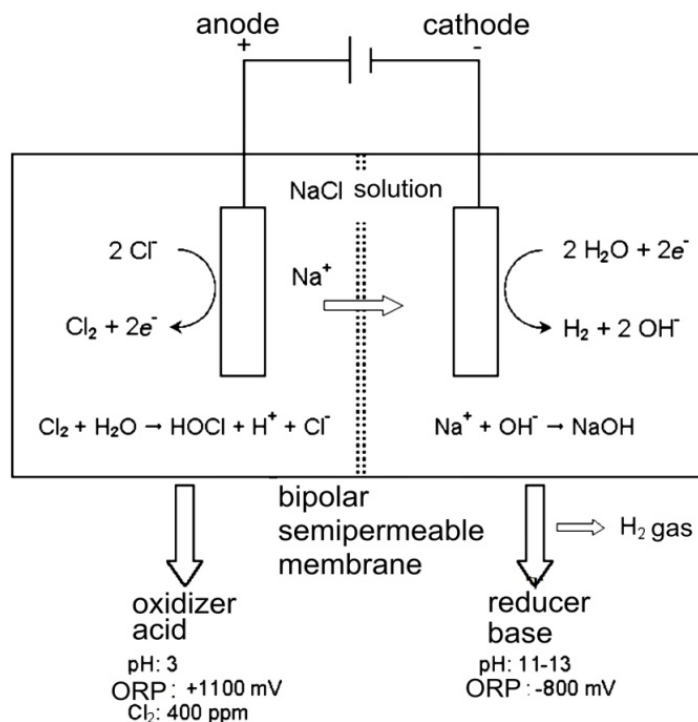


Figure 1. The diaphragm electrolysis apparatus for preparation of acid (anolyte) and alkali (catholyte) solutions via the electrochemical activation of sodium chloride

NES, and DNES methods were used for the estimation of energy of hydrogen bonds of the anolyte, the catholyte and deionized water in order to make a supposition about the spectrum characteristics. The device measured the angle of evaporation of water drops ranged from 72 ° to 0 °. As the main estimation criterion was used the average energy ($\Delta E_{H...O}$) of hydrogen O...H-bonds among H₂O molecules in water's samples. NES, and DNES spectra of water were measured in the range of energy of hydrogen bonds at 0,08–0,387 eV or $\lambda = 8,9\text{--}13,8 \mu\text{m}$ with using a specially designed computer program. Statistical processing of experimental data was performed using *t*-criterion of Student (at $p < 0,05$).

Results and Discussion

Electrolysis of water

The main stage of electrochemical treatment of water is the electrolysis of water or aqueous solutions with low mineralization as aqueous solutions of 0,5–1,0% NaCl [3], which occurs in the electrolysis cell, consisting of the cathode and the anode separated by a special semipermeable membrane (diaphragm) which separates water to alkaline fraction – the catholyte and acidic fraction – the anolyte (Figure 1). When the passing over the electric current through water, the flow of electrons from cathode as well as the removal of electrons from water at the anode, is accompanied by series of redox reactions on the surface of the cathode and anode [4]. As the result, new elements are formed, the system of intermolecular interactions, as well as the composition of water and the water structure are changed [5, 6].

The typical apparatus for electrochemical treatment of water comprises water preparation/treatment unit (1), the electrolyzer (2), and the processing unit after the electrochemical treatment of water (3) (Figure 2).

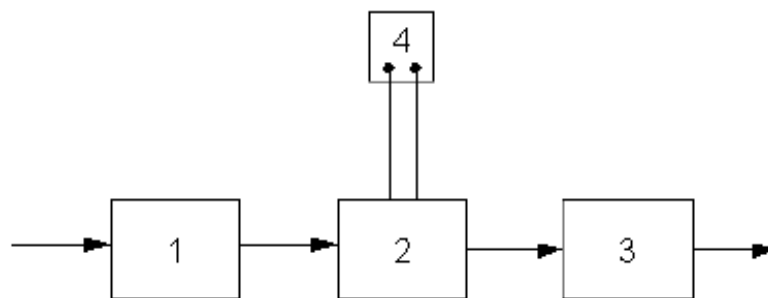


Figure 2. The apparatus for electrochemical water treatment: 1 – water preparation/treatment unit; 2 – electrolyzer; 3 – the block of post-treatment; 4 – rectifier of electric current.

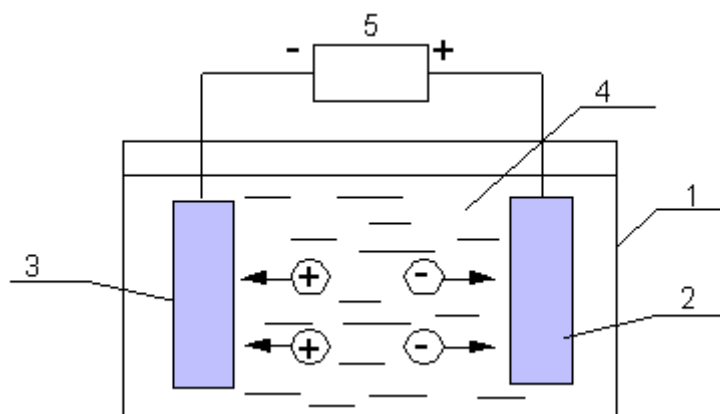


Figure 3. Scheme of the electrolysis cell: 1 – the case; 2 – anode; 3 – cathode; 4 – interelectrode space; 5 – DC power source.

The main element of the apparatus is electrolyzer consisting of one or more electrolysis cells (Figure 3). The typical electrolysis cell is formed by two electrodes – a positively charged anode and a negatively charged cathode connected to different poles to a DC source. Interelectrode space is filled with water, which is an electrolyte capable of conducting electrical current, or with 0,5–0,1% solution of NaCl. As a result it occurs the transferring of electric charges through the water – electrophoresis, i.e. migration of the polar particle charge carriers – ions for the electrode having an opposite sign. Wherein the negatively charged anions are moved toward the anode, the positively charged cations are moved toward the cathode. At electrodes the charged ions lose the charge and become depolarized, turning into the decay products. In addition to these charged ions, in the electrophoresis participate the polar particles with different particle sizes, including solid particles (emulsified particles, gas bubbles, etc.), but the main role in the transfer of electrochemical charges plays the ions possessed by the greatest mobility.

The products of electrode reactions are the neutralized aqueous admixtures, gaseous hydrogen and oxygen generated during the electrolytic destruction of H_2O molecules, metal cations (Al^{3+} , Fe^{2+} , Fe^{3+}) in the case of metal anodes made of aluminum and steel, and the molecular chlorine. Wherein at the cathode is generated the gaseous hydrogen, and at the anode – oxygen. Water also contains a certain amount of hydronium ions (H_3O^+) depolarizing at the cathode with formation of the atomic hydrogen ($H\cdot$):



In an alkaline environment there occurs the disruption of H_2O molecules, accompanied by formation of the atomic hydrogen ($H\cdot$) and hydroxide ion (OH^-):



The reactive hydrogen atoms are adsorbed on the surfaces of the cathode, and after recombination are formed the molecular hydrogen H_2 , released in the gaseous form:



At the same time at the anode is released the atomic oxygen. In an acidic environment, this process is accompanied by the destruction of H_2O molecules:



In an alkaline environment, the source of oxygen source is OH^- ions, moving under the electrophoresis from the cathode to the anode:



The normal redox potentials of these reactions compiles +1,23 V and +0,403 V, respectively, but the process takes place in certain conditions of electric overload.

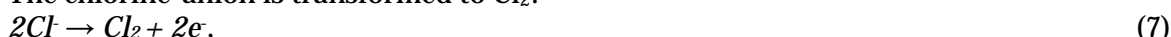
The cathodes are made of metals that require high electrical voltage (lead, cadmium), allow to generate the reactive free radicals as Cl^* , O^* , OH^* , HO_2^* , which react chemically with other radicals and ions.

In bulk oxidative processes a special role plays products of electrolysis of water – oxygen (O_2), hydrogen peroxide (H_2O_2) and hydrochlorine acid (HClO). During the electrolysis, an extremely reactive compound formed – H_2O_2 , the formation of which occurs due to hydroxyl radicals (OH^*), which are the products of the discharge of hydroxyl ions (OH^-) at the anode:



where OH^* – the hydroxyl radical.

The chlorine-anion is transformed to Cl_2 :



Gaseous Cl_2 forms highly active oxidants: Cl_2O ; ClO_2 ; ClO^- ; HClO ; Cl^* ; HO_2^* . The parameters of pH, the redox potential, ORP and the electrical conductivity of the anolyte/catholyte depend on different factors including the ratio of water volumes in the two electric chambers, the material of electrodes, NaCl concentration, the temperature, electric voltage and processing time [7, 8].

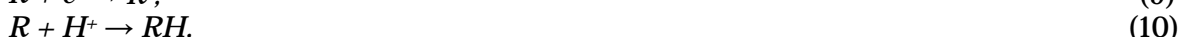
The electrolysis cell can be regarded as a generator of the above mentioned products, some of them, entering into the chemical interaction with each other and water impurities in the interelectrode space, providing additional chemical treatment of water (electrophoresis, electroflotation, electrocoagulation) [9]. These secondary processes do not occur on the electrode surface, but in the bulk water. Therefore, in contrast to the electrode processes they are indicated as the volume processes. They generally are initiated with increasing the temperature of water during the electrolysis process and with increasing the pH value.

There are distinguished the cathodic and anodic oxidation. When the cathodic oxidation the organic molecules absorbed on cathodes, accepting free electrons and reduced. The reduction process usually takes place in one step:



where R – the organic compound; RH – the hydrated form of the compound.

In other cases, the cathodic reduction takes place in two stages: at the first stage (9) the organic molecule is converted into an anion, in the second (10) – the hydrated anion interacts with the proton of H_2O water:



The cathodes made of materials that require high electrical voltage (lead, cadmium), allow for large amounts of electricity to generate the reactive free radicals – particles having on the outer orbits of atoms or molecules free unpaired electrons (Cl^* , O^* , OH^* , HO_2^*). The latter circumstance makes the free radicals the reactivity, i.e. to react chemically with other radicals and ions.

At the anodic oxidation the organic molecules, adsorbed on the anode, give up electrons to simultaneous or prior hydration:



The anodic oxidation of organic compounds often results in the formation of free radicals, which further transformations is defined by their reactivity. Anodic oxidation processes are multistage and proceed with the formation of intermediate products. Anodic oxidation lowers the chemical resistance of organic compounds and facilitates their subsequent destruction in volume processes.

The rate of the anodic oxidation depends on the temperature and the pH value. Often in the process of oxidation of organic compounds are formed intermediates, which differ from the original compounds by the resistance to further transformations and indicators of toxicity.

The source of active chlorine and its oxygen-containing compounds are chlorides generated in the electrolyser, and NaCl, which is added into the electrochemically treated water before the electrolysis. As a result of the anodic oxidation of Cl^- anions is generated the gaseous Cl_2 .

Depending on the pH value Cl_2 is either hydrolyzed to form hypochlorous acid (HOCl), or forms hypochlorite ions (ClO^-). The equilibrium of the reaction depends on the pH value; at pH = 4–5 all chlorine is present in the form of HClO, and at pH = 7 – half in the form of ClO^- ion and half – in the form of HClO (Figure 4).

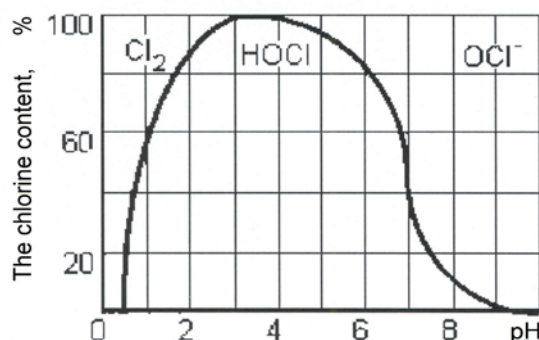


Figure 4. Content (%) of various forms of chlorine (Cl_2 , HOCl, OCl^-) in the electrochemically activated water depending on the pH value

The mechanism of interaction between the hypochlorite ions (ClO^-) with the oxidizing agent described by the following equation:



where A – the oxidizing substances; C – the oxidation product.

The electrochemical oxidation of organic compounds by hypochlorite ions (ClO^-) is accompanied by an increase of the redox potential E_h , indicating the predominance of oxidative processes. The E_h value growth depends on the ratio of active chlorine concentration in the interelectrode space to the content of organic impurities in water. As the purification and reducing the amount of impurities, the ratio increases, which leads to an increase of E_h , but after some time the rate stabilizes.

The amount of substance reacted at the electrodes by passing a constant electric current through the Faraday's law, is directly proportional to the current strength and the time of the electrochemical treatment:

$$G = A I_{cur} t, \quad (13)$$

where A – the electrochemical equivalent of an element (g/A·h); I_{cur} – the amperage (A); t – the processing time (h).

The electrochemical equivalent of an element is defined by the formula:

$$A = M/26,8z, \quad (14)$$

where M – the atomic mass of the element (g); z – its valence.

The values of the electrochemical equivalents of some elements are shown in Table. 1.

Table 1: Electrochemical equivalents of some elements

Element	The electrochemical equivalent of an element, g/A·h
H_2	0,0376
O_2	0,289
Fe (II)	1,042
Fe (III)	0,695
Al (III)	0,336
Cr (III)	0,647
Cr (VI)	0,324
Cu (II)	1,186
Zn (II)	1,22
Cl_2	1,324
Ca (II)	0,748

The actual amount of a substance, generated during the electrolysis is less than the theoretical, calculated from the formula (13) as part of the electric power is expended on heating the electrodes and water. Therefore, at calculations take into account the current efficiency $\eta < 1$, the value of which is determined experimentally.

The electrode processes are accompanied by an exchange of charged particles and ions between the electrodes and the electrolyte – water. For this the equilibrium must be established to provide an electric potential minimum value, which depends on the sort of the redox reaction and the water temperature measured at +25 °C (Table 2).

Table 2: The electrode potentials of some elements

Electrode reaction	Electric voltage [V]	Electrode reaction	Electric voltage [V]
$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$	-1,66	$\text{Cu} \rightarrow \text{Cu}^{2+} + \text{e}^-$	+0,345
$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	-0,763	$4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$	+0,401
$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$	-0,44	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	+1,23
$\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^-$	-0,403	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	+1,36
$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	0,0001	$\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}^+ + 2\text{e}^-$	+1,49

The electrical voltage generated in the electrode cell, should be sufficient to cause oxidation-reduction reactions at the electrodes. The voltage depends on the ionic composition of water, the presence of impurities in water, such as detergents, the electric current density (its power per unit area of the electrode), the electrode material, and others. Other things being equal the task of selecting the electrode material is to undergo the oxidation-reduction reactions at the electrodes, the voltage required to be minimized since it reduces the cost of electricity.

Some redox reactions are competing – they occur simultaneously and mutually inhibit each others. Their flow can be regulated by changing the electric voltage in the electrolytic cell. Thus, the normal electrical potential of the reaction of formation of molecular oxygen is +0,401 V or +1,23 V; when the voltage increases to +1,36 V (the normal potential of the reaction of formation of molecular chlorine) at the anode will be allocated only oxygen, and at the further increase in capacity – both oxygen and chlorine, and the evolution of chlorine will occur with insufficient intensity. At the voltage value +5,0 V the oxygen evolution will be almost ceased, and the electrolytic cell will only generate chlorine.

The physical-chemical properties of the catholyte and the anolyte

As a result of the cathode (catholyte) treatment water becomes alkaline: its ORP decreases, the surface tension is reduced, decreasing the amount of dissolved oxygen in water, increases the concentration of hydrogen, hydroxyl ions (OH^-), decreases the conductivity of water, changes the structure of hydration shells of ions [10]. By external characteristics the catholyte – is a soft, light, with an alkaline taste liquid, sometimes with white sediment; its pH = 10–11, ORP = -200...-800 mV.

On physical and chemical parameters the catholyte has the significantly enhanced electron-donating properties, and getting into the physiological fluids of an organism can enhance the electron-background for a few tens of millivolts [11]. The catholyte reportedly has antioxidant, immunestimulating, detoxifying properties, normalizing ORP, metabolic processes (increases the ATP synthesis, modification of enzyme activity), stimulates the regeneration of tissues, increases the DNA synthesis and stimulates the growth and division of cells by increasing the mass transfer of ions and molecules across the cell membrane, improves trophic processes in tissues and blood circulation [12]. It was also reported that catholyte with the redox potential at -700...-100 mV favors the development of anaerobes, whereas the anolyte with the redox potential at +200...+750 mV supports the growth of aerobes [13]. The antibacterial effect of the catholyte is differentiated: the bactericidal effect is appeared relative to *Enterobacteriaceae*, resistant to it are enterococci and the group of streptococci B, and against Gram-negative microorganisms – only the bacteriostatic effect [14].

The electrochemically activated solutions of the catholyte, depending on the strength of the transmitted electric current may be of several types:

C – alkaline catholyte (pH > 9,0; ORP = -700...-820 mV), the active components – NaOH, O₂, HO₂⁻, HO₂^{*}, OH⁻, OH^{*}, HO₂⁻, O₂;

CN – neutral catholyte (pH = 9,0; ORP = -300...-500 mV), the active components – O₂, HO₂⁻, HO₂^{*}, H₂O₂, H⁺, OH⁻.

As a result of the anode (anolyte) treatment water becomes acid reaction, the ORP increases slightly, the surface tension is slightly reduced, the conductivity increases, the amount of the dissolved oxygen and chlorine in water also increases, whereas the amount of hydrogen decreases [15]. The anolyte is a brownish, acid, with a characteristic odor and taste the liquid with a pH = 4–5 and ORP = +500...+1100 mV. The specific anolyte toxicity when being administered in the stomach and applying to the skin refers to the class 4 of harmful substances according to the Russian Standard GOST 12.1.007-76, with the minimal toxicity within this class. When being inhaled the anolyte with oxidants content of 0,02% and total mineralization 0,25–0,35% does not irritate the respiratory system and mucous membranes of the eyes. When introduced into the organism, the anolyte has no immunotoxic action and increased chromosomal aberrations in the bone marrow cells and other tissues, and it has no cytogenetic activity. When being heated to +50 °C the bactericidal activity of the anolyte is increased by 30–100% [16].

The electrochemically activated solutions of the anolyte are divided into four main types:

A – acidic anolyte (pH < 5,0; ORP = +800...+1200 mV), the active components – HClO, Cl₂, HCl, HO₂^{*};

AN – neutral anolyte (pH = 6,0; ORP = +600...+900 mV), the active components – HClO, O₃, HO⁻, HO₂^{*};

ANK – neutral anolyte (pH = 7,7; ORP = +250...+800 mV), the active components – HClO, ClO⁻, HO₂⁻, H₂O₂, O₂, Cl⁻, HO^{*};

ANKD – neutral anolyte (pH = 7,3; ORP = +700...+1100 mV), the active components – HClO, HClO₂, ClO⁻, ClO₂^{*}, HO₂^{*}, H₂O₂, O₂, O₃, Cl⁻, HO⁻, O^{*}.

The anolyte has antibacterial, antiviral, antifungal, anti-allergic, anti-inflammatory, antiedematous and antipruritic effect, may be cytotoxic and antimetabolite action without harming the human tissue cells [17]. The biocide elements in the anolyte are not toxic to somatic cells, as represented by oxidants, such as those ones produced by the cells of higher organisms.

Studies on the virucidal effect of the anolyte are rare and insufficient, basically on the possibilities of applying the anolyte in the implementation of effective control of viral diseases in humans and animals and especially on particularly dangerous viral infections, as staphylococcal Enterotoxin-A [18] and the classical swine fever (CSF) virus, caused by enveloped viruses belonging to the genus *Pestivirus* [19]. According to J.A. Sands [20] and U.S. Springthorpe [21], the effective disinfection of viruses whose infectivity is associated with the elements of the casing may be achieved by disinfectants dissolving fats, surfactants, disinfectants or fatty acids, organic solvents (ether and chloroform), detergents, proteases, and common disinfectants. It is believed that 2% solution of NaCl is most suitable for the disinfection of spaces contaminated with them. It is thought that to achieve the effective electrochemical disinfection it is necessary to irreversibly damage the RNA [22].

The research [23] carried out with of *E. coli* using as a desinfectant the anolyte with ORP equal or greater than +1100 mV and pH = 5,5, obtained via electrolysis of diluted NaCl solution demonstrated that within 5 min of influence all cells were inflated and burst. Also, it was occurred a full destruction of proteins, DNA and RNA. Supposedly the anolyte enters the cells provoking structural and functional damages on the cell's membrane and cell's wall.

Similar research was performed by S.V. Kumar et al. [24] to evaluate the inactivation efficacy of the anolyte at pH = 2,7 and ORP = +1100 mV on *E. coli* O157:H7, *Salmonella enteritidis* and *Listeria monocytogenes*. As it was demonstrated on five strains of *E. coli* E06 (milk), E08 (meat), E10 (meat), E16 (meat) and E22 (calf feces), all pathogens were significantly reduced (7,0 log CFU/ml) or fully destroyed (8,0 log CFU/ml) after 2 to 10 min inactivation by the anolyte within the temperature range from +4 °C to +23 °C. Supposedly, the low pH value of the anolyte makes sensitive the outer cell's membrane, thus facilitating HClO to enter into the cell and further destroy it. Unexpectedly, the stronger biocidal effect of the catholyte was observed when a strain of *E. coli* DH5 was treated by the anolyte and catholyte, respectively.

The virucidal action of the anolyte was studied by us on cell culture and suspensions of the CSF virus [25]. After inoculating them with cell cultures, the viral presence (the presence of viral antigen) was measured using the immunoperoxidase technique. It was found that anolyte did not affect the growth of the cell culture PK-15; viral growth during the infection of a cell monolayer with a cell culture virus was affected in the greatest degree by the anolyte in 1:1 dilution and less in other dilutions; whereas the viral growth at the infection of a cell suspension with the CSF virus was affected by the anolyte in dilution 1:1 in the greatest degree, and less by other dilutions; viral growth at the infection with a virus in suspension of the cell monolayer was affected by the anolyte in all dilutions. However, it should be noted that the pharmacological studies of electrochemically activated solutions of water and their virucidal effects and toxicity have not yet been completely evaluated.

The evaluation of the mathematical model of interaction of the catholyte and the anolyte with water

The peculiarities of the chemical structure of H₂O molecules and weak bonds stipulated by electrostatic forces and donor-acceptor interaction between hydrogen and oxygen atoms in H₂O molecules create favorable conditions for formation of directed intermolecular hydrogen bonds (O–H...O) with neighboring H₂O molecules, binding them into complex intermolecular associates which composition represented by general formula (H₂O)_n, where *n* can vary from 3 to 50 units [26]. The hydrogen bond – is a form of association between the electronegative oxygen O-atom and hydrogen H-atom, covalently bound to another electronegative oxygen O-atom, is of vital importance in the chemistry of intermolecular interactions, based on weak electrostatic forces and donor-acceptor interactions with charge-transfer. It results from interaction between electron-deficient H-atom of one H₂O molecule (hydrogen donor) and unshared electron pair of an electronegative O-atom (hydrogen acceptor) on the neighboring H₂O molecule; the structure of hydrogen bonding, therefore may be defined as O...H^{δ+}–O^{δ-}. As the result, the electron of the H-atom due to its relatively weak bond with the proton easily shifts to the electronegative O-atom. The O-atom with increased electron density becomes partly negatively charged – δ⁻, while the H-atom on the opposite side of the molecule becomes positively charged – δ⁺ that leads to the polarization of O^{δ-}–H^{δ+} covalent bond. In this process the proton becomes almost bared, and due to the electrostatic attraction forces are provided good conditions for convergence of O...O or O...H atoms, leading to the chemical exchange of a proton in the reaction O–H...O ↔ O...H–O. Although this interaction is essentially compensated by mutual repulsion of the molecules' nuclei and electrons, the effect of the electrostatic forces and donor-acceptor interactions for H₂O molecule compiles 5–10 kcal per 1 mole of substance. It is explained by negligible small atomic radius of hydrogen and shortage of inner electron shells, which enables the neighboring H₂O molecule to approach the hydrogen atom of another molecule at very close distance without experiencing any strong electrostatic repulsion.

The H₂O molecule has four sites of hydrogen bonding – two uncompensated positive charges at hydrogen atoms and two negative charges at the oxygen atom. Their mutual disposition is characterized by direction from the centre of regular tetrahedron (nucleus of oxygen atom) towards its vertexes. This allows to one H₂O molecule in condensed state to form up to 4 classical hydrogen bonds, two of which are donor bonds and the other two – acceptor ones (taking into consideration bifurcate (“two-forked”) hydrogen bond – 5) [27].

A hydrogen bond according to Bernal–Fowler rules [28] is characterized by the following parameters:

a) an oxygen atom of each H₂O molecule is bound with four neighboring hydrogen atoms: by covalent bonding with two own hydrogen atoms, and by hydrogen bonding – with two neighboring hydrogen atoms (as in the crystalline structure of ice); each hydrogen atom in its turn is bound with oxygen atom of neighbour H₂O molecule;

b) on the line of oxygen atom – there can be disposed only one proton H⁺;

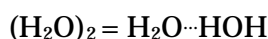
c) the proton, which takes part in hydrogen bonding situated between two oxygen atoms, therefore has two equilibrium positions: it can be located near its oxygen atom at approximate distance of 1,0 Å, and near the neighboring oxygen atom at the distance of 1,7 Å as well, hence both a usual dimmer HO–H...OH₂ and an ion pair HO...H–OH₂ may be formed during hydrogen

bonding, i.e. the hydrogen bond is part electrostatic (~90%) and part (~10%) covalent [29]. The state of “a proton near the neighboring oxygen” is typical for the interphase boundary, i.e. near water-solid body or water–gas surfaces.

d) the hydrogen bonding of a triad O–H...O possess direction of the shorter O–H (→) covalent bond; the donor hydrogen bond tends to point directly at the acceptor electron pair (this direction means that the hydrogen atom being donated to the oxygen atom acceptor on another H₂O molecule).

The most remarkable peculiarity of hydrogen bond consists in its relatively low strength; it is 5–10 times weaker than chemical covalent bond [30]. In respect of energy the hydrogen bond has an intermediate position between covalent bonds and intermolecular van der Waals forces, based on dipole-dipole interactions, holding the neutral molecules together in gasses or liquefied or solidified gasses. Hydrogen bonding produces interatomic distances shorter than the sum of van der Waals radii, and usually involves a limited number of interaction partners. These characteristics become more substantial when acceptors bind H-atoms from more electronegative donors. Hydrogen bonds hold H₂O molecules on 15% closer than if water was a simple liquid with van der Waals interactions. The hydrogen bond energy compiles 5–10 kcal/mole, while the energy of O–H covalent bonds in H₂O molecule – 109 kcal/mole [31]. The values of the average energy ($\Delta E_{H...O}$) of hydrogen H...O-bonds between H₂O molecules make up $-0,1067 \pm 0,0011$ eV [32]. With fluctuations of water temperature the average energy of hydrogen H...O-bonds in of water molecule associates changes. That is why hydrogen bonds in liquid state are relatively weak and unstable: it is thought that they can easily form and disappear as the result of temperature fluctuations.

Another key feature of hydrogen bond consists in its cooperativity coupling. Hydrogen bonding leads to the formation of the next hydrogen bond and redistribution of electrons, which in its turn promotes the formation of the following hydrogen bond, which length increasing with distance. Cooperative hydrogen bonding increases the O–H bond length, at the same time causing a reduction in the H...O and O...O distances [33]. The protons held by individual H₂O molecules may switch partners in an ordered manner within hydrogen networks [34]. As the result, aqueous solutions may undergo autoprotolysis, i.e. the H⁺ proton is released from H₂O molecule and then transferred and accepted by the neighboring H₂O molecule resulting in formation of hydronium ions as H₃O⁺, H₅O₂⁺, H₇O₃⁺, H₉O₄⁺, etc. This leads to the fact, that water should be considered as associated liquid composed from a set of individual H₂O molecules, linked together by hydrogen bonds and weak intermolecular van der Waals forces. The simplest example of such associate can be a dimer of water:



The energy of the hydrogen bonding in the water dimer makes up 0,2 eV (~5 kcal/mol) that is larger than the energy of thermal motion of the molecules at the temperature of 300 K. Hydrogen bonds are easily disintegrated and re-formed through an interval of time, which makes water structure quite unstable and changeable [35]. This process leads to structural inhomogeneity of water characterizing it as an associated heterogeneous two-phase liquid with short-range ordering, i.e. with regularity in mutual positioning of atoms and molecules, which reoccurs only at distances comparable to distances between initial atoms, i.e. the first H₂O layer. A liquid is a dynamic system: its atoms, ions or molecules, keeping short-range order in mutual disposition, participate in thermal motion, the character of which is much more complicated than that of crystals. For example H₂O molecules in liquid state under normal conditions (1 atm, +22 °C) are quiet mobile and can oscillate around their rotation axes, as well as to perform the random and directed shifts. This enabled for some individual molecules due to cooperative interactions to “jump up” from one place to another in an elementary volume of water. Random motion of molecules in liquids causes continuous changes in the distances between them. The statistical character of ordered arrangement of molecules in liquids results in fluctuations – continuously occurring deviations not only from average density, but from average orientation as well, because molecules in liquids are capable to form groups, in which a particular orientation prevails. Thus, the smaller these deviations are, the more frequently they occur in liquids.

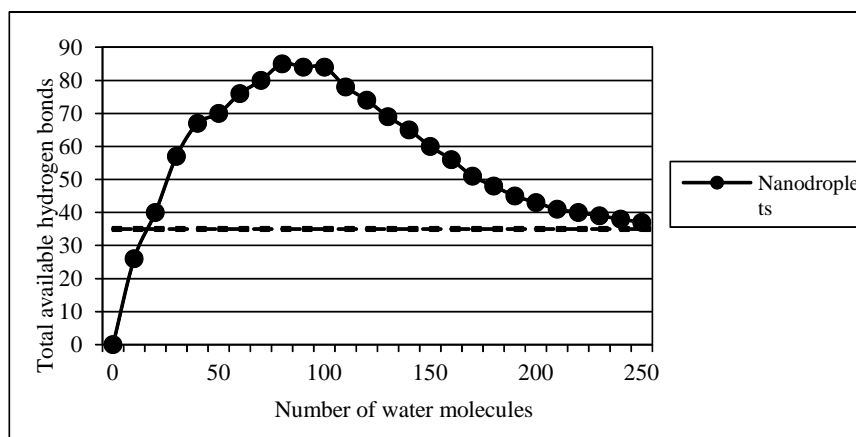


Figure 5. The total number of hydrogen bonds depending on the number of H₂O molecules in clusters.

Hydrogen bonds are easily disintegrated and re-formed through an interval of time, which makes water structure quite unstable and changeable. External influences can provoke changes in the water structure that will reflect on the number of hydrogen bonds, i.e. on the size of clusters. In 2005 R. Saykally [36] calculated the possible number of hydrogen bonds and the stability of water clusters depending on the number of H₂O molecules (Figure 5). The possible number of available hydrogen bonds (90) depending on the number of H₂O molecules (250) in clusters was also estimated [37]. O. Loboda and O.V. Goncharuk provided data about the existence of icosahedral water clusters consisting of 280 H₂O molecules with average size up to 3 nm [38].

It was noticed that under the influence of electric field the hydrogen bonds become highly polarized and get disrupted, therefore the cluster size is diminished to up to a few H₂O molecules, but not more than 20.

Another convenient method for obtaining useful information about the structural changes in water and the average energy of hydrogen bonds is the measuring of the energy spectrum of the water state (ESWS). It was established experimentally that at evaporation of water droplet the contact angle θ decreases discretely to zero, whereas the diameter of the droplet changes insignificantly [39]. By measuring this angle within a regular time intervals a functional dependence $f(\theta)$ can be determined, which is designated by the spectrum of the water state. For practical purposes by registering the ESWS it is possible to obtain information about the averaged energy of hydrogen bonds in an aqueous sample. For this purpose the model of W. Luck is used, which consider water as an associated liquid, consisted of O–H...O–H groups [40]. The major part of these groups is designated by the energy of hydrogen bonds ($-E$), while the others are free ($E = 0$). The energy distribution function $f(E)$ is measured in electron-volts (eV^{-1}) and may be varied under the influence of various external factors on water as temperature and pressure.

For calculation of the function $f(E)$ experimental dependence between the water surface tension measured by the wetting angle (θ) and the energy of hydrogen bonds (E) is established:

$$f(E) = bf(\theta) / [1 - (1 + bE)^2]^{1/2}, \quad (15)$$

$$\text{where } b = 14,33 \text{ eV}^{-1}; \theta = \arccos(1 - bE)$$

The energy of hydrogen bonds (E) measured in electron-volts (eV) is designated by the spectrum of energy distribution. This spectrum is characterized by non-equilibrium process of water droplets evaporation, thus the term “non-equilibrium energy spectrum of water” (NES) is applied.

The difference $\Delta f(E) = f(\text{samples of water}) - f(\text{control sample of water})$ – is designated the “differential non-equilibrium energy spectrum of water” (DNES).

The DNES-spectrum measured in milielectron volts (0,001 eV) is a measure of structural changes in the bulk water as a result of external factors. Figure 5 shows the characteristic NES-spectrum of deionized water made from 25 independence measurements done in a period of one year.

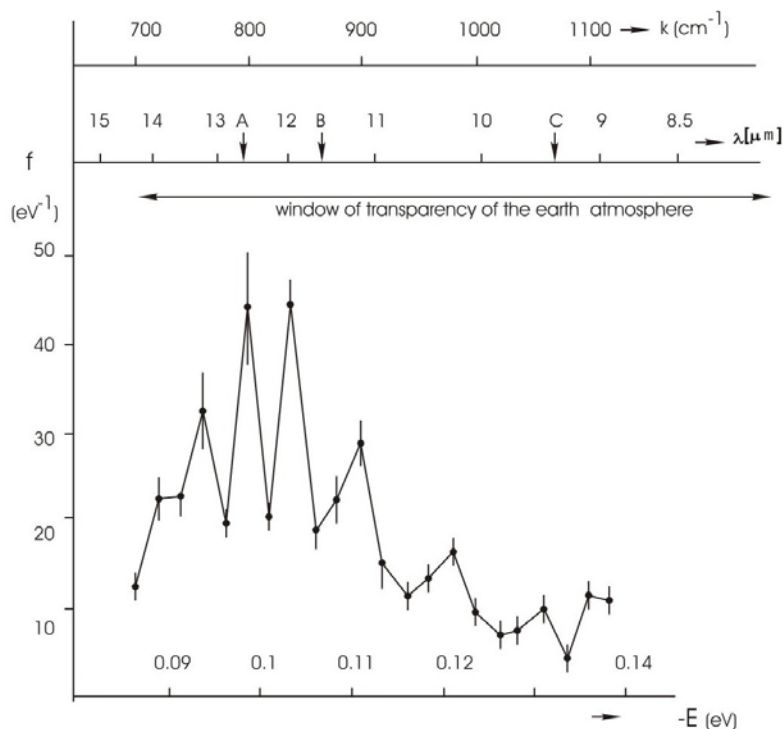


Figure 5. NES-spectrum of deionized water (chemical purity – 99,99%; pH – 6,5–7,5; total mineralization – 200 mg/l; electric conductivity – 10 $\mu\text{S}/\text{cm}$). The horizontal axis shows the energy of the H...O hydrogen bonds in the associates – E (eV). The vertical axis – energy distribution function – f (eV^{-1}). k – the vibration frequency of the H–O–H atoms (cm^{-1}); λ – wavelength (μm).

We studied the characteristics of NES and DNES-spectra of catholyte and anolyte solutions and distribution of local maximums in them. Also the average energy ($\Delta E_{\text{H...O}}$) of hydrogen H...O-bonds among individual molecules H_2O was calculated for the catholyte and the anolyte by NES- and DNES-methods. Local maximums of catholyte and anolyte solutions in NES- and DNES-spectra are shown in Table 3. The local maximum for the catholyte in the NES-spectrum was detected at -0,1285 eV, for anolyte – at -0,1227 eV, and for the control sample of deionized water – at -0,1245 eV. The calculations of $\Delta E_{\text{H...O}}$ for catholyte with using the DNES method compiles (-0,004 \pm 0,0011 eV) and for anolyte (+1,8 \pm 0,0011 eV).

The evaluation of the possible number of hydrogen bonds as percent of H_2O molecules with different values of distribution of energies for electrochemically activated catholyte and anolyte solutions is presented in Table 4. These distributions are basically connected with the restructuring of H_2O molecules having the same energies. These data serves as the mathematical model explaining the behavior of the anolyte and the catholyte regarding the distribution of H_2O molecules to the energies of hydrogen bonds in samples of electrochemically activated water solutions of the catholyte and the anolyte. These data testifies that not only the number of H_2O molecules with different energies of hydrogen bonds changes, but also the number of hydrogen bonds, the redistribution of H_2O molecules and the character of hydrogen bonding changes as well. This phenomenon may be explained by the fact that under the influence of electric field the hydrogen bonds between H_2O molecules become polarized and get disrupted, therefore the cluster size may be changed to up to a few H_2O molecules. However, these are our preliminary judgments, based on the character of NES and DNES-spectra and distribution of local maximums and minimums in spectra that will be continued in future studies.

Table 3: Local maximums of catholyte and anolyte solutions in NES- and DNES-spectra

-E(eV) x-axis	Catholyte	Anolyte y-axis (eV ⁻¹)	Control ample y-axis (eV ⁻¹)	DNES Catholyte	DNES Anolyte	-E(eV) x-axis	Catholyte y-axis (eV ⁻¹)	Anolyte y-axis (eV ⁻¹)	Control sample y-axis (eV ⁻¹)	DNES Catholyte y-axis (eV ⁻¹)
0,0937	0	0	0	0	0	0,1187	0	66,7	66,7	-66,7
0,0962	0	0	0	0	0	0,1212	66,7	0	0	66,7
0,0987	0	0	0	0	0	0,1237	0	0	0	0
0,1012	66,7	66,7	33,3	33,4	33,4	0,1262	0	0	66,7	-66,7
0,1037	0	0	33,3	-33,3	-33,3	0,1287	0	0	66,7	-66,7
0,1062	0	0	0	0	0	0,1312	33,3	100	33,3	0
0,1087	0	0	0	0	0	0,1337	33,3	33,3	33,3	0
0,1112	0	0	0	0	0	0,1362	0	0	0	0
0,1137	0	66,7	66,7	-66,7	0	0,1387	200	66,7	66,7	133,3
0,1162	0	0	0	0	0	-	-	-	-	-

Table 4: Energy distribution of catholyte and anolyte solutions in electrochemically activated solutions of sodium chloride

-E(eV) x-axis	Catholyte y-axis, % (-Evalue)/ (-Etotal value)	Anolyte y-axis, % (-Evalue)/ (-Etotal value)	-E(eV) x-axis, % (-Evalue)/ (-Etotal value)	Catholyte y-axis, % (-Evalue)/ (-Etotal value)	Anolyte y-axis, % (-Evalue)/ (-Etotal value)
0,0937	0	0	0,1187	0	16,7
0,0962	0	0	0,1212	16,7	0
0,0987	0	0	0,1237	0	0
0,1012	16,7	16,7	0,1262	0	0
0,1037	0	0	0,1287	0	0
0,1062	0	0	0,1312	8,4	24,8
0,1087	0	0	0,1337	8,4	8,4
0,1112	0	0	0,1362	0	0
0,1137	0	16,7	0,1387	49,8	16,7
0,1162	0	0	-	-	-

Conclusions

The electrochemical water treatment has several advantages compared to alternative chemical methods for disinfection of water. These advantages are the efficiency, stability, controllability and convenient automatic control of the electrolysis processes, as well as simplicity of the construction scheme. The devices for the electrochemical water treatment are compact, have a high level of reliability, easy operation and demand, and may be fully automated. In multi-stage schemes to improve water quality and its disinfection the electrochemical treatment can conveniently be combined with other water treatment methods. We have applied NES and DNES-methods for studying the physical-chemical properties of the catholyte and anolyte the evaluation of the possible number of hydrogen bonds as percent of H₂O molecules with different values of distribution of energies. These distributions suggest that not only the number of H₂O molecules with different energies of hydrogen bonds changes, but also the number of hydrogen bonds, the redistribution of H₂O molecules and the character of hydrogen bonding changes as well. These data serves as the mathematical model explaining the behavior of the anolyte and the catholyte regarding the distribution of H₂O molecules to the energies of hydrogen bonds.

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