

Results from the Research of Water Catholyte with Nascent (Atomic) Hydrogen

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Abstract

A reaction is published for forming of nascent (atomic) hydrogen (H^*) from hydronium ions (H_3O^+) in catholyte (Ignatov, Mosin et al., 2015). It is also observed the production of nascent hydrogen in electrolysis in the transition to H_2 (Mehandjiev et al., 2017). For checking of the theoretical suggestion experiments with potassium permanganate ($KMnO_4$) are conducted. Potassium permanganate is a strong oxidizing agent. In this compound, manganese is in the +7 oxidation state (Mn^{7+}). In reduction process the color of the aqueous solution of $KMnO_4$ is changed and thus the process could be examined spectrophotometrically. Described is a reaction that proves the presence of nascent hydrogen in catholyte using potassium permanganate (Parn et al., 2012). In order to avoid the influence of salts contained in water from other sources, deionized water is used for production of catholyte/anolyte.

Keywords: electrolysis, catholyte, anolyte, nascent hydrogen, reduction

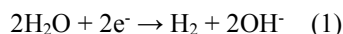
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1. Introduction

The interest towards electrochemically activated water (ECAW) increases due to its applications. It is gained from electrolysis with direct current where the electrodes are separated with semipermeable membrane. The liquid surrounding the cathode is called catholyte, and the liquid surrounding the anode is called anolyte. It is observed a higher pH in catholyte (>7.0) in comparison with the water before activation. Lower pH is observed in the anolyte (<7.0) compared to the water before activation. The catholyte has reduction properties, and the anolyte oxidative. The catholyte has beneficial effect over the human health. The strong oxidative action of anolyte enables its use as an antibacterial tool for disinfection, in agriculture, and for purifying contaminated water.

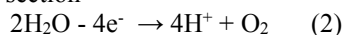
For the science however, still remains open the question what determines these specific properties of ECAW. A large number of scientific investigations are conducted in this field, and certain physical properties of ECAW are established.

The following reactions are known:



The hydrogen gas is separated and the water acquires alkaline reactivity. The catholyte has reduction properties, and it has increase in number of the electrons compared to the control sample, and a negative ORP.

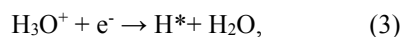
The following reaction happens in the anode section



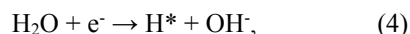
The anolyte has oxidative properties and there is reduction in number of the electrons in it, and a positive ORP, compared to the control sample.

The following is valid (Ignatov, Mosin et al., 2015).

The gaseous hydrogen is generated at the cathode while the oxygen is produced at the anode. Water also contains a certain amount of hydronium ions (H_3O^+) depolarizing at the cathode with formation of the atomic hydrogen:



In an alkaline environment a disruption of H_2O molecules, accompanied by formation of atomic hydrogen and hydroxide ion (OH^-) occurs:

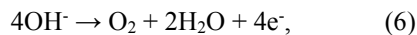


The reactive hydrogen atoms are adsorbed on the surface of the cathode, and molecular hydrogen H_2 released in the gaseous form after recombination is formed:



At the same time atomic oxygen is released at the anode. In an acidic environment this process is accompanied by the destruction of H_2O molecules according to formula (2).

In an alkaline environment the OH^- ions moving from the cathode to the anode during the electrolysis are a source of oxygen:



In a previous article (Mehandjiev et al., 2017) was shown that the mechanism of activation in ECAW can occur with the following intermediate reaction taking place:



In ECAW the mechanism includes two stages as it is for cathode and anode. At the first stage nascent hydrogen and nascent oxygen are released according to reactions (7) and (9). The gained products react with each other and produce a hydrogen molecule and an oxygen molecule respectively – reactions (8) and (10). Certain quantities of the nascent forms of hydrogen in catholyte, and oxygen in anolyte can be kept. Due to the strong reduction properties of the nascent hydrogen and the oxidative properties of the nascent oxygen, the obtained catholyte and anolyte have stronger reduction and oxidative abilities respectively. The experimental check of this statement defined the aim of the current scientific research. The check of the reduction property of catholyte was performed through a chemical reaction with potassium permanganate as a reagent, and a strong oxidant. It is well known that potassium permanganate dissolves in water to give intensely pink or purple solutions. Therefore the content of manganese ions (Mn^{7+}) in the permanganate anion (MnO_4^-) can be controlled spectrophotometrically.

2. Materials and methods

The production of catholyte is performed by the means of device called “Activator 2”, developed in the Institute of Information and Communication Technologies, BAS. The electrochemical treatment of water is processed in a glass container inside of which two electrodes from platinized titanium are put. These are cathode and anode at a distance 3 cm of each other. The electrodes of size 17/3 cm and thickness of 0.5 mm are separated by a semipermeable membrane. Direct current of 220 V is used. The anode space contains 400 ml of water, and the cathode one 1500 ml. Time for activation is 6 minutes, which is sufficient to reach the saturation point of the pH curve.

Methodology is based on defining the concentration of potassium permanganate in the catholyte. For this purpose potassium permanganate (KMnO_4) from Merck (Germany) is used. Initial solution of KMnO_4 is prepared with a concentration of 1000 mg/L through dissolving the necessary amount of salt into the deionized water. In volumetric flasks of 50 ml solutions of KMnO_4 of concentrations 1, 2.5 and 5 mg/L are prepared through dilution of the starting solution with deionized water or catholyte. The concentrations of solutions are measured spectrophotometrically using the apparatus Spekol 11 (Carl Zeiss Industrielle Messtechnik GmbH) via admeasurement of absorbance at λ_{max} of 560 nm. The width of cuvettes is 1 cm. Standard line is built within the interval of concentrations of KMnO_4 from 0.2 to 50 mg/L ($R^2 = 0.9988$). The concentrations of the working solutions are measured at different intervals of time - 1, 2, 3, 24 hours.

3. Experimental results and discussion

On Fig.1 are presented the results from the potassium permanganate concentration measurements at three initial concentrations of 1.0 mg/L; 2.5 mg/L; 5.0 mg/L, depending on the time. Over the course of time the concentration of potassium permanganate in the catholyte slightly decreases. This supports the supposition that active reduction forms are built in the catholyte, which reduce the manganese ions. In control study with the same deionized water but without electrolysis the concentration of potassium permanganate remains unchanged over a time period of 24 hours.

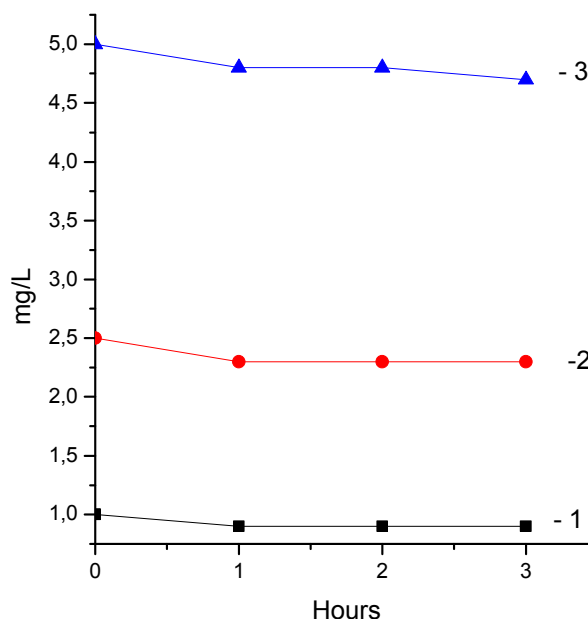


Fig.1 Change of concentration of potassium permanganate in the catholyte over time depending on the initial concentration of 1.0 mg/L; 2.5 mg/L; 5.0 mg/L.

From the conducted experiments we can conclude that during the electrolysis atoms of nascent hydrogen are created in the catholyte, according to the equations (3) and (7). Figure 1 shows that the activity of cations lasts for 24 hours with regards to the reduction process. We need to take into consideration that as per reaction (8) hydrogen molecules are also released into the solution, as they saturate it. In order to exclude the possibility that the observed reduction of concentration of permanganate ions is due to this hydrogen, trials were conducted under the same conditions using deionized water saturated with hydrogen at 20°C for a period of 30 minutes without electrochemical activation. The analysis of the contents of permanganate ions shows that their concentration is not diminished as a result of saturation of water with hydrogen. This proves that the observed reduction of concentration of these ions is due to the formation of nascent hydrogen during the electrochemical activation of deionized water.

In Table 1 the measurement results done 24 hours later are presented. The initial and residual concentration of permanganate ions, % of reduction, reduced Mn^{7+} - ions, and the quantity of nascent hydrogen for this reduction are also shown.

The content of nascent hydrogen remains the same for 24 hours even in the presence of a strong oxidizer such as the manganese ion (Mn^{7+}) in the permanganate anion (MnO_4^-). It can be concluded that the action of ECAW continues for at least 24 hours. From the Table 1 is also evident that with the increase of the initial concentration of potassium permanganate the quantity of reduced manganese ions increases. The explanation for this is that the probability for reacting in such low concentrations gets higher with the increase of the initial concentration of manganese ions.

Table 1

Initial and residual concentration of permanganate ions, % of reduction, reduced Mn^{7+} - ions, and the quantity of nascent hydrogen for this reduction

Initial concentration mg/L	Residual concentration mg/L	% of reduction	Reduced Mn^{7+} - ions mg/L	Nascent hydrogen mg/L 10^2
1.0	0.8±0.2	20.0	0.2	1.85
2.5	2.1 ±0.2	16.0	0.4	3.65
5.0	4.5±0.1	10.0	0.5	4.65

In the Table 1 is also calculated the quantity of nascent hydrogen contained in ECAW for up to 24 hours and acted as antioxidant agent. The amount of stabilized nascent hydrogen is low, in a range of $0.9 \cdot 10^{-2}$ mg/L, but it has to be taken into account that these are only the kept after reactions (5) (8) and forming of molecular hydrogen quantities.

4. Conclusions

The achieved results show that ECAW creates strong reducing agents in catholyte. The availability of free electrons contributes to the reduction properties of catholyte. Deionized water is used, as the reducing components in this case can be also based on hydrogen. These are atoms from nascent hydrogen (H^*), which can be achieved from hydronium ions (H_3O^+) and from the electrolysis itself, as an intermediate reaction of $2H^* \rightarrow H_2$. The atoms of nascent hydrogen (H^*) get stabilized within certain amounts in the catholyte, and by having strong reducing activity they define its antioxidant activity. The obtained results reveal that the mechanism of activation is also determined by nascent hydrogen in ECAW.

References

- Aider, M., Kastyuchik, A., Gnatko, E., Benali, M. & Plutakhin, G. (2012). Electro-activated Aqueous Solutions: Theory and Application in the Foodindustry and Biotechnology, *Innovative Food Science and Emerging Technologies*, **15**: 38-49
- Bakhrir, V.M., Zadorozhnyi, Y.G., Leonov, V. I., Panicheva, S.A. & Prilutsky, V.I. (2001). Electrochemical Activation; Water Purification and Production of Useful Solutions –Moscow: VNIIMT, **1**: 100-176 (in Russian).
- Fukuzaki, S. (2006) Mechanisms of Actions of Sodium Hypochlorite in Cleaning and Disinfection Processes, *Biocontrol Sci.*, **11** (4):147-57.
- Gluhchev, G., Ignatov, I., Karadzhov, S., Miloshev, G., Ivanov, N.&Mosin, O.V. (2015). Studying of Viruscidal and Biocidal Effects of Electrochemically Activated Anolyte and Catholyte Types of Water on Classical Swine, *Journal of Medicine, Physiology and Biophysics*, **13**: 1-17.
- Ignatov, I., Karadzhov, S., Atanasov, A., Ivanova, E.&Mosin, O. V. (2014) Electrochemical Aqueous Sodium Chloride Solution (Anolyte and Catholyte) as Types of Water, Mathematical Models, Study of Effects of Anolyte on the Virus of Classical Swine Fever Virus, *Journal of Health, Medicine and Nursing*, **8**: 1-28.
- Ignatov, I., Gluhchev, G., Karadzhov, S., Miloshev, G., Ivanov, I.&Mosin, O. V. (2015) Preparation of Electrochemically Activated Water Solutions (Catholyte/Anolyte) and Studying of their Physical-Chemical Properties, *Journal of Medicine, Physiology and Biophysics*, **13**: 18-38.
- Ignatov, I., Mosin, O.V., Gluhchev, G., Karadzhov, S., Miloshev, G.&Ivanov, N. (2015) The Evaluation of Mathematical Model of Interaction of Electrochemically Activated Water Solutions (Anolyte and Catholyte) with Water, *European Reviews of Chemical Research*, **2** (4): 72-86.
- Ignatov, I., Karadzhov, S., Gluhchev, G.&Yakimov, I. (2018) Electromagnetically Activated Water - Properties and Effects, *Bulgarian Journal of Public Health*, **10** (4): 63-69.
- Inoe, Y., Endo, S., Kondo, K., Ito, H., Omori, H. & K. Saito (1997). Trial of Electrolyzed Strong and Aqueous Solution Lavage in the Treatment of Peritonitis and Intraperitoneal Abscess, *Artificial Organs*, **21**(1): 28-31
- Komatsu, T., Kabayama, S., Hayashida, A et al. (2001). Suppressive effect of Electrolyzed Reduced Water on the Growth of Cancer Cells and Microorganisms, *Animal cell technology: From target to market*, Kluwer Academic Publishers, 220-223.
- Kyu-Jae Lee, Seung-Kyu, Jae-Won, Gwang-Young et al., Anticancer Effect of Alkaline Water, Korea
- Lee, M-Y., Kim.-K., Ryoo, K.-K et al. (2006). Electrolyzed-reduced Water Protects Against Oxidative Damage to DNA, RNA and Protein, *Applied Biochemistry and Biotechnology*, **135**: 133-144.
- Shirahata, S., Murakami, E., Kusimoto, K.-I., et al. (1999). Telomere Shortening in Cancer cells by Electrolyzed-reduced Water., *Animal Cell Technology: Challenges for the 21st Century*, 355-359
- Leonov, I.B., Bakhrir, V.M. & Vtorenko, V.I. (1999b). Electrochemical Activation in the Practice of Medicine, *2nd Int. Symposium "Electrochemical Activation"*, *Pros. Rep. and brief reports*, **1**: 15-23 (in Russian).
- Mehandjiev, D., Ignatov, I., Karadzhov, I., Gluhchev, G.& Atanasov, A. (2017) On the Mechanism of Water Electrolysis, *Journal of Medicine, Physiology and Biophysics*, **31**: 23-26.
- Mehandjiev, D., Ignatov, I., Karadzhov, S., Gluhchev, G., Atanasov, A. (2017) Processes in Catholyte and Anolyte as Result of Water Electrolysis, *European Journal of Molecular Biotechnology*, **5** (1): 23-29.
- Morita, C., K. Sano, S. Morimatsu, H. Kiura. T. Goto & T. Kohno. (2000). Disinfection Potential of Electrolyzed Solutions Containing Chloride at Low Concentrations, *Journal of Virological Methods*, **85**(2): 163-174
- Pham, V.H. et al. (2012) Chemical Reduction of an Aqueous Suspension of Graphene Oxide by Nascent Hydrogen, *Journal of Materials Chemistry*, **21**: 1-5.
- Prilutsky, V. I.&Bakhrir, V.M. (1997). Electrochemically Activated Water: Anomalous properties, Mechanism of biological action, *All Russian Scientific Research and Experimental Institute of Medical Engineering (VNIIMT)*, **1**: 124. (in Russian).
- Reinert, F., Kumar, S., Steiner, P.& Claessen, R., Hüfner, S. (1994) The Electronic Structure of $KMnO_4$ Investigated by Photoemission and Electron-energy-loss Spectroscopy, *Zeitschrift für Physik B Condensed Matter*, **94** (4): 431-438
- Shirahata, S. (2002). Reduced Water For Prevention of Diseases, *Animal cell technology: Challenges for the 21st*

century (pp. 25-30)

- N. Yahagi, M. Kono, M. Kitahara, A. Ohmura, O. Sumita & T. Hashimoto. (2000) Effect of Electrolyzed Water on Wound Healing. *Artificial Organs*, **24** (12): 984-987.
- Ye, J., Li, Y., Hamasaki, T., N., Komatsu, E. et al. (2008). Inhibitory Effect of Electrolyzed Reduced Water on Tumor Angiogenesis, *Biological and Pharmaceutical Bulletin*, **31**: 19-26.
- Kim, C., Y.C. Hung & R.E. Brackett. (2000). Roles of Oxidation-reduction Potential in Electrolyzed Oxidizing and Chemically Modified Water for the Inactivation of Food-related Pathogens, *Journal of Food Protection*, **63**: 19-24
- Kirkpatrick, R. D. (2009) The Mechanism of Antimicrobial Action of Electro-chemically Activated (ECA) water and its Healthcare Applications, *Doctoral Thesis, University of Pretoria*.
- Tanaka, H., Y. Hirakata, M. Kaku, R. Yoshida, H. Takemura & R. Mizukane. (1996). Antimicrobial Activity of Superoxidized Water, *Journal of Hospital Infection*, **34**(1): 43-49.
- Lee, M-Y., Kim.-K., Ryoo, K.-K et al. (2006). Electrolyzed-reduced Water Protects Against Oxidative Damage to DNA, RNA and protein. *Applied Biochemistry and Biotechnology* **135**, 133-144.