

NASCENT OXYGEN – ACTIVE COMPONENT OF ANOLYTE, OBTAINED BY MEANS OF ELECTROCHEMICAL ACTIVATION OF WATER

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ABSTRACT

In the present study the content of hydrogen peroxide in anolyte obtained through electrochemical activation (ECA) of water is investigated. The possibility of the obtained nascent oxygen (mono-atomic form of oxygen) to increase hydrogen peroxide and be responsible for the strong oxidation ability of anolyte is supposed. Anolyte obtained by two different apparatus is used and the content of hydrogen peroxide is analyzed by two different analytical methods. It is established that the content of hydrogen peroxide in the control water used for comparison is higher than its content in the anolyte in all cases. This proves that strong oxidation action of the anolyte is not due to the hydrogen peroxide, but rather to the nascent oxygen obtained in the process of ECA.

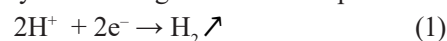
Keywords: *Electro-Chemical Activation (ECA), electrolyzer, catholyte, anolyte, nascent oxygen, hydrogen peroxide.*

INTRODUCTION

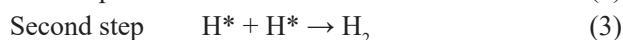
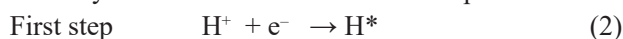
The interest to the electrochemically activated water permanently increases due to the possibility of its application in different processes [1 - 5]. It is produced in electrolyzers where the cathode and the anode are separated with semipermeable membrane and direct current is applied. The water in the cathode section is called catholyte, while the water in the anode section is called anolyte. Many investigations were and are still carried out to explain the mechanism of the process and the completely different properties of the two fractions of water [6 - 12]. A number of studies have proved that catholyte has antioxidant properties that make it interesting for biomedical applications [7, 8, 13, 14]. On the other side the anolyte possesses strong oxidation

property [15 - 17]. Many researchers have illustrated the effects of anolyte water – anti-inflammatory [1], anti-viral [17] anti-fungal [18] etc. It is interesting to know what components are generated in catholyte and anolyte during ECA that determine those properties.

In the catholyte following reactions take place:



Actually this reaction consists of two steps:

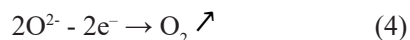


where H* denotes nascent hydrogen.

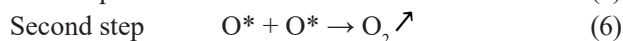
The presence of nascent hydrogen in catholyte was demonstrated in our preceding investigation using chemical analysis [19]. Thus, its decisive role as a strong reducer and deoxidizer was confirmed.

In the anolyte obtained at the anode following

reaction takes place:

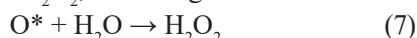


However, this process also develops in two steps, as follows.



where O^* stands for nascent oxygen.

In our work [20] we presumed that the nascent oxygen is stabilized in a similar way in the anolyte, as is the nascent hydrogen in catholyte. The nascent oxygen determines the oxidation properties and antibacterial activity of the anolyte. In the same work it was supposed that the preservation of the nascent oxygen was due to the hydrogen peroxide H_2O_2 , according to the reaction:



Therefore, it could be expected that the change in the content of hydrogen peroxide in the anolyte proves the presence of nascent oxygen. According to this the goal of present work is formulated as follows: evaluate the change in the amount of H_2O_2 in the anolyte, obtained through ECA of water.

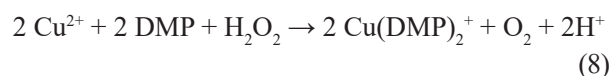
EXPERIMENTAL

For comparison of samples of anolyte two different equipments for ECA are used. For the anolyte marked as "Anolyte G" a glass jar of 2 L and a linen bag of 0.5 L is used. Two platinum coated electrodes are put in the jar as cathode and in the bag, as anode. The linen plays the role of semi permeable membrane. For ECA 1.5 L of de-ionized water is put in the jar, 0.4 L is put in the bag, and stabilized current is applied. The process takes 9 min and the liquids are separated [20]. For the anolyte marked as "Anolyte I" Wasserionisierer Hybrid PWI 2100 is used. It is equipped with four titanium electrodes coated with platinum. By analogy the electrodes are separated with a special semi permeable membrane (diaphragm).

Two procedures are applied for the evaluation of hydrogen peroxide concentration in the samples Anolyte I and Anolyte G.

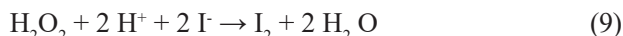
- Spectrophotometric determination of hydrogen peroxide at low concentration in aqueous solution according to Baga et al. [21]. The procedure is based on reduction of copper (II) ions by hydrogen peroxide of

excess of 2,9-dimethyl-1,10-phenanthroline (DMP) to form the copper(I)-DMP complex. The copper(I) - DMP complex is determined directly by spectrophotometric measurement at 454 nm.



In a 10 mL volumetric flask, 1 mL of the 0.01 mol L⁻¹ copper (II) sulphate solution and 1 mL of 1 % ethanolic DMP solution is mixed. A known volume of anolyte or hydrogen peroxide solution is added. The H_2O_2 concentration after dilution to 10 mL should be in the range 1 - 120 x10⁻⁶ mol L⁻¹. A blank sample is prepared in the same way with water substituted for H_2O_2 solution. The pH value of samples should be in the range 5 - 9.

- Spectrophotometric determination of hydrogen peroxide with toluidine blue (TB) as a reagent according Sunil and Narayana [22]. The proposed method is based on the liberation of iodine in acidic medium equivalent to the amount of hydrogen peroxide present. The liberated iodine bleaches the blue color of toluidine blue and is measured at 628 nm. The decrease in absorbance is directly proportional to hydrogen peroxide concentration and obeys Beer's law in the range 0.2x10⁻⁶ - 14x 10⁻⁶mol L⁻¹.



In a 10 mL standard flask 3 mL of anolyte is added, then 1 mL of potassium iodide followed by 1 mL of 2 M hydrochloric acid. The mixture was shaken well until the appearance of yellow color and then added 0.5 mL of 0.01% toluidine blue indicator solution followed by 2 mL of 2 M sodium acetate solution. The contents were made up to the mark and mixed well. Absorbance was measured at 628 nm. In the blank sample 3 mL water instead anolyte is added.

SP-V1000-Visible spectrophotometer (DLAB Scientific Co., Ltd., China) was used for the absorbance measurement. All reagents used were of analytical pure grade. Standard stock solution of hydrogen peroxide was prepared by suitable dilution of 30 % hydrogen peroxide. Three parallel measurements of each sample were carried out and average values are presented.

RESULTS AND DISCUSSION

Spectrophotometric determination of hydrogen peroxide with DMP

Initially experiments with solutions of known concentration of hydrogen peroxide - $11.5 \times 10^{-6} \text{ mol L}^{-1}$ were carried out. The results are shown on Table 1. The concentration of H_2O_2 in the samples is given by:

$$[\text{H}_2\text{O}_2] \text{ mol L}^{-1} = \Delta A_{454} / 1500 V, \quad (11)$$

where V is the volume of H_2O_2 solution, ΔA_{454} is the difference between the measured absorbance of the sample and blank sample.

The calculated concentrations for H_2O_2 are as follows: $[\text{H}_2\text{O}_2]$ - $11.4 \times 10^{-6} \text{ mol L}^{-1}$ and $11.3 \times 10^{-6} \text{ mol L}^{-1}$, i.e. an average value $11.35 \times 10^{-6} \text{ mol L}^{-1}$, which is a quite good coincidence with the actual concentration of the hydrogen peroxide - $11.5 \times 10^{-6} \text{ mol L}^{-1}$. The blank sample with distilled water also contains some quantity of hydrogen peroxide. This is very important as it will be used for the evaluation of the anolyte results.

Table 2 contains the measurement results of the absorption of the copper complex at 454 nm in the presence of Anolyte I.

The obtained results show that the measured absorption of the blank sample with distilled water used for the preparation of Anolyte I is almost two times higher than for the samples with Anolyte I. This allows assuming that the concentration of hydrogen peroxide in Anolyte I is smaller than its concentration in the distilled water.

Table 3 contains the results from the determination of absorption of the copper complex with Anolyte G.

Again, the measured absorption of the blank sample with deionized water is higher compared with the absorption when some Anolyte G is added to the solution, i.e. it could be assumed that the content of hydrogen peroxide is also smaller compared to the initial deionized water.

In addition, the results for deionized water and Anolyte G differ from those for distilled water and Anolyte I (Tables 2 and 3). This indicates that the content of hydrogen peroxide in the electrochemical activated water depends on the processing conditions, and probably on its preservation conditions. The important result, however, is that the content of hydrogen peroxide

Table 1. Absorbance of $\text{Cu}(\text{DMP})_2^+$ in the presence of H_2O_2 solution.

Sample	Volume of H_2O_2 solution, mL	Absorbance at 454 nm
1	0	0.127
2	5	0.213
3	8	0.263

Table 2. Absorbance of $\text{Cu}(\text{DMP})_2^+$ in the presence of Anolyte I.

Sample	Volume of Anolyte I, mL	Absorbance at 454 nm
1	0	0.127
2	5	0.070
3	8	0.087

Table 3. Absorbance of $\text{Cu}(\text{DMP})_2^+$ in the presence of Anolyte G.

Sample	Volume of Anolyte G, mL	Absorbance at 454 nm
1	0*	0.161
2	5	0.114
3	8	0.148

*The empty sample is prepared with deionized water used for preparation of Anolyte G.

in the anolyte samples is smaller than in the control water. The concentration of H_2O_2 in the samples Anolyte I and Anolyte G is smaller than $1 \times 10^{-6} \text{ mol L}^{-1}$.

Spectrophotometric determination of hydrogen peroxide with toluidine blue

Next Table 4 contains data from measured absorption of the solutions of toluidine blue containing anolyte and the blank samples.

It can be concluded from data listed in Table 4 that the content of hydrogen peroxide in the anolyte is smaller than in the water used for its preparation. The concentration of H_2O_2 in the anolyte samples is smaller than $0.2 \times 10^{-6} \text{ mol L}^{-1}$. The most important inference is that the content of H_2O_2 in anolyte is smaller than that in the water. Therefore, the content of H_2O_2 diminishes during the anolyte production.

Table 4. Absorbance of toluidine blue solutions containing anolyte and control water.

Sample	Type of sample	Absorbance at 454 nm
1	blank sample with distilled water	0.362
2	sample with Anolyte I	0.435
3	blank sample with deionized water	0.387
4	sample with Anolyte G	0.493

The obtained results show that hydrogen peroxide is not responsible for the strong oxidative action of the anolyte, otherwise the original water must have a higher oxidative capacity and disinfectant properties than anolyte. Therefore, when anolyte is produced with ECA, nascent oxygen O^* is obtained at the anode, according to reaction (5) and is stabilized in the water, thus giving a strong oxidation ability of the anolyte. These properties determine its biocidal and disinfecting action and give possibilities for its broad application as a cheap and effective disinfecting and therapeutic means.

CONCLUSIONS

The content of hydrogen peroxide in anolyte obtained through electrochemical activation of water is studied. It was established that the concentration of H_2O_2 in the anolyte is lower than in the control waters and is below $0.2 \times 10^{-6} \text{ mol L}^{-1}$ for both devices used for its production. These results prove that the nascent oxygen produced by the anode reaction in electrochemically activated water is responsible for the strong oxidative action of the anolyte and determines its bactericidal and disinfectant properties.

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