Modeling of physical and chemical processes in the electrical activator of water solutions

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Abstract. Agriculture needs new types of drugs to combat harmful microorganisms, the introduction of which will reduce the ingress of unnecessary chemical compounds into products. It is necessary to use anolytes more widely as alternative means of disinfection. The use of anolytes in various fields of industries has proven their high effectiveness and harmlessness. However, the production of anolyte is a complex electrochemical process, which results in a mixture of the necessary metastable elements. To obtain an anolyte with the required set of properties, it is necessary to study the physical and chemical processes of the activator in detail. The article proposes to use Comsol software for these studies. As a result of the modeling, the characteristics of changes in the concentrations of individual chemical elements over time and the main physical dependences of the activator itself were obtained. The analysis of changes in concentrations of chemical compounds confirmed the adequacy of mathematical models. There were installed points on electrodes with significant density of currents. Studies of changes in the hydrogen index and temperature allow you to set the required operating time of the activator. Analysis of concentrations of chlorine-containing compounds proves the difficulty of determining the rates of formation of individual chemical formations and their instability. On the basis of the obtained data, it is possible to recommend the mode of operation of the electrical activator depending on the properties of the source water and the requirements to the resulting solution.

1. Introduction

Agriculture forced to use a large number of disinfectant solutions for processing both equipment and products. In crop production, the use of chemicals is associated with the fight against insect pests and the destruction of various kinds of painful microflora, toxins, with the introduction of fertilizers. The appearance of mycotoxins in food and feed causes the emergence of new diseases of plants, animals and humans.

Researchers of the United States, Germany, the Czech Republic, Russia found that nitrates and nitrites cause many dangerous diseases in humans such as stomach cancer, also negatively affect the nervous and cardiovascular systems, the development of embryos. Poisoning occurred when drinking water and food with high content of these chemicals.
Unjustified use of high and ultra-high doses of nitrogen fertilizers leads to the formation of excess nitrogen in the soil, and it enters the plants, where it accumulates in large quantities. Today there is an intensive use of chemicals in the technology of growing crops. After their effect and subsequent decomposition of certain types of chemical compounds in food products appear and accumulate substances that are actually poisons, both for humans and animals. Russia occupies one of the leading places in the production of honey. However, it cannot compete successfully in the world market due to the excessive use of antibiotics and other chemicals. Beekeepers are forced today to use more and more active chemical means of combating bee diseases, which leads to the ingress of chemical compounds in bee products.

In the world there is a further trend to increase the use of chemicals to kill pathogens. However, bacteria and microbes constantly mutate, which leads to the need to increase the concentration of drugs used or constantly develop new ones. The current situation causes environmental damage to the world and becomes unsafe for humans. Some drugs cannot be even used without personal protective equipment.

One of the escapes of this situation is to use fundamentally new disinfectants based on the fundamental difference between macro- and microorganisms. Such remedies are electrically activated solutions – anolytes. Scientific studies [1-5] have established that the chemical nature of the disinfectant effect of such a solution is similar to the antimicrobial action of internal environment of living organisms - phagocytosis. In addition, most pathogens are particular to the pH level, and the pH=7 and above is optimal for them. By lowering the pH of the medium below 5.0, it is possible to inhibit the activity of pathogenic cultures. The use of electrically activated solutions in certain technologies is described in the literature [6-11] including under the authorship of Bakhir V. M. [5, 11]. In Kaban State Agrarian University, studies are also conducted on the use of activated media in agricultural production technologies [12, 13]. There are also positive results on the use of anolytes in greenhouses, beekeeping.

The anolyte production is obtained from diaphragm electrolysis. However, many scientists noted the difficulty of describing the processes occurring during activation, which is associated with a large number of electrochemical reactions. In addition, there is a loss of antimicrobial properties of the anolyte over time due to neutralization reactions of most metastable oxidants. In this regard, it is necessary to continue studying the processes occurring in the preparation of the anolyte, to study its properties and find new applications. The software product such as Comsol is quite appropriate for such studies.

2. Methodology
In Kaban State Agrarian University there was the geometric model of the activator of aqueous solutions and there were the research on changes in concentrations during the operation of individual chemical compounds. The basic physical processes occurring during activation are also modeled. The system of equations to describe the changes in the potential and concentration of substances in the electrolyte under the action of electric current is as follows:

\[
\begin{align*}
\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i \mu_i F \cdot \nabla \phi_i) + u \cdot \nabla c_i &= R_i \\
c_H - c_{OH} + \sum_{i} z_i c_i &= 0 \\
\nabla i_j = F \sum_{i=1}^{V} z_i R_i + FR_H - FR_{OH}
\end{align*}
\]

Also we write a system of equations for electric current:
\[
\begin{align*}
J_i &= -D_i \cdot \nabla c_i - z_i \cdot u_{mi} \cdot F \cdot c_i \cdot \nabla \phi_i \\
J_H &= -D_H \cdot \nabla c_H - z_H \cdot u_{mH} \cdot F \cdot c_H \cdot \nabla \phi_i \\
J_{OH} &= -D_{OH} \cdot \nabla c_{OH} - z_{OH} \cdot u_{mOH} \cdot F \cdot c_{OH} \cdot \nabla \phi_i \\
i_j &= F \sum_{\text{i}} z_i J_i + F J_H - F J_{OH}
\end{align*}
\]

where \(c_i\), \(c_H\), \(c_{OH}\) - concentration of a substance and hydrogen protons and hydroxyl ions respectively; \(z_i\) - charge of \(i\) ion; \(D_i\) - coefficient of diffusion of \(i\) substance; \(u_{mi}\) - mobility of \(i\) ion, \(\text{mol} \cdot \text{s} / \text{kg} \cdot \text{A} / \text{m}^2\); \(F\) - constant of Faraday; \(R\) - velocity of chemical reaction, \(\text{mol} / \text{m}^3 \cdot \text{s}\); \(\phi_i\) - falling of tension in electrolyte, \(\text{B}\); \(i_j\) - current density in electrolyte, \(\text{A} / \text{m}^2\).

The Joule’s heating will occur when the current flows through the liquid. In addition, exothermic and endothermic reactions occur in the fluid. The intensity of heat transfer by thermal conductivity depends on the temperature gradient of the thermal conductivity coefficient of the material and is described by the Fourier equation. The equation of fluid flow associated with thermal convection is described by the Navier-Stokes equations. Navier-Stokes equations and Darcy’s law were used to describe transport displacements in porous media.

Chlorine-containing compounds are formed mainly in the anode chamber, and the following chemical reactions will occur:

\[
\begin{align*}
2 \text{H}_2\text{O} - 4e^- &\rightarrow 4\text{H}^+ + \text{O}_2 \\
2\text{Cl}^- - 2e^- &\rightarrow \text{Cl}_2 \\
\text{Cl}_2 + \text{H}_2\text{O} &\rightarrow \text{HClO} + \text{HCl} \\
\text{HClO} &\leftrightarrow \text{H}^+ + \text{ClO}^- \\
2\text{ClO}_2 + \text{O}_3 + \text{H}_2\text{O} &\rightarrow 2\text{ClO}_3^- + \text{O}_2 + 2\text{H}^+ \\
\text{HCl} + 2\text{H}_2\text{O} - 5e^- &\leftrightarrow 5\text{H}^+ + \text{ClO}_2 \\
\end{align*}
\]

Hydrogen is released at the cathode, metals are reduced and reactions to form hydroxides and carbonates take place:

\[
\begin{align*}
2\text{H}_2\text{O} + 2e^- &\rightarrow \text{H}_2 + 2\text{OH}^- \\
\text{Fe}^{2+} + 2e^- &\rightarrow \text{Fe} \\
2\text{H}_2\text{O} + 2\text{Na}^+ + 2e^- &\rightarrow \text{H}_2 + 2\text{NaOH} \\
\text{Ca}^{2+} + 2\text{HCO}_3^- &\leftrightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} + \text{CO}_2
\end{align*}
\]

3. Results

Images of changes in the concentrations of elements, electrical characteristics and thermal changes were constructed based on the modeling results. For example, Figure 1 shows the current density lines in the activator from which it can be seen that the maximum current density is observed at the edges of the electrodes - up to 300 A / m², especially at the anode. You can also see the value of the current density directly between the electrodes is at the level of 150 A / m², and closer to the walls of the activator - 50 A / m².

The modeling of changes in the concentrations of all incoming and newly formed chemical compounds was carried out. There were the corresponding images and graphics in separate elements of the electrical activator. It was important to trace the change in the hydrogen index in chambers, since it is often taken as the main indicator of activation degree of the solution.

The changes in average values of the hydrogen index depending on time in cathode - anode chambers of the activator show that in both parts the changes are dynamic from the first minutes of operation (Figure 2). So, the pH equal 11 is mounted in cathode parts of the activator to 4th minute, and in anodic - equal 4 (in initial moment time pH=8.2). Further, the process of changing the
hydrogen index slows down and there is stabilization of values, which is associated with the end of the transfer of elements, but with the continuation of other chemical reactions.

Figure 1. Image of current density lines in the activator

Figure 2. Image of average values of the hydrogen index in dependence on time in the cathode chamber of the activator (left) and in the anode chamber (right)

In the experiments, the water ionizer "Iva" was used as an electrical activator. Measurement of temperature, pH and concentration of ions K, Ca, Cl, Na, Mg were carried out with the help of the water analyzer "Expert-001" with a set of necessary electrodes. Figure 3 presents theoretical and experimental graphs of changes in the concentrations of calcium and magnesium in the anode chamber. According to the graphs, the match is quite good, especially at the end of the activation period. There is a coincidence of the modeling results and experimental data, as shown by the graphs of changes in the concentration of chlorine in the anode chamber (Figure 4, left) and cathode (Figure 4, right). It is also possible to observe a satisfactory coincidence of model and experimental data on temperature and hydrogen index in the activator chambers (Figure 5).
Figure 3. Graphs of changes in calcium (left) and magnesium (right) concentrations over time.

Figure 4. Graphs of changes in chlorine concentrations in the anolyte (left) and catholyte (right) over time.
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Figure 5. Graphs of changes in the hydrogen index (left) and temperature (right) over time

4. Discussion
Comparison of modeling results with experimental data showed a good match. Studies of images of the hydrogen index (pH) in the activator indicate the unevenness of its state at individual points of the object. The analysis of images of calcium and magnesium distribution in the activator demonstrated their decrease in the anode chamber at a rate coinciding with the experimental data. It can also be seen that initially there are oscillatory processes of changes in the concentrations of these elements, which is associated with the formation of intermediate compounds and their possible decay. Changes in concentrations of chlorine ions also indicate the presence of intermediate reactions and the formation of metastable compounds-most likely, it is ClO$_2$, ClO$_3$, HCl, HClO. Graphs of temperature changes in the anolyte prove the validity of the use of mathematical models and show the correctness of calculations of the conductivity of solutions. Comparison of model and experiment data on hydrogen index showed the satisfactory coincidence and presence of stationary place of operation.

On the basis of obtained data, it is possible to develop an automated control circuit of the electric activator using a microprocessor. Having the initial data on the composition of individual chemical elements in water and the total level of mineralization, as well as entering the required level of concentration of an individual substance or a total complex of substances based on the hydrogen index, you can automatically obtain the activation time.

5. Conclusion
Thus, there were obtained the mathematical models of the processes proceeding in anode and cathode chambers as a result of research. There were defined the basic chemical reactions that form the active substance in the anolyte. Based on the modeling results, the current density lines in the activator are
constructed, from which it can be seen that the maximum current density is observed at the edges of electrodes. Comparison of theoretical and experimental results obtained in the stationary mode of the activator with working time of more than 16 minutes showed a sufficient coincidence in temperature and hydrogen index. The analysis of graphs on the concentrations of chlorine, sodium and magnesium confirmed the conclusion about the instability of compounds with these chemical elements. The results obtained on the hydrogen index, the concentrations of calcium, magnesium and chlorine in the anolyte show that there is a stationary process of the activator to the 12th minute, and most of the ions finish transportation through the diaphragm.

References
[1] Hricova D, Stephan R and Zweifel C 2008 J. of Food Protection 71(9) 1934–1947
[2] Stopforth J D, Mai T, Kottapalli B and Samadpour M 2008 J. of Food Protection 71(3) 625–628
[3] Udompijitkul P, Daeschel M A and Zhao Y 2007 J. of Food Science 72(9) M397–M406
[4] Satyawali Y, Van de Wiele T, Saveyn H, Van der Meeren P and Verstraete W 2007 J. of Chemical Technology & Biotechnology 82(8) 730–737
[5] Bakhir V M, Vtorenko V I, Leonov B I, Panicheva S A, Prilutsky V I and Shomovskaya N Yu 2003 Disinfection science 1 29–36
[6] Deza M A, Araujo M and Garrido M J 2007 J. of Food Protection 70(1) 102–108
[7] Koseki S, Isobe S and Itoh K 2004 J. of Food Protection 67(11) 2544–2549
[8] Vorobjeva N V, Vorobjeva L I and Khodjaev E Y 2004 Artificial Organs 28(6) 590–592
[9] Wilhelmsen E 2003 J. of Food Protection 66(9) 1540–1540
[10] Akurai Y S and Obayashi I K 2002 Digestive Endoscopy 14(2) 61–66
[11] Prilutsky V I, Dolgopolov V I and Barabash T B 2013 Medical alphabet. Epidemiology and hygiene [in Russian – Meditsinskiy alfavit. Epidemiologiya i gigiena] 35 2–61
[12] Oskin S V 2010 Emergencies: industrial and ecological safety [in Russian – Chrezvychainye situatsii: promyshlennaya i ekologicheskaya bezopasnost] 1(2) 107–115
[13] Oskin S V 2013 Land management, cadastre and land monitoring [in Russian – Zemleustroistvo, kadastr i monitoring zemel] 8(104) 75–80