Preparation of disinfectant solution for use in agricultural production and processing industry

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Abstract. To improve the ecological purity of agricultural products it is necessary to look for new ways of pest control. Earlier studies show the prospects of using electroactivated solutions – anolytes for bactericidal treatment of bee colonies. The article analyzes the problem of describing main physical and chemical processes occurring during the electrochemical water activation. It is proposed to carry out modeling of electrolysis processes in Comsol software package. As a result of the necessary settings, this package is able to describe the basic physical and chemical processes and obtain solutions with a high level of coincidence with experimental data.

1. Introduction
The cultivation of agricultural products and their processing is usually accompanied by the use of chemicals to protect plants from various pests. Today, the number of strains of microorganisms with high resistance to a number of chemicals is increasing. In this regard, the periodic replacement of antimicrobials occurs, but it only increases the degree of danger of products. All the above mentioned aspects are applied to such a special agro-industry as beekeeping. Russian beekeepers are forced to use a large number of chemicals to combat bee diseases. It leads to the inability to supply honey to the European market and increase of content of harmful substances in the main product. A big problem is the disinfection of various containers for products during their processing, as in this process it is necessary to observe safety for life with further consumption.

A specific agent for bactericidal treatment can be obtained using a diaphragm electrolyzer. The mixture of metastable active ingredients of the anolyte does not lead to adaptation of microorganisms to microbicide action. Low concentrations of active chlorine and oxygen compounds provide the necessary level of safety for humans and environment. All researchers note the difficulty of describing processes occurring in the process of electrolysis with the presence of a diaphragm. This is due to the large number of electrochemical reactions taking place in the interelectrode space. It is also noted that the sameness of chemical composition and equality of concentrations of existing and ballast substances, differences in antimicrobial activity of electrochemically obtained anolytes can be large [5-10]. Many researchers agree that the basis of high efficiency of anolytes is still the presence of chlorine- and oxygen-containing compounds. However, the leading role of bactericidal action is given to hypochlorous acid. A large number of studies on use of anolyte in JSC "Institute of electrochemical systems and technologies named after Witold Bahir" and they offer a range of appropriate equipment [1, 2]. This group of researchers found that there is a loss of antimicrobial properties of anolyte during storage, which is associated with the reactions of mutual neutralization of most metastable oxygen chloride and hydroperoxide oxidants,
which have a higher rate under higher total mineralization of anolyte [1, 2]. The studies of anolyte properties and its application in various fields of agricultural production are also engaged in Kuban State Agrarian University [3, 4]. The disinfection effect in beekeeping was confirmed in laboratories of the University and there was a decrease in the activity of anolyte over time. Thus, it is necessary to create conditions for the production of electroactivated anolyte and its rapid application.

It is very difficult to obtain anolyte with specific content of active substances and it is necessary to conduct theoretical and practical studies for this.

2. Materials and methods
It is proposed to describe the main physical and chemical processes occurring during electrolysis (electroactivation) using Comsol software. This software product has shown itself in the analysis of physical processes occurring in a hive [4]. In this case, as the object of research was chosen non-flowing electrical activator of small volume. There was developed the geometric model of the object, which is shown in Figure 1.

![Figure 1. Type of geometrical model of activator](image)

In accordance with this figure, you can see that there are: electrodes 1, to which a direct current is connected, total capacity 3, separated by a diaphragm 2. Accordingly, during the flow of current in some parts of the tank 3, anolyte and catholyte will be formed.

Modeling of thermal processes was carried out in the physical block "Heat Transfer". Interfaces "Solid", "Fluid", "Porous Medium" were used to distinguish between solid, current and porous media. As initial conditions, we assume that the initial temperature of all elements was 20°C. In the form of restrictions, it is assumed that the cooling of outer surface of the activator occurred by natural convection and the appropriate heat transfer coefficients on the surface were used for this purpose. The basic heat equation can be represented as follows:

\[
\rho \cdot c_p \cdot \frac{\partial T}{\partial t} + \rho \cdot c_p \cdot u \cdot \nabla T + \nabla q_i = \sum Q_g,
\]

where \(\rho\), \(c_p\) - density and heat capacity of medium; \(u\) - velocity of flow; \(q_i = -\lambda \nabla T\) - density of thermal flow; \(\lambda\) - coefficient of thermal conductivity of liquid, Wt/m·K; \(\sum Q_g\) - total intensity of heat generations and heat absorptions, Wt/m³.

The total intensity of heat generation and heat absorption will be determined by the formula:

\[
\sum Q_g = Q_j + \sum Q_{ch},
\]

where \(Q_j\) - Joule heating; \(\sum Q_{ch}\) - total amount of generated and absorbed heat at the expense of chemical reactions.

The equation of liquid medium flow connected with heat convection can be described on the basis of equations of Navier – Stokes.
There are various dissolved substances in the initial water. Under the influence of electric current and due to diffusion and convection, they begin to move. The transport of these substances is described by the Nernst-Planck equation:

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot (D_i \cdot \nabla c_i + z_i \cdot u_{mi} \cdot F \cdot c_i \cdot \nabla V) + R_i,
\]

where \( c_i \) - concentration of \( i \) substance, mol/m\(^3\); \( D_i \) - coefficient of diffusion of \( i \) substance, m\(^2\)/s; \( z_i \) - charge of \( i \) of ion; \( u_{mi} \) - mobility of \( i \) of ion, mol·s/kg; \( u_{mi} = \frac{D_i}{RT} \); \( F \) - constant of Faraday; \( R_i \) - velocity of chemical reaction, mol/m\(^3\)·s.

The current density in the electrolyte can be determined in accordance with Faraday's law and is calculated by the equation:

\[
i_i = F \sum_{i=1}^{n} z_i (-D_i \cdot \nabla c_i - z_i \cdot u_{mi} \cdot F \cdot c_i \cdot \nabla V).
\]

The transfer processes occurring in the diaphragm were also taken into account. Navier-Stokes equations and Darcy's law were used to describe transport displacements in porous media.

All electrolytic processes were modeled in the interface "Tertiary Current Distribution". As the initial conditions there were given the concentrations of main chemical elements and compounds: Na, Cl, Mg, SO\(_4\), HCO\(_3\), K, Ca, Cl\(_2\), O\(_2\), H\(_2\), Fe, HClO, HCl, ClO\(_2\), CaCO\(_3\), O\(_3\), NaOH, ClO\(_3\), ClO\(_4\). The values of diffusion coefficients were taken from scientific literature data or from the program itself. The formation of following elements was modeled in interfaces of "Electrode Surface": oxygen, ozone and chlorine at the anode, and hydrogen and iron at the cathode. Chlorine-containing compounds were formed in the anode chamber in accordance with following chemical reactions:

\[
\begin{align*}
2H_2O - 4e^- & \rightarrow 4H^+ + O_2 \\
2Cl^- - 2e^- & \rightarrow Cl_2 \\
Cl_2 + H_2O & \rightarrow HClO + HCl \\
HClO & \leftrightarrow H^+ + ClO^- \\
2ClO_2 + O_3 + H_2O & \rightarrow 2ClO_3^- + O_2 + 2H^+ \\
HCl + 2H_2O - 5e^- & \leftrightarrow 5H^+ + ClO_2
\end{align*}
\]

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

\[
\begin{align*}
2H_2O + 2e^- & \rightarrow H_2 + 2OH^- \\
Fe^{2+} + 2e^- & \rightarrow Fe \\
2H_2O + 2Na^+ + 2e^- & \rightarrow H_2 + 2NaOH \\
Ca^{2+} + 2HCO_3^- & \leftrightarrow CaCO_3 + 2H_2O + CO_2
\end{align*}
\]

The solutions were carried out in a non-stationary mode with a total operating time equals to 16 minutes. The initial concentrations of chemical compounds were taken on the basis of analysis of the available water, in order to be able to conduct a full-scale experiment and compare the data with the theoretical ones in further.

3. Results and discussion

The analysis of images of liquid speeds (Figure 2) at the expense of heat convection showed that small speeds were 2·10\(^{-3}\)m/s. The highest speeds are observed in the anode chamber and closer to water surface - to 4·10\(^{-3}\)m/s.
Figure 2. Image of speeds of liquids in the activator

Figure 3 shows thermograms of the activator after 4 and 14 minutes of operation, from which it can be seen that the most heated is anolyte – excess over the catholyte is 6-8 degrees. Inside the anode chamber is visible rise of more heated part of the anolyte.

The formation of chlorine gas fraction in the anolyte is shown in Figure 4, where it is possible to see the following: chlorine gas is mainly behind the anode and has concentration of up to 0.075 mol/m³ by 6th minute; the part of gas has gone out by 16th minute, and the other part has spread throughout the anolyte. Partial dissolution of chlorine occurs in the anolyte, maximum concentrations are near the anode and have value of 0.035 mol/m³. It is also seen that the formation of chlorine gas fraction does not occur in the cathode chamber.

Figure 3. Images of temperature fields in the activator via 4 minutes (left) and 14 minutes (right)

Figure 4. Images of gas chlorine spreading in the anode chamber via 6 minutes (left) and via 16 minutes (right)
Modeling of formation of hydroxides in the catholyte by the example of sodium was also carried out and studies showed that after 4 and 12 minutes of the activator operation, an increased concentration is observed near the cathode and diaphragm from the anolyte. The analysis of changes in Cl and ClO concentrations in anolyte shows that their concentration increases from 0 to 0.001 mol/m$^3$. The formation of ClO$_2$, ClO$_3$ is slower as they appear as a result of secondary reactions and therefore the concentrations of these elements have lower values compared to HCl. Images of ozone concentrations in the activator showed the maximum value of this parameter near the anode - up to 20 mol/m$^3$ (after 16 minutes of operation). Thus, there is an intensive formation of ozone and it changes little over time near the electrode, but ozone spreads gradually near the walls of activator, and concentration increases reaching in some places to 4 mol/m$^3$.

The task of experimental studies was to confirm values of obtained solutions in the modeling. As the object of experimental researches there was chosen the ionizer "Iva", which is identical in design with the model and has the same value of activation current. Temperature, hydrogen rate and element concentrations were measured using an ionometer with a set of appropriate sensors. Time graphs were constructed and compared with similar simulation graphs based on the results of experiments. Thus, there were presented the graphs of concentrations of sodium and calcium in the anolyte in Figure 5. From these images it is seen that the modeling and experimental graphics in most parts show good matching after the 12th minute. There is a decrease in concentrations of these elements in this part of the activator by transferring them to the catholyte chamber. Experimental values have fluctuations in first moments of time, but the trend coincides with the theoretical graph. The relative error of differences between values of theory and experiment at the end of non-stationary period is in the range from 2 to 6%. The maximum deviation of data is available in time interval from 5 to 12 minutes on the first chart and from 2 to 8 minutes on the second. Such deviations can be explained by a large number of chemical reactions and their different flow rates. In this case, many intermediate unstable compounds are formed, which are noted in scientific literature.

**Figure 5.** Diagrams of time dependences of sodium concentration changes (left) and calcium (right)

In addition, comparative diagrams were obtained for other chemical elements and compounds.
Diagrams of changes in hydrogen rate over time in the anode and cathode chambers are shown in Figure 6. According to these diagrams, it is possible to determine small discrepancy in the range of 8 - 12 minutes (relative error of about 11%) and a good match on the stationary site (relative error of less than 4%).

Figure 6. Diagrams of time dependences of hydrogen rate changes in the anolyte and catholyte

4. Conclusion
The obtained models and their solutions reflect quite correctly the processes taking place in the diaphragm electrolyzer. Models allow making additions on chemical reactions, changing values of current densities, modernizing a geometrical design of the activator. The constructed images of temperature fields allow seeing the most heated parts and analyzing the surface with high heat efficiency. Images of changes in concentrations in the anolyte and catholyte chambers make it possible to trace the rate of transfer of individual chemical elements and, if necessary, make adjustments to the throughput of the diaphragm (replaced by another material). These images show locations of maximum concentrations of chemical compounds, which will allow sampling at a particular location. Experimental testing of the activator showed a good match of main characteristics of the activator on the stationary part of the work - relative error was at the level of 5%. Comparison of obtained data on the non-stationary part (up to 12 minutes) shows a big difference for individual elements, but the trend remains correct. This discrepancy is reasoned by the large number of chemical reactions taking place with different flow rates. Thus, if there are specific requirements for anolyte as a disinfectant on the part of processors of agricultural products, it is possible to obtain a safe antimicrobial agent in electrolyzers of the diaphragm type and recommend its parameters and modes.

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