

Preparation and Application of Environmentally Friendly Electroactivated Solutions for Use in Beekeeping in Disinfection of Hives and Equipment

Sergey Oskin, Dmitry Tsokur and Elena Shcherbakova*

Kuban State Agrarian University named after I. T. Trubilin, Krasnodar, Russia

Abstract. Analysis of the health status of bee colonies has shown that constant prevention and treatment of bees from concomitant diseases is necessary. The health of bees is directly related to their productivity. Most beekeepers use highly active chemicals to process beehives and inventory. To change this situation, it is necessary to search for new solutions for the treatment of bees. One of the ways to solve the problem is the use of environmentally friendly and harmless to bees and beekeepers electroactivated solutions obtained using diaphragm electrolyzers of water. The conducted studies of the developed model of a diaphragm electrolyzer using the Comsol program allowed us to obtain information about the physicochemical processes occurring in it over time. Comparison of simulation results and experimental data showed their good coincidence. Studies on the treatment of bee colonies in the apiary with electroactivated solutions can halve the use of chemicals and reduce the likelihood of drugs getting into bee products.

1 Introduction

To obtain high-quality beekeeping products in large quantities, it is necessary to carefully monitor the health of the bees themselves. The relevance of this issue is related to the fact that bees are social insects and with the disease of one individual, the disease can be rapidly transmitted to the whole family. In the bee family, both diseases of bees and their brood larvae can be present. The causes of infectious diseases can be bacteria, fungi, viruses, parasites. The most widespread are the following infectious diseases of bees: hafniasis, nosematosis, paratyphoid, braulosis, acarapidosis. In addition to infectious diseases, bees also suffer from non-infectious diseases, for example, toxicosis. The strength of the bee family largely depends on its timely replenishment with new bees from the brood. One of the most frequent diseases of the brood is its defeat by foul brood, the causative agent of which are bacteria of several species. The source of this disease is the bees themselves. They begin to remove the dead larvae and at the same time infect the mouthparts, which leads to the spread of infection throughout the brood nest. Foul brood spores can remain

* Corresponding author: dmitry_tsokur@mail.ru

viable for many years and are also particularly resistant to chemicals. In this regard, concentrated solutions and mixtures of highly active disinfectants are used for treatment. A particularly serious disease of bee colonies is varroaosis, which is accompanied by the death of larvae and a strong weakening of the family. The cause of this disease is the ectoparasitic mite *Varroa jacobsoni*. Female mites lay eggs in cells and by the time the bees leave the honeycomb, the mites become adults. Treatment and prevention are carried out with the help of physical, chemical and biological preparations. In Russia, chemical methods of combating bee diseases have become the most widespread, and most often with the use of antibiotics. The use of formic and oxalic acids, which are sprayed in compliance with precautionary measures (gas masks, special clothing, etc.), proves its effectiveness. The use of various chemicals leads to the fact that toxic drugs get into bee products. Over time, there is an adaptation of pathogenic microorganisms to chemicals, and beekeepers increase the dose.

This situation can be changed if other methods of combating bacterial diseases of bees are used, which are based not on increasing the concentration of chemicals, but on blocking individual processes of the vital activity of microorganisms. Ozonation and the use of electroactivated solutions of anolyte can be recommended as such methods [1, 2].

2 Materials and methods

Diaphragm electrolysis of water leads to the appearance of solutions (in particular anolyte) with unique properties compared to traditional disinfectants [3]. On the part of beekeepers, the following requirements can be formulated for an antimicrobial agent: a wide spectrum of action, effective defeat of bacteria, viruses, fungi and spores, safety for humans during the preparation of the product and after its use, having minimal corrosion activity in relation to the materials used in beekeeping, maximum ease of use, low cost.

The production and further decomposition of H_2O_2 in the process of diaphragm electrolysis of water is accompanied by the formation of compounds with high antimicrobial activity. The resulting radicals and atomic oxygen also take part in the destruction of microorganisms. [3]. Thus, a solution with the presence of such elements acquires a universal spectrum of action: it damages pathogenic microorganisms, while it is safe for humans. The main active substances in anolyte are peroxide and chloro-oxygen compounds. Their combination makes it impossible for microorganisms to adapt to the biocidal action of the anolyte, and low concentrations of these compounds make these solutions safe for their use in the apiary.

Household diaphragm electrolyzers are on sale. They are easy to operate and suitable for use by beekeepers (Figure 1).



Fig. 1. Household diaphragm water electrolyzers

There are studies [4] proving the strengthening of the antimicrobial effect of anolyte due to its bubbling with ozone. In the Kuban State Agrarian University, studies have been conducted to combat bee diseases by dissolving ozone in anolyte [5]. The results obtained show the high efficiency of the use of such solutions.

When the current passes through the diaphragm electrolyzer, various chemical reactions occur in the anode and cathode chambers. The speed and presence of these reactions depends on the initial salt content in the water, the operating mode of the electrolyzer, as well as on the materials used in it, in particular, the materials of the electrodes. In the cathode chamber, weakly mineralized water acquires alkaline properties due to the transformation of salts into hydroxides, and metal reduction processes are also underway in this chamber. Reactions associated with the formation of chlorine-containing substances occur in the anode chamber of the diaphragm electrolyzer. It was found that as a result of electrolysis, the anolyte is saturated with such oxidizing agents as: HClO , HCl , ClO , ClO_2 , ClO_3 , O_3 . Hypochlorous acid HClO is the most powerful oxidizer.

Based on the chemical nature of the disinfecting effect of electroactivated aqueous solutions, it is necessary to determine the parameters of the electrolyzer and its operating modes. As our research shows, the solution should be used 1-2 hours after preparation. The time is limited by a decrease in the concentrations of active compounds after electrolysis.

The main chemical reactions were established and included in mathematical models [6]. The Comsol program was used to solve mathematical models. Initially, a geometric model of the investigated diaphragm electrolyzer was developed (Figure 2).

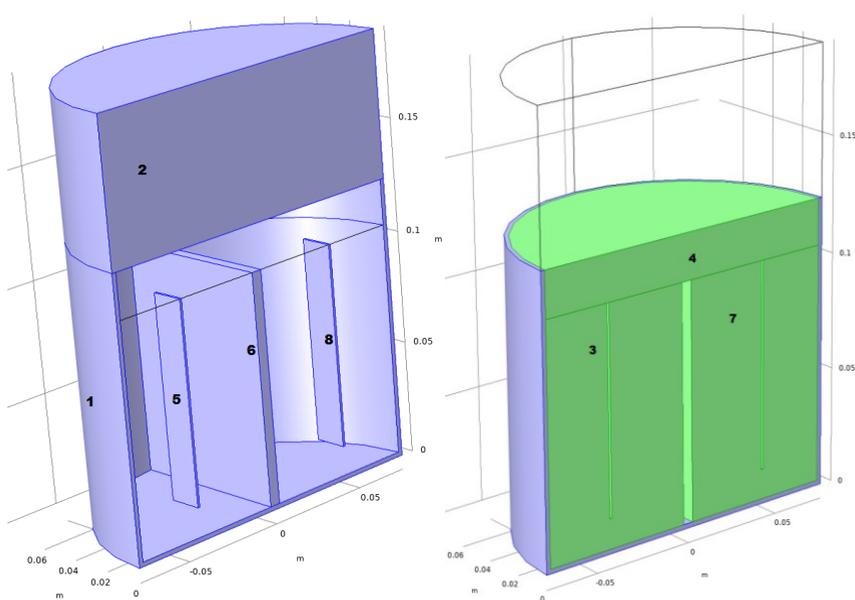


Fig. 2. The geometric model of the electrolyzer under study: 1 – the main part of the electrolyzer housing into which the source water is poured; 2 - the upper part of the housing containing the control circuit of the installation; 3, 7 – the cathode and anode chambers of the electrolyzer, respectively; 4 - the air part above the electrolyte surface; 5, 8 - the cathode and anode, respectively; 6 - the diaphragm.

Interfaces for the study of physical processes were selected in the software product and multiphysical connections were established.

Modeling of thermal processes occurring in a diaphragm electrolyzer was obtained using the Heat Transfer interface, in which the equations of thermal conductivity in solids

(electrodes, installation housing), liquids (electrolyte) and porous media (diaphragm) were solved. Steel and ruthenium were chosen as the cathode and anode materials, respectively (as a rule, in household diaphragm electrolyzers, the anode is a steel electrode coated with ruthenium). The diaphragm material is a tarpaulin. The initial temperature was assumed to be 20 °C. Convective heat flow was described by the following equation [7]:

$$-nq = h\Delta T, \quad (1)$$

where h is the coefficient of heat transfer through the surface.

Using the "Heat Flux" functions in the Comsol environment and accepting the condition of natural convection on the outer part of the electrolyzer, heat transfer coefficients were calculated.

The solution of the hydrodynamic problem was carried out using the "Laminar Flow" interface, since the fluid velocities are low and caused by natural convection.

Electrochemical processes were modeled using the interface "Tertiary Current Distribution". The concentrations of the following chemical compounds were set as initial conditions: Na, Cl, Mg, SO₄, HCO₃, K, Ca, Cl₂, O₂, H₂, Fe, HClO, HCl, ClO₂, CaCO₃, O₃, NaOH, ClO₃, ClO. The kinetics of electrode processes was implemented using the "Electrode Surface" interface. As electrode reactions, reactions at the anode proceeding with the formation of O₂ и Cl₂, as well as reactions at the cathode with the reduction of H₂ and Fe were modeled.

The rates of the main chemical reactions occurring in the electrolyte were calculated in the "Chemistry" block.

As a result of solving the described physico-chemical problems, fields of fluid velocities, concentrations of the resulting chemical compounds, temperature and pH were obtained.

The analysis of images of fluid velocities during thermal convection inside the electrolyzer is carried out. It can be seen from Figure 3 that the highest speeds are in the anode chamber - up to $4 \cdot 10^{-3}$ m/s, liquid circulation zones are also observed near and behind the electrodes.

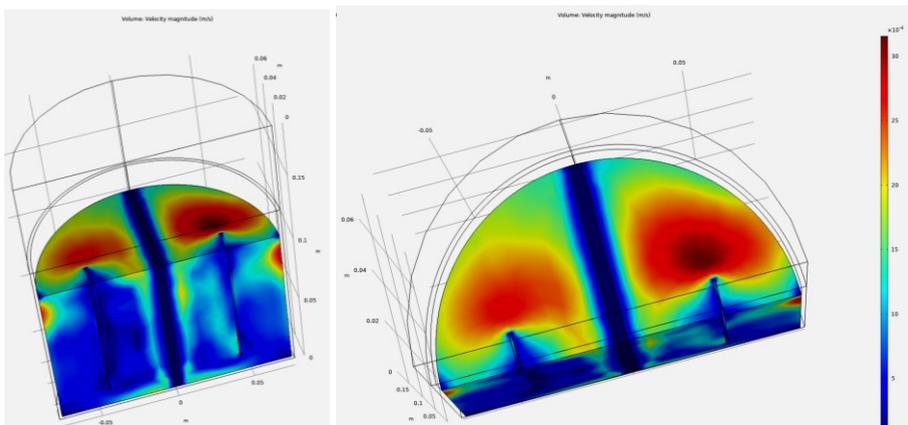


Fig. 3. Image of the fluid velocity in the electrolyzer

Changes in the concentrations of various chemical elements in individual cells of the electrolyzer were studied. Figure 4 shows graphs of the dependence of changes in iron concentrations on time, where you can see the process of metal reduction at the cathode.

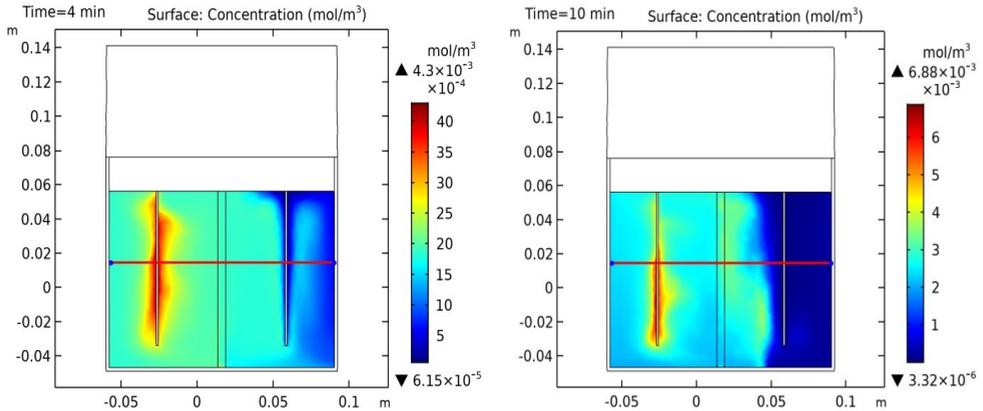


Fig. 4. Images of the Fe concentration in the diaphragm electrolyzer after 4 (left) and 10 (right) minutes

Of particular importance is the formation of Cl_2 in the anolyte. Figure 5 shows that after six minutes the concentration of chlorine gas is mainly behind the anode and its maximum value is about 0.075 mol/m^3 , and after sixteen minutes the gas fills the entire anode chamber of the electrolyzer and the process of its dissolution is underway.

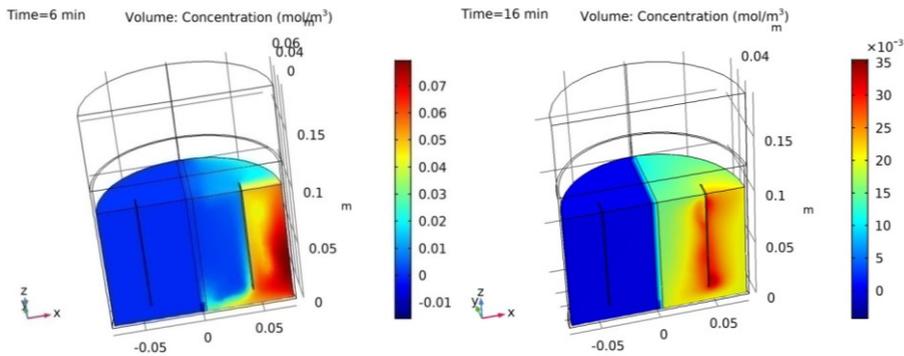


Fig. 5. Images of Cl_2 concentrations in the anode chamber of the diaphragm electrolyzer of water after 6 minutes (left) and after 16 minutes (right)

Figure 6 (left) shows graphs of changes in HCl and ClO concentrations, where an increase in their content in the anode chamber can be observed. The formation of ClO_2 , ClO_3 , occurs very slowly in the anode chamber of the electrolyzer, since they appear as a result of secondary reactions and therefore the concentrations of these elements have lower values compared to HCl.

As a result of dissociation of HClO acid, ClO is formed. At the same time, the HClO concentration drops by an order of magnitude. Figure 6 (right) shows the state of HClO concentration after 16 minutes of operation of the electrolyzer with a zone of elevated concentrations near the anode of the order of $20 \cdot 10^{-7} \text{ mol/m}^3$.

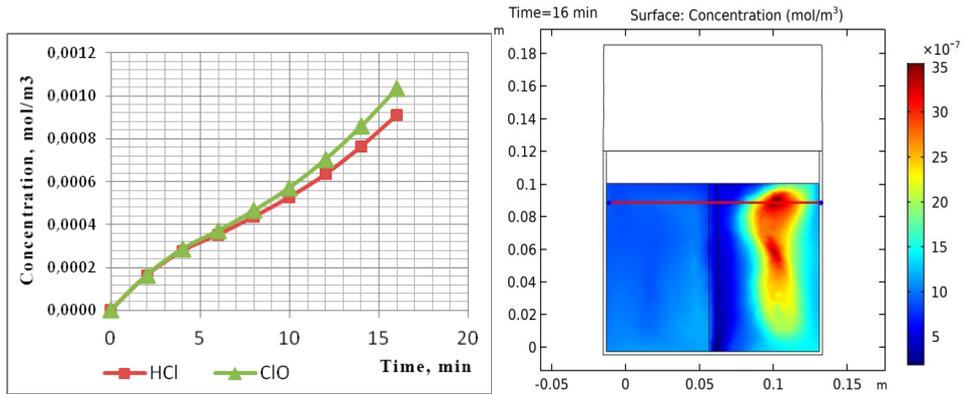


Fig. 6. Graphs of the dependence of HCl and ClO concentrations in the anode chamber on time (left) and an image of HClO concentrations in the anolyte after 16 minutes (right).

Experimental studies were conducted to confirm theoretical studies.

For the experiments, a laboratory installation was assembled using the Iva ionizer. To saturate the anolyte with ozone, a plate-type electric detonator was additionally used, the capacity of which was 600 mg/h. To measure ion concentrations, an Expert-001 water analyzer with electrodes was used: ESC-10603/7 pH, ALICE-121 Ca, ALICE-121 K, ALICE-112 Na, HC-Mg-001, ALICE-131 Cl, ESr-10103/3.5. The conductivity of water was measured by a TDS meter.

The assessment of the disinfecting effect of the obtained anolyte on beekeeping objects (beehives, bee inventory) was carried out as follows. We took 1 ml of microbial solution and added it to an anolyte with a volume of 9 ml. After 3 minutes, inoculation of a Petri dish was carried out. Quantitative analysis of viable microorganisms was carried out using the Koch cup method.

3 Results and discussion

The experimental data obtained were compared with the simulation results. Figure 7 shows graphs of changes in the concentration of Cl in the anolyte over time and with different values of the exchange current density i_0 at the anode-electrolyte interface. It was determined that the value of this current slightly affects the change in the concentration of chlorine in the anolyte. By the 14th minute, the concentration of Cl has stabilized.

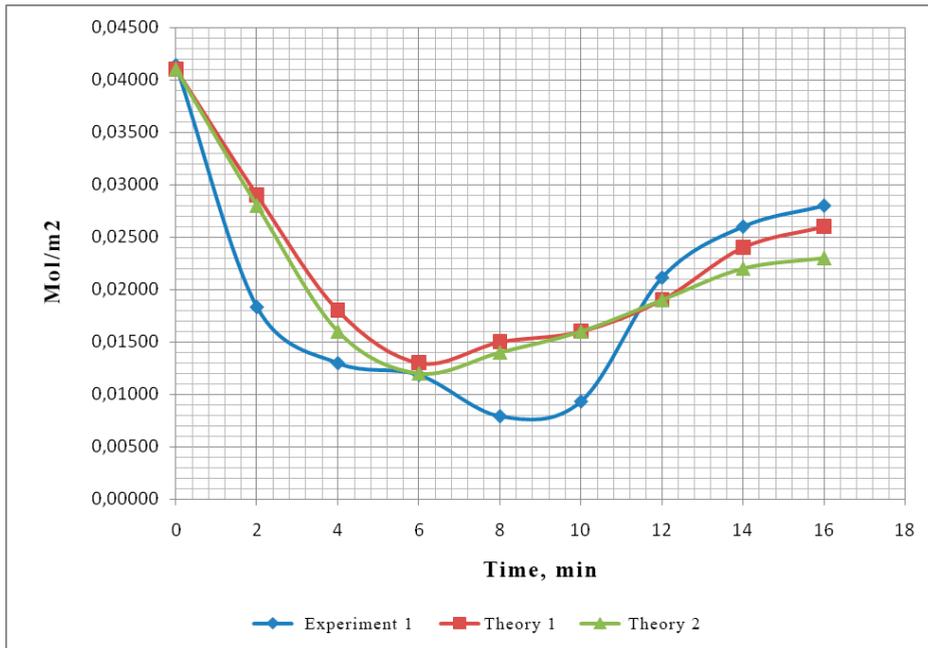


Fig. 7. Graphs on comparison of experimental dependences of changes in chlorine concentrations with model data

The slight difference between the theoretical and experimental graphs in Figure 7 can be explained as follows. Initially, the concentration of Cl in the anolyte decreases due to the high reaction rate of Cl₂ formation. During this period, Cl ions flow from the cathode chamber, but this process is slower than the formation of Cl₂. At the same time, chlorine-containing elements (HCl, HClO, ClO, ClO₂, ClO₃) are formed in the anode chamber and the concentration of Cl is leveled. There is a process of accumulation of chlorine-containing elements and their transition from one compound to another. There is also a dissolution of part of the Cl₂ released at the anode, which leads to an increase in Cl ions and the graph takes an increasing form. Experimental and model data were also compared for all incoming chemical elements [4, 8].

Experimental studies were conducted on the effect of ozone-bubbled anolyte on microbial solution. The analysis of such experiments showed that the maximum effect is observed during electrolysis for 12.5 minutes and subsequent bubbling of the resulting anolyte with ozone for 2.2 minutes. A regression model of the effectiveness of the effect of the resulting solution on pathogenic microorganisms from the time of electrolysis and bubbling with ozone was obtained. Figure 8 shows the boundaries of the rational parameters of electrolysis x_1 (11 minutes) and ozonation x_2 (1.4 minutes).

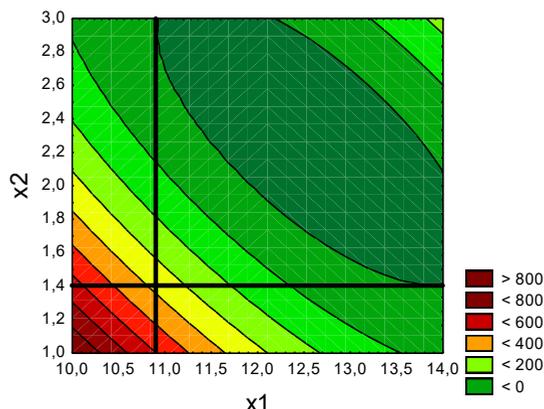


Fig. 8. Diagram of the effect of the parameters of electroactivation and saturation of the anolyte with ozone on the CFU parameter field

At a separate apiary in the Krasnodar Territory of the Russian Federation, a field experiment was conducted to study the effectiveness of the use of electroactivated solutions for the maintenance of bee colonies. Using the resulting disinfectant solution, 20 hives were periodically treated after wintering, as well as bee equipment. There were also 5 control hives that were periodically treated with Nosemat (including Metronidazole and Oxytetracycline). The results of such comparative experiments showed the following: the number of antibiotics used (such as Oxytetracycline) for the treatment of bees has decreased by 2 times, the number of diseases has decreased, the probability of antibiotics getting into bee products has decreased.

4 Conclusions

The use of the Comsol medium made it possible to implement mathematical models of the main physico-chemical processes occurring in the diaphragm electrolyzer and to link them through the appropriate interfaces.

As a result of solving the obtained models, it was found that changes in HCl and ClO concentrations in the anolyte occur with an increase in concentrations from 0 to 0.001 mol/m³. The effective operating time of the considered diaphragm electrolyzer in terms of the number of Cl compounds in solution is from 10 to 14 minutes at a current of 0.5 A and an initial content of Cl ions is 0.03 mol/m³.

Experimental studies have confirmed the rates of change and the values of the concentrations of the main chemical compounds obtained during the simulation. At the same time, by the end of 12 minutes, the relative errors of the values of experimental concentrations differed from the model ones in the range from 2 to 6%.

Experiments on the effectiveness of the anolyte's effect on pathogens have shown that the greatest effect is exerted by the anolyte during the electrolysis time from 12 to 14 minutes and its subsequent bubbling with ozone from 2 to 3 minutes.

References

1. V. M. Bakhir, A. R. Atadzhanov, U. D. Mamadzhanov, S. A. Alekhine, N. A. Mariampolsky, A. H. Najimitdinov, Proceedings of the Academy of Sciences of the Uzbek SSR, 5 (1981).

2. V. M. Bakhir, P. A. Kirpichnikov, A. G. Liakumovich, L. E. Spector, U. D. Mamadzhanov, *Proceedings of the Academy of Sciences of the Uzbek SSR*, **4** (1981).
3. V. I. Prilutsky, V. M. Bakhir, *Electrochemically activated water: abnormal properties, mechanism of biological action*, **228** (1997).
4. S. V. Oskin, A. S. Oskina, S. P. Voloshin, *Engineering for Rural Development*, **18**, 1210-1214 (2019).
5. S. V. Oskin, D. A. Ovsyannikov, *Emergencies: Industrial and Environmental Safety*, **21** (2015).
6. S. V. Oskin, A. S. Oskina, D. S. Tsokur, S. P. Voloshin, V. D. Shaforostov, *IOP Conference Series: Earth and Environmental Science*, **488**, 1 (2020).
7. *Documentation for the Heat Transfer module of the Comsol Multiphysics program*, Comsol.Inc, 876 (2021).
8. S. V. Oskin, D. S. Tsokur, *Lecture Notes in Electrical Engineering*, **729**, 143-151 (2020).