Method of preparation and biological activity of aqueous hydrogen peroxide solution

Mukhsindjan Ashurov¹, Sergej Belov², Yurij Danyleiko², Nodirbek Otamirzaev³, Alexandr Korshunov³, Dmitry Demin⁴,⁵, and Inna Bogun⁶

¹Statescientific productionen terprise “Fonon”, Tashkent, republic of Uzbekistan
²Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia
³Institute of Rice Growing, Tashkent, republic of Uzbekistan
⁴All-Russia Research Institute for Phytopathology, B. Vyazyomy, Moscow Region, 143050 Russia
⁵Institute of Basic Biological Problems of the Russian Academy of Sciences, 2 Institutskaya st., Pushchino, Moscow Region, 142290 Russia
⁶Peter the Great Saint Petersburg Polytechnic University, Saint Petersburg, 195251, Russia

Abstract. The possibility of increasing the concentration of hydrogen peroxide by using an electrolyte based on aqueous solutions of sodium sulfate or potassium sulfate salts is substantiated and implemented. Limit values of acidity and values of electrochemical potential of the activated aqueous solution are established. The obtained experimental confirmation of the possibility of the use of activated solution "Plasmolite" as a plant growth regulator.

1 Introduction

The electrochemical effect on weak solutions of strong electrolytes is the basis for the production of biologically active aqueous preparations – "activated water". It is known that biologically activated water containing the optimal concentration of hydrogen peroxide is an effective and absolutely environmentally safe stimulator of plant growth and development [1-3]. It is noted in the literature that after the treatment of plants with activated water, the acceleration of seed germination was observed, as well as an increase in the rate of plant biomass recruitment. There was also an increase in the resistance of crops to fungal and bacterial diseases [3, 4].

The classical method of obtaining activated water is the use of electrochemical activation of aqueous solutions by electrolysis. Aqueous solutions are electrolyzed in diaphragm electrolyzers with separate output of acidic and alkaline water [5-7]. This method is known to activated solutions: "living water" – the Catholyte and the "dead water" Anolyte. However, such methods are very time-consuming and expensive due to the short service life of the electrolyzer membrane and significant energy costs of the installation as a whole. In addition, the activity of such water is very low.

In contrast to the known methods, in this paper we consider a fundamentally new method for obtaining an activated aqueous solution using a low-temperature plasma of a
high-frequency electric discharge of a glow type, a plasma-forming gas in which water vapor is [8, 9]. For activation of aqueous solutions using high-frequency glow discharge plasma-chemical reactor is used in which activation of an aqueous solution occurs in the area of electrical contact glow discharge with aqueous electrolyte, as well as in the condensation of active param of the water leaving the combustion zone of the plasma. The device of the reactor will be described below, and activated it water rated brand "Plasmolite". In the result of plasma chemical treatment of diluted aqueous solutions of strong electrolytes obtained aqueous solution Plasmolite become biologically active. In particular, its redox potential can vary from – 900 mV to + 1000 mV depending on the activation conditions. By analogy with the known biologically active drugs Plasmolite can also be used in various sectors of the economy, however, the most interesting is its use in agriculture for seed treatment and for foliar watering plants as antibacterial and antivirus capabilities in the area of maintenance of agricultural animals, in food industry etc. According to the results of preliminary studies, the solution of Plasmolite indifferent concentrations can be used as the basis for a new agricultural technology. Especially important is the use of such technology in areas with a short light day, the Arctic circle in the polar night, as well as in conditions of long Autonomous diving, polar expeditions and long-term space flight.

2 Materials and methods

On the basis of the results obtained in the study of the mechanism of combustion of high-frequency glow discharge in an atmosphere of saturated water vapor at atmospheric pressure, a method was developed to produce biologically active drug Plasmolite and install to get it.

2.1 A method of producing Plasmolite

For the preparation of Plasmolite used a one per cent solution of NaCl or KCl in distilled water. To obtain a discharge in the volume of the liquid electrolyte, an electric circuit was used including: a high-frequency generator, a metal active electrode, a plasma layer with a plasma-forming gas from water vapor, a layer of a weak aqueous solution of a strong electrolyte and a passive electrode from a well-conducting electric current material. Plasma was generated on an active electrode of nichrome wire 0.3 mm in diameter immersed in the electrolyte volume. To reduce the energy costs of the formation of water vapor necessary for the combustion of plasma, the initial solution was heated to a temperature of 40 °C. as a passive electrode, a rod of pyrolytic graphite of the PGI brand was used (see Fig.1). The electrodes were connected to a high-frequency generator with an operating frequency of 110 kHz. The form of the output voltage – meander. Since at the moment of ignition of the plasma discharge in the electrolyte volume at the initial time, a short-term increase in the generator power (power 4-5 times higher than the stationary mode) is required, the amplitude of the output voltage was regulated within 250-500 V.

After the occurrence of a stable plasma discharge, the current in the active electrode circuit was automatically set so as to ensure stable plasma combustion Gorenje. In the case of using NaCl solution stable burning of the plasma were recorded by the characteristic yellow glow of the plasma that is associated with the emission of excited sodium atoms. The study of the current-voltage characteristics of the discharge showed that the normal working discharge in its properties is close to the anomalous glow-type discharge. In the transition of the discharge to the arc mode, the plasma radiation spectrum changed markedly with an increase in the luminescence in the blue region of the spectrum.
As a result of burning of plasma in an aqueous solution of plasma-chemical reactions occur, among which are the decomposition of water with release of hydrogen peroxide and free hydrogen [10]:

\[
\begin{align*}
    \text{H}_2\text{O} + e + 4.25 \text{eV} & \rightarrow \text{H}^- + OH^{-} + \text{H}_2 \\
    \text{H}^- + \text{H}^- & \rightarrow \text{H}_2 + e + 3.8 \text{eV} \\
    \text{HO}^- + \text{OH}^- & \rightarrow \text{H}_2\text{O}_2
\end{align*}
\] (1)

In this case, one molecule of hydrogen peroxide is synthesized per molecule of hydrogen. The General equation is as follows:

\[
2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}_2
\] (2)

It should be noted that such reactions are observed in the optical breakdown of water induced by laser radiation [11], under the influence of ultraviolet radiation [12], plasma [13] and other physical and not only physical effects [14], but the method proposed in the article is the most rational (cost/effect) and easily scalable for industrial applications.

Hydrogen peroxide \( \text{H}_2\text{O}_2 \) is the main stable oxidizer generated in aqueous electrolyte solutions under the action of plasma. As can be seen from the above reaction, hydrogen peroxide is formed as a result of recombination of radicals \( \cdot \text{IT} \). It is in an amount proportional to the amount of electricity that has passed. During the accumulation of peroxide in the solution, its decomposition reactions occur simultaneously, which eventually leads to the establishment of a stationary concentration of \( \text{H}_2\text{O}_2 \). In this experiment, the amount of hydrogen peroxide formed in the solution during the passage of a certain amount of electricity was estimated by the amount of hydrogen released, not exceeding \( 10^{-4} \text{m} \). As can be seen from the oscillogram (figure 2), the glow discharge plasma in the electrolyte solution burns at a negative polarity of the “hot” electrode. This is the reason for the appearance of a constant current component in the negative region, which is due to the reaction of the electrolysis of water with the formation of oxygen and hydrogen:

\[
2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2
\] (3)

On the one hand, this leads to the formation of alkali (sodium hydroxide, potassium hydroxide), the interaction of which leads to the decomposition of hydrogen peroxide. On the other hand, molecular oxygen appears in the aqueous solution, which serves as an electron acceptor [15]. If acceptee electron by molecular oxygen forms superoxide anion radical. This compound is immediately protonated in aqueous solutions [16], which leads to
the formation of hydroperoxide radical. Dismutation of hydroperoxide radicals also leads to generation of hydrogen peroxide [17]. It should be noted that this mechanism is polycyclic, that is, two molecules of molecular oxygen form one molecule of hydrogen peroxide and one molecule of molecular oxygen:

\[
O_2 + e \rightarrow O_2^* \\
O_2^* + H^+ \rightarrow HO_2^* \\
HO_2^* + HO_2^* \rightarrow H_2O_2 + O_2
\] (4)

Taking into account the competing processes of generation of hydrogen peroxide and electrolysis of water occurring in the process of obtaining Plasmolite, as the electrolyte, it is advisable to use aqueous solutions of salts of sodium sulfate or potassium sulfate containing acid residues of sulfuric acid. The use of such an electrolyte will protect the peroxide solution from decomposition and the ability to increase its concentration by increasing the operating time. Assuming that the degree of activation of a solution of Plasmolite proportional to the concentration of hydrogen peroxide, the concentration of peroxide H2O2 was performed using the method of iodometry [18].

It should be noted that hydrogen peroxide plays a dual role in living cells. On the one hand, it can cause harmful oxidative stress, which is accompanied by negative processes for cell activity, such as lipid peroxidation, oxidative modification of proteins and nucleic acids [19]. Oxidative DNA damage is associated with such processes as mutagenesis and carcinogenesis [20]. On the other hand, hydrogen peroxide plays an important signal-regulatory role [21]. It was established that living cells have several types of "H2O2 sensors" aimed at adaptation of the organism to oxidative stress [22].

Fig. 2. Oscillogram of voltage (yellow curve), current (red curve) and plasma glow (blue curve) on the working electrode.

The results of an experimental study of the method of obtaining a Plasmolite using a glow discharge plasma can be taken as a basis for evaluating the effectiveness of this method. In particular, the processing solution volume of 200 ml was carried out for 2-3 hours at RMS value current (true RMS) level 2-3 A. thus the characteristic length of the combustion region of the plasma column was 40-50 mm. After processing, the solution is allowed to stand for one day and filtered. The pH of the fresh solution was about 8.3. Oxidation-reduction potential (ORP measure) was of the order of 800 mV (measured with tool RNT-028).
2.2 Installation to receive Plasmolite

For the realization of the considered method an experimental setup was developed to obtain Plasmolite. The unit contains an electrochemical cell with two electrodes immersed in the electrolyte, a high-frequency generator, a programmable sensor for monitoring the amount of hydrogen released, a controlled mixer and a working container.

The functional diagram of the installation is shown in figure 3. The electrolyte 1 flows into cell 3, where the generation of hydrogen peroxide upon application of high frequency voltage from the generator 2 to the anode 4 and the cathode 5. The control of the amount of hydrogen released is carried out programmed in accordance with the calibration schedule, the sensor 6 which controls the mixer 7 to which water 9 is supplied. The working solution 10 with a given concentration of hydrogen peroxide enters the container 11. The installation allows for operational control of the amount of hydrogen released. Determination of the amount of hydrogen peroxide in the solution was carried out by iodometry. To quickly determine the numerical value of the amount of hydrogen peroxide in the plasma Plane solution based on the amount of hydrogen released, a calibration graph is used.

![Functional diagram of the installation for obtaining a Plasmolite.](image)

Generator – 2 is a powerful high-frequency generator operating at a frequency of 110 kHz with dynamic control of values of current and voltage to determine the phase of ignition and the stable combustion phase of the high frequency plasma. The microprocessor control and output parameters of the RF generator allows you to optimize the ignition and maintain the burning plasma is stable. Oscillogram of voltage and current during steady burning of a plasma is shown in figure 4.
2.3 Experimental study of the effectiveness of Plasmolite on agricultural plants

The main purpose of experimental research is a quantitative assessment of some indicators of the effectiveness of Plasmolite on the process of growth and development of crop plants. The analysis of the effectiveness of the Plasmolite effect on plants was carried out at the early stages of their development with the help of morphological tests. This took into account:

a) number of sprouted seeds;

b) entry of plants into the next phase of development by the number of plants with the first leaf;

c) root system development;

d) the number of viable plants to a certain.

The obtained results allow to draw the following conclusions about the effectiveness of the use of Plasmolite for the treatment of agricultural plants.

1. Plasmolite solution can be classified as plant growth regulators. Its use in high concentrations partially or completely blocks the growth and development of plants, as noted earlier the use of a solution in lower concentrations, with a dilution of 500 or more times stimulates their growth, that is, the effect of hormesis is observed. The choice of the optimal concentration for a particular type of processing of agricultural plants will significantly increase their yield resistance to negative factors.

2. Activation of plant growth at low concentrations of a solution of Plasmolite retains its activity for a long time, which ensures its use as a finished drug as indoors and in the field. Processing of sowing material in a semi-dry way can also be effective in the field.

3 Conclusion

A plant for producing activated carbon an aqueous solution of the plasma Torch in the combustion of low-temperature plasma of high-frequency electrical discharge uses a fundamentally new method of obtaining activated water solution is relatively simple and unexpensive device. It allows for the activation of an aqueous solution with an oxidation-reduction potential in the range from -1000 mV to +1500 mV with a pH Index of ORP from 7.0 to 8.5. Due to the simplicity and low energy consumption, the use of the installation in some cases is advisable directly in the field. Activated aqueous solution of Plasmolite can be used as a plant growth regulator. The effectiveness of its application, both in the
processing of plants themselves and soils confirm the results of testing on seeds of agricultural plants. The new scientific results obtained as a result of our studies are in good agreement with the data of various scientific studies that have been obtained by other scientists [23-34].

The work was done at the Prokhorov General Physics Institute RAS with partial support of the Research project "Physical methods in agriculture and ecology" (№0024-2019-0004).

References

1. G. Komissarov, *Photosynthesis: physico-chemical approach* (URSS, Moskow, 2003)
2. R. Shin, D. Schachtman, PNAS, 101 8827-8832 (2004)
3. A. Lobanov, N. Rubtsova, Yu. Vedeneeva, G. Komissarov, DAN, 421 773–776 (2008)
4. T. Baranova, V. Kalaev, A. Voronin, Bulletin of the Baltic University, 7 96–102 (2014)
5. V.V. Davydov, N.S. Myazin, Measurement Techniques, 60(5) 491-496 (2017)
6. D. Paskalov, M. Borodkin, V. Sokolov, RF patent 2272787 (2003)
7. V. Pindak, A. Mitrophanov, V. Lagutin, A. Yushkin, RF patent 2203 861 (2005)
8. N. Baburin, S. Belov, Y. Danyleiko, A. Egorov, T. Lebedeva, S. Nefedov, V. Osiko, V. Salyuk, Reports of Academy of Sciences, 426 468-470 (2005)
9. S. Belov, Yu. Danileiko, S. Nefedov, V. Osiko, V. Salyuk, S. Sidorov, Biomedical Engineering, 5 59–63 (2011)
10. V. Rusanov, A. Friedman, G. Sholin, Advances in physical Sciences, 134 2 (1981)
11. A. Simakin, M. Astashev, I. Baimler, O. Uvarov, et al., J. Phys. Chem. B. 123 1869-1880 (2019)
12. M. Piskarev, High Energy Chem. 52 212 (2018)
13. B. Locke, K-Y. Shih, Plasma Sources Sci. Technol. 20 034006 (2011)
14. S. Gudkov, A. Chernikov, V. Bruskov, Rus. J. Gen. Chem. 86 1531–1538 (2016)
15. M. Travers, D. Cowles, J. Ellison, Chemical Physics Letters, 164 449-455 (1989)
16. V. Bruskov, O. Karp, S. Garmash, I. Shtarkman, et. al., Free Radical Research, 46 1280-1290 (2012)
17. J. Van Hemmen, W.J. Meuling, Biochimica et Biophysica Acta, 402 133-141 (1975)
18. O. Nevrova, A. Lobanov, G. Komissarov, Macrotetacycles, 2 264-267 (2009)
19. M. Sharapov, V. Novoselov, N. Penkov, E. Fesenko, et. al., Free Radic. Biol. Med. 134 76-86 (2019)
20. T. Kryston, A. Georgiev, P. Pissis, A. Georgakilas, Mutat Res. 711 193-201 (2011)
21. S. Gudkov, M. Grinberg, V. Sukhov, V. Vodeneev, J. Env. Radioact. 202 8–24 (2019)
22. V. Skulachev, Biochemistry (Mosc), 66 1153-1156 (2001)
23. A.V. Moroz, V.V. Davydov, V.Yu. Rud, Yu.V. Rud, V.C. Shpunt, A.P. Glinushkin, Journal of Physics: Conference Series, 1135(1) 012060 (2018)
24. V.B. Fadeenko, V V Davydov, V Yu Rud’, A P Glinushkin, Yu V Rud’, V Ch Shpunt, Journal of Physics: Conference Series, 917(9) 092015 (2017)
25. I.A. Zharkov, R.V. Davydov, V.A. Lyapisheva, V.Yu. Rud, Yu.V. Rud, A.P. Glinushkin, Journal of Physics: Conference Series, 917(5) 052011 (2017)
26. I.S. Kudryashova, V.Yu. Rud, Yu.V. Rud, V.Ch. Shpunt, A.P. Glinushkin, N.N. Bykova, Journal of Physics: Conference Series, 929(1) 012021 (2017)
27. N. Grebenikova, A. Korshunov, V. Rud, I. Savchenko, M. Marques, MATEC Web of Conference, 245 11006 (2018)
28. R. Davydov, M. Sokolov, W. Hogland, A. Glimushkin, A. Markaryan, MATEC Web of Conference, 245 11003 (2018)
29. J. Stenis, W. Hogland, M. Sokolov, V. Rud, R. Davydov, IOP Conference Series: Materials Science and Engineering, 497(1) 012061 (2019)
30. I.S. Kudryashova, V.Yu. Rud, V.Ch. Shpunt, Yu.V. Rud, A.P. Glinushkin, Journal of Physics: Conference Series, 741(1) 012106 (2016)
31. N.M. Grebenikova, K.J. Smirnov, V.V. Davydov, V.Y. Rud, Journal of Physics: Conference Series, 1124(4) 041011 (2018)
32. I.A. Zharikov, V.Yu. Rud, Yu.V. Rud, E.I. Terukov, V.V. Davydov, N.N. Bykova, Journal of Physics: Conference Series, 1038(1) 012100 (2018)
33. R.V. Davydov, V.Yu. Rud, Yu.V. Rud, E.I. Terukov, Journal of Physics: Conference Series 1124(8) 081039 (2018)
34. V.A. Lyapishev, V.Yu. Rud, M.S. Sokolov, A.V. Cheremisin, Proceedings of the 2018 IEEE International Conference on Electrical Engineering and Photonics, EExPolytech 2018, 8564387 292-294 (2018)