A new method of potenciacion of aqueous media using high-frequency glow discharge plasma

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Abstract. A method of activation of aqueous solutions of strong electrolytes using high-frequency glow discharge plasma in water vapor at atmospheric pressure is considered. An experimental setup for activation of aqueous solutions of NaCl and KCl salts, sodium sulfate Na2SO4, potassium sulfate K2SO4, etc. is presented. Experimental studies were conducted using an activated solution based on potassium sulfate K2SO4, at a concentration of 5.7 × 10⁻² M. The limit values of acidity, redox potential (Eh) and hydrogen peroxide concentration of the prepared activated solution were: pH ≈ 8.3, Eh ≈ 800, H₂O₂ concentration ≈ 5 × 10⁻⁴ mol. %. The effectiveness of the K₂SO₄-based activated aqueous solution was evaluated at test sites of typical crops, such as soybeans and corn. Based on the results obtained, it is concluded that the method of activation of aqueous solutions using high-frequency glow discharge plasma is quite simple, technological and low-cost.

Keywords: method, activation, installation, aqueous solution, hydrogen peroxide, technology, agricultural plants.

1. Introduction

The basis of obtaining biologically active aqueous solutions, then activated water, is the electrochemical effect of various physical factors on poorly concentrated aqueous solutions of electrolytes. Biologically activated water containing hydrogen peroxide is an effective and absolutely environmentally safe plant growth stimulant and activator of plant development phases [1-4]. In the literature it is noted that after treatment of plants with activated water, there was an acceleration of seed germination, an increase in the rate of plant biomass recruitment, an increase in resistance to stress. There is an increase in the resistance of agricultural plants to fungal and bacterial diseases [4, 5]. Ultimately, treatment of crops with activated water increases the yield of agricultural products.

The main industrial methods of treatment of aqueous solutions for the purpose of their activation are electrochemical methods based on the electrolysis process [6]. Other methods of water activation are: mechanical and ultrasonic treatment, treatment with gas-discharge plasma, exposure to ultraviolet radiation and a number of other, non-specific types of exposure [7]. In contrast to conventional activation methods, the article considers a fundamentally new method for producing activated water using low-temperature plasma of high-frequency glow discharge in water vapor [8, 9]. In this case, to
activate the aqueous solution of the electrolyte, a plasma chemical reactor is used, in which the interaction of the plasma with the aqueous solution occurs in the zone of electrical contact. The activation process takes place at the active condensation of water vapor coming from the combustion zone of the plasma. Thus the redox potential of the activated solution can vary from −900 mV to +900 mV depending on the mode of burning plasma and the physical characteristics of the used electrodes. The pH value of activated water is usually in the range of 5.7 – 6.9. By analogy with the known biologically active preparations, activated water obtained with the help of glow discharge plasma can be used in agriculture for processing seeds of foliar watering of plants, as an antibacterial and antiviral agent in the field of keeping farm animals, as well as for routine preventive treatment of premises for keeping farm animals. It should be borne in mind that the water activated in this way is absolutely clean, from the point of view of ecology, biologically active drug.

The purpose of this article is to describe the method of activation of aqueous solutions using high-frequency glow discharge plasma, as well as to evaluate the effectiveness of the drug taking into account the roadmap of product development, starting from the preparation stage to the process of its application directly at the site of use. Thus, consideration of a new method of activation of BP using low-temperature plasma of high-frequency glow discharge is relevant and of practical interest.

2. Methods
The study of an aqueous electrolyte solution exposed to high-frequency glow discharge plasma in an atmosphere of saturated water vapor indicates a change in its physical and chemical characteristics. Preliminary data confirm the biological activity of the aqueous electrolyte solution, which appears after the combustion of high-frequency plasma in it. This fact became the basis for the development of a new method of activation of aqueous solutions.

2.1. Method of activation of aqueous solutions using high-frequency glow discharge plasma
The method of activation of aqueous solutions by means of glow discharge plasma is based on the process of burning of high-frequency plasma in an aqueous solution of a strong electrolyte of low concentration. As the electrolyte component of aqueous solutions can be used dissolved in water salts NaCl and KCl, sodium salt of sulfuric acid Na2SO4, potassium sulfate K2SO4, etc. Burning glow-discharge plasma in a volume of liquid electrolyte is provided with an electric circuit consisting of a high-frequency generator, an active electrode metal, a layer of plasma gas from water vapor, a layer of an aqueous electrolyte solution and a passive electrode, closing an electrical circuit. The ignition of the plasma and its burning is taking place on the metal active electrode in the volume of aqueous electrolyte solution (see Fig.1). The amplitude value of the igniting high-frequency voltage with a frequency of 0.44 MHz is (250-300) V and depends on the size of the active electrode and the frequency of electric current generation. The level of power supplied to the active electrode is selected from the condition of formation of a vapor-gas layer on its surface, completely covering the electrode. The value of this power, used in laboratory conditions, is about 150 Watts.

Figure 1. Plasma on the surface of the active electrode.

The process of activation of aqueous solutions using glow discharge plasma occurs as follows. When a high-frequency current flows in the electrolyte volume, a high-resistance vapor-gas layer is formed
around the electrode. The voltage drop leads to the appearance of a high-frequency glow-type plasma discharge in this layer [8, 10].

As a result of burning of plasma in water vapor occur in the plasma-chemical reaction (1), among which are the reactions of water decomposition according to the mechanism of dissociative adhesion [10]:

\[
\begin{align*}
H_2O &+ e + 4.25 \text{ eV} \rightarrow H^- + \cdot OH \\
H^- + \cdot H &\rightarrow H_2 + e + 3.8 \text{ eV} \\
\cdot OH &+ \cdot OH + M \rightarrow H_2O_2 + M
\end{align*}
\]

(1)

Here M is a molecule (ion) in the gas subsystem of the plasma. As can be seen from the above reactions, hydrogen peroxide is formed as a result of heterogeneous recombination of radicals \(\cdot OH\) with the participation of a molecule or ion M. in this case, one molecule of hydrogen peroxide is synthesized per molecule of the released hydrogen. The General equation (2) is as follows:

\[
2H_2O \rightarrow H_2 + H_2O_2
\]

(2)

In the chain of reactions, hydrogen peroxide \(H_2O_2\) is the main stable oxidant generated in an aqueous electrolyte under the action of a glow discharge plasma in water vapor and in contact with a solution [11]. Hydrogen peroxide \(H_2O_2\) is the main stable oxidant generated in aqueous electrolyte solutions under the action of plasma. As can be seen from the above reactions hydrogen peroxide is formed as a result of dimerization of radicals \(\cdot OH\) in an amount proportional to the amount of electricity passed. In addition to hydrogen peroxide in an aqueous solution under the action of high-frequency plasma, hydrogen, active oxygen and other active components can be formed due to the complete collapse of water molecules, as well as metal ions formed in the process of electrochemical erosion of electrodes [12]. Due to the formation of hydrogen and active oxygen during the accumulation of peroxide in solution, its decomposition reactions occur simultaneously, which eventually leads to the establishment of a stationary concentration of \(H_2O_2\). The amount of peroxide formed in solution by passing a certain amount of electricity can be estimated by the amount of hydrogen released. Taking into account the competing processes of peroxide generation and decomposition, it is advisable to use aqueous solutions of sodium sulfate or potassium sulfate salts containing acid residues of sulfuric acid as an electrolyte. 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.

### 2.2 Installation for activated water production

With the purpose of realization of the considered method of activation of aqueous solutions experimental setup was developed, which is a plasma-chemical reactor where activation occurs in the area of electrical contact plasma glow discharge with aqueous electrolyte. The functional diagram of the installation is shown in figure 2.

Plasma generation took place on an active electrode made of nichrome wire with a diameter of 0.4 mm immersed in the electrolyte volume. As a passive electrode, a plate of pyrolytic graphite of the PGI-1 brand was used. The electrodes were connected to a high-frequency generator with an operating frequency of 440 kHz and the shape of the output voltage close to the sine wave. The amplitude of the output voltage was regulated within \((250 – 450)\) V. The operating modes of the unit were chosen for the case of using an aqueous solution of \(K_2SO_4\) in a concentration of \(5.7 \cdot 10^2\) M as an electrolyte, or an aqueous solution of \(NaCl\) in a concentration of \(0.17\) M. The Solution was preheated to a temperature \((40 – 50)^\circ C\). The Peculiarity of igniting a plasma discharge in the electrolyte volume is that at the initial moment a high (3 - 4 times higher than the operating mode) short-term power of the generator is needed. Its value was determined by the conductivity of the electrolyte solution and the size of the active electrode. After the occurrence of a steady plasma discharge, the magnitude of the current in the circuit of the active electrode were automatically set so as to ensure stable burning of the plasma. Normal combustion plasma were recorded the nature of the current-voltage characteristics in which the current value fell a few times, and then stabilized at this level.
Figure 2. Functional diagram of the installation for obtaining activated water.
1-control unit; 2-hydrogen sensor; 3-working cell; 4-mixer; 5-accumulator of water; 6-container for activated water solution; 7-plasma chemical reactor; 8-high-frequency generator.

3. The results of the experimental study of the method for obtaining activated aqueous solutions using glow discharge plasma can be taken as a basis for evaluating the effectiveness of this method. In particular, having a solution volume of 200 ml was carried out for 2-3 hours at RMS value current level 2-3 A. thus the characteristic length of the combustion region of the plasma column was 40-50 mm. After receiving the solution, the latter is allowed to stand for one day and filtered. The pH of the fresh solution was about 8.3 The redox potential was of the order of 800 mV (measured by the device РНТ-028). The concentration of hydrogen peroxide was of the order \((10^{-3} – 10^{-4})\) mol. %. Assuming that the degree of activation of the aqueous solution is proportional to the concentration of peroxide, the concentration level of \(\text{H}_2\text{O}_2\) peroxide was carried out using the method chemiluminescence [13].

2.3 Experimental studies of the effect of activated water on agricultural plants

The main objective of experimental studies is to quantify the effectiveness of the action of activated water on the growth and development of agricultural plants. The analysis of the effectiveness of the effect of activated water on plants was carried out at the early stages of their development using morphological tests. This takes into account:

a) number of germinated seeds;
b) the entry of plants into the next phase of development by the number of plants with the first leaf;
c) development of the root system;
d) the number of viable plants by a certain time of the experiment.

To assess the effectiveness of the activated aqueous solution (hereinafter PAS) on the process of growth and development of agricultural plants, experiments were conducted on germination of seeds of cereals and legumes. PAS based on potassium sulfate \(\text{K}_2\text{SO}_4\) was used as the study drug. During the experiment, the treatment of seeds planted in the soil was carried out by watering them with a solution of PAS with different degrees of dilution. The analysis of indicators of efficiency of action at different dilutions was carried out at early stages of development of plants.

| Breeding options, % | Soy  | Corn  |
|---------------------|------|-------|
| Control             | 85.6 ± 0.1 | 95.5 ± 0.1 |
| 0.0075              | 90.0 ± 0.1 | 98.5 ± 0.1 |
| 0.005               | 87.2 ± 0.1 | 94.5 ± 0.1 |
| 0.05                | 86.0 ± 0.1 | 96.0 ± 0.1 |

4. The experiment used soybean seeds (grade "selekt-102") and corn (grade "Uzbekistan-601"). Seeds were treated with an aqueous solution of PAS in breeding variants: 0.0075%, 0.005%, 0.05% and tap water was used as a control. Germination was determined in accordance with GOST 12038-84 “Seeds
of agricultural crops". Methods for determining germination" on filter paper. The results obtained on seed germination are given in Table 1.

From the data given in Table 1, it can be seen that the best effect on germination was shown by seeds treated with PAS at a concentration of 0.0075%, which were ahead of the control for soybeans by 4.4%, corn by 3.0%.

During the research, an experiment was conducted on the effect of PAS on the growth of seedlings, including the above-ground and underground parts. A photo of corn seedlings 7 days after planting, treated with PAS of different concentrations, is shown in Fig. 3a. In Fig. 3b shows the seedlings of corn seeds after 10 days: untreated (control, left) and treated PAS with a concentration of 0.0075% (right).

![Figure 3. Effect of PAS solution on corn seedlings.](image)

The effect of the degree of dilution of PAS on the growth and development of corn and soybean seedlings is shown in table 2. Underground part Overhead.

| Breeding options, Concentration | Corn seedlings growth, cm | Soybean seedlings growth, cm |
|--------------------------------|---------------------------|-------------------------------|
|                                | Underground part          | Overhead part                 | Underground part | Overhead part |
| Control                        | 14.7 ± 0.2                | 10.7 ± 0.2                    | 10.0 ± 0.2       | 8.0 ± 0.2     |
| 0.0075                         | 17.3 ± 0.2                | 12.9 ± 0.2                    | 12.1 ± 0.2       | 10.6 ± 0.2    |
| 0.005                          | 15.5 ± 0.2                | 12.0 ± 0.2                    | 10.4 ± 0.2       | 8.6 ± 0.2     |
| 0.05                           | 12.7 ± 0.2                | 13.2 ± 0.2                    | 10.7 ± 0.2       | 8.0 ± 0.2     |

Seeds, which were treated with an activated solution based on K_2 SO_4 with varying degrees of concentration, mainly exceeded the growth of seedlings of the control group. Soybean seeds treated with PAS solution with a concentration of 0.0075% were 2.6 cm ahead of control on seedlings and 4.8 cm ahead of corn seedlings. At the same time, the concentration PAS solution equal to 0.0075% is optimal. Treatment of soybean and corn seeds with PAS solution of optimal concentration allows to increase their germination rate by 2.0% - 3.0%. The obtained results allow to draw the following preliminary Plasma activated water solution can be attributed to the category of plant growth regulators. Its use in high concentrations partially or completely blocks the growth of plants. The use of the solution in lower concentrations, with dilution of more than 500 times stimulates their growth. The optimal concentration of PAS for each type of technological processing of agricultural plants allows to increase productivity and their resistance to negative factors.
Evaluation of the effectiveness of the use of activated aqueous solutions based on salts of NaCl, KCl, sodium salt of sulfuric acid Na2SO4 and other water-soluble compounds requires additional experimental studies.

3. Conclusion
The method of activation of aqueous solutions using high-frequency glow discharge plasma is quite simple, technological, low-cost and, in this regard, is of practical interest. As the electrolyte component of aqueous solutions can be used dissolved in water salts NaCl and KCl, sodium salt of sulfuric acid Na2SO4, potassium sulfate K2SO4, etc., which in low concentrations can form a nutrient medium. The unit for producing activated aqueous solution with the help of low-temperature plasma of high-frequency discharge of glow type implements a fundamentally new method for producing activated aqueous solution and is a relatively simple and inexpensive device. It allows the activation of an aqueous solution with redox potential in the range from −1000 mV to +1500 mV with a pH of 7.0 to 8.5. Due to its simplicity and low energy consumption, the high-frequency plasma reactor can be used directly in agricultural facilities. Obtaining RAS directly at the site of use eliminates the cost of storage and transportation and thus reduces the cost of the drug used.

Plasma-activated aqueous solution based on soluble salts of NaCl, KCl, sodium sulfate Na2SO4, potassium sulfate K2SO4, etc. can be used as a plant growth regulator. The effectiveness of its application, both in the treatment of plants themselves and soils is confirmed by the results of testing on seeds of agricultural plants.

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