Activation of aqueous solutions by high-frequency glow discharge plasma in water vapor to stimulate growth and control diseases of agricultural plants

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Abstract. The results of an experimental study of the activation of weak aqueous solutions of a strong electrolyte with a low-temperature glow discharge plasma are presented. A method for producing an activated aqueous solution based on 0.9% NaCl solution in a glow discharge plasma at atmospheric pressure is presented. The main characteristics of the activated aqueous solution, including the Raman spectrum at a wavelength $\lambda = 514.53$ nm, are shown. The results of experiments on the test objects give an assessment of the effectiveness of the effect of the obtained activated aqueous solution on various crops. In particular, experimental confirmation of the possibility of using this activated solution as a plant growth regulator was obtained.

1 Introduction

Increasing the production of agricultural products, improving the quality and reducing the cost of its production is an important task to ensure food security of any state. The solution to this problem is impossible without the introduction of technologies that increase productivity, increase the volume of agricultural production and reduce its cost. To date, various methods of chemical or biological treatment of agricultural plants are traditionally used in agricultural technological processes, the use of which is associated with negative side effects that ultimately affect human health [1]. These circumstances make it necessary to use more efficient and environmentally friendly agricultural technologies, among which the most promising are technologies based on the dosed effect of physical factors on crops [2]. The result of the impact of physical factors in different combinations can be manifested

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in the stimulation of development processes, such as crops, and in the suppression of pathogenic and opportunistic microorganisms, pathogens and pests [3].

One of the promising directions in the creation of such technologies is the use of biologically active water or aqueous electrolyte solutions obtained by means of low-temperature plasma of high-frequency glow discharge. Burning high-frequency glow discharge in water vapor on the surface or in the liquid volume causes activation of aqueous electrolyte solutions by increasing their redox potential and enrichment of pure (unstabilized) hydrogen peroxide. Hydrogen peroxide at high concentrations causes damage to biological macromolecules [4], but at low concentrations it can cause activation of growth processes and give resistance to negative external conditions [5]. In particular, treatment of plant seeds with water solutions activated by low-temperature plasma is close in nature to the impulse effect of concentrated sunlight [6,7]. Seeds after processing have a greater energy potential, they occur structural and functional restructuring of membrane formations and macromolecules, resulting in a wide range of biological changes in plants. In General, semenah processes similar to hormesis [8]. In favor of this is evidenced by the fact that one of the main effects of the biochemical effects of activated aqueous solution is the generation of plant seeds induced free radicals that affect the enzymatic properties of seeds. At the same time in the treated plants there is an increase in the content of chlorophyll, which causes an increase in the intensity of photosynthesis [9]. For this reason, activated aqueous solutions containing an optimal concentration of pure hydrogen peroxide are an effective and absolutely environmentally safe stimulant of plant growth and development [10]. At the test sites it was found that after treatment of plants with activated water, there was an acceleration of seed germination, as well as an increase in the speed of plant biomass recruitment. The aim of this work was to study the possibility of using plasma-activated high-frequency glow discharge aqueous solutions to stimulate growth and combat diseases of agricultural plants.

2 Materials and methods

2.1 The subject of the study

During the experimental study of the activation of weak aqueous solutions of a strong electrolyte with a low-temperature glow discharge plasma, taking into account the performance of the installation, the following were optimized:
- electrical parameters of plasma excitation;
- the shape and dimensions of the electrodes;
- the chemical composition of the electrode material.

Activated aqueous solution resulting from the combustion of low-temperature plasma of high-frequency electric discharge, then Plasmolite (Plazmolite) can be used in various sectors of the economy where traditionally used activated water in agriculture for seed treatment and for foliar watering plants as antibacterial agents in animal husbandry, food industry etc.

2.2 Method of obtaining Plasmolite

Various methods and devices for producing activated water using electrochemical methods are known [11]. Typically, water is activated in diaphragm electrolyzers with separate output of acidic and alkaline water Known apparatus for producing activated water (acidic and alkaline), containing a generator of radio frequency plasma for exposure to radio waves to processed water [12, 13]. In this case, production of activated aqueous solution of
Plasmolyte is a fundamentally different way compared to traditional methods of producing activated water, and substantially different in their properties. In particular, the redox potential may reach the magnitude of -1000 mV to +1500 mV at the time of synthesizing Plasmolite. A method of producing Plasmolite using low-temperature plasma of high-frequency electrical discharges of the glow type, developed in General physics Institute. A. M. Prokhorov, RAS [14, 15].

Plasma generation was carried out using two types of "hot" electrodes.

1. Loop platinum electrode was immersed in 0.9 % sodium chloride solution in distilled water. The diameter of the electrode wire was 0.25 mm, the depth of immersion of the electrode in the solution was 20 mm. The electrode was supplied from the RF generator voltage with the parameters: the repetition frequency of 110 kHz and the amplitude up to 300 V.

2. Needle electrodes of stainless steel with wire diameter of 0.3 and 0.5 mm were also immersed in 0.9 % sodium chloride solution in distilled water to a depth of 25 – 30 mm. The electrodes were supplied from the RF generator voltage with the parameters: the repetition rate of 110 kHz and amplitude up to 370 V.

To maintain a uniform temperature in the container with the electrolyte, its mixing was carried out using a magnetic stirrer. The electrolyte temperature was controlled and maintained at (50-55ºC) by forced air cooling.

2.3 The Scheme of obtaining Plasmolite

Glow discharge is an effective tool for initiating a number of chemical reactions in the liquid phase. Direct decomposition of water vapor in high-frequency discharge plasma with formation of H$_2$O$_2$ peroxide and release of free hydrogen according to the scheme:

\[
H_2O_2 \rightarrow H_2 + \frac{1}{2}O_2 \quad \Delta Q \approx 2.6 \text{ eV} \quad (1)
\]

it can occur due to intensive direct excitation of high-energy electron-vibrational States. However, the highest efficiency in the decomposition of water should be expected at a temperature (energy) of the electron gas insufficient for direct excitation of the electron-vibrational States. Energy is more advantageous process of decomposition of water molecules due to the dissociative adhesion of a free electron in the plasma to form a negatively charged H$_2$O– ion. This mechanism of decomposition of water molecules prevails at an electron gas temperature above (1.5 – 3.5) eV [14]. In the first case, there is a reaction:

\[
H^* + H_2O^* \rightarrow H_2 + *OH \quad *OH + H_2O^* \rightarrow H_2O_2 + H^* \quad (2)
\]

and in the second:

\[
e + H_2O \rightarrow H^* + *OH \quad H^* + e \rightarrow H^* + 2e \quad *OH + *OH \rightarrow H_2O_2 \quad (3)
\]

The second reaction, which occurs under the action of electronic shock, provides a chain process of dissociative adhesion reaction, increasing its efficiency [16]. For both reactions, the final products are free hydrogen and hydrogen peroxide dissolved in an aqueous electrolyte (0.9 % NaCl solution), in which one molecule of the released hydrogen is synthesized by one peroxide molecule. In the experimental setup, by selecting the amplitude of the supply high-frequency voltage in the range of 250-380 V and the frequency of 110 kHz, the process of hydrogen peroxide generation was carried out mainly due to the reaction of the dissociative adhesion of the free electron to the water molecule. In General, such radical and redox reactions are observed under the influence of other physical
factors, namely ionizing radiation [17], ultraviolet radiation [18], pulsed laser radiation [19], EMI kWh [20], but the most economically feasible is the method proposed in this article.

The level of activation of the produced solution Plasmolite was estimated according to the concentration of dissolved hydrogen peroxide. The initial $\text{H}_2\text{O}_2$ content was between 60 and 100 μm. The change in the level of activation of a solution of Plasmolyte during storage were recorded at concentrations of hydrogen peroxide using the method of iodometry. Analysis of the dynamics of changes in the concentration of peroxide in the resulting solution for several days showed that the change in the amount of $\text{H}_2\text{O}_2$ in the direction of reduction begins after 5 days of storage.

The resulting solution of Plasmolyte also been studied by Raman (red). For excitation spectra, we used the line 514.53 nm radiation of an argon laser. The scattering spectra obtained on the U1000 spectrometer are shown in Fig.1. The spectrum shows well-known Raman scattering lines: $1640 \, \text{cm}^{-1}$ and $2800 + 3800 \, \text{cm}^{-1}$. The band in the region of $2800 + 3800 \, \text{cm}^{-1}$ is due to the vibrations of hydrogen atoms along the O-H bond. A strip with a maximum at $1640 \, \text{cm}^{-1}$ is associated with vibrations of hydrogen atoms relative to each other (the angle of 104.5° changes). With a further increase in the recording time of the spectrum (black upper curve, Fig.1) there are four new bands: $875 \, \text{cm}^{-1}$, $930 \, \text{cm}^{-1}$, $1050 \, \text{cm}^{-1}$ and $1123 \, \text{cm}^{-1}$, uniquely associated with the plasma treatment of an aqueous electrolyte solution.

2.4 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 efficiency of Plasmolyte on the process of growth and development of crop plants. Analysis of the effectiveness of Plasmolyte on plants was carried out at the early stages of their development with the help of morphological tests.

Test objects for determining the effectiveness of Plasmolite on plants was significant agricultural plants, representing different families, which is essential in determining the
possible flexibility of use of the drug, including: 1. Cucumber variety "Competitor" and "far Eastern"; 3. Radish variety 18 days; 5. Safflower variety "Zavolzhsky"; 6. The Asteraceae family, the sort of "Thompson"; 7. Tuber cuttings of potatoes sort of Luck; 8. Family nightshade, tomatoes "Aurora"; 9. The representative of the shrub — Japanese Quince.

The level of activation of a solution of Plasmolite was monitored for 6 days at concentration of peroxide using the method of iodometry. The solution was stored in the dark at a temperature of +20°C. The concentration of peroxide in the solution is shown in table.1.

Table 1. The dependence of the concentration of H2O2 in solution Plasmalite from time to time.

| Density | H2O2 mole/liter |
|---------|-----------------|
| 1 day   | 6 ×10^{-5}      |
| 3 day   | 6 ×10^{-5}      |
| 6 day   | 3 ×10^{-5}      |

Example 1 Cucumber seeds of the "far Eastern" variety were soaked in Petri dishes. Cups with seeds were placed in a thermostat at a temperature of +20 °C. On the third day the number of sprouted seeds was determined. Test data are shown in table. 2.

Table 2. Dependence of seed germination on the concentration of the moisturizing solution.

| Option     | The Number of germinated seeds % | Dampening solution |
|------------|----------------------------------|--------------------|
| Control    | 60                               | Distilled water    |
| Experiment 1 | 95                             | Plasmalite (1:100) |
|             | No                               | Plasmalite (1:100) |
|           | Plasmalite (1:100) on the basis of NaCl |
| Experiment 2 | 90                             | Plasmalite (1:100) |
|             | No                               | Plasmalite (1:1)   |
|           | Plasmalite (1:1) on the basis of NaCl |

Example 2 Seeds of cucumber cultivar "Competitor" were placed in Petri dishes, moistened in the distilled water control, in the experiment 1 and 2 solutions Plasmolite. Experience 1 dilution 1:10, 2 experience a dilution of 1:100. After incubation of seeds in a thermostat at a temperature of 20 °C in 48 hours, the number of sprouted seeds was taken into account. And after 72 hours, take into account the number of seeds with a root length of 8-9 mm. test Data is given in table.3.

Table 3. The dependence of the root system development on the concentration of the moisturizing solution.

| Option     | The Number of germinated seeds % | Dampening solution |
|------------|----------------------------------|--------------------|
| Control    | 60                               | Distilled water    |
| Experiment 1 | 95                             | Plasmalite (1:100) |
|             | No                               | Plasmalite (1:1)   |
|           | Plasmalite (1:1) on the basis of NaCl |
| Experiment 2 | 90                             | Plasmalite (1:100) |
|             | No                               | Plasmalite (1:1)   |
|           | Plasmalite (1:1) on the basis of NaCl |

Example 3 The seeds of radish cultivar "18 days" preset for 20 hours moistened in the distilled water control, in the experience of solutions of Plasmolite. Experiment 1 – dilution 1:10, experience 2 – the dilution of 1:100. Then the seeds were planted in cultural vessels with sand, which was once moistened in the control of distilled water, in experiments 1 and 2 with water of corresponding dilution. Plants were grown in a culture Cabinet with a lighting rhythm of 12-12. On the 6-th day of the experiment, the number of surviving plants
with an open cotyledon leaf was taken into account. Such plants were: - in control 15%; - in experiment 1 – 20%; - in experience 2 – 65%.

**Example 4** Safflower (the sort of “Zavolzhskoye”) seeds soaked for 4 hours in control – distilled water, in the experiment with a solution of Plasmolite (dilution 1:100). Further, the moistened seeds were planted in cultural vessels with sand. The sand is moistened in control – distilled water, in experience - solution Plasmolite (dilution 1:100) in the same volume. The plants were growing up in luminette (rhythm lighting 12:12) took into account the number of plants from the first open leaf. In the control was 16%, in the experience – 40%. On the seventh day, the height of the above-ground part of the plants was measured. The average plant height in the control is 4.5 cm, in the experiment 6.5 cm.

**Example 5** Of sprouted potato tubers were cut tuber cuttings. After two days of drying they were planted in cultural vessels with sand. The sand is moistened in control – distilled water, in the experiment with a solution of Plasmolite (dilution 1:100). After eight days, the number of viable cuttings and the degree of root system formation were estimated. 10% of cuttings died in the control, 100% survived in the experiment. The root system in the experiment was more developed. Intensively green in the experiment was 30% of cuttings, in the control – no more than 10%.

**Example 6** The seeds of Japanese Quince were washed with water for 24 hours then seeds were divided into a control that continued to germinate in water, experienced that germinated in a solution of Plasmolite (dilution 1:100). To interrupt the rest period, stratification of seeds was carried out in a thermostat with a temperature of +40°C. After 20 days of incubation, the number of accumulated seeds was recorded. In the experiment, they were 15%, in the control of only 4% of the accumulated seeds.

2.5 Analysis of results

Analysis of the effectiveness of the impact of Plasmolite plants were in the early stages of their development using 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 by a certain time of the experiment.

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. The use of the solution in lower concentrations, with dilution of 100 or more times stimulates their growth. 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. When using activated aqueous solutions based on sodium chloride and potassium chloride salts, there were no noticeable differences in the degree of impact on plants when used as a growth regulator.

3 Conclusion

The use of low-temperature plasma of high-frequency glow discharge in water vapor to activate aqueous solutions of strong electrolytes is an effective and environmentally
friendly method not only for pre-sowing preparation of seeds, but also at different stages of development of agricultural plants. Activated aqueous solution resulting from the combustion of low-temperature plasma of high-frequency electric discharge, can be considered as a plant growth regulator. At the same time, the efficiency of its application both in the processing of plants and soils is shown. Such treatment is the most gentle method that preserves the viability of the microflora of plants and the soil itself.

A method of obtaining activated water solution as a result of the combustion of low-temperature plasma of high-frequency electric discharge is fundamentally new compared with traditional ways of obtaining activated water solution, and substantially different in their properties. In particular, the redox potential can have a value of -1000 mV to +1500 mV at the time of synthesis of the Plasmolite. In addition, this method is not expensive, technological and low-cost. So, for example, to obtain 100 g. the activated solution within 30 minutes will require a power source of no more than 150 watts. For this reason, obtaining an activated solution using a low-temperature plasma is economically advantageous directly at the place of its application. It is enough just to have access to a conventional source of electricity.

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 [21-32].

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