MECHANISM OF PHYSICO-CHEMICAL-BIOLOGICAL PROCESSES OCCURRING IN MATERIALS AS A RESULT OF IMPACT ON THEM OF VARIOUS TYPES OF HIGH-VOLTAGE GAS DISCHARGES

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The impact of an electric field, various types of high-voltage gas discharges and the use of ozone in the purification and disinfection of drinking, technical, industrial waste and irrigation water, other food products, including seeds of grain plants and cotton from various harmful viruses and bacteria has entered the sphere of interests of researchers in solving environmental problems. The work provides brief information on the physicochemical-biological mechanisms of the processes occurring in materials as a result of the impact of an electric field, various types of high-voltage gas discharges and the use of ozone, studied by various scientists.

Keywords: environment, environmental problem, ozone, pulsed barrier discharge, electric discharge plasma, electrical stimulation, oxidation reactions, aromatic ring opening, non-toxic end products, disinfection, cleaning.

I. Introduction

The development of industrial production, emissions of harmful gases into the atmosphere, discharge of industrial wastewater onto land and water bodies, factors of increasing population on earth cause a number of negative changes in the environment, create disturbances in the ecosystem, and have a negative impact on flora and fauna.

The high degree of pollution of surface and groundwater and growing requirements for water quality create a significant need for water treatment systems that would be effective, easy to operate and would not ultimately lead to environmental pollution due to the use of toxic chemicals [1]. In the second half of the twentieth century, significant advances were made in the field of high-voltage pulse technology, which laid the foundation for a new direction in the science of high-voltage electrophysics and the development of a number of technologies called electric pulse or electric discharge.

Electric discharge technologies are based on the transformation of low-temperature and nonequilibrium discharge plasma in gases, liquid and solid dielectrics or semiconducting materials into the energy of phase transitions, chemical reactions, mechanical work, etc. Their fundamental difference lies in the possibility of targeting a substance with a high energy density in a pulsed mode. This ensures high rates of change in physical and thermodynamic parameters in the processed substance. The impact on the substance being processed in electric discharge technologies is multifactorial: powerful electromagnetic radiation (from UV to radio range), electric fields changing at a speed of up to 1010...1011 V/ms, charged particles and high-energy atoms, shock and acoustic waves. As a rule, due to disequilibrium, the effect is synergistic, i.e. the interaction energy is greater than the sum of the contributions of individual factors.

It should be noted that the effects of an electric field, various types of high-voltage gas discharges and the use of ozone in the purification and disinfection of drinking, technical, industrial waste and irrigation waters, other food products, including grain seeds from various harmful viruses and bacteria have become the area of interest of researchers in solving environmental problems [2-5]. In the research conducted in these areas, there is not enough work to determine the physical, chemical, and biological mechanisms of the processes occurring in materials as a result of exposure of materials to an electric field, various types of high-voltage gas discharges, and the use of ozone. Carrying out applied work in this direction and continuing scientific research highlights the importance of performing optimization processes that ensure increased efficiency of methods.

II. Among environmentally friendly water treatment technologies, ozonation has become widespread.

Ozonation is one of the most progressive modern technological processes aimed at creating environmentally friendly, favorable working conditions and human life. Ozone is formed from ordinary oxygen under the influence of glow, barrier electrical discharge or ultraviolet radiation. Ozone, being one of the strongest oxidizing agents, has a very high electron affinity (1.9 eV), which determines its properties as a strong oxidizing agent, second only to fluorine in this regard. Despite the high oxidation potential of ozone, it interacts extremely selectively. The reason for this selectivity is the polar structure of the ozone molecule, or more precisely, the positively polarized oxygen atom, which gives the entire molecule an electrophilic character. Therefore, molecules with high electron density are the most preferred reactive elements.

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Ozonation has a number of disadvantages, the main one being inefficient use of energy. Ozone synthesis in an electrical discharge is a reversible reaction, with a significant part of the energy lost to maintain the equilibrium between ozone and oxygen. Due to the low solubility of ozone in water, installations are needed that increase the contact time of ozone with water, the dimensions of which can be quite significant. The system is further complicated by the need to dry the air supplied to the ozonizer. Ozone decomposes in water to form a strong oxidizing agent - hydroxyl radical (OH), which, unlike molecular ozone, is capable of destroying many toxic organic compounds. However, two molecules of ozone are required to produce one OH radical. Some OH radicals recombine and react with ions of mineral impurities. Short-lived particles are also formed in the electrical discharge zone: free radicals, ions and electrons, many of which can play an important role in water purification processes, however, due to the short lifetime, most of them are uselessly lost and do not leave the discharge zone. Ozone only partially stores and delivers the energy of these particles to the water. To reduce energy costs, it is desirable to ensure the generation of active particles in the treated water, which can be achieved in the case of direct contact of water and electric discharge plasma. The initial stage of research in this direction involves the use of pulsed discharges in water. These studies continue to this day. It has been shown that a discharge in water causes disinfection and decomposition of dissolved organic compounds [5-9], and both drinking and waste water can be purified. The main disadvantage of the method is the rather low efficiency of energy use.

The process of chemical oxidation of pollutants in soils is based on the release of electrons from the outer unstable layer of the electronic shell of atoms of substances and elements, which leads to the transition of the pollutant into a less toxic and reactive form. Atoms of elements that have a small number of electrons in their outer electron layer are prone to losing electrons. The process is an integral part of the redox interaction between a pollutant and a chemical or reactive surface. Chlorine, oxygen, ozone and atmospheric air are used as reagents that create redox conditions and free electrons in the pore solution of soils and soils [6-18]. Oxidation with oxygen and air is used primarily for cleaning soils, natural and man-made soils of heterogeneous permeability or low permeability. This method can reduce the initial contaminant content to 3% (<200 ppm).

During ozonation, unlike chlorination, oxidation reactions occur such as the opening of the aromatic ring and the production of non-toxic end products. These products are easily removed by filtration. With metals, ozone forms non-reactive oxides (oxide of iron, manganese, aluminum, etc.). Oxides precipitate and are easily removed by filtration. Organic substances containing iron and manganese are first destroyed by ozone, and then the metals form oxides [6,10]. Ozone easily oxidizes iron and manganese salts to form insoluble substances, which can then be removed mechanically. If iron and manganese are contained in the form of organic compounds or colloidal particles (with sizes of 0.1-0.01 microns), then deferrization and demanganization of water by traditional methods are ineffective. In this case, it is necessary to pre-oxidize complex organic compounds with ozone, leading to their breakdown, after which it becomes possible to remove iron and manganese using one of the usual methods. By oxidizing complex compounds, ozone converts soluble salts into insoluble ones, which are subsequently easily removed.

Ozone - oxidizes almost all metals (with the exception of gold, platinum and iridium) to their highest oxidation states, many non-metals. The reaction product is mainly oxygen.

$$2Cu^{2+} + 2H_2O^+ + O_3 \rightarrow 2Cu^{3+} + 3H_2O + O_2$$

Ozone reacts with sulfides to form sulfates:

$$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$$

Oxidation of lead oxide hydrate by ozone:

$$Pb(OH)_2 + O_3 \rightarrow PbO(OH)_2 + O_2.$$

Oxidation of silver with ozone.

$$4Ag + 2O_3 \rightarrow 2Ag_2O + 2O_2.$$

Treatment of a solution of calcium in ammonia with ozone results in the formation of ammonium ozonide, not calcium:

$$3Ca + 10NH_3 + 7O_3 \rightarrow Ca \cdot 6\,NH_3 + Ca(OH)_2 + Ca(NO_3)_2 + 2NH_4O_3 + 3\,O_2 + 2H_2O$$

Ozone can be used to remove manganese from water to form a precipitate that can be separated by filtration:

$$2Mn^{2+} + 2O_3 + 4H_2O \rightarrow 2MnO(OH)_2\downarrow + 2O_2 + 4H^+$$

When a spark discharge occurs in water, radiation, shock waves, cavitation, electrolysis phenomena and local heating occur. In this case, only part of the energy expended is effective in removing target contaminants. For example, disinfection occurs mainly due to ultraviolet radiation (70...90%), the contribution of shock waves is 20...40%, and other phenomena accompanying the discharge are practically useless. The works also show that the disinfecting effect is almost entirely due to UV radiation. Thus, most of the energy of the spark discharge in water is spent uselessly - the method is not able to compete with ozonation [19-21].

III. Formation of active oxidizers and synthesis of hydrogen peroxide in electric discharge plasma

In the area of electric discharge near the surface of the liquid, at currents of the order of 20-30 mA, water evaporates, and the characteristics of the electric discharge radiation correspond to the spectral system of emission bands of the dissociation products of water molecules in the range of 304-316 nm. Plasma discharges generate chemically active particles that have a high oxidizing ability (hydrogen peroxide (H2O2), atomic oxygen (O•), hydroxyl radical (HO•), hydroperoxide radical (HO2•), ozone (O3) [22-25]. Oxidation potentials of active particles generated in electric discharge plasma.

Active particles generated in electric discharge plasma	Oxidation potential, (mV)
Hydroxyl radical	2,56
Ozone	2,07
Atomic oxygen	1,78
Hydrogen peroxide	1,77
Oxygen	1,23

Below are diagrams of the main processes characteristic of the electric-discharge plasma-water system:

$H_2O \rightarrow OH\cdot + H\cdot$

$2H_2O \rightarrow H_3O + + OH\cdot + eaq –$

$H \cdot + O_2 \rightarrow HO_2 \cdot$

$H \cdot + H_2O_2 \rightarrow H_2O + OH\cdot$

$eaq - + OH\cdot \rightarrow OH-$

$eaq - + H\cdot + H_2O \rightarrow OH- + H_2$

$eaq - + H_2O_2 \rightarrow OH\cdot + OH-$

$H \cdot + OH\cdot \rightarrow H_2O$

$OH\cdot + OH\cdot \rightarrow H_2O_2$

$HO_2 \cdot + HO_2 \cdot \rightarrow H_2O_2 + O_2$

$H \cdot + HO_2 \cdot \rightarrow H_2O_2$

$H \cdot + H\cdot \rightarrow H2$

$HO_2 \cdot + OH\cdot \rightarrow H_2O + O_2$

$H_3O + + OH- \rightarrow 2H_2O$

$OH\cdot + H_2O_2 \rightarrow H_2O + HO_2 \cdot$

In recent years, a number of studies have been carried out on pulsed barrier discharge (PBD) in gas with a voltage pulse duration of 50...300 ns. Such a discharge turned out to be an effective way to generate OH radicals in air containing water vapor [23]: e– +H2O→e– +H+OH (1) O(1 D)+H2O→2OH (2) The data from these studies allow us to conclude that IBR is a promising method for the oxidation of organic and inorganic pollutants in air and aerosols. The concentration of OH radicals in the discharge zone can significantly exceed the concentration of ozone. Increased gas humidity hinders the formation of ozone and accelerates the formation of OH radicals. The lifetime of OH radicals in air is several hundred microseconds [24,25]. The OH concentration after the discharge is 1014...1015 cm–3. The maximum concentration is achieved 30...50 μs after the end of the voltage pulse, which makes it possible to transfer radicals from the gas phase into water with subsequent oxidation of contaminants dissolved in water.

Thus, the electrical parameters of a pulsed barrier discharge in a water-air flow differ from the characteristics of a discharge in air. In a water-air environment, an increase in active power and a decrease in the discharge ignition voltage are observed. The energy yield of nitrateions in IBR is 0.6...0.8 g/kW. h. As the voltage applied to the electrodes increases, the yield of nitrogen-containing products increases, which is most likely caused by an increase in the temperature and concentration of excited particles in the microdischarge channels.

Studies of the emission spectra of the discharge show that a discharge in a water-air environment is a source of hydroxyl radicals (OH). The high oxidation potential of OH radicals makes electric discharge treatment a promising direction, provided that a significant part of the radicals is transferred from the gas phase into the treated water. A discharge in a water-air medium ignites predominantly near the water-air interface. It is this type of discharge that is most preferable for the effective use of active particles.

The action of pulsed electric discharges causes the formation of defects in the cell membrane of bacteria, which allows highly active oxidants to freely penetrate into the internal environment of cells and disrupt their metabolic processes. This principle is used to inactivate microorganisms. The cell membrane acts as a semi-permeable barrier and controls the passage of nutrients into the cell, as well as the removal of waste products. A study of electrical pulse inactivation showed that to achieve a reduction in the number of yeast cultures of Saccharomyces 35 cerevisiae in food liquid media, less than 10% of electrical energy is required than for heat treatment.Cells die as a result of breakdown of cell membranes that protect bacteria from the external environment. For example, compared to ultrafiltration, electric pulse technology in the pasteurization of liquid food products shows a more effective bacteriostatic effect. The impact of pulsed electrical discharges on bacterial flora is caused by the generation of chemically active short-lived compounds, including ozone, hydrogen peroxide, hydroxyl and hydroperoxide radicals, UV radiation, acoustic and shock waves. In studies devoted to the processing of food products with electric discharge plasma, a fundamentally different design of plasma-chemical reactors is used, using a high-voltage generator (6) with the following parameters: voltage pulse amplitude $U \leq 20$ kV, pulse repetition frequency $f \leq 100$ Hz, pulse duration $\tau \approx 5$ ms. The disinfecting effect of using this type of device was determined using the example of inactivation of Escherichia coli cells. It was shown that with an increase in the energy input of water treatment, the bactericidal properties manifested themselves to a greater extent [26-29].

IV. The mechanism of the influence of the electric field of various discharges on grain and cotton seeds before sowing.

The yield of agricultural crops largely depends on the sowing qualities of the seeds. Therefore, along with improving the cultivation and harvesting of agricultural crops, much attention should be paid to the development and implementation of new environmentally friendly methods (use of biological agents, physical factors, ozone) aimed at improving the sowing and yield qualities of seeds. Thus, when pre-sowing seeds are treated with physical factors in optimal conditions, an increase in viability, accelerated and intensive germination of seeds and an increase in productivity are achieved, due to a more complete realization of the biological potential of plants with a simultaneous destructive effect on phytopathogens. The introduction of these methods into practice is hampered by insufficient knowledge of the optimal regimes for treating seeds of various agricultural crops, the lack of necessary equipment, as well as theoretical models of the impact of physical factors on biological objects [31-36].

The main product of cotton is fiber, which is a valuable export material. Compliance with cultivation technology and the application of mineral fertilizers increases the yield, but not significantly, and the main reason for the decrease in yield is the low sowing quality of the seeds. The germination of seeds, in turn, is greatly influenced by the presence of pathogenic fungi and bacteria that cause various plant diseases. In order to improve the sowing qualities of seeds and combat their diseases, seeds need additional processing before sowing. To prevent the spread of plant diseases through seeds and increase their productivity, chemical, biological and physical treatment methods are used. Experimental studies have shown that seed treatment in an electric field reduces seed disease and, in a cyclic mode, almost completely destroys pathogens, which improves the quality of seed material. For the correct and timely organization of pre-sowing seed treatment, as well as measures to combat seed diseases, various chemical disinfectants are used, which have been used for a very long time and have been sufficiently researched; however, pesticides, along with protecting seeds from seed and soil infections, have a negative impact on the environment and operating personnel. It has been experimentally established that cotton seeds, which have a lift and a hard peel, almost completely absorb UV radiation in a single grain layer, which does not allow the use of multilayer technologies and the use of the flux attenuation indicator “a” when calculating installations. The positive effect of pre-sowing UV irradiation and NTP radiation of cotton seeds on the yield and quality of cotton fiber was established in comparison with the control option. Experimental studies have shown the stimulating effect of an electric pulse field on grain and cotton seeds treated before sowing. The high result of the stimulating effect is explained by the increase in the course of biological processes in the seed due to the receipt of additional energy during processing. Activation of the initial stages of development of seeds exposed to an electric field leads to changes in the morphological characteristics of seedlings. In plants, the first internodes lengthen, and a more powerful root system is formed, compared to the control. Very important is the fact that root growth contributes to faster rooting of plants and better use of spring moisture and nutrients.

The degree of influence of electrical stimulation depends on the treatment mode. The best results were recorded using an electric pulse current when exposed to seeds for 15 minutes. The observed increase in morphophysiological parameters of seedlings contributes to an increase in yield. Electrical stimulation, using an electric pulse field, allows you to transfer the physiological state of the embryo, up to a change in the chemical composition, from a state of “rest” to a state of “awakening” and active growth. That is, at the moment of exposure to an electric field, a redistribution of electrical charges occurs inside the seed, which, in turn, somewhat changes the course of physical and chemical processes that affect the subsequent growth and development of plants. The stimulating effect of an electric pulse field on cotton seeds helps solve the problem of minimizing pests in agrobiocenoses and maximizing the circulation of entomophages. The consequence of this is the formation of plant resistance to a complex of harmful factors, including economically dangerous pests and infectious diseases. During the experiments, it was found that processing seed material in the electric field of a pulsed discharge helps reduce the number and harmfulness of phytophages by 46.5-68.3% and 13.1-88.5%, respectively. Moreover, the effectiveness of this technique in protecting plants from various pests is directly dependent on the treatment mode.

The electrophysical methods most used today in crop production involve the use of electromagnetic fields. The action of this factor is based on the fact that most of the physiological processes occurring in a living organism are accompanied by electromagnetic phenomena. A constant component of electromagnetic oscillations in a plant organism is bioelectric potentials, which are regenerated in the process of life activity and reflect its physiological state. As a result of treating barley seeds with an alternating electromagnetic field (50 Hz), there was an increase in the mass of roots and seedlings, an increase in germination energy and laboratory germination of seeds [37-45].

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