Comparison of mechanisms for the action of cold electric discharge plasma and hot pulsed discharge plasma emission on water solutions

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Abstract. Cold electric discharge plasma can be in direct contact with the water solution being treated. Active species are generated directly in the discharge and penetrate into the solution through the gas-liquid interface. Hot plasma of pulsed electric discharge can remotely affect an object without causing any thermal damage to it, e.g., by means of irradiating it. The effect of light penetrating into the solution is fundamentally different from the effect of cold plasma which is in contact with the solution: cold plasma already contains all active species, while radiation does not contain any of them. The species are generated in water solution when radiation passes through it. It is shown that the penetration depth of radiation into distilled water can be considerable. The method for activated water production based on the effect of plasma radiation can be more advantageous than that based on its treatment with cold plasma.

1. Introduction

All types of reactive oxygen and nitrogen species form in cold plasma of surface electric discharge [1]. These active species penetrate into the sample of treated solution through the gas-liquid surface. The contribution of reactive nitrogen species to this process and the possible applications of Plasma Activated Water (PAW) containing reactive nitrogen species were analyzed in [2]. Hot plasma radiation contains no active species; they begin to form and accumulate when radiation penetrates into the solution. The additional active factor of hot plasma is the presence of nitrogen compounds forming in the discharge region in the gas phase and diffusing to the sample surface [3]. Hot plasma radiation, as well as cold plasma, can be used to obtain activated water [4]. The characteristics of activated water produced by means of its exposure to hot plasma radiation are similar to those that can be obtained when water is treated with cold plasma of the surface discharge.

It is of interest to consider the specific features of the action of hot plasma radiation on distilled water. The goal of this work is to compare the actions of active species on water in two cases: active species form in cold plasma and penetrate into water or they form just in water volume during its exposure to hot plasma radiation.

2. Materials and methods

The IR50 spark discharge generator was the source of pulsed radiation [3]. The spark discharge occurred between the stainless steel electrodes with a diameter of 2 mm connected to the discharge capacitor C = 680 pF by means of the copper strip. The discharge gap was 3 mm, and the breakdown voltage was 6 kV. A high voltage of 11 kV was supplied to the capacitor through the ballast resistor R = 8 MΩ. When the high voltage was switched on, the self-sustained discharge was initiated. The total duration of current pulse was 5 μs, the pulse rise time was 50 ns, the pulse energy was $8.1 \times 10^{-3}$ J,
the pulse repetition rate was 50 Hz, and the discharge power was 0.4 J/s. The duration of current pulse was determined by the charge dissipation time. The average current consumed from the current supply was 0.7±0.02 mA. The spark discharge plasma emission can be considered as the black body emission with the peak of the emission spectrum at a wavelength of 220 nm [3].

Water was processed in the test tubes of different heights. The neck diameter of the test tubes was 27 mm. The test tubes were filled with water. The heights of the test tubes were 10, 20, 40, 60, 80 and 100 mm; and 5, 10, 20, 30, 40 and 50 ml of water was poured into them, respectively. The thicknesses of water layers were from 10 to 100 mm, respectively. In all experiments, the distance from the water surface to the discharge region was 30 mm. The water samples were processed for 3 minutes. There were two modes of water processing: the “light” mode corresponds to the processing, during which emission of the hot spark discharge plasma directly fell onto the water surface; and when the samples were processed in the “without” mode, the opaque screen was installed across the radiation path. In this mode, only the products formed in the gas phase could reach the water surface. Immediately after the processing, the absorption spectrum of water in the wavelength range of 250–400 nm was measured using the SF-102 spectrophotometer (Russia). In this case, the main product identified directly is nitrous acid [3]. The yield of nitrous acid was determined by means of analyzing the 371-nm-peak, $\epsilon = 51 \, \text{l} \cdot (\text{mol cm})^{-1}$ [3]. The distilled water was used with pH = 5.5.

3. Results and discussion
The amount of nitrous acid in water samples after the processing as a function of the sample volume is shown in Figure 1. It can be seen that in the "without" mode, the amount of the produced nitrous acid does not depend on the sample volume. In this case, only gaseous products that formed in the discharge region can reach the water surface as a result of diffusion. As these products were absorbed, nitrous acid was formed [3]. The volume of the gaseous products was constant in all experiments. During the discharge, the steady-state concentration of products formed in the gas phase, and it remained the same with a change in the water sample volume. Therefore, the amount of nitrous acid formed in all samples was the same.

In the "light" mode, the amount of the formed nitrous acid is higher due to the action of light, and it increases with an increase in the volume of treated liquid. This means that light penetrates deep into the liquid, and the active species are formed in the sample volume.

The mechanisms for the action of cold plasma and hot plasma emission on the water samples are illustrated in Figures 2 and 3. The cold plasma (Figure 2), which already contains a full set of active
species, is in contact with the sample surface. In the interface, the species penetrate into the water through the gas-liquid surface. As a result of their interaction, the secondary products can form that will diffuse deep into the water. At the high concentrations of active species in the superficial layer, they will be lost when interacting with each other, and this reduces the processing efficiency.

The hot plasma emission (Figure 3) penetrates deep into the water layer. Active species are formed when radiation passes through the water. The production of active species under the action of hot plasma emission is discussed in [3]. The local concentration of active species is much lower than that formed under the action of cold plasma. The probability of their loss during mutual interaction is much less. Therefore, during the PAW production, the efficiency of water treatment with hot plasma emission can be much higher than that in the case, when using cold plasma for this purpose.

Let us consider to what depth the radiation can penetrate into distilled water. The linear absorption coefficient of light as a function the wavelength can be found in [5]. Based on these data, the attenuation of the light beam was calculated with wavelengths in the range from 200 to 700 nm after it passed through the water layers with thicknesses of 10 and 100 cm. Results are given in Table 1.

| $\lambda$, nm | $a_w$, m$^{-1}$ [5] | $L = 100$ cm | $L = 10$ cm |
|------------|-----------------|---------|--------|
| 200        | 3.01            | 0.049   | 0.74   |
| 220        | 1.31            | 0.269   | 0.87   |
| 250        | 0.559           | 0.57    | 0.94   |
| 300        | 0.141           | 0.868   | 0.98   |
| 415        | 0.0044          | 0.995   | 0.999  |
| 700        | 0.624           | 0.535   | 0.939  |

The minimum absorption coefficient corresponds to a wavelength of 415 nm. At the lower and higher wavelengths, the absorption coefficient increases. Table shows that for the 10-cm-thick water layer, in the entire wavelength range under consideration (from 200 to 700 nm), the beam with

\[ \lambda_{\text{max}} \sim 220 \text{ nm} \]
intensity of at least 74% of the initial beam intensity is transmitted through water and can create the active species in it.

In [6], it was ascertained that the main mechanism for the initiation of chemical processes in liquid under the action of pulsed radiation with the parameters similar to those used in this work is the indirect action. The indirect action mechanism means that after exposure of the water sample with a substance dissolved in it to the pulsed radiation, the chemical reaction yield turns out to be the same as in the case when first water is treated directly by radiation, and then the substance under study is dissolved in the treated active water. The active species are first produced in water under the action of radiation, and then they can interact with the solutes. Thus, the pulsed emission of hot spark discharge plasma initiates the chemical transformations by means of creating the active water. The yield of oxidants and reducing agents under the action of hot plasma emission is of the order of 6 l-(100 eV)-1 [6]. Therefore, the technology for producing the activated water using the pulsed hot plasma emission can be promising [4].

Continuous radiation has no indirect effect, even in those cases, when its average power is much higher than that of the pulsed radiation [6]. Continuous radiation cannot be used to obtain the activated water, since the instantaneous concentration of active species formed under the action of continuous radiation is much less than that when water is exposed to the pulsed radiation.

4. Conclusions
Radiation with the wavelengths in the range from 200 to 700 nm is attenuated in the 10-cm-thick water layer by not more than 26%, so it can create active species in the bulk of water. The mechanism for the action of pulsed hot plasma emission is indirect, that is, the active species are first produced in water, and then they can enter into chemical reactions that determine water activity. Therefore, pulsed radiation can be used to obtain activated water. The generation efficiency of activated water under the action of pulsed hot plasma radiation can be higher than that under the action of the surface discharge plasma.

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