Production of chemically active water using pulsed radiation of spark discharge plasma

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Abstract. The possibility of producing chemically active water using the spark discharge plasma radiation is considered. This process is more efficient as compared to the production of active water using cold plasma processing. Long-lived products forming in the discharge region and diffusing to the liquid surface also contribute to the total process. The distinctive features of the process kinetics are established. The yield of oxidative and reductive equivalents, ORP, pH and conductivity of the processed water were determined.

1. Introduction
Cold plasma that does not damage the processed object is used to produce Plasma Activated Water (PAW) [1]. This water can be used for food sterilization. The distinctive feature of this type of processing is high concentration of active particles in plasma, so the probability of their loss during interactions with each other is high. This highly affects the efficiency of plasma processing.

It was shown that the spark discharge plasma radiation also has a strong chemical effect on the liquid sample [2]. The plasma radiation is generated in a spark discharge ignited between the solid electrodes at a considerable distance from the sample. There is no gas flow from the discharge region onto the sample, so the products formed in the spark discharge plasma do not directly interact with the processed liquid. The relatively long-lived gaseous products formed in the discharge can diffuse to the surface of the liquid and be absorbed in it. They also contribute to the chemical effect occurrence.

The goal of the work is to study the distinctive features of reaction kinetics occurring under the effect of plasma radiation of the spark discharge in air and the characteristics of the processed water determining its chemical activity.

2. Materials and Methods
The SD50 spark discharge generator was used as a source of pulsed radiation [3]. The spark discharge occurred between the solid electrodes connected to the discharge capacitor C = 680 pF. A high voltage of 11 kV was applied to the capacitor through a ballast resistor of R = 11 MΩ. After supplying high voltage to the electrodes, the self-sustained spark discharge began. The total current pulse duration was 5 μs, pulse rise time was 50 ns, pulse energy was $8.1 \times 10^{-3}$ J, pulse repetition rate was 50 Hz, and the discharge power was 0.4 J/s. The duration of the current pulse was determined by the plasma-discharge time. The current consumed from the power supply was $0.7 \pm 0.02$ mA.

Three processing modes were used. In Mode 1 ("all" mode), the liquid surface was directly irradiated by the spark discharge radiation. In this case, both plasma radiation and products formed in the discharge region processed the water sample. In Mode 2 ("gas" mode), an opaque plate was placed...
between the discharge region and the liquid sample, but the products formed in the discharge could freely diffuse towards the water surface. In Mode 3 (“quartz” mode), the discharge cavity was completely closed by a 2.3-mm-thick quartz glass. The passage of the gaseous products from the discharge cavity to the processed sample was completely excluded.

The outlet of the discharge cavity had a diameter of 20 mm, and the distance from the discharge region to the surface of the processed liquid was 30 mm. The light spot on the sample surface had a diameter of 40 mm. The samples were processed in the Petri dish with a diameter of 40 mm (liquid volume was 5 mL, and the thickness of the processed liquid layer was 4 mm).

To determine the chemical effect, the oxidation-reduction reactions with the test substances were used. Two kinds of processing were studied: (case 1) direct irradiation of the sample with dissolved test substance and (case 2) irradiation of water, after which the processed water was mixed with the test substance.

The yield of oxidative equivalents in the sample formed during the processing was determined from the oxidation of bivalent iron in the Mohr’s salt Fe²⁺ → Fe³⁺. In cases 1 and 2, the Mohr’s salt concentrations were 20 and 2 g/L, respectively ([Fe²⁺] = 5.1×10⁻² and 5.1×10⁻³ mol/L, respectively). Concentrated sulfuric acid 21 ml/L (0.4 M) and 50 mg/L of NaCl were added to the solution. The acidity of the solution was pH = 0.8. In all experiments, Fe²⁺ concentration in the sample was chosen so that not all ferrous iron ions were consumed for oxidation. The concentration of oxidized Fe³⁺ was determined from the absorbance of the 304 nm band, ε = 2100 ± 50 L/(mol·cm)⁻¹. The extinction coefficient was directly determined for the calibrated solution.

The yield of reduction equivalents was determined from manganese reduction Mn⁷⁺ → Mn²⁺ in solution of potassium permanganate. The concentration of potassium permanganate used during the processing was 1.58 g/L (0.05 N). Concentrated sulfuric acid 21 ml/L (0.4 M) was added to the solution. To observe the absorption peaks in the range of 400 – 650 nm, the initial and processed solutions were 10 times diluted with water. Concentration of Mn⁷⁺ was determined from the 527 nm band. The extinction coefficient, measured directly for the calibrated solution, was ε = 2160 ± 50 L/(mol·cm)⁻¹. The absorption spectra of the samples were measured by the SF-102 AKVILON spectrophotometer (Russia). The thickness of the cavity was 10 mm. Absorbance A = log(I₀/I) (B) was determined relative to that of the distilled water. The pH and ORP (Ag/AgCl) values were measured by the Expert-001 instrument; conductivity was measured by the Expert-002 conductometer (EKONICS, Moscow, Russia). Twice distilled water with pH = 6.5, ORP = 420 mV, and conductivity 10 μS/cm and chemically pure reagents were used.

3. Results and discussion
Under the effect of plasma radiation, we have observed the formation of HO₂⁺ radicals, hydrogen peroxide, nitrous acid, decaying into nitric acid, and complex compounds, which were not observed directly, but decayed up to 14 days to peroxynitrite and peroxynitrous acid [3, 4]. Nitrogen compounds are also formed after the active species diffusing from the discharge region were absorbed by water. All species generated in water can have oxidative and reductive properties. For different species, the reaction rate constants with the test substances are different, and this determined the total reaction time. The decay of the long-lived complex compounds can also contribute to the yield of redox reactions until this contribution becomes less than the measurement error. Therefore, reactions with each oxidizing or reducing agent formed under specific processing conditions were studied separately. It was found that the total reaction time does not exceed 4 days, so the yield of oxidizing and reducing equivalents was determined 4 days after the processing basing on the reaction yields.

After processing the distilled water by the spark discharge generator for 3 minutes, the water becomes active. The achieved values were: pH = 3.1 ± 0.03, ORP = 530 ± 10 mV (Ag/AgCl), and conductivity was 700 ± 50 μS/cm. These values are of the same order as those achieved after cold plasma processing [1]. Energy costs for obtaining active water using plasma radiation are less than those in the case of processing by plasma itself [2].
3.1. Indirect mechanism of radiation activity

In the case when the object is exposed to the cold plasma, all active species, which initiate chemical reactions in liquid, are present in plasma. The concentration of active species in plasma is constant, so the reactions initiated by plasma begin immediately after the plasma generator is switched on and continue with the reaction rate determined by the composition of the processed sample and the concentration of active species.

In the case of processing by plasma radiation, the situation is different. When the object is exposed to radiation, both direct absorption of photons by molecules of a chemical substance dissolved in water and the formation of secondary active species in water under the effect of radiation, which will determine further chemical transformations, are possible. If there are no chromophores in the sample directly absorbing radiation, the radiation itself does not have chemical activity. At time of switching on radiation, there are no active species in the sample; they are just beginning to be generated, and their concentration becomes considerable only some time after the start of processing. Therefore, the reactions occurring under the effect of radiation begin with a delay.

To estimate the contribution of the indirect mechanism affecting sample by means of formation of secondary active species, experiments were carried out in two cases: (case 1) the direct effect on the test substance dissolved in water and (case 2) the effect on pure water, into which the test substance was then introduced. The table presents the results of measurements of the oxidation and reduction yields, in which solutions of ferrous iron in the Mohr’s salt (oxidation) and KMnO₄ (reduction) were used as test substances. In all cases, the processing time was 3 minutes. It can be seen that, in cases 1 and 2, in the “all” and “gas” processing modes, oxidation and reduction yields are close within the measurement errors. This means that the mechanism of indirect effect of radiation by means of formation of secondary active species is determinative. The table also shows that the mechanism of indirect effect takes place for the processes occurring under the effect of only UV discharge radiation, when the sample is irradiated through the quartz glass (“quartz” mode). The yield of oxidizing and reducing equivalents is less in the case of processing through quartz glass. This may be due to the attenuation of the photon flux by the quartz glass in the wavelength range of 200–250 nm. The attenuations are 30 and 20% at wavelengths of 200 and 250 nm, respectively. The result indicates a significant role of the short-wavelength radiation. In addition, a decrease in the yield can occur due to the delay in the production of active species in the liquid under the effect of radiation after switching on the radiation source, which will be discusses further.

Table. The yield of oxidants and reductants (mol equiv/L) for different modes of processing by the SD50 generator in cases 1 and 2. Sample volume is 5 mL. The processing time for all samples was 3 minutes.

| Mode     | Oxidation | Reduction |
|----------|-----------|-----------|
|          | Water, case 2 | Mohr's salt, case 1 | Water, case 2 | KMnO₄ solution, case 1 |
| "All"   | (2.3 ± 0.3) × 10⁻² | (2.6 ± 0.3) × 10⁻² | (8.3 ± 0.6) × 10⁻³ | (9.3 ± 0.8) × 10⁻³ |
| "Gas"   | (2.0 ± 0.3) × 10⁻² | (2.1 ± 0.3) × 10⁻² | (8.1 ± 0.6) × 10⁻³ | (8.2 ± 0.6) × 10⁻³ |
| "Quartz"| (3.5 ± 0.7) × 10⁻³ | (2.4 ± 0.6) × 10⁻³ | (3.8 ± 0.4) × 10⁻³ | (4.1 ± 0.4) × 10⁻³ |

3.2. Delay of active species formation

The dependence of the oxidized Fe³⁺ ions concentration on the processing time was studied to estimate the delay time of the beginning of active species formation relative to time of the radiation source switching on. The dependences of concentration of the oxidized trivalent iron in the Mohr's salt (case 1, the Mohr's salt solution is directly processed), formed during samples processing by the SD50 generator radiation during time from 1 to 5 minutes in the modes “all” and “gas”, are shown in figure (curves 1 and 2, respectively). Similar dependences were obtained in case 2 (water is processed; and then the solution of the Mohr's salt is introduced). The dependences can be approximated by straight lines. The processing time, required for the oxidation reaction rate to become considerable, can be found by extending these approximations till the intersection with the time axis.
Figure. Concentrations of oxidized trivalent iron as functions of the processing time of samples by the SD50 spark discharge generator. (1) and (2) correspond to "all" and "gas" processing modes.

The delay in the beginning of the reaction may occur due to the fact that there are no active species in the solution before processing, and the reaction rate constants for the active species formed under the effect of radiation are small. The reaction rates will become considerable after the concentrations of species exceed a certain minimum value. Similar delay was observed for the reduction reaction.

4. Conclusions
Under conditions of water processing by plasma radiation, the indirect mechanism of radiation activity prevails, when, under the effect of radiation, the active species are first formed in water. After being produced, they can interact with chemicals dissolved in water.

At time of switching on the radiation source, there are no active species in the liquid yet. They are just starting to be produced. The reaction begins after the concentration of active species becomes considerable. Therefore, the reaction under the effect of radiation is delayed. Under the experimental conditions under consideration, this delay time is about 1 minute.

The results obtained should be taken into account when creating industrial methods for food sterilization by water activated by plasma radiation.

References
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