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## The effect of multispark discharge plasma on solutions of ethylenediaminetetraacetic acid

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The research focused on investigating the impact of a multispark discharge plasma on solutions containing different concentrations of ethylenediaminetetraacetic acid and its disodium salt. It is shown that with the observed erosion of the electrodes, it is possible to vary the qualitative and quantitative composition of particles in solution by changing the parameters of the liquid. The measuring of hydrogen peroxide and iron ion concentration was carried out, alongside the formulation of assumptions concerning the creation of chelate compounds and the shapes of precipitation observed.

**Keywords:** multispark discharge, nanoparticles, electrode erosion, hydrogen peroxide, EDTA.

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The study of physical and chemical processes occurring in a liquid when it is exposed to a low-temperature gas discharge plasma is being actively developed at present [1–3]. Particular attention is paid to systems where one or both electrodes are immersed in the medium to be treated and erosion occurs during the discharge process. One of the directions of application of such systems (in addition to formation of reactive oxygen and nitrogen intermediate, hydrated electrons, etc.) — synthesis of nanoparticles for tasks of medicine, agriculture, chemical industry, engineering [4,5].

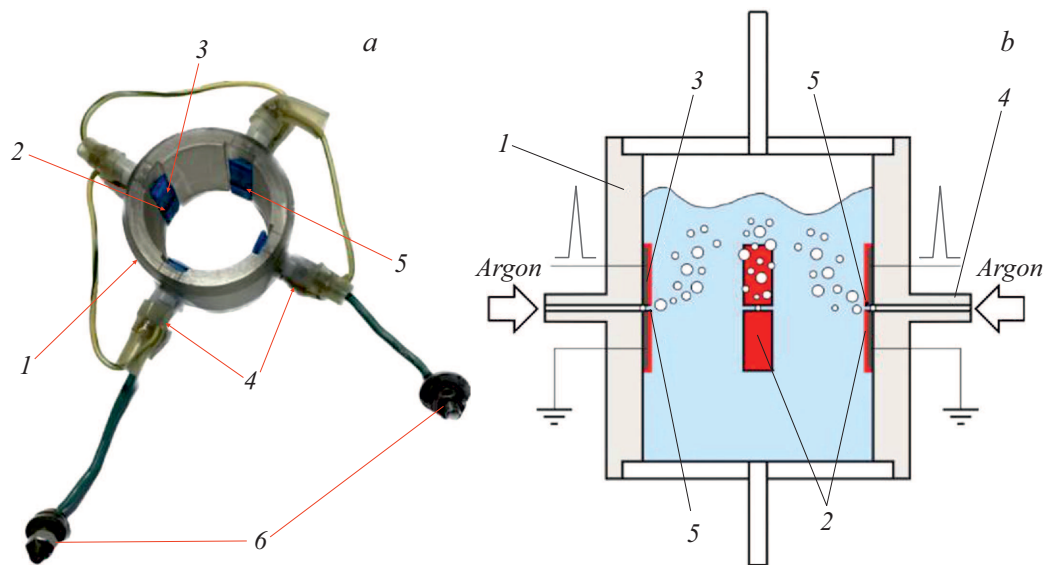
Often, ethylenediaminetetraacetic acid (EDTA) is used for chemical synthesis of nanoparticles as a reducing or enriching component in order to adsorb metal ions from aqueous solutions [6,7]. On one hand, we consider the possibility of absorption of metal ions from a discharge-treated solution of EDTA and its disodium salt to create their chelate compounds with hydrogen peroxide content as plant fertilizer. On the other hand, the controlled production of electrode material particles depending on the conductivity of the solution, which affects erosion processes in gas discharge treatment, is of interest. In [8] it is noted that when the source of metal nanoparticles is the electrode material, synthesis occurs either by electrochemical erosion of the electrodes or by their sputtering similar to classical plasma sputtering. The plasma-treated fluid acts as a stabilizer or a reducing agent (or both at the same time). Stabilization of nanoparticles involves stopping the agglomeration process. By varying the experimental conditions (working gas, electrode material, exposure time, treated liquid), it is possible to control the composition of both the obtained nanoparticles and the solution.

In the present work, we investigated the preparation of iron oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ), which can be used for

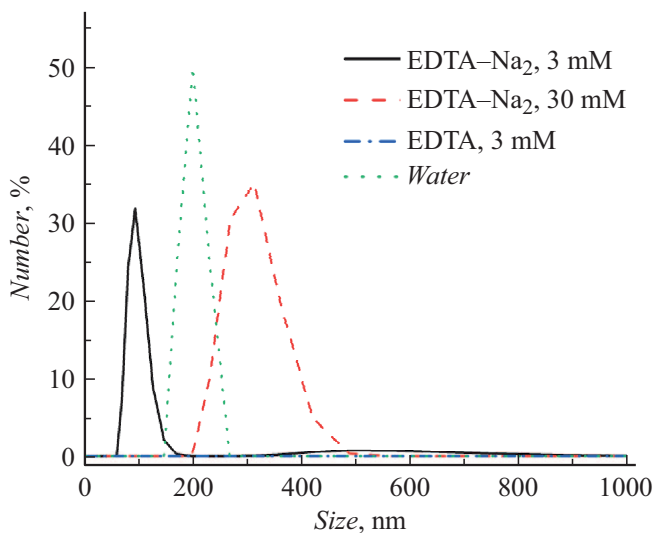
medical applications [9] among others. The formation of iron [10] chelate compounds for agriculture was also investigated. In work was used installation (Fig. 1) with realization of high-voltage pulse-periodic multi-electrode ring discharge in liquid with gas injection in interelectrode gaps [11,12]. The voltage applied to the arrester was  $U = 20$  kV, and the high-voltage pulse repetition rate was  $f = 50$  Hz, pulse duration  $2 \mu\text{s}$ . The energy invested in the discharge was  $\sim 0.5$  J. The plasma concentration ( $10^{17} \text{ cm}^{-3}$ ) was determined in [12]. Temperature of heavy particles  $T = 4000$ – $5000$  K along the continuum of radiation. In the presented experiment, the electrodes were made of 12X18H10T stainless steel, and argon with a flow rate of 6 l/min was used as the working gas. Exposure time 10 min, liquid volume 120 ml.

The effects on aqueous solutions of EDTA with concentrations of  $300 \mu\text{M}$ ,  $3 \text{ mM}$  and EDTA– $\text{Na}_2$  (Trilon B) with concentrations of  $300 \mu\text{M}$ ,  $3 \text{ mM}$ ,  $30 \text{ mM}$ , where M — mol/l, were investigated. The concentration of hydrogen peroxide was measured using FOX (ferrous oxidation-xylenol orange) [13] by absorption spectrum at 560 nm, and the concentration of  $3+$  — metal ions was measured with XO (xylenol orange) [14] by absorption spectra at 560 nm using a HACH LANGE DR- 5000 spectrophotometer (HACH LANGE GmbH, Germany). The hydrodynamic radius of particles (Fig. 2) was determined using dynamic light scattering (DLS) (Zetasizer ULTRA, Malvern Panalytical, Ltd., UK). Conductivity, hydrogen index, and oxidation-reduction potential of the medium were determined using a SevenExcellence multichannel meter (Mettler Toledo, Switzerland).

Three characteristic types of precipitation were observed (see Table): 1 — orange precipitate  $\text{Fe}(\text{OH})_3$  or  $\text{FeO}(\text{OH})$ , changing to  $\text{Fe}_2\text{O}_3$  in  $\alpha$ - phase, which is



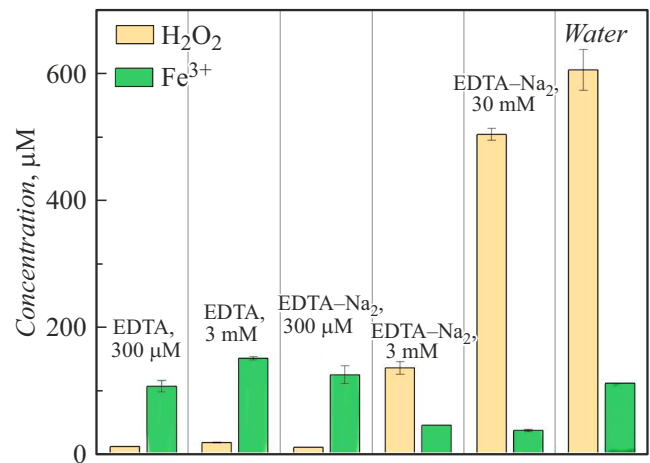
**Figure 1.** *a* — one of the reactor sections; *b* — the cross-section of the discharge chamber. 1 — dielectric chamber; 2 — electrodes; 3 — electrical insulating material; 4 — gas injection port 5; 6 — high voltage terminals.



**Figure 2.** DLS of samples after 10 min exposure to a multi-spark discharge with argon injection into the interelectrode gaps.

a weak ferromagnet at room temperature, which was confirmed in the experiment by the slow reaction with a permanent neodymium magnet; 2 — mixed oxide  $\text{Fe}_3\text{O}_4$  (magnetite) in black color, which exhibits strong magnetic properties and is rapidly attracted to the magnet, is a ferrimagnet; 3 — grey unidentified particles, which exhibit weaker magnetic properties than precipitate 2. For samples other than EDTA 3 mM, in addition to precipitation by DLS, the presence of colloid with agglomerates of nanoparticles was also recorded (Fig. 2).

When the concentration of EDTA  $-\text{Na}_2$  was increased, there was a decrease in the concentration of Fe ions



**Figure 3.** Concentrations of hydrogen peroxide  $\text{H}_2\text{O}_2$  and iron ions  $\text{Fe}^{3+}$  in solutions after 10 min exposure to a multi-spark discharge with argon injection into the interelectrode spaces.

$\text{Fe}^{3+}$  (Fig. 3), which is probably due to the formation of  $\text{Fe(II)} - \text{EDTA}$  or  $\text{Fe(III)} - \text{EDTA}$ . The iron-based chelate compound is stable and prevents the fixation of ions with oxidation degree +3 by XO [15]. The use of EDTA and its disodium salt solutions also affected the hydrogen peroxide concentration. A decrease in the concentration of  $\text{H}_2\text{O}_2$  and consequently its degradation or complex formation with EDTA was found experimentally. Hydrogen peroxide is involved in the oxidation reactions of  $\text{Fe(II)} - \text{EDTA} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} - \text{EDTA} + \text{OH} + \text{OH}\cdot$  and others. [16] and the formation of  $\text{Fe(II)} - \text{EDTA} - \text{H}_2\text{O}_2$  [17], which is consistent with a decrease in the concentration of  $\text{H}_2\text{O}_2$  compared to the result in deionized water. It should be noted that the highest concentration of hydrogen

Parameters of aqueous solutions before (values with index 1) and after (values with index 2) exposure to argon-injected multi-spark discharge

Substance	C, mM	$\sigma_1$ , $\mu\text{S}/\text{cm}$	$\sigma_2$ , $\mu\text{S}/\text{cm}$	pH <sub>1</sub>	pH <sub>2</sub>	Redox <sub>1</sub> , mV	Redox <sub>2</sub> , mV	Particles
EDTA	0.3	191.6	46.0	3.5	4.9	505	305	Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub>
	3	727.2	333.9	2.9	3.5	491	278	
EDTA–Na <sub>2</sub>	0.3	67.4	60.7	5.0	6.7	429	218	Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub>
	3	469.9	411.4	4.9	7.1	439	160	
Water	30	3663.2	3223.2	4.7	5.5	420	210	Fe <sub>3</sub> O <sub>4</sub> , * Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub>
		0.1	25.0	5.7	5.7	420	368	

Note. C — concentration; unspecified particles are marked with an asterisk.

peroxide was diagnosed in EDTA–Na<sub>2</sub> with a concentration of 30 mM and perhaps this fact is related to the different pH result from other EDTA–Na<sub>2</sub> solutions.

The increase in solution conductivity in deionized water is due to the appearance of metal ions in solution. When EDTA solutions are used, the contribution of electrochemical erosion becomes significant because the initial conductivity of the solutions ranges from 67.4 to 3663.2  $\mu\text{S}/\text{cm}$ . Note that after treatment, it decreased several-fold with EDTA and decreased slightly with –Na<sub>2</sub>. This fact indicates the inhibition of solution supersaturation [18]. In the case of EDTA –Na<sub>2</sub>, sodium ions are released instead of the metal ion bound in the complex, due to which the conductivity of the solution decreases slightly, which also indirectly confirms the formation of chelate compounds.

Thus, the first experimental study of gas-discharge treatment of EDTA solutions has been carried out. The formation of chelate compounds and agglomerates of Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> particles has been qualitatively demonstrated. It is shown that by varying the concentrations of EDTA in solution, erosion processes, particle composition and water-soluble compounds can be influenced.

### Conflict of interest

The authors declare that they have no conflict of interest.

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