Investigation of the mechanism of microplasma impact on iron and aluminum load using solutions of organic substances

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Abstract. The paper reports on the study of mechanism of electroeffects on iron and aluminum and pellets with using solutions of organic substances. Methylene blue solution, furacilin and eosin were used. It is observed the reactions of the pulse at the time and after switching off the voltage source. It is shown that there are two developing process in the conditions studied. The first process depends on material of electrodes and pulse parameters. The second process occurs spontaneously and it is determined by the redox reaction and sorption processes. The products of electrode erosion and active particles react in the redox reactions. Active particles are formed in solution by the action of pulsed electric discharge in water. The highest efficiency of the process was demonstrated on an iron pellets.
Key words: *pulsed electric discharge erosion, aluminum, iron, an aqueous solution of methylene blue, eosin furatsilin.*

1. Introduction

The using of pulse electric discharge in heterogeneous mediums is the great scientific interest. For instance, for production of metal nanoparticles and their compounds and for waste and natural water purification due to a wider variety of chemical processes depends on electrode material.

The scientific interest in this field is due to the particular conditions of chemical reactions in a pulsed electric discharge (PED), their kinetics and mechanism.

On the one hand different kinds of dissolved substances (impurities) are involved in different types of reactions: redox, acid-base, ion-exchange, chemisorption, coprecipitation, etc. On the other hand, the type and behavior of reactions can depend on the type of PED and the chemical nature of electrode.

The use of various types of electric discharges for cleaning water due to their ability to initiate the formation of a wide spectrum of short-lived reactive species - radicals and ions, which form with the influence of degradation and oxidation of impurities in water [1 – 3]. Recently it is known papers which are devoted to the electric discharge wastewater treatment in reactors with aluminum and iron loadings [4 – 6]. Some developments brought to the level of patents [7]. However, there is no clear opinion of the processes.

The pulsed electric discharge in a layer of iron or aluminum granules placed in different aqueous solutions of organic substances differs from other types of discharges. It is due to the input energy influence on the electrodes. Metal pellets disintegrate to form highly dispersed materials. When using PED there are different physical and chemical processes with the active particles. Active particles have oxidizing and reducing properties. The study process of formation of active partials in the aquatic environment and chemical reactions with them are difficult due to time of life.

the mechanism of their transformation identified by chemical methods. For example, in papers [2, 3], it is investigated the formation of active particles when exposed to water an electric corona discharge with using solutions: $KMnO_4$, KJ and oxalic acid.

Most of the energy of pulsed electrical discharges expended on the dispersion of the metal by melting and evaporation.

Metal dispersed particles react with the medium to form the oxidized form metal erosion products. Products erosion of metallic granules determine the future direction of chemical reactions. There is no consensus explanation of these processes. Currently, many research groups engaged in the study of the process on electropulse with the solution of organic substances [1 – 4]

The objective of the work is to study the mechanism of physical and chemical processes occurring in reactors under the action of pulsed electrical discharges with iron and aluminum load using aqueous solutions of organic substances.

2. Experimental approach

The experimental setup is presented in [5]. The apparatus consists of a reactor volume of 1.5 L and power source. The reactor was made of a dielectric material. At the bottom of the reactor filled with aluminum or iron granules. Selection of different granules determined electrochemically active metal in an aqueous medium. The two external electrodes immersed in the metal loading was applied pulse voltage amplitude of 500 V with a pulse repetition rate of 300 s-1 and a duration of 15 ms. The maximum discharge current was 250A. Pulse energy 0.5 J / pulse.

A breakdown of intergrain space occurs with electroconductive canal formation and much energy liberation on the surface of contacting grains –"hot" spark formation. At that the main energy consumption is for metal dispersion, due to melting, evaporation, spraying.

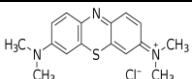Figure 1 shows the sketch of spark erosion process.
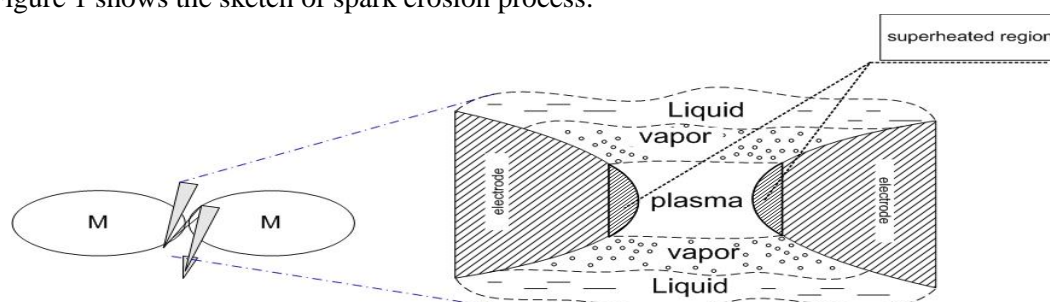
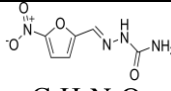**Figure 1.** Sketch of spark erosion process.

On the left are two electrodes immersed in a dielectric liquid and connected to a pulsed power source. When the field strength in the gap is sufficiently high, a spark is produced. The spark results from the breakdown of the dielectric fluid as depicted in the enlarged view of the reaction zone on the right-hand side of Fig. 1.

A plasma channel of small diameter (perhaps 50 μm) is established in approximately 10 ns after the electric field is applied. The temperature in the plasma channel has been determined to be in excess of 10000 K.

The colored aqueous solutions of organic substances with well-studied properties: methylene blue, furacilin and eosin were used to determine the mechanism of physical and chemical processes in reactors. Selected organic substances can demonstrate the possibility of chemical reactions such as oxidation-reduction, and adsorption. Chemical formulas and properties of organic substances listed in the table 1.

Table 1. Chemical formulas and properties of organic substances

| Name of substances	Formula	Properties
thylene blue	$C_{16}H_{18}ClN_3S \cdot HCl$	Reversible redox and cation adsorption indicator. Dissociation of the cation forms a shape in the form of $[C_{16}H_{18}ClN_3S]H^+$

osin $NA_2[C_{20}H_6O_5Br_4]$	Dissociation of forming anionic form as $[C_{20}H_6O_5Br_4]^{2-}$
Furacilin $C_6H_6N_4O_4$	Participates in redox processes and oxidized with decomposition

Treatment of aluminum or iron pellets electrical discharges in the solutions leads to the formation of a homogeneous suspension. The concentration of solids in the suspensions depends on the time of the metal processing load.The suspensions is centrifuged in a centrifuge slurry «Allegra 64R» firm «Beckman-Coulter» US at 20.000 rpm for the separation of the solid phase and the solution. Changing the intensity of the color solutions of organic substances upon the action of the pulsed electric discharge was determined after 15 min.

Absorbance of the solution was measured at the maximum of the absorption bands of the instrument ApelPD-303UV, the company «ApelCo., LTD», Japan. For methylene blue is at a wavelength of 590 nm to 440 nm at furatsilina and eosin is at 490 nm.

3. Results and discussion

The concentration of different forms of iron are measured to study the dynamics of accumulation of erosion products of an iron charge in various forms in water. The data on iron accumulation in various forms in solid erosion products are shown on figure 2.
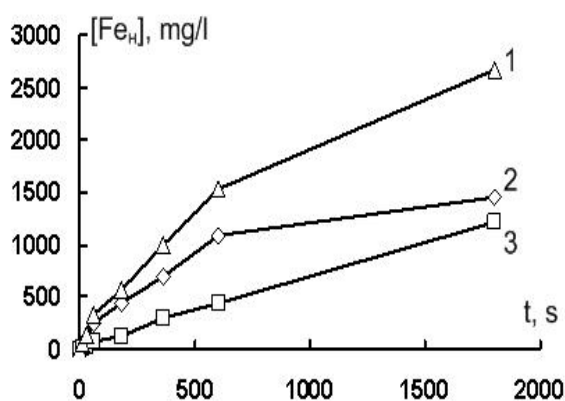
Figure 2. Data on accumulation of erosion products of the iron grains in various forms (1) – ∑Fe, (2) – Fe^{2+} и Fe^0, (3) – Fe^{3+} in water.
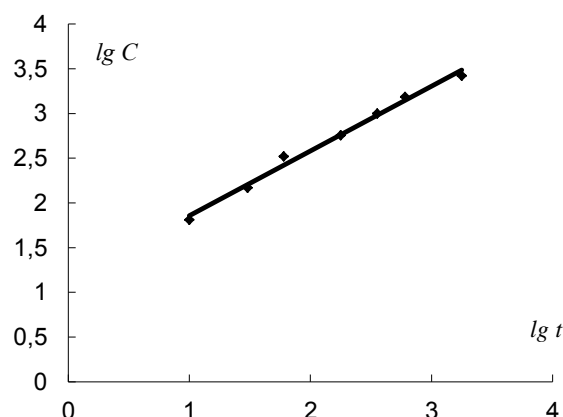
Figure 3. Concentration ∑Fe of iron ions in erosion products (in suspension) vs. (versus) the treatment time t.

The experimental data obtained were processed and dependence plotted in the log-log coordinates (Figure 3). The total amount of iron (mg/L) removed from the electrodes (charge) is described as a function of the time of action of the discharge by the following empirical relations:

$$lg\ C_{Fe} = 0{,}72\ lg\ t + 1{,}1331 \tag{1}$$
$$or\ C_{Fe} = 13{,}6\ t^{0,72} \tag{2}$$

Thus, the kinetic equation describing the spark-erosion process of iron grains in water can be represented as a general formula:

$$[M_н] = k_e \cdot t^\nu, \tag{3}$$

where $\nu \leq 1$.

The index ν was determined experimentally and it is connected with the change of contact geometry in a layer of iron grains and electrophysical characteristics of medium.

The value k_e is an empirical constant which depends on intensity and other characteristics of discharge, properties of electrodes and medium mg/(l·s$^\nu$).

3

The mechanism of this process can be represented by the following reactions, which form dispersed metal particles.

$$Me \xrightarrow{\text{PED}} Me_{\text{H}} \quad (4)$$

$$Me_{\text{H}} \rightarrow Me^{+n} + ne^{-} \quad (5)$$

$$Me_{\text{H}} + n\,H_2O \rightarrow Me(OH)_n + H_2 \quad (6)$$

$$Me^{+n} + n\,OH^{-} \rightarrow Me(OH)_n \quad (7)$$

$$4H_2O + 4\,e^{-} \rightarrow 2H_2 + 4OH^{-} \quad (8)$$

$$4OH^{-} + 4\,e^{-} \rightarrow 2H_2O + O_2 \quad (9)$$

In the above reactions 4, 8 and 9 react on the electrodes and depend on parameters of the electrical discharge pulse. Reactions 5, 6 and 7 are spontaneously, even after turning off the voltage source. As follows from equations 5-7, the reactions start at the interface "metal solution". The solutions of methylene blue, eosin and furacilin were used to identify reactions in the reactor.
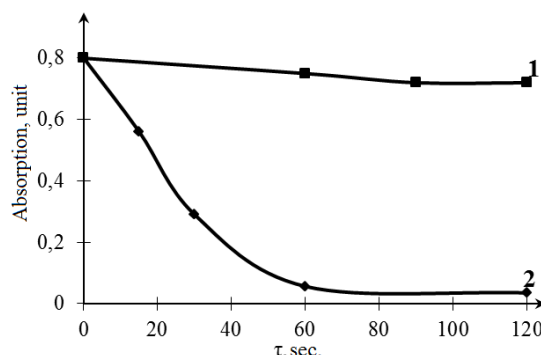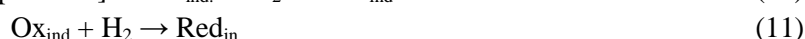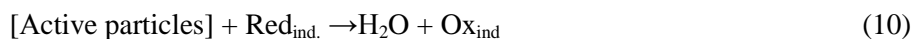
Exposure to pulsed electric discharge on the methylene blue solution leads to a reduction of the intensity of its color. Metal particles in its oxidized form as oxides and hydroxides are deposited on the bottom of the reactor after switching off the voltage source.

Aluminum (III) react with water and form a sediment in the form of $Al(OH)_3$ when dealing with aluminum loading ions. The result of this process is the return methylene blue in initial color partly. Intensity of colors methylene blue in this case depends only weakly on the number of submitted pulses.

Figure 4 (curve 1) shows the change in the color intensity of methylene blue solution when pulsed electric discharge exposed for 15 s, 30 s and 60 s. The color intensity of methylene blue on the aluminum load varies slightly. This change does not reflect the actual mechanism of the process. The oxidation process proceeds to form electrons in reaction (5) due to the high electrochemical activity of aluminum.

Active particles that are obtained during discharge were involved in the oxidation of methylene blue is losing color.

The hydrogen which are formed by the reaction (6), involved the methylene blue by oxidation reactions (11). Methylene blue has a reversible indicator. It allows evaluating the development of the processes of oxidation and subsequent recovery. Reduction reactions involving hydrogen occur primarily.

$$[\text{Active particles}] + Red_{\text{ind.}} \rightarrow H_2O + Ox_{\text{ind}} \quad (10)$$

$$Ox_{\text{ind}} + H_2 \rightarrow Red_{\text{in}} \quad (11)$$

Figure 4. The dependence of the optical density of methylene blue on the time of exposure to pulsed electric discharge: curve 1–on aluminum loading curve; 2 – on iron loading.

Processes which is occurring on the iron granules, more intense than aluminum. This can be seen in Figure 4 curve 2. Intensive reduction of methylene blue staining is associated with a longer time of the process in comparison with the processes occurring on the aluminum granules. This is due to variable valence of iron and participation of free electrons in the oxidation of methylene blue and the lower electrochemical activity of iron as compared with aluminum.

Confirmation of a slow recovery of the color intensity of methylene blue can serve kinetics are shown on the Figure 5.
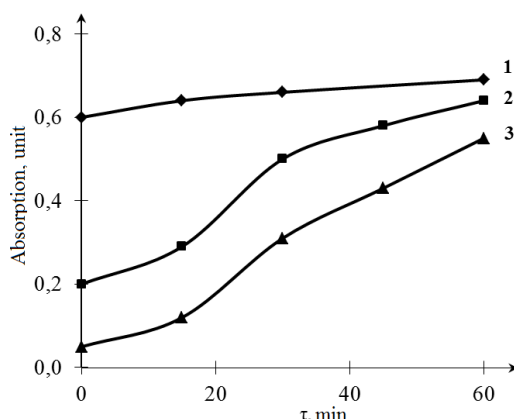
Figure 5. Restoring the color intensity of methylene blue solution after cessation of exposure PED iron loading at different time processing solution discharge
$(1 - 15$ s., $2 - 30$ s ., $3 - 60$ s.$)$.

The same experiments were performed with a solution furacilina. Furacilin is irreversible in oxidation-reduction reactions and may show only the oxidative processes. Change the color intensity of the solution furacilina under the action of pulsed electric discharge is shown in Figure 6.
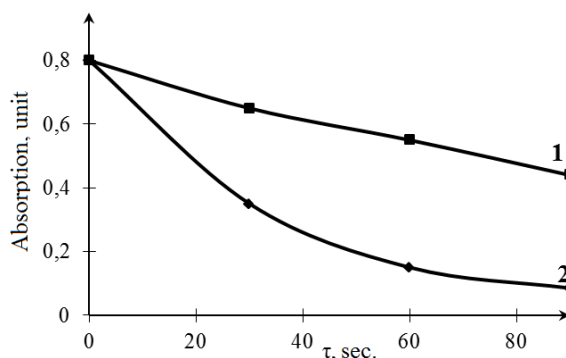
Figure 6. Dependence of the optical density furacilina from the time of exposure PED: 1-on aluminum load, 2 - on iron loading.

View kinetic dependences indicates that the oxidation furatsilina on aluminum and iron loads flows through different mechanisms. This is due to different kinetics of accumulation of products electrolytic erosion solution. In [5, 6], the dependence of the amount of metal eroded by time is described by the general formula (12):
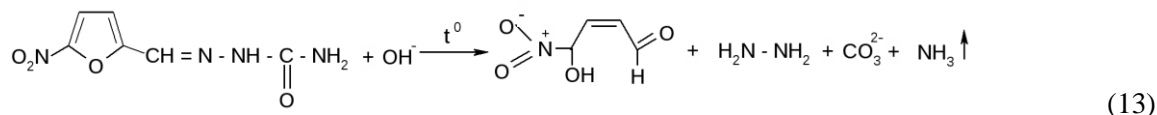
$$[Me_H] = A\, t^n, \tag{12}$$

where $[Me_H]$ –is concentration of electrolytic erosion products, mg/L;
A is empirical constant that depends on the intensity and other characteristics of the discharge, properties of the electrodes and the medium, mg/L c^n.
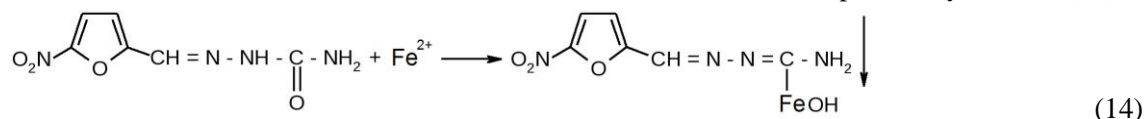
The exponent n is associated with a change in the geometry of the contacts in the layer of granules and electrical characteristics of the medium. For the aluminum loading of n equals 1, while for iron n equals 0.72.

The presence of hydroxide ions formed in reaction (8) and high local temperatures due to electrical discharges suggest to the reaction (13). This reaction is accompanied by cleavage of the furan ring to form the hydrazine and ammonia regardless of the material load.

$$O_2N\!-\!\underset{O}{\diagup\!\!\!\!\diagdown}\!-\!CH=N-NH-\underset{\underset{O}{\parallel}}{C}-NH_2 \;+\; OH^- \;\xrightarrow{t^0}\; \underset{OH}{O_2N}\!=\!\diagup\!\!\!\!\diagdown\!\!=\!O \;+\; H_2N-NH_2 \;+\; CO_3^{2-} \;+\; NH_3\!\uparrow$$

(13)

involved in the processes of recovery furacilina.

However, the most intensive decrease color of the solution of furacilina is observed at iron pellet. This can be attributed to its interaction with iron ions to form insoluble compounds by reaction (14)

$$O_2N-\text{furan}-CH = N - NH - \underset{\underset{O}{\|}}{C} - NH_2 + Fe^{2+} \longrightarrow O_2N-\text{furan}-CH = N - N = \underset{\underset{FeOH}{|}}{C} - NH_2 \downarrow \qquad (14)$$

The possibility of this reaction was confirmed by reaction of furacilina solution with a model solution of $FeSO_4$. Oxidation of hydroxide Fe (II) leads to the formation of hydroxide Fe (III) with a developed adsorption of surface. This leads to a decrease in the intensity of color furatsilina due to sorption processes.

Established facts confirm the important role of material of loading in oxidation-reduction reactions during the processing of materials that are prone to oxidation in the PED reactors.

Adsorption processes have been examined for adsorption of the eosin solution. The results are shown in Figure 7.
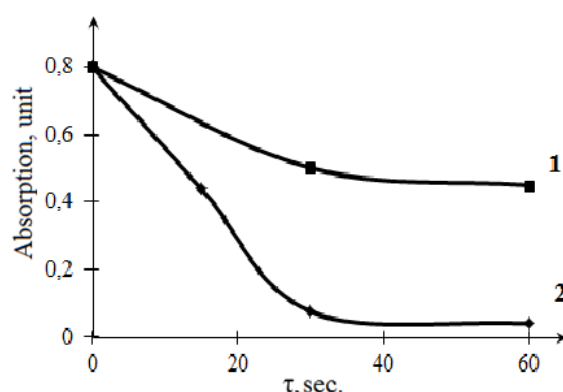
Figure 7. Dependence of the optical density of the solution of eosin from time of PED: 1–on aluminum loading; 2 – on iron loading.

Figure 7 shows the change in color of eosin at the initial time exposure pulses. It cannot be explained only by the adsorption process due to a solid phase with a minor amount.

In this case it may be assumed other reactions that lead to changes in the intensity of eosin staining. For example, a redox reaction with the active particles or destruction with the influence of the discharge.

According to figure 7 the sorption properties of erosion products of iron loading is much more efficient than aluminum. This is associated with the positive charge of the surface of the iron hydroxide having basic properties [7]. Aluminum hydroxide is amphoteric and it may contain two types of surface ions - H^+ and OH^-. Efficient sorption of eosin having anionic form ($[C_{20}H_6O_5Br_4]^{2-}$) is reduced.

4. Conclusion
1. It is shown that the main process in the reactors are redox reactions that developing during operation a pulsed electric discharge. Efficacy of redox reactions is dependent on the material load.
2. It is found that methylene blue is involved in redox reactions.
3. It is shown that furacilina simultaneous occurrence of two processes such as the destruction due to high local temperatures and the formation of insoluble compounds with heavy metal ions.
4. Flow adsorption processes are shown in eosin solution. The effectiveness of which is determined by the surface charge of the oxidized products of erosion.

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