

Electropulse treatment of water solution of humic substances in a layer iron granules in process of water treatment

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Abstract. The present work is a part of a continuations study of the physical and chemical processes complex in natural waters containing humic-type organic substances at the influence of pulsed electrical discharges in a layer of iron pellets. The study of humic substances processing in the iron granules layer by means of pulsed electric discharge for the purpose of water purification from organic compounds humic origin from natural water of the northern regions of Russia is relevant for the water treatment technologies. In case of molar humate sodium – iron ions (II) at the ratio 2:3, reduction of solution colour and chemical oxygen demand occur due to the humate sodium ions and iron (II) participation in oxidation-reduction reactions followed by coagulation insoluble compounds formation at a pH of 6.5. In order to achieve this molar ratio and the time of pulsed electric discharge, equal to 10 seconds is experimentally identified. The role of secondary processes that occur after disconnection of the discharge is shown. The time of contact in active erosion products with sodium humate, equal to 1 hour is established. During this time, the value of permanganate oxidation and iron concentration in solution achieves the value of maximum permissible concentrations and further contact time increase does not lead to the controlled parameters change.

1. Introduction

Currently, water purification processes from impurities by means of various electrical discharge types' application are widely explored [1, 2]. In the paper [3] the effect of glow and diaphragm discharges of aqueous solutions of organic dyes is investigated. It is shown that the effect of glow and diaphragm discharges on water solutions of organic substances leads to their destruction. Along with that [4] the effects of pulsed electric discharge (PED) in the layer of metal pellets which are placed in water solutions of organic substances are investigated.

The difference of PED in the layer of metal granules from other discharges types is a complex phenomenon. The primary effects are initiated by discharges channels in the developing system. Reducing properties of active surface of eroding metal and the tendency of substances present in the solution to redox reaction stimulate the development of secondary phenomena. These phenomena are able to determine the further way of chemical reactions which are developing in electroerosion reactors.

The pulsed electric discharge is a unique tool to influence either liquid [5] or solid phase [6] in a heterogeneous system with conducting particles. The destruction of the metallic phase in the areas of discharge channel formation leads to a mass transfer processes intensification, the water solution activation, the gaseous products formation and the conjugate oxidation - reduction reactions development.



In the papers [7-10] the mechanism of the reactions which are taking place at electric pulse impact on water solutions of methylene blue, eosin and furatsilina are studied. It is shown that redox reactions and adsorption processes occur as a result of pulsed electric discharge. Process efficiency depends on the material load. The investigated water solutions of organic substances are involved in redox reactions and adsorption processes in different ways due to the different structure and properties of methylene blue, eosin and furatsilina.

The present work is a part of a continuations study of the physical and chemical processes complex in natural waters containing humic substances at the influence of pulsed electrical discharges in a layer of iron pellets.

The objective of the work is to investigate the influence of phenomena initiated by the discharge channels and secondary redox processes on the stability of humic substances in the model solution and groundwater.

2. Experimental approach

For the experiments concerning the effect of the discharge on the stability of humic substances, the installation was used according to the paper [6]. The installation consisted of a 1.5-liter reactor fitted with electrodes and a switching power supply. The iron pellets weighing 300 g were located in the reactor. Voltage pulses were supplied to the electrodes from a pulse generator with the energy output of 0.5 J and variable pulse repetition rate. The voltage amplitude was 500 V, pulse repetition frequency was 500 imp·s⁻¹, the energy and the duration of voltage pulses was 15 ms. The volume of the model solution was varied in the range 0.3...0.9 L.

For synthesis and analytical study, the model solution of humic substances was used. Humic organic substances for experiments were extracted from peat bogs in Tomsk region [11, 12].

The organic substances concentration was determined by the analysis of the chemical oxygen demand (COD), permanganate oxidation (PO) and the total organic carbon (TOC) content.

The iron and silicon concentrations in the solution were determined by means of ICP-OES plasma optical emission spectrometer (Varian, USA). The concentration of iron (II) was determined according technique State Russia Standard 4011-72 with o-phenanthroline. The pH value was measured by means of a WTW Multiline P4 multifunctional device (WTW GmbH, Germany).

Centrifugation was carried out immediately after the PED solutions processing to stop the oxidation-reduction reactions in the systems "eroded metal – investigated substances". The suspension was centrifuged by means of a centrifuge Allegra 54 R (Beckman-Coulter, USA) with a shaking frequency 20000 rounds / min for 10 min.

The influence of active particles was evaluated by exclusion. To do this, the appropriate amounts of distilled water were treated with PED. The suspensions made were injected into the humic substances solution with the contact time was 10 seconds. Thus, humic substances were not involved in the processes initiated by the discharge channels, but only came into contact with eroded metal.

3. Results and discussion

The model solutions of sodium humate were used to determine the water treatment process parameters. The sodium humate concentration in model solution 1 was 8 mg/L whereas in solution 2 it was 16 mg/L. This sodium humate concentration corresponded to that in the groundwater of the Western Siberian region [12].

It is known [8] that as a result of pulsed electric discharge, water solutions are characterised by eroded iron particles formation, redox reactions of $\text{Fe}^0 \rightarrow \text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ transition occurrence, pH changes in the range of 6.5 ... 9.5.

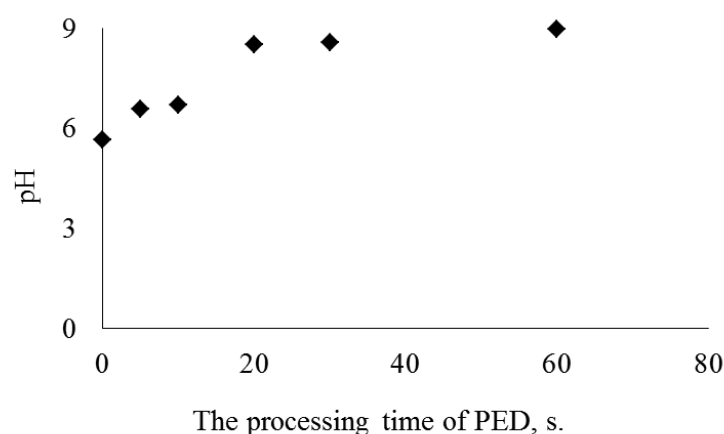


Figure 1. pH change in the model solution from processing time of PED.

The influence of processing time on the humic substances insoluble form was investigated to determine the conditions of effective of humic substances coagulation in the process of electropulse effect.

Fig. 2 demonstrates that the colour of humate sodium solution and concentration of iron (II) formed by the reaction of iron eroded with water depend on the processing time of PED.

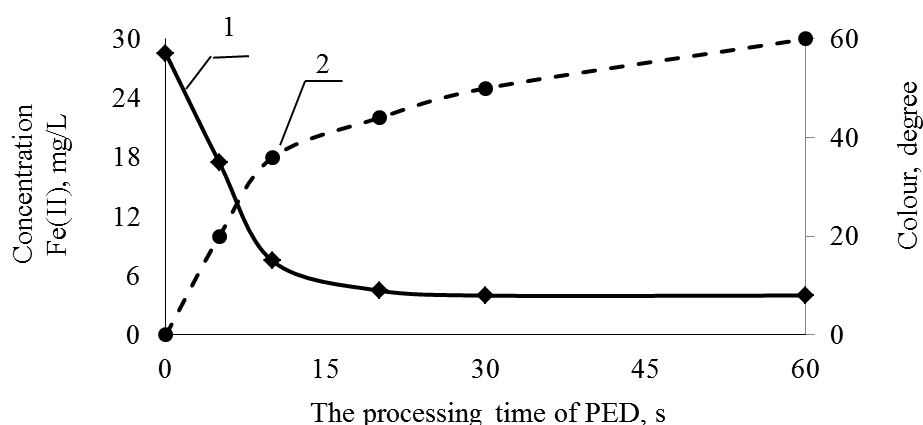


Figure 2. Dependence of the processing time of PED on colour of humate sodium solution (1) and the iron (II) concentration (2).

It is seen in Fig. 2 that the most intense color reduction to maximum permissible concentration values occurs when the processing time is not more than 10 seconds, whereas the iron ions (II) concentration in solution corresponds to 18 mg/L. Experimental treatment time is 10 seconds, which is sufficient to obtaining a humic substances to iron ratio of 2: 3. A further increase in the processing time can be considered inappropriate. The iron ions reactions with the sodium humate occur followed by coagulation to form precipitate at the determined ratio. The residual concentration of iron ions does not exceed the maximum permissible concentration for drinking water which equals 0.3 mg/L in the solution.

Reduced color solution as an indicator of the sodium humate concentration was confirmed by measuring the permanganate oxidation (PO), chemical oxygen demand (COD) and measuring the concentration of total organic carbon (TOC). The dependence of these parameters on the processing time of the solution by a pulsed electric discharge is shown in the Fig. 3. This figure demonstrates that the change of COD and PO are well correlated with the changes in solution color (Fig. 2). The maximum decrease in the concentration of humic substances is also achieved with the processing time of 10 seconds.

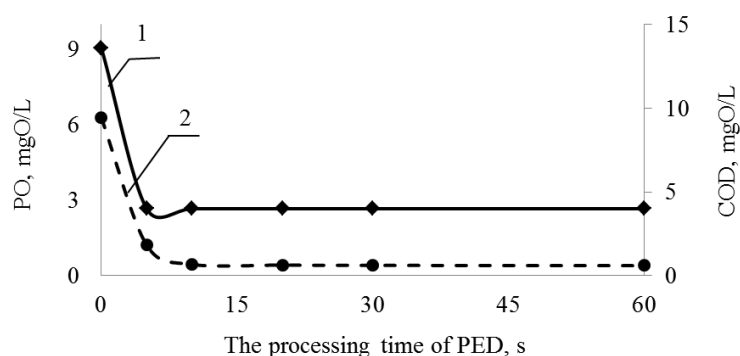


Figure 3. Dependence of the processing time of PED on value of COD (1) and PO (2).

As shown earlier [7, 8], the secondary processes occurring after discharge shutdown make a major contribution to the process of electro-processing solutions involving metal loading.

The distilled water was treated for 10 seconds and the solution added to a suspension of sodium humate after discharge disconnection to study the suspension activity. The sodium humate concentration was selected in the amount to equal the concentration of a stock solution. The suspension activity was evaluated relative to dissolved sodium humate at stated intervals (1-6 hours). The result of the interaction was observed for changes in the total iron concentration and PO values and it was compared with indicators of a stock sodium humate solution.

Fig. 4 shows the dependence of the iron total concentration and PO on the contact time with the active iron erosion products.

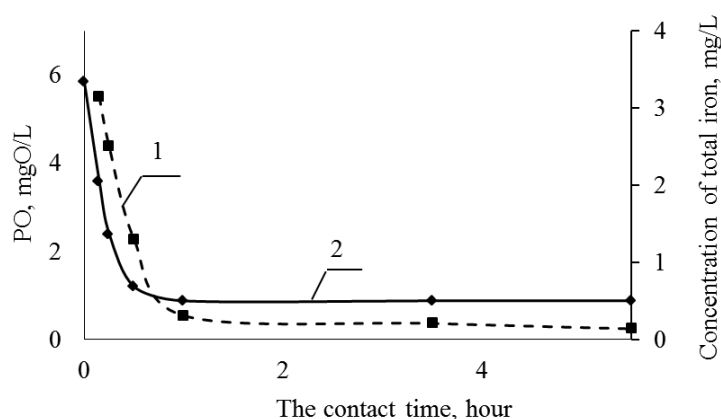


Figure 4. Dependence of the contact time on total iron concentration (1) and PO value (2).

It is seen in Fig. 4 that the optimum contact time of sodium humate with active erosion products is one hour. The value of PO and the iron concentration in solution come up to the maximum permissible concentration and further increase contact time does not lead to a change in the monitored parameters. The contact time experimentally ascertained shows that the load remains active for at least 1 hour after discharge disconnection for a sodium humate solution at TOC concentration 8 mg/L. The load activity is connected with the interaction of iron erosion products, water and sodium humate.

The groundwater of village Belyy Yar of Tomsk region was used as natural water. That water has a complex chemical composition and it contains such impurities as humic substances, iron ions and silicon compounds. Several papers [12, 13] show that the ability to form colloidal compounds in this type of water causes problems in the process of water purification. The difficulty of removing colloid

impurities are related to their stability to physical and chemical effects used in water treatment technology.

Fig. 5 shows the dependence of the permanganate oxidation and the color solution at the processing time of PED. The minimum processing time is 5 seconds, the maximum is 60 seconds.

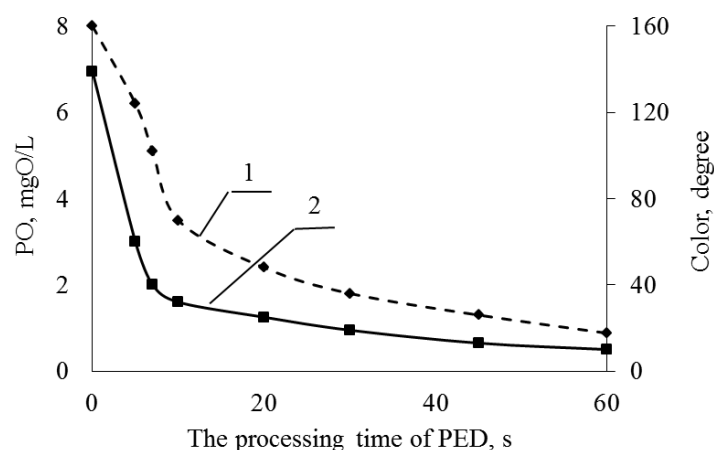


Figure 5. Dependence of the processing time on PO value (1) and color of solution (2).

Fig. 6 show, the changes of total iron concentration and silicon at the same processing time of PED.

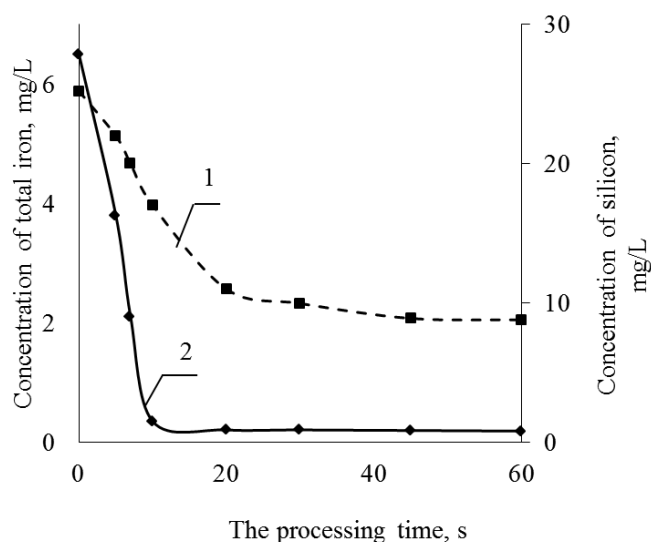


Figure 6. Dependence of the processing time of PED on silicon (1) and total iron (2) concentration.

Fig. 5 and 6 demonstrate that humic substances concentration is decreased and also the iron ions and silicon concentration are decreased at the groundwater treatment of village Belyy Yar, Tomsk region. The maximum parameters decrease is observed at the processing time close to 10 seconds. It fully corresponds to the results obtained for model humic solutions.

4. Conclusion

1. It is shown that the most intense color reduction to the maximum permissible concentration occurs at the processing time equal to 10 seconds. Experimental processing time is sufficient to obtain molar humic substances iron ion at the ratio of 2:3 and further processing time increase can be considered inappropriate.
2. It is found out that load activity is maintained for 1 hour after the discharge disconnection.
3. The role of secondary processes that occur after discharge disconnection, which are conditioned by suspension of activity is shown. The contact time of active erosion products with sodium humate, equal to 1 hour is established. The value of permanganate oxidation and iron concentration in solution achieves maximum permissible concentration during this time. Furthermore, the increase of contact time does not lead to the change in the monitored parameters.

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References

- [1] Piskarev I M 2000 *Journal of Physical of Chemistry Journal High Energi Chemistry* **74** 546-551
- [2] Piskarev I M, Spirov G M, Selemir V D, Karelin V I, Shlepkin S I 2007 *Journal High Energi Chemistry* **41** 334-336
- [3] Maksimova A I, Xlustova A V, Subbotina N N 2009 *Chemistry and Chemical Technology* **52** 116-120
- [4] Boev S, Yavorovsky N A 1999 *Digest of Technical Papers-IEEE International Pulsed Power Conference* **1** 181-184
- [5] Zerba A A, Petrichenko S V 2004 *Technical electrodynamics* **3** 27-32
- [6] Danilenko N B, Savelev G G, Yavorovsky N A Yyrmazova T A 2008 *Russian Journal of Applied Chemistry* **81** 803-810.
- [7] Aristova N A, Piskarev I M 2003 *Journal of Physical of Chemistry* **77** 723-726
- [8] Lobanova G L, Shiyan L N, Yyrmazova T A, Galanov A I 2014 *Proceedings of the universities. Physics* **57** 141-145
- [9] Parkansky N 2013 *Journal Plasma Chemistry Plasma Process* **33** 907-919
- [10] Kim J R 2013 *American Journal of Analytical Chemistry* **4** 115-122
- [11] Shiyan L N, Tropina E A, Machekhina K I, Gryaznova E N, An V V 2014 *SpringerPlus* DOI: 10.1186/2193-1801-3-260, URL: <http://www.springerplus.com/content/3/1/260>.
- [12] Machekhina K I, Shiyan L N 2014 *Advanced Materials Research* **1040** 342-346
- [13] Voyno D A, Machekhina K I, Shiyan L N 2014 *Advanced Materials Research* **971-973** 266-269