

Destruction of humic substances by pulsed electrical discharge

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Abstract. Currently, the water recourses in the territory of Tomsk region are groundwater which is limited to the high concentration of iron and manganese ions and organic substances. These impurities present in water in different forms such as soluble salts and the colloid forms. Therefore, the present work is a part of a continuations researcher of the processes in natural waters containing humic substances at the influence of pulsed electrical discharges in a layer of iron pellets. It is shown that the main stage of water purification process of humic substances during treatment by pulsed electric discharge in the layer of iron granules is a difficult process including several stages such as formation of iron oxyhydroxide colloid particles, sorption and coagulation with humic macromolecules substances, growth of particle dispersed phase and precipitation. The reason for the formation and coagulation of the dispersed phase is a different state of charge of the colloid particles (zeta potentials of $(\text{Fe}(\text{OH})_3)$ is +8 mV, zeta potentials of (Humic substances) is -70 mV. The most intense permanganate oxidation reduction to the maximum permissible concentration occurs at the processing time equal to 10 seconds. The contact time of active erosion products with sodium humate is established and it equals to 1 hour. The value of permanganate oxidation achieves maximum permissible concentration during this time and iron concentration in solution achieves maximum permissible concentration after filtration.

1. Introduction

The formation of stable colloid systems occurs in groundwater containing dissolved humic substances, silicates and heavy metal ions. In the papers [1-3] the formation of colloid solution is investigated. It is shown that the stable colloid solution forms at the molar ratio of iron ions, the silicates and humic substances equal 1: 7: 2, respectively.

Currently, there are various water treatment technologies to clean groundwater such as aeration, ozonation, treatment of pulsed electric discharge, membrane filtration [4-6]. Along with that [7-9] the existing methods do not allow to reduce the humic substances concentration by more than 30-40% of the initial concentration (20 mg/L) and the humic substances concentration exceeds the maximum permissible concentration after treatment. However, the removal of iron from natural waters is a complex scientific and technical problem, even when the concentration of humic substances does not exceed the limits of standard values. Therefore, the development of technology with integrated physical and chemical effects of the water are required. In view of this the use of spark electric discharges in combination with electro metal erosion in water purification technology is promising due to redox reactions, stimulation of sorption processes, destruction of organic matter, water disinfection.

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 groundwater.

2. Experimental approach

Object of the research is the groundwater containing humic substances from the village Vertikos Tomsk region. The experimental work was carried out in an accredited laboratory of Radiation spectroscopy in Tomsk polytechnic university using attorney equipment. For the experiments concerning the effect of the discharge on the stability of humic substances, the installation was used according to the paper [10]. This installation was constructed in the 12th laboratory of High Technologies Physics Institute in TPU.

Russian standard methods were used to determine the chemical composition of natural waters in accordance with the sanitary standard 2.1.4.1074-01 and GOST 51232-98.

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).

The colloid particle size distribution and the ζ -potential in the model solutions were determined using a Zetasizer Nano ZS analyzer (Malvern Instruments, UK), which allows measuring the particle size in the range 0.6...6000 nm. The particle size was determined by dynamic light dispersion (at a dispersion angle of 173°). The measurement result was in the form of numerical particle distribution $s\varphi(r)=dN/dr$. The mode δ_m was found from the maximum of this distribution and was taken as an average particle size because the distribution functions approximated normal log functions.

The chemical composition of the surface formed by electro metal granules in water and aqueous solutions was studied using infrared diffuse reflectance spectroscopy FTIR using a spectrometer Nicolet 5700 (USA).

3. Results and discussion

Indicators of the quality of groundwater for different wells Vertikos village are shown in Table 1. Table 1 demonstrates that the main indicators exceeding the maximum permissible concentration values are color, iron, manganese and permanganate oxidation.

Table 1. Quality indicators of groundwater v. Vertikos Tomsk region.

Determined parameters	The groundwater of v. Vertikos	
	№ 1	№ 2
pH, ед. pH	6.9	6.9
Color, grad	39	31
Turbidity, mg/L	29.3	27.8
Hardness, °H	4.8	4.6
PO, mgO/L	7.2	7.3
HCO ₃ ⁻ , mg/L	329.5	328.5
Iron, mg/L	6.3	5.9
Manganese, mg/L	0.55	0.53
Silicon, mg/L	10.8	11.1

Processing groundwater in a pulsed electric discharge (PED) v. Vertikos brought to change parameters such as pH, permanganate oxidation the total iron concentration (Fig. 1).

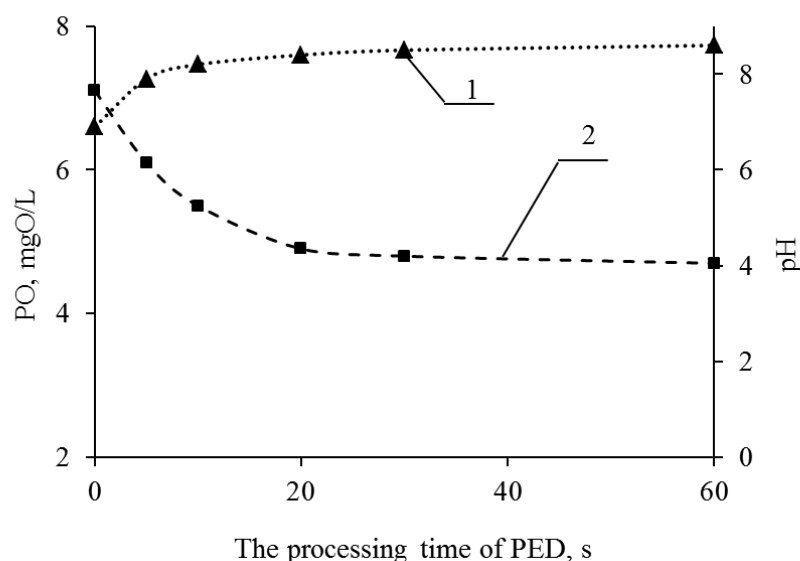


Figure 1. Dependence of the processing time of PED on pH (1) and value PO (2) (holding time before analysis - 1 hour)

It is seen in Fig. 1 that pH of the solution increases due to the interaction erosion products with water and decomposition of water by the action of the pulse electric discharge on iron pellets. The reduction of permanganate oxidation (PO) indicates that the impurities oxidize by the action of discharge on the water.

The formation and growth of colloidal particles occurs under the influence of electrostatic interaction forces. Value of ζ -potential (mV) for particle erosion products has a positive value and it equals +8 mV. After the interaction of iron compounds hydrolysis products having a positive ζ -potential with the humic substances (ζ -potential = -70 mV) occurs recharge of surface erosion products and value ζ -potential becomes negative and equals -27 mV.

The qualitative composition of deposits obtained after coagulation of erosion products with humic substances from groundwater n. Vertikos determined by IR - spectra presented is shown in the Fig. 2 and Table 2. The IR-specters of sodium humate and erosion products present on the fig. 2 for comparison.

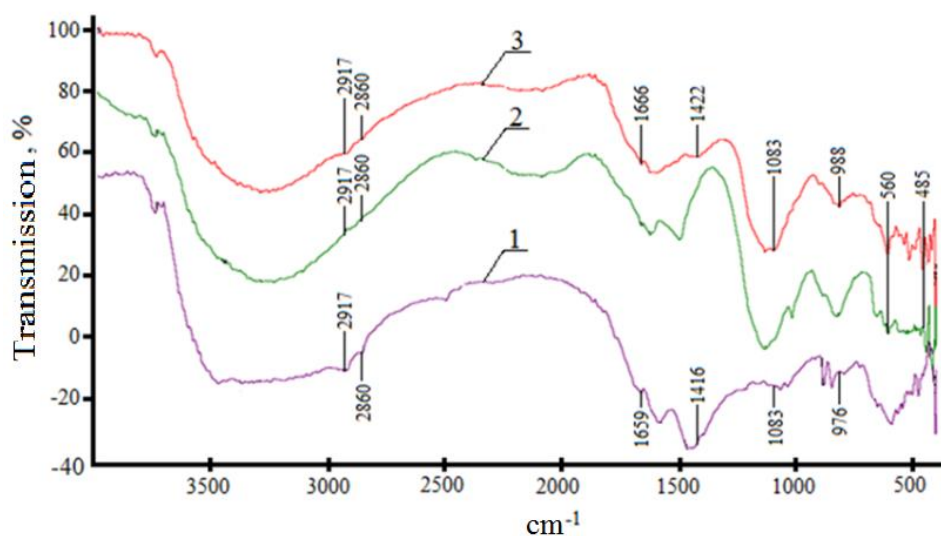


Figure 2. IR-spectra: 1 – sodium humate; 2 – erosion products; 3 – sodium humate with erosion products.

Table 2. Characteristic vibrational frequencies bands in the IR-specters.

Humic substances	Sodium humate	Erosion products of iron pellets	Sodium humate, besieged on erosion products	Functional groups
2920	2917	2917	2917	–OH
2860	2867	2867	2853	–OH
1650	1659	отс.	1666	–C–H
1400	1416	отс.	1422	–C–O
1063	1083	отс.	1083	COO [–] , HOH, ⁺ NH ₃
980	976	отс.	988	C ₆ H ₅ –

The analysis of IR–spectra is shown that there are three spectrum bands: 560 cm^{–1}, attributable to stretching vibrations and Fe₂O₃ strip 485 cm^{–1} attributable to the stretching vibrations FeOOH. There are 3 bands of stretching vibrations 1420 cm^{–1} related to the symmetric stretching vibrations of carboxylate ions (C–O), characterized by the presence of humic substances in the sediment, and stretching vibrations at a frequency of 1650 cm^{–1}, is characterized by fluctuations due (C–H) in their aromatic fragments at the same curve. The band 1083 cm^{–1} refers to fluctuations –COO– bonds, HOH, ⁺NH₃, and the band 988 cm^{–1} characterize vibrations of the aromatic ring fragments.

Ground water from v Vertikos was treated by pulsed electric discharge in a layer of iron pellets and it had been settled during 1 hour. The upper layer was analyzed for total iron and the total organic carbon (Fig. 3).

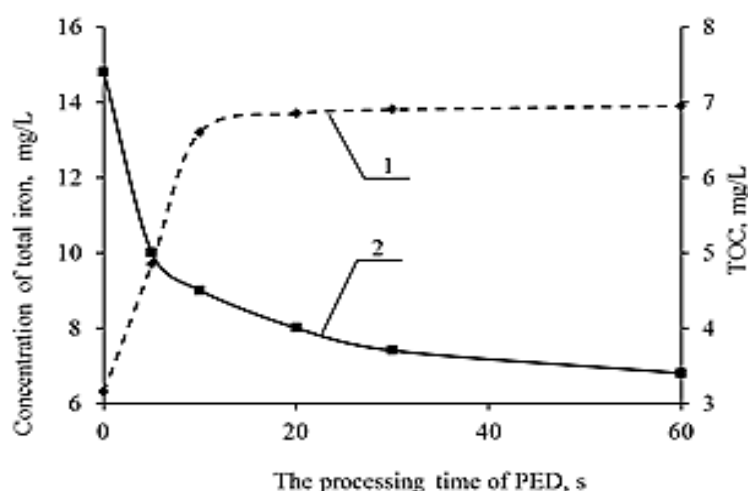


Figure 3. Dependence of the processing time on total iron concentration (1) and TOC (2)

Figure 3 demonstrates that the concentration of humic substances decreases according to the processing time of PED, whereas the iron ions (II) concentration in solution corresponds to 14 mg/L. Iron remaining after interaction with the humic substances as hydroxides can be removed by filtration. Table 3 shows that the main indicators of water quality after all treatment steps do not exceed the maximum permissible concentration for drinking water.

The two stage of process have been established based on the results obtained by the action of a pulsed electrical discharge in a layer of iron pellets in groundwater. The first stage - is electro-erosion stage and destruction of organic substances which takes place at the discharge action is short time ($\tau = 10$ c), the second stage is a long and it occurs after discharge shutdown ($\tau = 1$ hour).

Table 3. Quality indicators of groundwater v. Vertikos Tomsk region before and after treatment

Parameter	Units	Ground water v. Vertikos				MPC
		source of water	PED (10 s)	Contact (1 h)	Filtration	
pH	units pH	6.9	7.5	7.5	7.5	6–9
Color	grad	39	7	5	5	20
Turbidity	mg/L	29.3	56.3	23.5	1.0	1.5
hardness	$^{\circ}\text{K}$	4.8	4.8	4.8	4.8	7.0
PO	mgO/L	7.2	5.2	1.0	1.0	5.0
Iron		6.3	35.1	14.0	0.2	0.3
Manganese	mg/L	0.55	0.55	0.1	0.05	0.1
Silicon		10.8	10.7	6.9	6.9	10.0

4. Conclusion

1. It is found that the limiting stage water purification process of humic substances during spark treatment in the layer of iron granules is a complex of processes including formation of iron oxyhydroxide colloid particles, sorption and coagulation together with humic macromolecules substances, growth of particle dispersed phase and precipitation. The reason for the formation and coagulation of the dispersed phase is a different state of charge of the colloid particles (zeta potentials $\zeta(\text{Fe}(\text{OH})_3) = +8 \text{ mV}$, $\zeta(\text{Humic substances}) = -70 \text{ mV}$).
2. It is shown that the most intense permanganate oxidation reduction to the maximum permissible concentration occurs at the processing time equal to 10 seconds.
3. It is shown the role of secondary processes. The contact time of active erosion products with sodium humate is established and it equals to 1 hour. The value of permanganate oxidation achieves maximum permissible concentration during this time and iron concentration in solution achieves maximum permissible concentration after filtration.

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References

- [1] Shiyani 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>
- [2] Machekhina K I, Shiyani L N 2014 *Advanced Materials Research* **1040** 342-346
- [3] Voyno D A, Machekhina K I, Shiyani L N 2014 *Advanced Materials Research* **971-973** 266-269
- [4] Serikov L V, Tropina E A, Shiyani L N, Frimmel F H, Metreveli G, Delay M 2009 *Journal for Soils and Sediments* **9** 103-110
- [5] Svetleishaya E M, Mitchenko T E, Astrelin I M 2014 *Journal of Water Chemistry and Technology* **36** 25-30
- [6] Kornev J, Yavorovsky N, Preis S, Khaskelberg M, Isaev U, Chen B-N 2006 *Ozone: Sci. and Engineering* **28** 207-215
- [7] Zherlitsyn A G, Shiyani V P, Shiyani L N, Magomadova S O 2015 *Journal of Physics: Conference Series* **652**
- [8] Machekhina K I, Titova E N, Kornev Y I, Shiyani L N, Preys S, Magomadova S O 2016 *Key Engineering Materials* **685** 648-652
- [9] Kornev I, Preis S, Gryaznova E, Saprykin F, Khryapov P, Khaskelberg M, Yavorovskiy N 2014 *Industrial and Engineering Chem. Res.* **53** 7263-7267
- [10] Danilenko N B, Savelev G G, Yavorovsky N A, Yirmazova T A 2008 *Russian Journal of Applied Chemistry* **81** 803-810