

# Study of adsorption process of iron colloid substances on activated carbon by ultrasound

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**Abstract.** The paper reports on the adsorption of iron colloid substances on activated carbon (PAC) Norit SA UF with using ultrasound. It is found that time of adsorption is equal to three hours. High-frequency electrical oscillation is 35 kHz. The adsorption capacity of activated carbon was determined and it is equal to about 0.25 mg iron colloid substances /mg PAC. The iron colloid substances size ranging from 30 to 360 nm was determined. The zeta potential of iron colloid substances which consists of iron (III) hydroxide, silicon compounds and natural organic substances is about (-38mV). The process of destruction iron colloid substances occurs with subsequent formation of a precipitate in the form of  $\text{Fe}(\text{OH})_3$  as a result of the removal of organic substances from the model solution.

*Keyword:* iron colloid substances, adsorption, activated carbon, ultrasound

## 1. Introduction

The present work relates to the problem of high-quality drinking water supply using processes of adsorption on activated carbon with using ultrasound with the oscillation frequency 35 kHz. In papers [1, 2] it is shown that iron containing groundwater of Western Siberian can be divided into two types. The first type is the water with a high concentration of hydrocarbonate where iron presents in the form of hydrocarbonate iron. The second type is water where iron presents partly in the form of hydrocarbonate iron and partly as a complex with dissolved organic substances. The classical water treatment which includes such step as the aeration, sedimentation and filtration is successfully applied for producing potable water from the water of the first type [2]. Using traditional methods of water treatment for the second type is not always allowed to provide the necessary quality of water. This is due to the ability to form iron colloid solutions during the oxidation [3]. These solutions are stable for a long time. This complicates the water treatment process and significantly reduces the performance of the facilities used in [1].

Currently, many research groups engaged in the study of the processes of absorption for the removal colloid substances [4, 5]. In addition there is work studying the adsorption processes of organic substances on activated carbon [6, 7]. Therefore, this work is relevant.

The objective of the work is to investigate the processes of adsorption for the removal iron colloid substances on activated carbon with using ultrasound.

## 2. Experimental approach

For synthesis and analytical study, reagents  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  and distilled water were used. Organic substances for experiments were extracted from peat bogs of the Tomsk region. The concentration of organic substances was determined using an analyzer of dissolved organic carbon (DOC) with subsequent IR-analysis of  $\text{CO}_2$  evolved. The molar mass of organic substances was determined by the gel-chromatography method [8]. The samples contained fractions of 200–20000 Da.



All model solutions were synthesized at room temperature. A shaker GFL 3005 (Germany) with a shaking frequency 100 rounds / min was used for mixing.

The iron and silicon concentrations in the solution were determined using an ICP-OES plasma optical emission spectrometer (Varian, USA). The pH value was measured using a WTW Multiline P4 multifunctional device (WTW GmbH, Germany). The colloid particle size distribution and the  $\zeta$ -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  $\delta_m$  was found from the maximum of this distribution and was taken as an average particle size because the distribution functions approximated normal log functions.

For the adsorption experiments activated carbon Norit SA UF was used, which was produced by Norit, table 1. The specified sorbent has high kinetic characteristics due to the superthin structure of its particles.

**Table 1.** Specification of the sorbate Norit SA UF

Characteristic	Value
Produce	Norit
Name	Norit SA UF
Total surface area m <sup>2</sup> /g	1200
Particles size, $\mu$ m	7
Apparent density, kg/m <sup>3</sup>	160
Moisture, mass., %	5

The ultrasonic bath (PSB-4035-05, Russia) was used to power source. The operating frequency was  $35 \pm 10$  kHz. The power supply was the ultrasonic generator that connects to electricity 220 V and 50-60 Hz. Amplitude modulation is up to 90%.

### 3. Results and discussion

Adsorption is the accumulation of atoms or molecules on the surface of a material. The substance on whose surface there is an adsorption, is referred to as adsorbent, and the substance which is adsorbed as adsorbate. Forces of interaction between adsorbent and adsorbate, determining adsorption, are various, and usually consider two extreme cases when adsorption is characterized by physical or chemical interactions: so-called physical and chemical adsorption [9].

The equation of adsorption shows functional dependence of the following kind:

$$f(q, C, T) = 0 \quad (1)$$

where  $q$  is the amount of adsorbed substance (in kmol), designed on 1m<sup>2</sup> adsorbent surfaces (or on 1 kg adsorbent);  $C$  is the equilibrium concentration in the solution;  $T$  is the temperature.

If the temperature is constant, the adsorbed amount of substance is a function of the amount of adsorbent and the concentration of adsorbate. This equation is referred to as adsorption isotherm.

There is no general theory which correctly enough would describe all kinds of adsorption on various adsorbents and different interfaces. Common theories are the monomolecular adsorption theory from Langmuir and the Freundlich isotherm [9].

The Langmuir isotherm is described by the following equation:

$$q = q_m (K_1 C / (1 + K_1 C)) \quad (2)$$

where  $q$  is the amount of the substance adsorbed on 1 m<sup>2</sup> of a surface (or 1g) adsorbent (specific adsorption of a substance), g/m<sup>2</sup> or g/g;  $q_m$  is the maximum amount of the substance adsorbed 1 m<sup>2</sup> of a surface (or 1g) adsorbent in g/m<sup>2</sup> or g/g;  $C$  is the equilibrium concentration of the adsorbent in the gas phase or the solution;  $K_1$  is the Langmuir adsorption coefficient which depends on the structure of the adsorbed molecules.

Concerning adsorption from water solutions, the Langmuir isotherm suitable for the adsorption of big molecules, like humic substances which cause the color of natural waters [10].

During adsorption two kinds of intermolecular interactions compete: hydration of molecules of the dissolved substance, i.e. their interaction with molecules of water in a solution, and interaction of

molecules of adsorbed substance with atoms of a surface of a firm body. The energy difference of these two processes also represents energy from which the substance taken from a solution is kept on a surface shipped in a solution of eluate. The strongest adsorptive interaction is observed if in the structure of the molecules there are the double bonds formed with participation of  $\pi$  - electrons. Therefore, adsorption of aromatic compounds is much better than of aliphatic substances.

Adsorption decreases at increase in molecules of number hydroxide groups possessing the big energy of hydration due to hydrogen bonds. Adsorption also decreases with the presence of electric charge focusing around of dipoles of water.

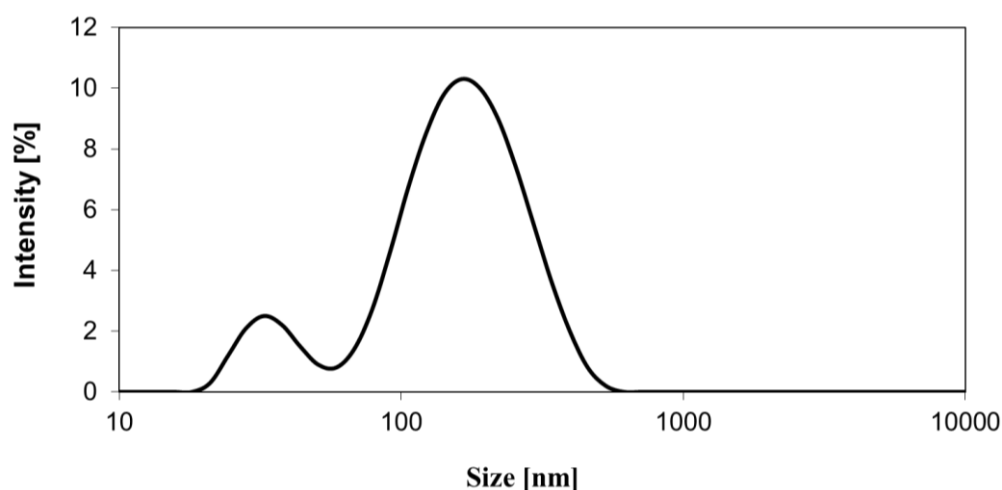
The model solution has been prepared with a technique [11]. Different properties of the solution have been investigated: pH-value and electroconductivity were analyzed with a multipurpose device WTW Miltiline P4, particle-sizing interferometry and measurement of  $\zeta$  -potential in solution have been performed. The basic parameters are shown in the table 2.

**Table 2.** Comparison of different properties of the model solution and groundwater

Parameter	Model solution	Groundwater
pH	6.5	6.0...7.0
Electroconductivity, $\mu\text{S}/\text{cm}$	205	-
$\zeta$ - potential, mV	-21...-32	-20...-120
Concentration of organic substances (DOC), mg/L	2.43	2.0...14.0
Concentration of iron, mg/L	6.92	1.0...25.0
Concentration of silicium, mg/L	24.13	10.0...28.0

Table 2 shows that the model solution corresponds to real groundwaters of northern regions of Tomsk area [12]. Hence, it could be used as model system for the investigation of adsorption processes as well as ultra and nano filtration in the experiments.

Figure 1 shows a distribution of particle size in the model solution.

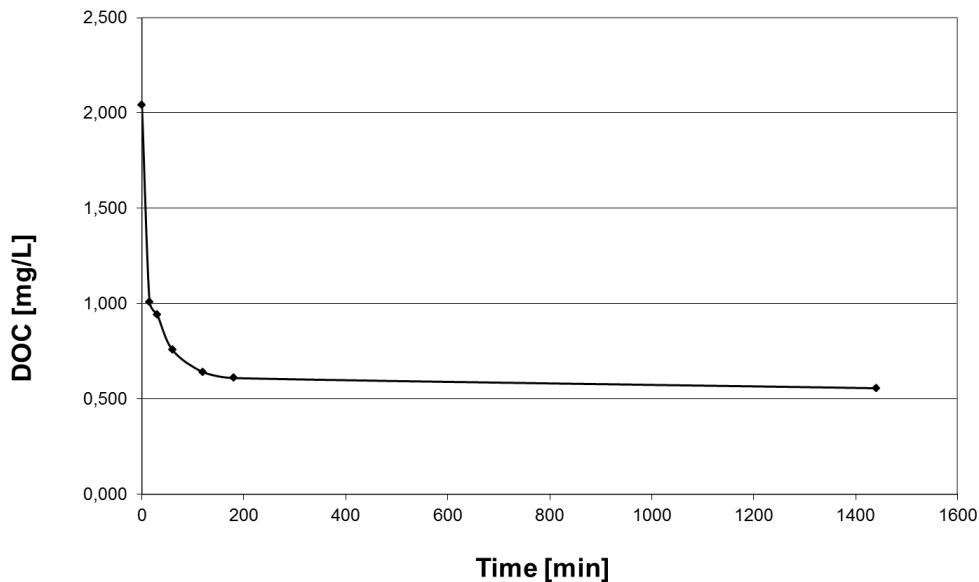


**Figure 1.** Size distribution of the colloid particles in the model solution.

Figure 1 shows that the solution contains basically two types of particles (maxima at 33 and 165 nanometers).

Adsorption experiment consisted of two basic parts. The first part is analysis of the adsorption kinetics and second one is analysis of the adsorption isotherm. Activated carbon was used as adsorbent for the analysis of the adsorption kinetics. The mass of activated carbon was 12.5 mg in 250 ml solution (50mg/L). The activated carbon ( $m=12.5\text{mg}$ ) was put into a flask (volume 250 ml) filled with model solution. After that the model solution with activated carbon was shaken with using ultrasound. The flasks were removed after 15, 30, 60, 120, 180 and 1440 minutes after the beginning of shaking. After that solutions were filtrated through a membrane with a pore size of  $0.4\mu\text{m}$  (Millpore, USA).

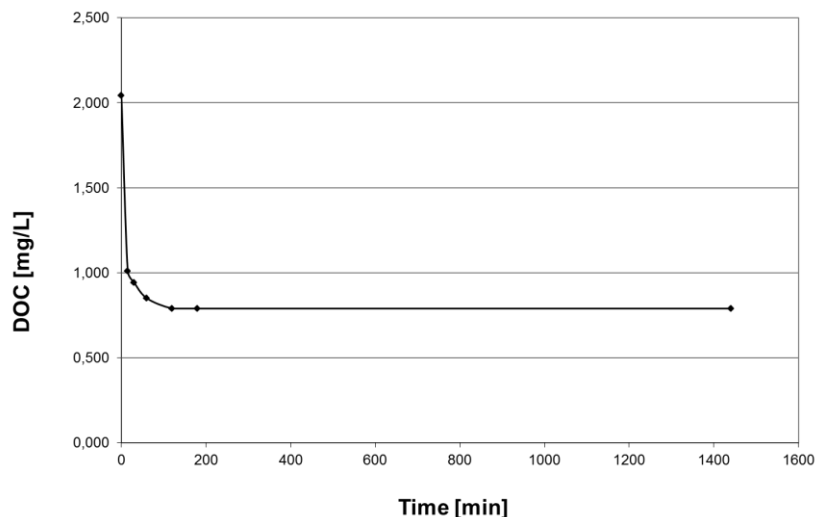
Concentrations of DOC, Fe and Si were measured in the solution after filtration. The results are presented in figure 2.



**Figure 2.** Adsorption kinetics of the model solution on activated carbon with ultrasound.

Figure 2 shows that silicium and iron practically did not adsorb, but the concentration of organic substances decreased from 2.24 mg/L to 0.6mg/L.

The adsorption process without sonication proceeds less efficiently. Changes in the concentration of DOC are presented in Figure 3.



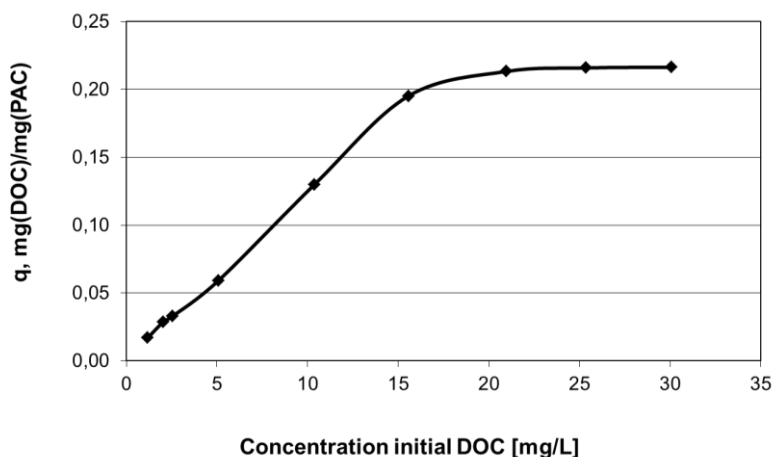
**Figure 3.** Adsorption kinetics of the model solution on activated carbon without ultrasound.

Figure 3 shows that the concentration of organic substances decreased from 2.24 mg/L to 0.79 mg/L. This is due to the fact that the rearrangement of the organic molecules and their division into smaller occurs under the action of ultrasound. This process dominates the desorption of organic molecules from activated carbon. Thus three hours were found as minimum to achieve an adsorption-equilibrium and were hence chosen as adsorption time for the determination of the isotherm. Concentration of activated carbon remained 50 mg/L, concentration of iron and silicium in initial solutions remained at 6.73 mg/L for iron and 25.61 mg/L for silicium. The concentration of DOC increased from 1.2 mg/L to 30.1 mg/L.

The Langmuir model was applied for the calculation of the adsorption isotherm. For this purpose eq. 3. was used in the form formula:

$$\frac{C}{q} = \frac{C}{q_m} + \frac{1}{q_m \cdot K_l} \quad (3)$$

It was not possible to fit the entire data set to the Langmuir model. For the four points of highest initial concentrations.  $K_l$  and  $q_m$  were determined, and  $K_l$  is equal to 0.26 and  $q_m$  is equal 0.25mg/mg. The bad results for the fitting of the whole data set might be due to experimental mistakes in the lower concentration range. Figure 4 shows the adsorption isotherm.



**Figure 4.** The adsorption isotherm of model solution on activated carbon Norit SA UF.

The maximum adsorption capacity of activated carbon to organic substances is 0.25 mg / mg. Thus, the destruction of iron colloid substances occurs due to the removal of organic substances from the model colloid solution through the adsorption process on activated carbon with formation of a precipitate in the form of  $\text{Fe}(\text{OH})_3$ .

#### 4. Conclusion

1. Experimental modelling was performed to study the chemical properties of colloid solutions containing iron ions, dissolved organic substances, and silicon ions.
2. The iron hydroxide nanoparticles size is in the range from 30 to 360 nm and characterizes the steady state of the colloid system.
3. The adsorption capacity of activated carbon was determined and it is equal to about 0.25 mg iron colloid substances /mg PAC.

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