IOP Conf. Series: Materials Science and Engineering **110** (2016) 012097 doi:10.1088/1757-899X/110/1/012097

Study the properties of activated carbon and oxyhydroxide aluminum as sorbents for removal humic substances from natural waters

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Abstract. The present work relates to the problem of high-quality drinking water supply using processes of adsorption on activated carbon and aluminum oxyhydroxide for removal humic-type organic substances. Also the paper reports on sorbtion properties of the activeted carbon Norit SA UF and oxyhydroxide aluminum for removal humic substances. It was found out that the maximum adsorption capacity of activated carbon to organic substances is equal to 0.25 mg/mg and aluminum oxyhydroxide is equal to 0.3 mg/mg. It is shown that the maximum adsorption capacity of activated carbon Norit SA UF to iron (III) ions is equal to 0.0045 mg/mg and to silicon ions is equal to 0.024 mg/mg. Consequently, the aluminum oxyhydroxide has better adsorption characteristics in comparison with the activated carbon for removal of humic substances, iron and silicon ions. It is associated with the fact that activated carbon has a large adsorption surface, and this is due to its porous structure, but not all molecules can enter into these pores. Therefore, the fibrous structure of aluminum oxyhydroxide promotes better sorption capacity. The presented results suggest that activated carbon Norit SA UF and aluminum oxyhydroxide can be used as sorbents for removal humic substances or other organic substances from groundwater and natural waters.

1. Introduction

The present work relates to the problem of high-quality drinking water supply using processes of adsorption on activated carbon and aluminum oxyhydroxide for removal organic substances from natural water. The present of organic substances in natural water is one of the reasons of formation colloid solutions with high stability [1-3]. The stability of the colloidal system has both positive and negative sides. On the one side stable colloid systems are used to increase productivity in chemical industry and technology, agriculture and animal industry. They are also used to manufacture highly effective pharmaceutical products [4] and to obtain lubricants with high tribological properties [5]. On the other side it is necessary to reduce the stability of colloidal systems. Various types of colloid systems exist in the nature or arise spontaneously in industrial and natural processes, e.g., on extraction and purification of natural waters. This is due to high stability of colloid solutions based on iron compounds. Colloids of iron compounds are found in natural waters of Germany, Finland, Russia, USA, etc. It is shown that humic-type organic substances play an important role in the formation of iron colloid compounds [6, 7]. In Russia, where boggy areas occupy half the country and iron ions are present almost in all water sources, the problem of colloid removal is of immediate interest.

Marshes and small rivers, which contain humic-type substances, are most likely to contribute to the formation of stable colloid iron compounds. There are different methods of water treatment from humic-type substances such as aeration, ozonation, filtration and etc. [8]. However, some of them are not effective or economically impractical. Therefore, the question of finding methods of treatment remains open.

Currently, many research groups engaged in the study of the processes of absorption for the removal colloid substances [9, 10]. In addition there is work studying the adsorption processes of organic substances on activated carbon [11, 12]. Therefore, this work is relevant.

The objective of the work is to investigate the adsorption processes for removal humic substances from natural water on activated carbon and on aluminum oxyhydroxide.

2. Experimental approach

For synthesis and analytical study, reagents $FeSO_4 \cdot 7H_2O$, $Na_2SiO_3 \cdot 9H_2O$ and distilled water were used. Organic substances for experiments were extracted from peat bogs in the Tomsk region. The organic substances concentration was determined by analysis of the total organic carbon (TOC) content. The initial organic substances concentration varied in the range 0.05...4.0 mg/L. The organic substances molar mass was determined by the gel-chromatography method [13]. 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).

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. The second sorbent which was used it is aluminum oxyhydroxide. For synthesis aluminum oxyhydroxide, the method was used according technique [14].

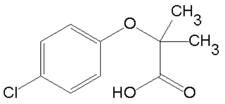
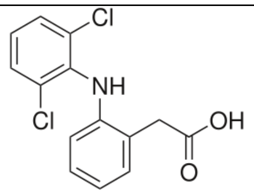
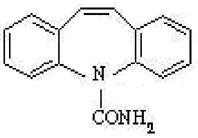
Table 1. Specification of the sorbents Norit SA UF and aluminum oxyhydroxide.

Characteristic	Value	
Sorbent	Norit SA UF	Aluminum oxyhydroxide
Produce	Norit	Laboratory product
Name	Norit SA UF	Aluminum oxyhydroxide
Total surface area (m^2/g)	1200	215
Particles size,(μm)	7	-
Apparent density, (kg/m^3)	160	-
Moisture, mass., (%)	5	-

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 and aluminum oxyhydroxide 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=12.5mg) was put into a flask (volume 250 ml) filled with model solution. After that the model solution with activated carbon was shaked. 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 0.4μm (Millpore, USA). The mass of aluminum oxyhydroxide was 100 mg in 250 ml solution (400 mg/L). The aluminum oxyhydroxide (m=100 mg) was put into a flask (volume 250 ml) filled with model solution. After that the model solution with aluminum oxyhydroxide was shaked. The flasks were removed after 15, 30, 60, 120, 180, 240 and 360 minutes after the beginning of shaking. After that solutions were filtrated through a membrane with a pore size of 0.4μm (Millpore, USA).

Three pharmaceutically active compounds were used: clofibric acid, diclofenac and carbamazepinee. All of them have different properties (table 2).

Table 2. Pharmaceutically active compounds used for the experiments.

	Clofibric acid (97%), Aldrich	
Application	Blood lipid regulator agent	
Formula	$C_{11}H_{11}ClO_3$	
M (g/mol)	216	
Charge	negative	
	Diclofenac sodium salt, Sigma	
Application	Anti-rheumatic	
Formula	$C_{11}H_{11}Cl_2NO_2$	
M (g/mol)	296	
Charge	neutral	
	Carbamazepinee (99%), Aldrich	
Application	Anticonvulsant agent	
Formula	$C_{15}H_{12}N_2O$	
M (g/mol)	236	
Charge	neutral	

3. Results and discussion

It was experimentally found that silicon and iron ions do not practically adsorb on activated carbon but the concentration of humic-type organic substances reduces by 3 times. The time of adsorption is equal to 3 hours. The concentrations of iron and silicon ions did not change in the initial solutions and it was 6.73 mg/L for iron ions and 25.61 mg/L for silicon ions. The initial concentration of organic substances was varied in the range 1.2...30.1 mg/L. The Langmuir model was applied for the calculation of the adsorption isotherm. For this purpose eq. 1. was used in the form formula:

$$\frac{C}{q}=\frac{C}{q_m}+\frac{1}{q_m\cdot K_l}, \tag{1}$$

where

q is the amount of the substance adsorbed on 1 m² of a surface (or 1g) adsorbent, g/m ² or mg/mg;
q_m is the maximum amount of the substance adsorbed on 1 m² of a surface (or 1g) adsorbent, mg/mg;
C is the equilibrium concentration of the adsorbent in the gas phase or the solution; K_l is the Langmuir adsorption coefficient which depends on the structure of the adsorbed molecules.

Figure 1 shows the adsorption isotherm which was constructed according to the Langmuir model.

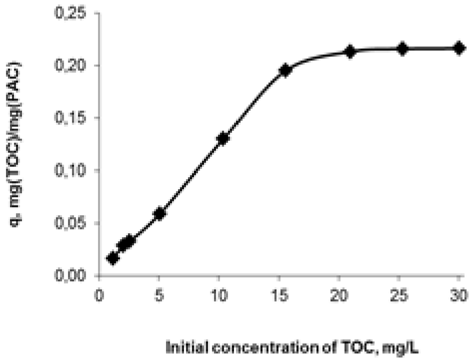


Figure 1. The adsorption isotherm of model solution on activated carbon for organic

substances

As it is seen in Fig. 1, the maximum adsorption capacity of activated carbon to organic substances is 0.25 mg/mg.

For comparison further adsorption experiments have been performed with diclofenac, clofibric acid and carbamazepine in demineralized water because these substances can be in natural waters [15]. Comparing the maximum adsorption capacity (q_{max}), which was calculated with the Langmuir model (table 3) it is possible to draw the conclusion that at the given experimental conditions, diclofenac adsorbs better on activated carbon than the humic-type organic substances of the model solution, but carbamazepine and clofibric acid did not.

Table 3. Process of adsorption on activated carbon.

Substances	Adsorptive capacity (q_{max})
Humic-type organic substances	0.25 mg TOC/mg PAC
Diclofenac	0.45mg Diclofenac /mg PAC
Clofibric acid	0.12 mg Clofibric acid/mg PAC
Carbamazepine	0.23 mg Carbamazepine/mg PAC

For the aluminum oxyhydroxide, the effects of humic-type organic substances are similar, but the time of adsorption is equal to 2 hours. Comparison of activated carbon shows that silicon and iron ions practically adsorb on aluminum oxyhydroxide. It was necessary to increase the iron and silicon concentration in the solution to obtain the adsorption isotherm. But it is impossible due to the model colloid system is stable at a certain ratio of iron - silicon - organic substances. Therefore, another method is used to construct isotherms. The mass of aluminum oxyhydroxide was varied in the range 0.1...60.0 mg. Figure 2 shows the adsorption isotherm which was constructed according to the Langmuir model for organic substances.

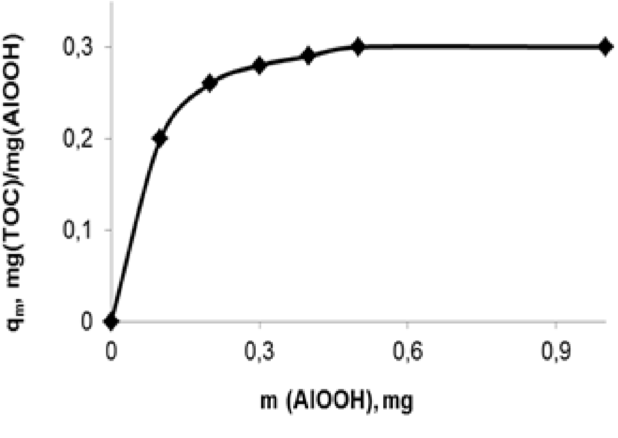
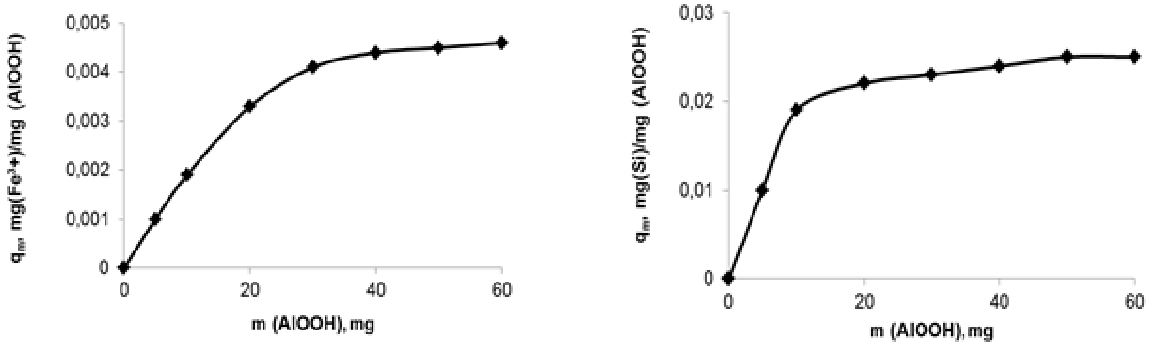


Figure 2. The adsorption isotherm of model solution on aluminum oxyhydroxide for organic substances

As it is seen in Fig. 2, the maximum adsorption capacity of aluminum oxyhydroxide to organic substances is 0.3 mg/mg. Comparison of activated carbon shows that adsorption capacity of aluminum oxyhydroxide more than it. This may be due to the fact that the aluminum oxyhydroxide has a positive charge on the surface, while the humic-type organic substances have negative charge, as shown earlier [6]. Figure 3 show the adsorption isotherm which was constructed according to the Langmuir model for iron and silicon ions.



a b

Figure 3. The adsorption isotherm of model solution on aluminum oxyhydroxide for: a) iron ions; b) silicon ions.

Figure 3 demonstrates that the maximum adsorption capacity of aluminum oxyhydroxide to iron ions is 0.004 mg/mg and to silicon ions is 0.024 mg/mg. The results obtained in the work suggest that the aluminum oxyhydroxide has better sorption capacity than activated carbon is associated with the fact that activated carbon has a large adsorption surface, and this is due to its porous structure, but not all molecules can enter into these pores. Therefore, the fibrous structure of aluminum oxyhydroxide promotes better sorption capacity.

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 aluminum oxyhydroxide with formation of a precipitate in the form of $Fe(OH)_3$.

4. Conclusion

The application of aluminum oxyhydroxide is most effective in relation to organic substances, iron and silicon ions. The adsorption capacity of aluminum oxyhydroxide was determined and it is equal to about 0.30 mg/mg for humic-type organic substances. Consequently, the aluminum oxyhydroxide has better adsorption characteristics in comparison with the activated carbon (0.25 mg/mg). Furthermore, aluminum oxyhydroxide can be used for treatment of colloidal solution for natural waters containing silicon and iron ions.

Acknowledgements

The study was supported by National Research Tomsk Polytechnic University, the project No. 7.1504.2015.

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