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Water Purification with Natural Sorbents: Effect of Surface Modification with Nano-Structured Particles

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Abstract

Modified nanostructured sorbents are widely used in water treatment processes. In this work, aluminum and iron particles prepared by electro-spark dispersion have been applied as modifiers. Zeolite samples from “Holinskoe” mineral deposit (Russia, Republic of Buryatia), with a size smaller than 0.1 mm, have been modified with aluminum and iron particles, using a sol-gel process. The properties of the modified materials have been determined by means of sorption test, when removing ions Pb^{2+} , Fe^{3+} and Cd^{2+} from the model solutions in static conditions. Using the method of thermal desorption of nitrogen (BET) it has been shown that increasing the iron content in the samples of nanostructured modified sorbents does not affect the increase in specific surface area and pore volume of the samples. Ions concentrations have been analyzed by stripping voltammetry and photocolourimetry. As a result, modified sorbents revealed a high efficiency sorption of heavy metals.

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Keywords: nanoparticles; sorbent; water purification; lead; iron; cadmium; heavy metals; electro-spark dispersion; sol-gel process.

1. Introduction

One of the important problems, currently facing the society, is the provision of clean drinking water. According to the forecasts, the situation will worsen in the future due to the reduction of fresh water supplies and population

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growth^{1,2}. Among the various methods of water purification, filtration plays a major role. That is why new types of nanostructured materials become more and more widely used³⁻⁵. Heavy metals are among the most common of the various types of hydrosphere pollution^{6,7}. Ions of heavy metals are toxic and bioaccumulative, with further biomagnification. Therefore, the purification of drinking water of heavy metal compounds is an important process for life safety, and the design of new types of nanostructured sorbents for the removal of heavy metals from water is a very relevant task. There are various physical and chemical methods for preparing samples of nanostructured materials, such as a sol-gel process, electro-spark dispersion, and electric explosion⁸. The choice of nanoparticles preparation approach depend on the physical and chemical characteristics required for the final product, such as size, dispersion, chemical miscibility and total cost of it, especially for widely used products⁹. In this work, we consider the method of electro-dispersion for preparation of nanostructured materials, for the purpose of their further application to create modified zeolites. The resulting nanostructured product can be used in designing a new filter system for water purification. Detail process description and confirmation nanoscale size of the materials prepared by this method, are reflected in works⁹⁻¹¹. The aim of this work was to create and study the physicochemical and sorption properties of new modified sorbents with nanostructured surface based on aluminum and iron, obtained by the electro-dispersion method. The sorption studies of the samples were carried out in aqueous solutions containing ions of lead Pb^{2+} , iron Fe^{3+} and cadmium Cd^{2+} .

2. Materials and methods

2.1 Preparation of modifiers for sorbent surface

Electric-spark dispersion method was used for preparation of nanostructured materials based on aluminum and iron, as following. The dispersion was carried out in an aqueous medium. Figure 1 shows the scheme of the experimental apparatus for nano-powder preparation. The experimental device consisted of a pulsed power supply and reactor made of a dielectric material (porcelain container, $V = 1.0 \text{ dm}^3$), in which aluminum electrodes, metal loading and a working fluid were placed. Under the action of the pulse, many micro discharges appeared between the aluminum granules, causing erosion of granules with evaporation in the contact area and spraying of the small metal particles from the granules. The power supply generated voltage pulses with a duration of $15 \mu\text{s}$ with the voltage amplitude of 500 V, the current amplitude of 250 A, and pulse frequency of 400 Hz. The inter-electrode gap was filled with cylindrical aluminum granules with the diameter from 3 to 5 mm, total weigh 100 g. Thickness of the granular layer was 10 mm. Aluminum rods with a diameter of 4mm were used there as electrodes. The distance between the electrodes was 100 mm. The general scheme of the reactor for electric spark dispersing is shown in Figure 1.

Distilled water was used as a working fluid for preparation of the sample #1. For preparation of the samples #2, 3, 4, an aqueous solution of iron sulfate (containing 1 g, 2 g and 3 g of $FeSO_4$ respectively) was used as a working fluid. The volume of the working fluid was 500 cm^3 for all samples. The working solution was treated by pulsed electric discharge within 5 minutes. The samples were obtained as colloidal solutions, which were placed in glass beakers for further procedure.

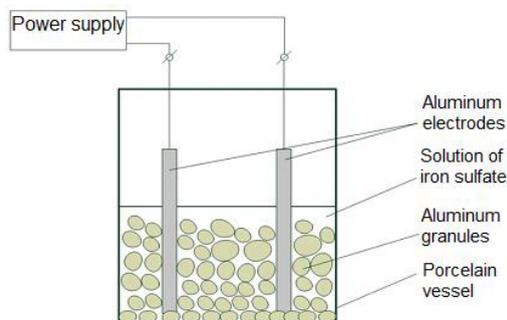


Fig. 1. Scheme of the device for preparing samples of nanomaterials by electro-spark dispersion

2.2 Modification of sorbent surface

Zeolite samples from “Holinskoe” mineral deposit (Russia, Republic of Buryatia), with size smaller than 0.1 mm were modified by the following procedure to obtain a highly efficient sorbent. In each vessel with a colloidal solution (solutions #1-4 with different iron content) 10 g of zeolite was placed. Further, zeolite was modified with nanostructured materials in the form of iron and aluminum compounds by the sol-gel process. Modification was carried out at a constant temperature $T = 80\text{ }^{\circ}\text{C}$ and pH of the medium was maintained in the range of 10-11. The modification process was performed within 3 hours. The contents of the suspension was washed to neutral pH, filtered and dried at $150\text{ }^{\circ}\text{C}$. As a result, we obtained the following modified sorptive materials: sorbent #1 (zeolite modified with colloidal solution #1), sorbent #2 (zeolite modified with colloidal solution #2), sorbent #3 (zeolite modified with colloidal solution #3), sorbent #4 (zeolite modified with colloidal solution #4).

Prepared samples of modified sorbents were tested to determine the physico-chemical and sorption properties. The specific surface area and porosity were determined by the method of nitrogen thermal desorption (BET method) by means of analyzer Sorptometer M (CJSC «Catacon»).

Morphology of nanoparticles was studied by using transmission electron microscopy (TEM) using an electron microscope JEM-2100 (JEOL, Japan) with a system of sample preparation EM-09100IS Ion Slicer.

2.3 Study of sorption properties of modified material

The study of the sorption properties of the modified material was carried out in a static mode with constant magnetic stirring. Salts solutions with a certain concentration of Pb^{2+} , Fe^{3+} and Cd^{2+} were used as simulated solution.

Test sample in amount of 0.5 g taken for each experiment. Sorbent was placed in a glass beaker ($V=100\text{ cm}^3$), added a simulated solution of 50 cm^3 (V) with the initial concentration of (C_0) $\text{Cd}^{2+} = 12.65\text{ mg/dm}^3$ (C_0) $\text{Fe}^{3+} = 11.33\text{ mg/dm}^3$ (C_0) $\text{Pb}^{2+} = 17.9\text{ mg/dm}^3$ was added and pH of stock solutions was as follows, Fe^{3+} - 2; Cd^{2+} - 2.5; Pb^{2+} - 2.2. Simulated solutions were prepared with bidistilled water using state standard samples (GSO) of solutions of lead, cadmium and iron ions. Adsorption test time for each sorbent sample was 0.5, 1, 5, 15, 30, 60 and 150 minutes. After the sorption, the sorbent was separated from the solution by centrifugation at 10000 rpm and the equilibrium concentration (C_e) of adsorbates (Pb^{2+} , Fe^{3+} , Cd^{2+}) was determined. Ion concentration of Pb^{2+} , Cd^{2+} , was determined by stripping voltammetry¹², and the concentration of Fe^{3+} ions was analyzed by photocolourimetry.

3. Results and discussion

Transmission electron microscopy is used to study the surface morphology of the modified sorbents. Figure 1 shows a sample of the sorbent #1 at a magnification of 19 thousand times. There is a visible surface of the sorbent having immobilized nanofibers of oxohydroxide aluminum sized of 50-200 nm in length and width of 2 nm in width. Figure 2 shows a sample of sorbent #2 at a magnification of 5800 times. The picture shows the same as in previous image. On the surface sorbent particles have immobilized nanofibers of oxohydroxide aluminum sized of 50-200 nm in length and 2 nm in width. Iron oxohydroxide particles, both in a free state, and on the surface of the sorbent are also visible in the image. Moreover, the individual particles of iron oxohydroxide are coated with nanofibers of aluminum oxohydroxide. Table 1 summarizes some physico-chemical parameters of the studied materials: the specific surface area (S_{sp}) and specific pore volume (P).

Table 1. Physicochemical characteristics of the studied materials samples

Sample	$S_{sp}, \text{m}^2/\text{g}$	P, cm^3/g
Zeolite “Holinskiy”, fraction < 0.1 mm	17.2	0.007
Sorbent #1	78.1	0.034
Sorbent #2	22.9	0.01

Sorbent #3	21.6	0.009
Sorbent #4	22.5	0.01

Results presented in Table 1 show that a non-modified zeolite "Holinsky" has the lowest values of the specific surface area and pore volume, as compared to modified sorbents. However, the sorbent 1 values of specific surface area and pore volume of about three and a half times higher than sorbents #2, 3, 4, where these values are almost equal. Figure 2A shows a particle of sample #1 with a very dense coating of aluminum nanoparticles. It can partly explain the results in Table 1.

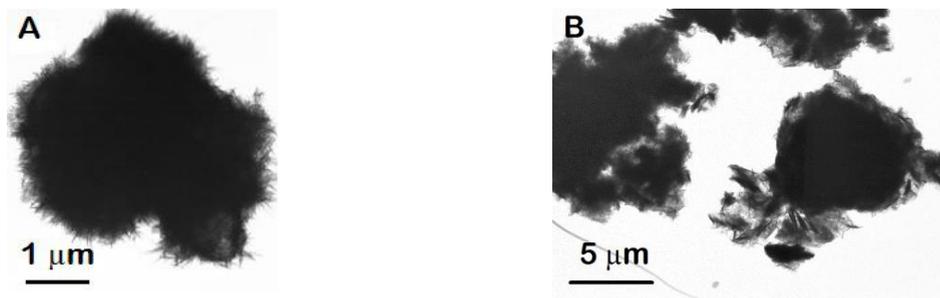


Fig. 2: **A.** Electron micrograph of tested sample (sorbent #1), with immobilized aluminum oxyhydroxide nanofibers on the surface (magnification $\times 19000$). **B.** Electron micrograph of sorbent #2, with immobilized aluminum oxyhydroxide nanofibers and iron oxyhydroxide agglomerates on the surface (magnification $\times 5800$).

Similar structure is revealed for sample 2 (Fig. 2B). However, the sorbent immobilizes on the surface agglomerates of iron and aluminum oxyhydroxides that causes big differences in properties between different samples and visible changes in the surface structure.

The sorption characteristics of the materials tested samples, during the purification of simulated solutions from ion Pb^{2+} , Cd^{2+} in static sorption processes, are presented in Table 2.

Table 2 - Sorption efficiency of tested materials under static sorption.

Sample	Removed ions	Concentration of the ions before adsorption, mg/dm^3		Concentration of the ions after adsorption, mg/dm^3		Sorption percentage, %
		After 60 min				
Zeolite	Pb^{2+}	17.90	0.049	99.72		
	Cd^{2+}	12.65	10.60	16.21		
Sorbent #1	Pb^{2+}	17.90	0.082	99.54		
	Cd^{2+}	12.65	3.190	74.79		
Sorbent #2	Pb^{2+}	17.90	0.038	99.78		
	Cd^{2+}	12.65	2.310	81.74		
Sorbent #3	Pb^{2+}	17.90	0.051	99.71		
	Cd^{2+}	12.65	7.400	41.51		
Sorbent #4	Pb^{2+}	17.90	0.039	99.78		
	Cd^{2+}	12.65	4.700	62.85		
After 150 min						
Zeolite	Pb^{2+}	17.90	0.066	99.63		
	Cd^{2+}	12.65	8.750	30.83		

Sorbent #1	Pb ²⁺	17.90	0.166	99.07
	Cd ²⁺	12.65	6.500	48.62
Sorbent #2	Pb ²⁺	17.90	0.031	99.82
	Cd ²⁺	12.65	6.200	50.99
Sorbent #3	Pb ²⁺	17.90	0.028	99.84
	Cd ²⁺	12.65	7.020	44.51
Sorbent #4	Pb ²⁺	17.90	0.033	99.81
	Cd ²⁺	12.65	7.700	39.14

According to the data from Table 2, sorbents #2, 3 and 4 have slightly better sorption characteristics compared to the natural zeolite "Holinsky" during the extraction of Pb²⁺ ions from simulated solutions. Meanwhile, sorbent #1 shows slightly worse sorption properties for Pb²⁺ ions than zeolite. Figure 3 shows the sorption properties of the four modified sorbents and zeolite "Holinsky", for extraction of Fe³⁺ ions from simulated solutions. The lowest relative sorption properties have been revealed for intact zeolite "Holinsky" regarding to Cd²⁺ ions. The properties of the modified sorbent have changed regarding to cadmium as following. There is inversely proportional dependence of the sorption characteristics on the increasing content of iron oxyhydroxide in the sample. Notably, the sorption level of the modified sorbents at 60 minute of the process is higher than that at 150 minutes of the process. This can be explained by saturation and further desorption of cadmium during time process with release of Cd²⁺ ions from the sorbent to solution.

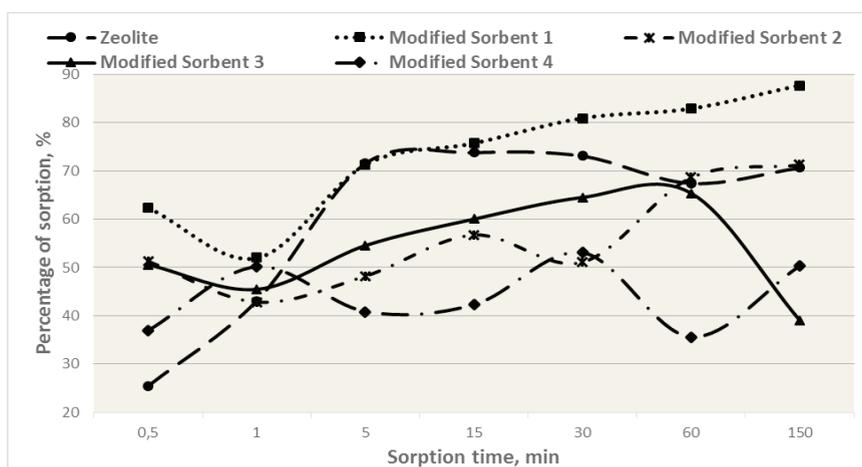


Fig. 3. Extraction degree of the Fe³⁺ ions vs time.

As shown in Figure 3, zeolite "Holinsky" at the initial stage (during the first minute of adsorption) shows the lowest adsorption efficiency when extracting the Fe³⁺ ions from the test solution as compared to the modified sorbents. However, after 5 minutes, zeolite sorption efficiency increases, yielding only to the sorbent #1. Sorbent #1 has the best relative parameters on the sorption efficiency of the iron ions throughout the test time. In a row of sorbents #1, 2, 3 and 4, the sorption efficiency decreases with increasing iron content in the sample. This is likely due to the fact, that a test solution containing ions Fe³⁺ has a pH level 2. In this environment, the iron-containing modifier on the zeolite surface partly dissolves, thereby increasing the level of iron in the test aqueous solution. Nevertheless, sorption properties of modified sorbents #2, 3 and 4 retain at a satisfactory level.

4. Conclusions

The method for the effective sorbent production has been developed using electro-spark dispersion and a sol-gel

process. Zeolite "Holinsky" has been modified by immobilization of the nanofibers of oxyhydroxide aluminum and iron oxyhydroxide agglomerates on the surface that provides extended sorption properties. Increasing of the specific surface area and pore volume of the modified examples of the sorption material has been found. Increasing content of iron oxyhydroxide in the sample causes no significant changes in the specific surface area and pore volume. Decreasing adsorption capacity has been detected in samples while extracting Fe^{3+} ions from a simulated solution. It is likely due to the acidic environment of the solution (pH 2), which implies that some of iron oxyhydroxide on the surface dissolves with allocation of dissolved iron in the aqueous phase. Sorbents #2, 3, and 4 have revealed relatively better sorption properties compared to zeolite ones during the extraction of Pb^{2+} and Cd^{2+} ions. Thus, the modified sorbents are suggested for the efficient water purification under certain environmental conditions.

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