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Investigation of the Sorption Properties of Materials Based on Wastes from Wood Production and Mineral Raw Materials

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Abstract

Method of obtaining a sorbent based on bentonite clay and saw dust was studied. Different kinds of saw dust modification were considered, the kinetics and statics of the sorption of copper ions from aqueous solutions on the indicated materials were investigated. The mechanical characteristics were determined and the choice was mode for the composition of the material which is optimal for the purification of waste water from the ions of heavy metals.

Key words: sorbent, modification, saw dust, bentonite clay, sorption, statics and kinetics of sorption, water purification

INTRODUCTION

Environmental protection from various types of pollution (solid, liquid, gas) is an urgent problem. A crucial solution of this problem is to design and implement environmentally friendly and low-waste technologies.

Among dangerous pollutants, heavy metals such as copper, lead, iron, nickel and zinc are widespread; they are formed at the plants of ferrous and non-ferrous metallurgy, machine building. They are hazardous substances and can form highly toxic compounds in the interaction with other substances. Heavy metals, included in a food chain, are able to get concentrated in the body to the amounts hundreds or thousands times greater than their contents in the environment. In addition, metals have a pronounced additive effect, because of which the joint presence of several elements significantly increases their toxicity [1].

Currently, sorption and ion exchange methods are considered as efficient ways to purify waste water from the ions of heavy metals. However, the widespread use of sorption materials at the plants is limited by their high cost, the lack of efficiency and a narrow assortment. Investigations carried out during the recent years show that instead of expensive synthetic sorbents it is possible to use the sorbents produced from natural raw materials or waste products.

Various products of plant origin can be used for these purposes, such as the seeds of alfalfa, clover, beans [2], rice husk [3], stump wood of peat layer [4], sawdust [2, 5, 6], as well as minerals, for example, basalt fibres [7], bentonite clay [8].

Taking into account the large number of wood processing enterprises in Russia, one of the promising directions of the development of sorbents based on natural materials is the use of wood wastes, including sawdust. Wood processing is usually characterized by the low coefficients of using raw materials and the formation of a large number of piles, because of which large territories are excluded from economic circulation. During prolonged storage, wood wastes decompose into carbon dioxide, phenolic compounds and other substances that have toxic and mutagenic properties. In this context, the problem of the rational use of wood raw material is important in terms of preventing environmental pollution and selecting the optimal directions of the use of wood wastes.

However, the low sorption characteristics of natural materials constrain their direct application as sorbents. In this connection, the problem of increasing the sorption properties of natural materials by using different ways to modify them with the help of available reagents and simple manufacturing operations appears to be urgent. The aim of this work is to develop a new sorption material based on sawdust and minerals (bentonite clay) to purify wastewater from copper ions.

EXPERIMENTAL

As a basis for the sorbent, we suggested to use sawdust, which is the waste product of wood industry. Previous research results showed that the sorption capacity of sawdust for copper ions is small and equal to about 7 mg/g [9].

In order to increase the absorptive capacity of sorbents, different methods of processing the raw material are applied: mechanical, physical, chemical and physicochemical treatment, including thermal processing of raw materials. In order to increase the sorption capacity, bentonite clay was deposited on sawdust with preliminary activation using 5 % sodium carbonate solution. The powdered clay sorbent was introduced directly into the solution of soda in the amount of 10 g of sorbent per 100 g of soda solution. Tank contents were stirred and left for 1 day for swelling and exchange reactions, then washed with water to remove residual salts. Rinsed suspensions were separated and exposed to thermal activation at 150 °C and then crushed.

Sawdust was also subjected to preliminary modification. The solutions of phosphoric acid (5 %), hydrochloric acid (0.5, 1.0 M) and sodium hydroxide (0.5 %) were used as modifiers. Processing consisted of sawdust impregnation with solutions for 24 h at room temperature, washing excess modifying substances off with distilled water and drying at 120 °C.

The sorption capacity of the materials was studied under static conditions at a constant temperature of 20 °C. For this purpose, we prepared model solutions containing copper ions from 10 to 1000 mg/L. To each flask with solution, we added 1 g of the sorbent. The flask contents were stirred continuously during the specified time interval, then the suspension was settled, and the clarified solution was analyzed for copper ions using the photocolorimetric method described in [10]. Experimental error did not exceed 10 %.

To obtain the kinetic curves of sorption, we placed the sorbent samples in the model solution of copper ions and incubated for 2–48 h, measuring the current concentration of copper ions in the solution after fixed time intervals.

The amount of adsorbed metal was calculated using equation

$A = [(C_{\text{ini}} - C_{\text{equil}})/m1000]V$

where A is a sorption capacity, mg/g; C_{ini} and C_{equil} are the initial and equilibrium concentrations of copper ions in the solution, respectively, mg/L; m is the mass of the sorbent sample, g; V is sample volume, mL.

RESULTS AND DISCUSSION

A comparative analysis of the effect of different methods of sawdust processing on sawdust sorption properties showed that the adsorption capacity of modified sawdust with respect to copper ions is about 1.5 times higher than that of unmodified sawdust.

Figure 1 shows the sorption isotherms of copper ions on modified sawdust. The maximum

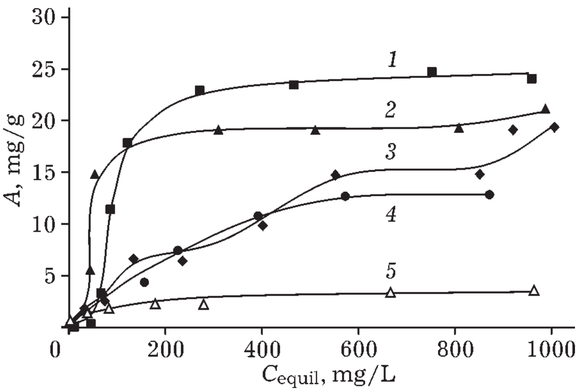

Fig. 1. Dependence of adsorption capacity of modified sawdust (A) on the equilibrium concentration (C_{equil}) of copper ions in the solution. Modifiers: *1* – 5 % NaOH solution; *2*, *3* – 1.0 M (*2*) and 0.5 M (*3*) HCl solutions; *4* – 5 % H_3PO_4 solution; *5* – without modification.

degree of copper ions extraction was observed for sawdust processed using the alkaline solution (curve *1*), it reaches 24 mg/g. High results (up to 21 mg/g) were shown by sawdust modified with 1.0 M HC1 solution (curve *2*). Sawdust modified with the solution of 0.5 M HC1 and 5 % solution of orthophosphoric acid (curves *3* and *4*, respectively) have comparable sorption capacity within a wide range of concentrations, but it is lower than the values reported above.

Curves *1*, *2* (see Fig. 1) correspond to copper ion sorption isotherms of type V according to BET classification [8], which describes the strong intermolecular interactions in the sorbate material. The sorption isotherm of sawdust sample modified with the solution of 0.5 M HCl (curve *3*) refers to type IV, indicating the presence of micro-, meso- and macropores in the material, and therefore the manifestation of polymolecular adsorption. The exception is unmodified sawdust and sawdust modified with orthophosphoric acid; the adsorption isotherms of copper ions on these samples can be attributed to type I and described by the theory of monomolecular adsorption in micropores.

The improvement of sorption properties of modified sawdust compared to unmodified sawdust is apparently connected with the fact that processing with reagents is likely to increase the specific surface area of sawdust and the number of active functional groups and their accessibility to the metal ions.

Bentonite clay is a natural inorganic material, with low cost, good availability, advanced microporous structure, and therefore high sorption properties. As shown in the previous studies of the extraction of heavy metal ions, bentonites have a greater sorption capacity than sawdust [9]. Earlier we investigated the adsorption capacity of bentonite clays from the Taganskoye and Khakasskoye deposits, which amounted to 25 and 50 mg/g, respectively.

In order to increase and govern the porous structure, to change the chemical nature of the surface and increase the sorption capacity, bentonite clays were subjected to different kinds of activation. Previous studies showed that sodium carbonate solution is more efficient to activate bentonite clays than sodium chloride, because in this case the adsorption capacity increases significantly (up to 65 mg/g for the

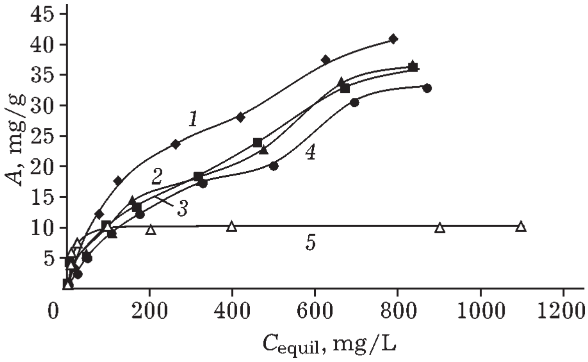

Fig. 2. Dependence of sorption capacity (A) of materials based on bentonite and sawdust on the equilibrium concentration(C_{equil}) of copper ions in the solution. Modifiers: *1* – 5 % NaOH solution; *2*, *3* – 1.0 M (*2*) and 0.5 (*3*) M HCl solutions; *4* – 5 % H_3PO_4 solution; *5* – without modification.

Taganskoye bentonite and 70 mg/g for Khakasskoye) [11]. It was the soda-activated bentonite that was used for the preparation of sorption ion-exchange material.

To obtain the sorption material, sawdust of different modifications were mixed in turn with soda activated bentonite at the ratio of bentonite/sawdust 1 : 2. The mixture was dried, ground and subjected to thermal treatment.

Figure 2 shows the sorption isotherms of copper ions on the material with soda-activated bentonite of Khakasskoye deposits and sawdust modified using different methods. One can see that the use of modified sawdust in the material promotes a substantial increase in its sorption capacity. The maximum degree of extraction of copper ions is observed when sawdust was preliminary processed with NaOH solution (curve *1*), it reached 40 mg/g. For materials processed with the solutions of 1.0 M and

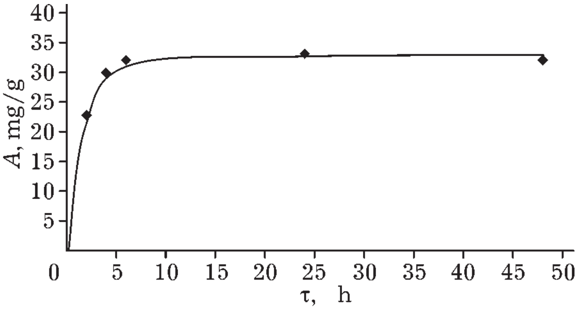

Fig. 3. Sorption kinetics of copper ions on the material of soda-activated bentonite from the Khakasskoye deposit and sawdust modified with a solution of 0.5 M HCl. A – sorption capacity, τ – sorption time.

TABLE 1

Mechanical properties of the sorbent

Parameters	Modifier (solution)			
	5 % H_3PO_4	0.5 M HCl	1 M HCl	0.5 % NaOH
Abrasion strength, %	48.9	42.5	41.0	26.5
Total pore volume, g/g	2.2	3.3	2.4	3.0

0.5 M HCl (curves *2* and *3*), the adsorption capacity was 36 mg/g.

On the basis of the shapes of dependences of the sorption capacity on the equilibrium concentration, it may be concluded that the sorption isotherms for all materials (see Fig. 2), except for the sorbent based on sawdust without any preliminary processing, refer to type IV according to BET classification. This fact points to a mixed structure of the material with a combination of micro- and macropores. Sorption isotherms for the unmodified sample (curve *5*) correspond to type I, and in this case the interaction of the sorbate with the solvent dominates.

We determined the time of equilibrium establishment for the sorption of Cu(II) from aqueous solutions on the obtained materials. The dependence of adsorption capacity on sorption time for copper ions on the material from soda-activated bentonite from the Khakasskoye deposit and sawdust modified with a solution of 0.5 M HCl is shown in Fig. 3. One can see that the equilibrium distribution of copper ions between the solution and the sorbent is set relatively slowly, about 6 h after the start of sorption. With sawdust modified using other methods, sorption equilibrium gets established within the same time.

When sorbents are used in filtering devices, the mechanical properties of sorbents are also important along with their sorption properties. These properties allow us to determine the possibility to carry out regeneration of the material, which depends on the degree of abrasion. Thus, one of the main characteristics of the sorbent is mechanical abrasion strength. Other important characteristics are the parameters of the porous structure of the material, which determines the macro properties of the sorbent.

To select the best modifier for the material, we determined the abrasion strength and total pore volume of sorbents (Table 1) [12, 13].

The highest mechanical strength is observed for the material with sawdust modified with a 5 % solution of phosphoric acid. The sorbents modified with hydrochloric acid solutions have a similar strength. The lowest mechanical strength is characteristic of the material with sawdust modified with sodium hydroxide. The material with the largest total pore volume is that obtained using a solution of 0.5 M HCl as a modifier.

The used sorbents can be repeatedly regenerated with soda solution. Worked out sorbent after regeneration (that is, without pollutants) can be disposed through combustion; the unburned mineral fraction (bentonite clay and ash) can be repeatedly used to prepare the new portions of the material. The studies showed that the sorbent based on soda-activated bentonite and modified sawdust can be used to purify water from copper compounds. In order to improve the sorption properties of sawdust and better fix bentonite, we recommend using a 0.5 M HCl solution as the modifier because this provides sufficient mechanical and sorption properties.

The use of this material will reduce the cost of water purification and create a closed water cycle, thus decreasing the load on the environment.

SUMMARY

1. It was determined that the modification of sawdust raises the adsorption capacity with respect to heavy metal ions by a factor of 1.5 as an average.

2. It was established that the sorbent based on soda-activated bentonite and sawdust is efficient for removing copper ions, and the use of modified sawdust in the material increases its adsorption capacity by a factor of 3.5 as an average.

3. It was revealed that it is preferable to use a solution of 0.5 M HCl as a modifier of saw-

dust, because this helps one to achieve the largest increase in the mechanical and sorption properties of the material.

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