Sorption Properties of Modified Wood Chips

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Abstract

Kinetics and equilibrium of the sorption of Cu(II), Zn(II) and Cd(II) ions on a natural cellulose-containing material – wood pine chips – were investigated. The effect of different methods of modifying the wood chips on their sorption properties was studied. Optimal regimes of the chemical modification of wood chips were determined. The results of tests of the modified chips as sorbents for the purification of industrial wastewater showed efficiency of their use to extract heavy metal ions, as well as oil products and surface-active substances.

INTRODUCTION

Development of sorbents based on natural polymeric materials of plant origin is important in the aspect of developing resource-saving technologies. The cost of the sorbents of this kind is much lower than that of the synthetic ion-exchange resins because the former are manufactured from renewable raw material, namely wood, flax, cotton, of from the wastes of pulp and paper, woodworking or food industry.

There are publications [1–17] concerning the use of polymeric materials of plant origin to extract heavy metal ions from wastewater. For instance, purification of wastewater from metal ions is carried out by mixing wastewater and active silt in the turbulent mode in a biosorption reactor [1, 2]. Preliminary treatment of the silt mixture with a solution of acids, alkalis or organic solvents improves its sorption properties.

To purify industrial wastewater from copper, chromium, iron, zinc, nickel, it is possible to use granulated peat; the degree of metal ion extraction is 92–96 % [3]. The sorbent may be well regenerated with the solutions 0.5–1.0 M HCl or 0.25–0.5 M H_2SO_4.

However, along with evident advantages (cheapness and availability of the raw material, simplicity of performance, high extraction degree), these methods have some substantial disadvantages. For instance, natural sorbents are suitable only for the purification of wastewater with relatively small concentrations of heavy metals. In addition, the working exchange capacity of peat is achieved with the duration of sorption cycle 20–26 h. Also the problem of dehydration and utilization of sorbents after purification arises.

Natural cellulose materials – the waste products of woodworking industry – can be used as the sorbents. A method is known to purify wastewater containing Ag(I), Cu(II), Zn(II) ions with the help of wood chips [4, 5]. Chip modification with sodium or ammonium sulphides or the deposition of surface-active films on their surface allows one to increase the degree of metal extraction from 41 to 100 % [5]. Neutralization of chromium-containing wastewater is carried out with the help of wood dust (waste material from furniture production works) preliminarily treated with concentrated sulphuric acid [6]. In order to remove copper salts from aqueous solutions, along with wood chips one may use such materials of plant origin as bamboo mass, jute fibres and cotton [7]. The efficiency of Cu(II) ion extraction with cotton and bamboo mass is about 40 and 70 %, respectively. Coloration of natural sorbents with active dyes of monochlorotriazine type improves their sorption characteristics, which helps one to increase the degree of Cu(II), Pb(II), Zn(II), Ni(II), Fe(II), Fe(III) ion recovery from aqueous solutions of their salts up to 84–98 % [8]. An increase in the efficiency of sorption process is connected with the formation of chelate compounds between the functional groups of dyes and metal ions. It should be noted that the application of jute, bamboo and cotton as sorbents is economically reasonable in places where these plants naturally grow.

Special attention is paid today to the investigation of sorption properties of the products of plant origin which are agroindustrial wastes: wheat straw, buckwheat husk, peelings of sunflower seeds, beet pulp [9], onion peel [10], peanut shells and rice husk [7].

Investigation of zinc ion sorption on different types of cellulose – wheat bran, apple pulp and cellulose itself – showed that the largest sorption capacity is that of wheat bran [11, 12]. The completeness of metal ion extraction is almost independent of the solution pH, while for Zn(II) ion sorption on rye bran and cellulose such a dependence has a clearly exhibited character.

Many biological polymers of plant origin – moss [13], algae [14], pectin [15], tree bark, starch [17] – are able to extract heavy metal ions from solutions; however, their use is possible only under the conditions of small works located close to the sources of raw material.

So, analysis of literature data on metal ion sorption by natural cellulose-based materials showed that, taking into account the geographical location of Russia, the most promising direction of the development of sorbents based on the natural raw material is the use of waste products of woodworking industry and agro industrial enterprises.

However, the direct use of natural materials as sorbents is limited due to their low sorption kinetic characteristics. Therefore, the problem of increasing the surface activity of natural polymers by means of different modification procedures involving various cheap reagents and simple technological operations becomes urgent.

The goal of the present work was to investigate the effect of pine chip modification methods on the kinetics and equilibrium of the sorption of Cu(II), Zn(II) and Cd(II) ions from aqueous solutions of electrolytes on pine chips.

EXPERIMENTAL

Metal ion sorption was carried out under static conditions from aqueous solutions of salts under mixing and thermostating at 293 K. Wood pine chips 0.5–1 mm in size were used as sorbents.

In order to record kinetic curves and sorption isotherms, weighed portions (m) 0.1 g of chips were put into a series of test tubes, then 10 ml (V) of the electrolyte solution with different initial concentrations (C_0) of metal ions (0.250–0.005 mol/l) was poured into each tube. After a given time interval or after the sorption equilibrium was established, the solution was separated from the sorbent by filtering, and the current (C_τ) or equilibrium (C_e) concentrations of metal ions were determined by means of atomic absorption spectroscopy. The sorption capacity ($A_{\tau,e}$) of wood chips was calculated using equation

$$A_{\tau,e} = (C_0 - C_{\tau,e})V/m \quad (1)$$

The degree of process completeness (F) was determined suing equation $F = A_\tau/A_p$ where A_τ is the sorption capacity at a moment τ, A_e is the equilibrium sorption capacity.

RESULTS AND DISCUSSION

The time of sorption equilibrium establishment was determined from the kinetic experiments for the sorption of Zn(II), Cd(II) and Cu(II) ions on wood chips from aqueous solutions of metal sulphates (Fig. 1). One can see that the sorption equilibrium is achieved within 60 min after the start of sorption process.

In order to determine the stage that limits the sorption process, we used the graphic-analytical method of constructing the

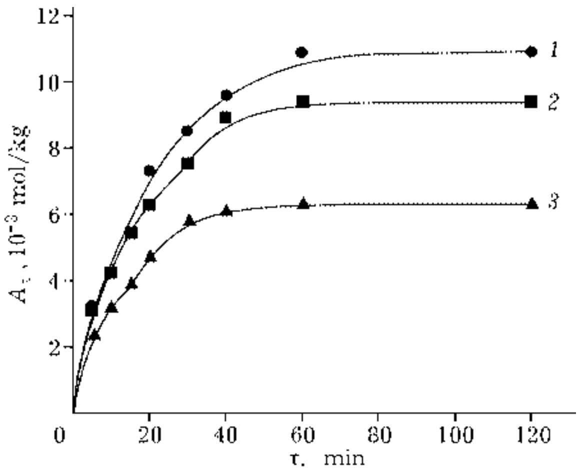

Fig. 1. Sorption kinetics of metal ions on non-modified chips from aqueous solutions of electrolytes ($C_0 = 1.5 \cdot 10^{-4}$ mol/l): *1* – Cu(II), *2* – Zn(II), *3* – Cd(II). A_τ is metal ion concentration in the polymer; τ is sorption time.

dependencies of sorbent filling degree (F) on time (τ). The semisorption period for Zn(II) ions is about 10 min (Fig. 2, *a*), which is also characteristic of other investigated metals. On the basis of the linearity of the initial region of $F-\sqrt{\tau}$ dependence (see Fig. 2, *b*), it may be assumed that the diffusion inside the polymer makes a substantial contribution into the mechanism of Zn(II) and Cd(II) sorption by wood chips. The final conclusion concerning the limiting stage of the process is made on the basis of the comparison between the kinetic curves of sorption obtained with an interruption for 2 h and withous any interruption of the contact between phases. Discrepancy between these curves plotted as $F-\tau$ (Fig. 3) provides evidence that the rate of zinc sorption on wood chips is limited by the diffusion of the ions inside the polymer granules, that is, the internal diffusion kinetics takes place.

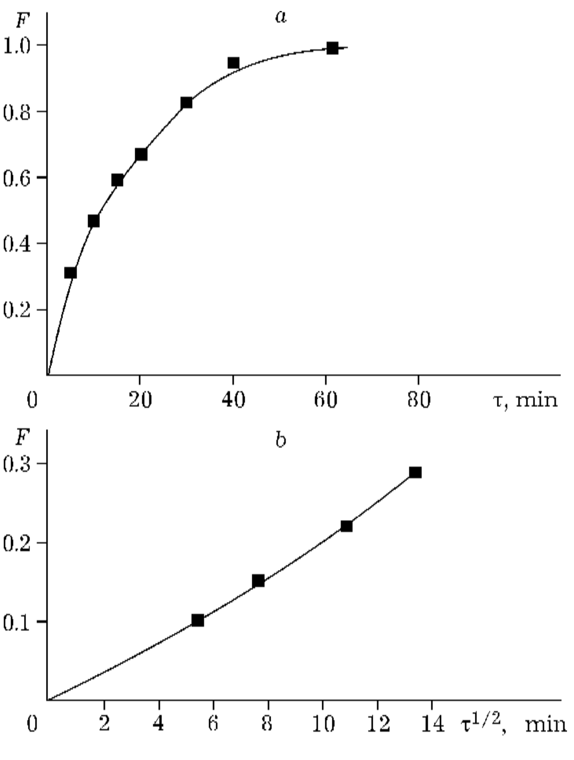

Fig. 2. Dependence of the degree of process completeness (F) for Zn(II) ion sorption on non-modified chips on τ (*a*) and $\tau^{1/2}$ (*b*).

In order to determine the parameters characterising the sorption properties of natural polymers, we obtained sorption isotherms for Zn(II), Cd(II) and Cu(II) ions. The experimental data can be described by Langmuir adsorption isotherm equation:

$$A_e = A_\infty K C_e/(K C_e + 1) \qquad (2)$$

where A_∞ is the limiting sorption capacity; K is the concentrat constant of sorption equilibrium characterising the sorption intensity, l/mol.

Linearization of sorption isotherms, calculated using equation

$$1/A_e = 1/A_\infty + (1/A_\infty K)(1/C_e)$$

allowed us to determine the coefficients in Langmuir equation (Table 1). Total specific surface of the polymer, taking into account the hydrated form of a metal to be sorbed [18]

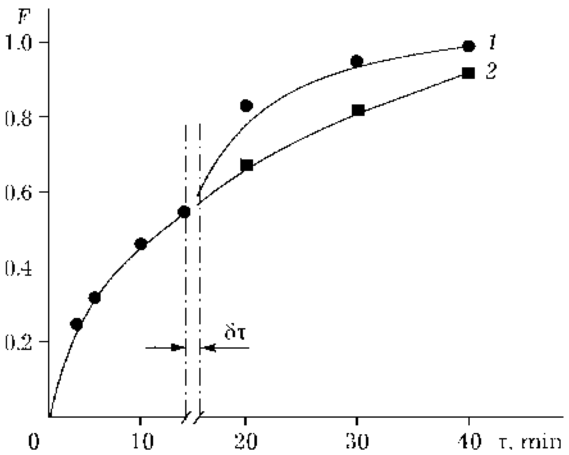

Fig. 3. Kinetics of Zn(II) ion sorption on non-modified chips with the interruption of the process (*1*) and without interruption (*2*). δτ is time of interruption of the contact of the sorbent with the solution phase, equal to 2 h.

TABLE 1

Sorption and kinetic characteristics of wood chips

Sorbent	A_∞, mol/kg			τ_e, min		
	Zn^{2+}	Cd^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Cu^{2+}
Non-modified chips	0.71	0.69	0.73	60	60	60
Chips modified with alkali	0.93	0.90	0.95	30	30	30

and the limiting sorption value, was determined to be 200–220 m^2/g.

In order to improve the sorption kinetic characteristics of wood chips, they were modified using different procedures: exposure at high and low temperature, treatment with NaOH solutions of different concentrations. To determine the optimal mode of modification with a chemical reagent, we studied the effect of different treatment parameters on the sorption properties of wood chips: the concentration of alkali solution was varied from 0.1 to 0.5 g/l NaOH, treatment time from 5 to 60 min, the mass ratio of modifying solution to the sorbent (module) from 3 to 20.

The optimal conditions of the treatment of wood chips with the chemical reagent were determined as a result of these investigations: alkali NaOH concentration is 0.5 g/l, treatment time (τ_{tr}) is 30 min, module is 20.

A comparative analysis of the effect of different kinds of wood chip treatment on the sorption properties showed that among the indicated modification procedures the most efficient one is the treatment of the chips with the chemical agent (Table 2). The equilibrium sorption capacities of the chips towards zinc and cadmium ions, as well as metal ion extraction degrees, are higher than the values for the non-treated polymer. Other treatment methods only insignificantly increase the sorption capacity of the chips towards metal ions.

The kinetic characteristics of the chips modified by alkali solution improve substantially: the time within which the sorption equilibrium gets established is much shorter than that with the non-modified polymer; the former is equal to 30 min for Zn(II), Cu(II) and Cd(II) ions. Semisorption time decreases approximately by a factor of 3 and is about 3 min for all the metals under investigation (Fig. 4). The limiting sorption values (see Table 1) were calculated on the basis of metal ion sorption on modified chips (Fig. 5).

An improvement of sorption and kinetic properties of modified wood chips in comparison with non-modified ones can be explained by the fact that treatment with the chemical reagent causes swelling of the polymer, its specific surface, the amount of active functional groups and their availability increase.

On the basis of the chemical nature of cellulose functional groups (–OH, –O–, –CO, –COOH) containing unshared electron pairs at the oxygen atom, it may be stated that sorption of transition metal ions M from solution can occur due to complexation with the electron-donor groups of natural ligands L according to the scheme

$$\overline{L} + M \Leftrightarrow \overline{LM}$$

TABLE 2

Effect of modification method on the sorption capacity of wood chips (sorption time $\tau = 60$ min, initial concentration of metal ions $C_0 = 1.5 \cdot 10^{-4}$ mol/l)

Modification method	A, 10^{-2} mol/kg		α, %	
	Zn^{2+}	Cd^{2+}	Zn^{2+}	Cd^{2+}
Non-modified chips	0.93	0.63	60	71
Treatment with alkaline solution	1.39	0.81	91	89
Thermal (T = 200 °C, τ_{tr} = 2 h)	1.16	0.45	76	51
Freezing out (T = –18 °C, τ_{tr} = 5 days)	1.19	0.61	78	70

Note. Here and in Table 3: α is the degree of metal ion extraction.

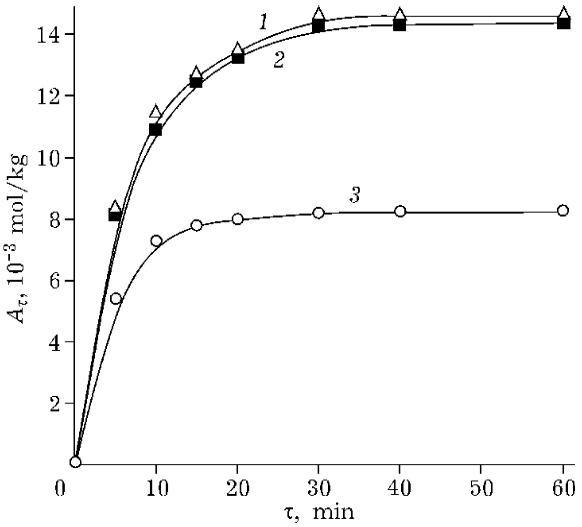

Fig. 4. Kinetics of metal ion sorption on modified chips ($C_0 = 1.5 \cdot 10^{-4}$ mol/l): *1* – Cu(II), *2* – Zn(II), *3* – Cd(II). A_τ is the concentration of metal ions in the sorbent phase.

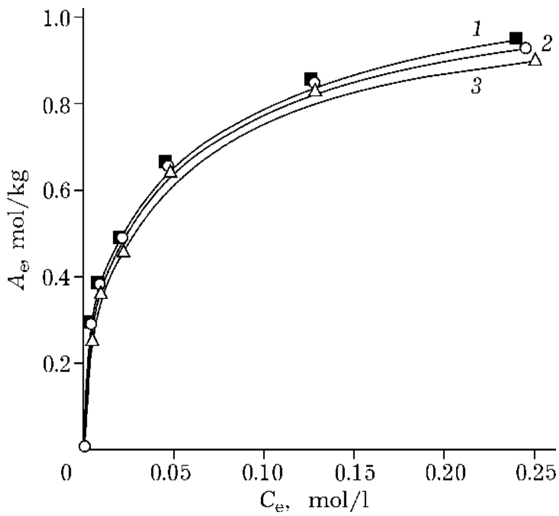

Fig. 5. Metal ion sorption isotherms for modified chips: *1* – Cu(II), *2* – Zn(II), *3* – Cd(II). A_e is metal ion concentration in the sorbent; C_e is the equilibrium concentration of metal ions in the solution.

The coefficient of metal ion distribution K_D is determined as a ratio of metal ion concentration in the sorbent phase to that in the solution. Therefore, K_D would increase with a decrease in the concentration of metal ions in solution. This regularity is of practical significance: it is reasonable to use cellulose-containing natural sorbents to sorb micro-impurities of transition metal ions [19], for the purification of industrial waste water with metal ion concentrations close to the maximal permissible level.

It should be noted that the selectivity of heavy metal ion sorption on a cellulose material and on wood chips is similar to the selectivity sequence for sorption on carboxylic cationites [19]: Cu(II) > Zn(II) > Cd(II).

The features of sorption process during the purification of real wastewater originate from the fact that the wastewater of a plant is a multicomponent aqueous-organic solution of a salts of various metals containing also oil products and surfactants.

The presence of surfactants in aqueous solutions decreases the surface tension of a solution, which promotes solubilization of oil products by the molecules of ionogenic and non-ionogenic surfactants. Because of this, the extraction of solubilized oil products from solutions will be determined mainly by the

TABLE 3

Results of the tests of modified wood chips with general industrial wastewater of Ivkhimprom JSC (Ivanovo city)

Component	MPC, mg/dm^3	Content, mg/dm^3		α, %
		in industrial wastewater	after treatment with the sorbent	
Copper	0.011	0.0029	0.0014	52
Cadmium	0.007	0.0732	0.0300	60
Zinc	0.02	0.132	0.068	49
Iron	0.4	3.77	3.02	20
Oil products*	0.9	4.5	0.24	95
nSSAC**	0.25	2.049	Abs.	100

Note. For designations, see Table 2.
*I-12A, I-20A, I-40A, S-9.
**nSSAC are non-ionigenic synthetic surface-active compounds (oleox-5, and stearox-6).

character of the interaction of the sorbent and organic molecule of a solubilizing agent.

The interaction of hydroxyl groups of a molecule of non-ionogenic surfactant with the basic groups of a cellulose containing sorbent (–OH, –COO, –O–) may result in the formation of a hydrogen bond, and it may be expected that wood chips would sorb oil products and non-ionogenic surfactants.

Anyone active surfactants in an alkaline medium (pH > 7) cannot interact with the basic groups of cellulose and therefore should not get sorbed on wood chips.

The results of tests of the modified wood chips as sorbents for the purification of industrial and conditionally pure wastewater of Ivkhimprom JSC (Ivanovo city) from heavy metal ions confirmed these assumptions. One can see in Table 3 that the use of the proposed sorbents helps one to decrease the concentrations of metal ions – zinc, cadmium and copper – in the waste water of Ivkhimprom JSC by a factor of 2 as a mean. The concentration of oil products in wastewater decreases by a factor of 20 and reaches the maximum permissible level; non-ionogenic surfactants are completely removed.

So, chemical modification of wood chips seems a promising method for the purification of industrial wastes from heavy metal ions, as well as from oil products and non-ionogenic surfactants.

CONCLUSIONS

1. It is established that a natural material – pine wood chips – is able to extract Cu(II), Zn(II) and Cd(II) ions from aqueous solutions of electrolytes.

2. It is determined that chemical modification of pine wood chips results in an increase in the sorption capacity of the sorbent with respect to heavy metal ions by 30 % as a mean, while semi-sorption time decreases by a factor of 3.

3. It was discovered that the extraction of heavy metal ions during the purification of industrial wastewater with the help of modified wood chips is accompanied by the sorption of oil products and solubilizing agents – non-ionogenic surfactants.

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