Sorption Properties of Hydrolytic Lignin from Sunflower Husk towards Cr(VI) Ions

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Abstract

The composition and morphology of hydrolytic lignin obtained from sunflower husk are studied before and after alkaline modification. The sorption properties of hydrolytic lignin towards Cr(VI) ions were studied under static conditions (at the solid to liquid phase ratio 1 : 1200, and a temperature of 20 °C) from the aqueous solutions of potassium dichromate with different initial concentrations of Cr(VI) ions (0.05–1.0 mg/L). Sorption kinetics was studied, and the analysis of the integral kinetic curves of sorption was carried out in accordance with chemical kinetic models.

Keywords: hydrolytic lignin, sorption kinetics, sunflower husk, sorption, heavy metals, chromium

INTRODUCTION

Liquid wastes and waste waters containing hazardous admixtures of heavy metals are formed in technological industrial processes. It is known that heavy metals including chromium are the most dangerous ecotoxicants. Hexavalent chromium is a carcinogenic substance of the 1st class of danger. The maximum permissible concentrations of Cr(VI) compounds in waters for different purposes are within the range of 0.05–0.083 mg/L [1, 2].

The formation of a substantial amount of dangerous sources of pollution, such as worked out electrolytes, rinsing and waste waters, requires the development and introduction of modern systems for neutralization and purification from heavy metal ions. Technological solutions to solve the problem of neutralization of concentrated chromium-containing solutions (including the solutions containing seawater), worked out electrolytes (including the electrolytes from galvanic chromium plating with Cr(VI) concentration more than 50 g/L), high-temperature (up to 90 °C waste waters formed as a result of rinsing the components after chromium plating) and inhibiting solutions were proposed in [3–5].

The sorption method is used for the thorough purification of waste waters from the ions of heavy metals. Sorption purification is efficient within the whole range of admixture concentrations in water, however, its advantages are most clearly pronounced at low concentrations of pollutants [6]. The search for promising natural and synthetic sorption materials for the purification of aqueous solutions from chromium ions is an urgent task, which is

confirmed by the studies carried out in Russia and abroad [7−11].

Among natural compounds considered as potentially efficient materials for the purification of aqueous media, lignin is distinguished. It is a complicated natural polymer that is present in nearly all terrestrial plants, comprises about 30 % of organic carbon in the biosphere and holds the second place after cellulose among the most widespread biopolymers of lignocellulose biomass.

Lignin is obtained in the industry as a waste product from cellulose production (sulphate lignin, lignosulphonic acids) and from the hydrolysis of plant materials (hydrolytic lignin). Hydrolytic lignin (HL) belongs to the most widespread large-scale industrial wood wastes and is transported almost completely into dumps in spite of the existing possibility of its processing into useful products [12].

Lignin and materials based on it are widely used as fuel in construction, in the chemical industry and agriculture, etc. [13]. Lignin and materials based on it are under active investigation for the purpose of using it to recover heavy metals (including chromium) from aqueous solutions. These materials include chemically modified lignin, resins, as well as other materials based on lignin and the oxides of titanium and (or) silicon, magnesium [14−22].

At the same time, the properties of HL from non-wood material, in particular sunflower husk, are poorly studied. The outlooks for the use of this raw material are demonstrated in [23−25].

The goal of the present work was to study the sorption properties of HL obtained from sunflower husk with respect to Cr(VI) ions.

EXPERIMENTAL

Preparation of hydrolytic lignin and its alkaline treatment

Hydrolytic lignin was obtained from 2.4 g of preliminarily crushed husk from the Kuban crops of 2015 (size fraction 0.5−1.0 mm). The process was carried out under heating to 190 °C in a 1 % aqueous solution of H_2SO_4 (reagent grade Kh. Ch. − chemically pure, Khimreaktivsnab, GOST 4204−77) at a ratio of lignin/H_2SO_4 = 1 : 14.6 (module 1 : 14.6) under mixing in a closed CEM XP-1500Plus vessel in the MARS-Xpress microwave furnace (CEM, USA) according to the procedure described in [26]. Then the mixture was

cooled, filtered and washed with distilled water to achieve the neutral medium. The resulting HL sample was dried to the constant mass.

Alkaline treatment of a weighted portion of HL 0.5 g in mass was carried out by boiling in round-bottomed flasks 25 cm³ in volume in 1 % (HL-1 sample) and 3 % (HL-3 sample) NaOH solutions (Kh. Ch. reagent grade, EKOS, GOST 4328−77) for 30 min at a ratio of lignin/NaOH = 1 : 20 (module 1 : 20). Then the mixture was cooled, filtered, washed with distilled water to the neutral medium and dried to the constant mass.

Sorption of Cr(VI) ions by the samples of hydrolytic lignin

Sorption experiments were carried out with lignin samples without additional modification (HL) and after alkaline treatment (HL-1 and HL-3) under static conditions (with the solid to liquid phase ratio equal to 1 : 1200 at a temperature of 20 °C) from the aqueous solutions of potassium dichromate ($K_2Cr_2O_7$, Kh. Ch. reagent grade, REAKHIM, GOST 4220−75) with different initial concentrations of Cr(VI) ions (0.05−1.0 mg/L) under mixing in an orbital shaker for 30 min. Along with the samples under investigation, a weighted portion of the sorbent was placed in a flask with distilled water and mixed (a reference experiment). Then the solutions were separated from the sorbents by filtering (through a dense 'Blue ribbon' paper filter), and the concentration of Cr(VI) ions in them was determined.

To record the kinetic curves of sorption under the same conditions, weighted portions of the sorbent (25 mg) were placed in a series of conical flasks 50 cm³ in volume, then 30 mL of the aqueous solution of $K_2Cr_2O_7$ with initial Cr(VI) concentration equal to 0.25 mg/L was poured into each flask, and mixing was carried out for different time intervals from 10 to 480 min. Then the solutions were separated from the sorbents by filtering, and the residual concentration of Cr(VI) ions was determined. Filtration time was not taken into account.

Analysis methods

X-ray diffraction patterns of precipitates were recorded with a D8 ADVANCE automatic diffractometer (Bruker, Germany) with sample rotation in CuK_α-radiation. X-ray phase analysis was carried out using an EVA search programme with the powder database PDF-2.

The determination of strongly acidic (carboxylic) groups in lignin was carried out using chemisorption according to a standard procedure [27].

The specific surface area of lignin samples was measured with the help of a Sorbtomer-M analyzer of specific surface area (CC KATAKON, Russia) on the basis of low-temperature (−196 °C) sorption of nitrogen. Calculation of specific surface area was carried out using the software based on Brunauer−Emmett−Teller method and a comparative method proposed by Gregg and Sing [28].

The IT spectra of the initial lignin sample and the samples obtained by means of alkaline treatment were recorded with a Spectrum BX II spectrophotometer (PerkinElmer, USA) in KBr tablets.

Investigation of the surface morphology of lignin samples was carried out using a scanning electron microscope S-5500 (Hitachi, Japan).

The concentration of Cr(VI) ions in solutions was determined with the help of a DR/2800 spectrophotometer (HACH-LANGE, Germany). The limit of Cr(VI) ion detection in aqueous solutions did not exceed 0.01 mg/L. The square mean deviation of determination was 2 %.

The sorption capacity (A_s, mg/g) of the samples was calculated using equation

$$A_s = \frac{C_{init} - C_{eq}}{m} V$$

where C_{init} and C_{eq} are initial and equilibrium concentrations of Cr(VI) ions in solution, respectively, mg/L; V is solution volume, l; m is sorbent mass, g.

The degree (α, %) of Cr(VI) ion recovery was calculated using equation

$$\alpha = \frac{C_{init} - C_{eq}}{C_{init}} 100\ \%$$

The kinetic data on the sorption of Cr(VI) ions were analyzed according to the kinetic models of pseudo-first and pseudo-second order [29, 30].

The kinetic equation of pseudo-first order (Lagergren equation):

$$\frac{dA_t}{dt} = k_1(A_e - A_t) \tag{1}$$

where k_1 is the rate constant of sorption for the pseudo-first order model; A_e, A_t are the values of sorption capacity in the equilibrium state and at the moment of time t, respectively.

Equation (1) in the linear integral form with the initial conditions ($A_t = 0$ for $t = 0$ and $A_t = A_t$ at the moment of time $t = t$) appears as

$$\log(A_e - A_t) = \log A_e - \frac{k_1}{2.303} t \tag{2}$$

The pseudo-second order kinetic model is:

$$\frac{dA_t}{dt} = k_2(A_e - A_t)^2 \tag{3}$$

where k_2 is the rate constant of sorption in the model of pseudo-second order.

Equation (3) may be transformed as follows:

$$\frac{dA_t}{dt} = \frac{1}{k_2 A_e^2} + \frac{1}{A_e} t \tag{4}$$

RESULTS AND DISCUSSION

To obtain HL from sunflower husk, microwave treatment of the biomass in the MARS-Xpress microwave furnace was applied. This method of lignin isolation is efficient and causes lower degradation than usual acidolysis under the same conditions [31−35].

The scheme according to which lignin was obtained is presented in the general form in Fig. 1.

The resulting HL samples are uniform, amorphous and black-coloured. According to the data of X-ray phase analysis (Fig. 2), the composition of the resulting samples is characterized by the presence of X-ray amorphous phases, which is confirmed by the observation of a halo within angle range 10−30°.
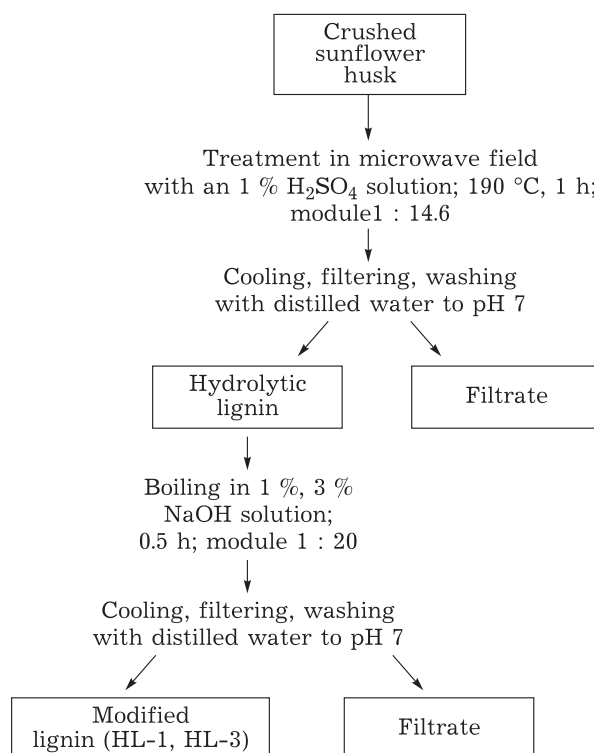

Fig. 1. Scheme according to which lignin was obtained.
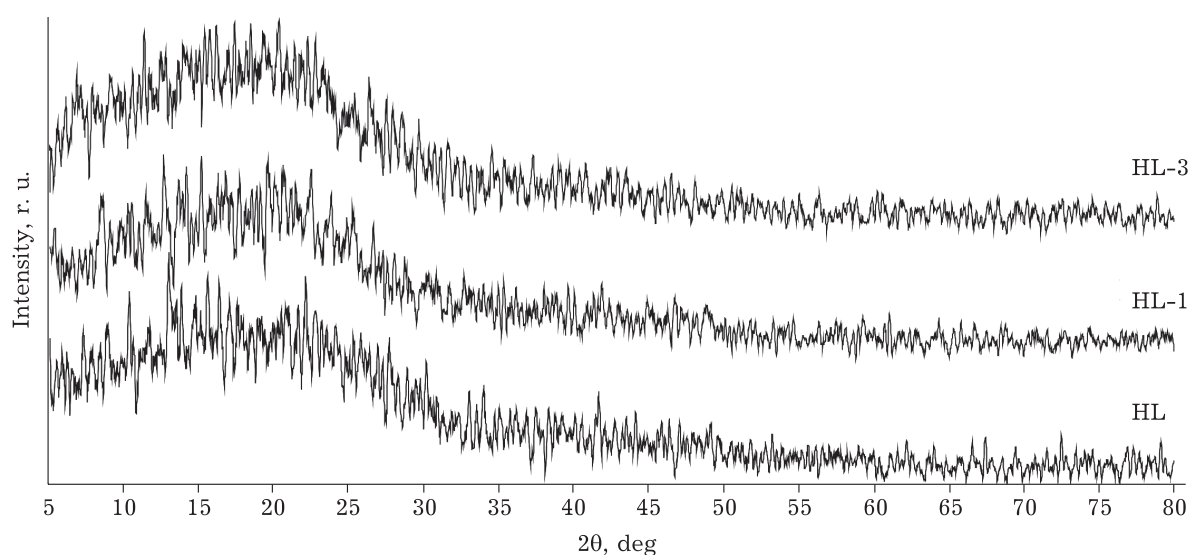
Fig. 2. X-ray diffraction patterns of the samples of hydrolytic lignin. <Intensity, r. u. deg HL-3 HL-1 HL>

The results of the measurement of the specific surface area of lignin samples are presented in Table 1. One can see that the specific surface area of all the studied samples does not exceed 5 m^2/g. The largest specific surface area is that of HL-3 sample.

Characteristic features of the surface morphology of samples are shown in Fig. 3.

HL-3 sample possessed the most branched porous structure. The surface morphology of this sample is represented by the elements of irregular geometric shapes forming a porous framework.

The yields of HL-1 and HL-3 samples (with respect to initial raw material) are independent of alkali concentration and a lower by 7 % that the yield of HL sample not treated with the alkali (Table 2). It was established that strongly acidic (carboxylic) groups are absent from lignin after the treatment with NaOH, while their content in the initial sample is 1.1 % (see Table 2). This fact may be explained by the neutralization of carboxylic groups by alkali.

The IR spectra of the initial sample [26] and the samples after alkaline treatment contain similar absorption bands characteristic of lignin (Fig. 4). The stretching vibrations of free and bound OH groups are observed within the region 3393−3424 cm^{-1}. The bands corresponding to the stretching and bending vibrations of C-H bonds of methyl and methylene groups are present in the regions 2927, 2934, 1461−1462 and 1368−1375 cm^{-1} respectively. The bands related to the stretching vibrations of carbonyl groups are observed as a shoulder in the region of 1689−1692 cm^{-1}, and this shoulder is less pronounced for HL-1 and HL-3 lignin samples. The presence of this absorption band in HL-1 and HL-3 samples may be assigned to aldehyde fragments because the absence of carboxylic groups in these samples was established. The presence of a broad absorption region at 1600−1700 cm^{-1} may be explained by overlapping of the absorption bands of bending vibrations of OH groups and the vibrations of other bonds. The skeletal vibrations of the aromatic ring appear at 1591−1595 and 1510−1511 cm^{-1}, and the intensities of these bands are higher for modified lignin samples. The bands corresponding to the stretching vibrations of C−O

TABLE 1

Specific surface area of lignin samples

Sample	Specific surface area, m^2/g	
	Multi-point BET method	Gregg−Sing method
HL	1.4	1.6
HL-1	1.9	1.1
HL-3	3.7	4.8

TABLE 2

Yields of lignin samples and the content of carboxylic groups in the samples

NaOH concentration, %	Sample	Average yield±standard deviation, %	COOH content, %
0	HL	34.3±2.7	1.1
1	HL-1	27.0±1.2	0
3	HL-3	27.6±2.3	0

S5500 15.0 kV−0.1 mm × 50.0 k SE   S5500 15.0 kV 0.2 mm × 100 k SE   S5500 15.0 kV 0.4 mm × 45.0 k SE
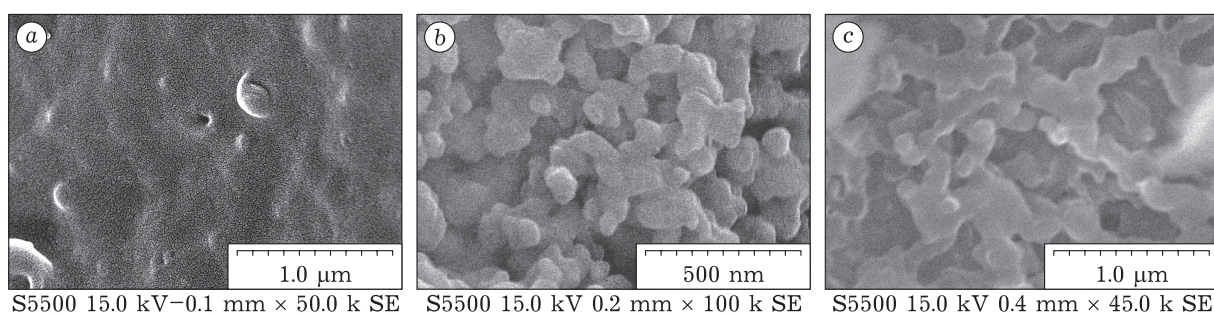
Fig. 3. SEM images of the surface of lignin samples: HL (*a*), HL-1 (*b*) and HL-3 (*c*).
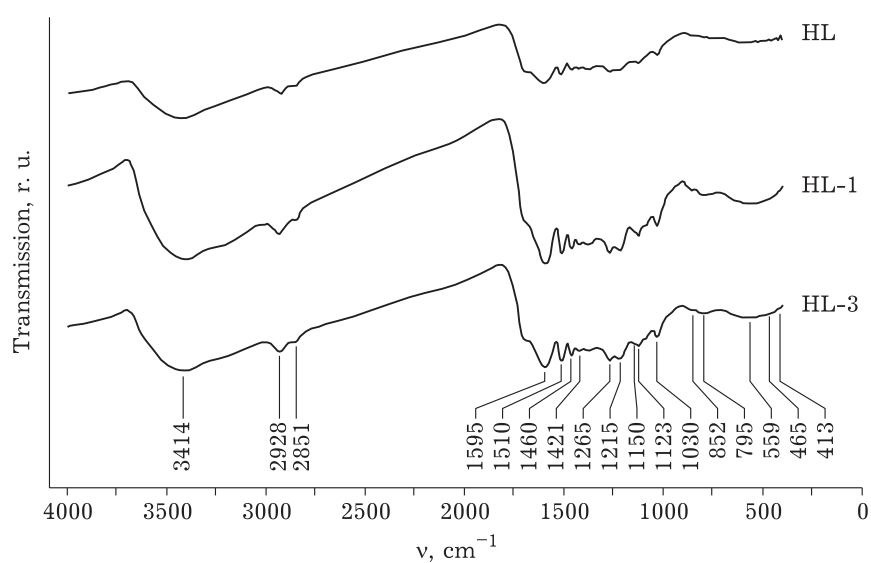

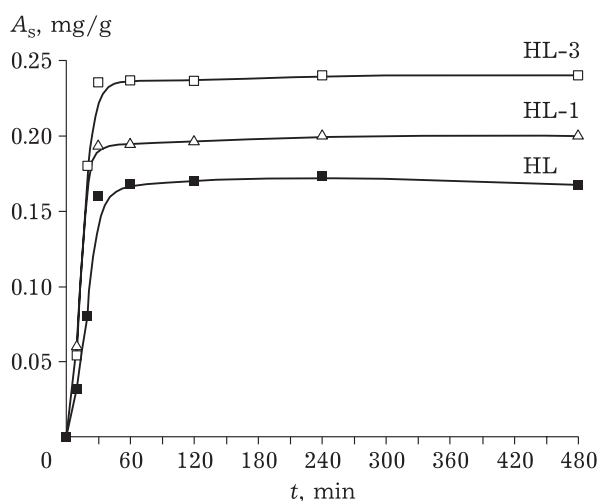Fig. 4. IR spectra of lignin samples.

Fig. 5. Integral kinetic curves of the sorption of Cr(VI) ions by the samples of lignin from sunflower husk (initial concentration of Cr(VI) ions: 0.25 mg/L).
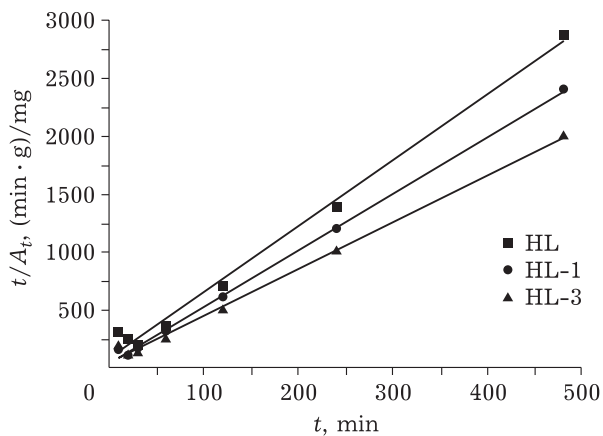
Fig. 6. Kinetic model of pseudo-first order according to the experimental data on the sorption of Cr(VI) ions by the samples of hydrolytic lignin.

TABLE 3

Results of the treatment
of the kinetic curves of the sorption of Cr(VI) ions
by the samples of hydrolytic lignin

Sample	Kinetic model			
	Pseudo-first order		Pseudo-second order	
	k_1, min^{-1}	R^2	k_2, g·mmol^{-1}·min^{-1}	R^2
HL	0.033	0.724	0.340	0.989
HL-1	0.024	0.523	0.750	0.998
HL-3	0.025	0.493	0.384	0.994

bonds are observed at 1265−1267 and 1214−1216 cm^{-1}, while the medium absorption band of the bending in-plane vibrations of C−H bonds in the aromatic ring and bending vibrations of C−O bands appear at 1029-1031 cm^{-1}.

To evaluate sorbent efficiency, it is important to take into account the time within which the sorption equilibrium is achieved. The integral kinetic curves of the sorption of Cr(VI) ions by lignin samples under investigation are shown in Fig. 5.

It was established that the time to achieve sorption equilibrium is 30 min, and the highest sorption capacity is characteristic of the HL-3 sample, which may be connected with better developed surface (see Fig. 5).

Apparent pseudo rate constants (k_1 and k_2) and the corresponding squared correlation coefficients R^2 demonstrating the correctness of attributing to the kinetic models of pseudo-first and pseudo-second order are presented in Table 3. It follows from the presented data that the sorption of Cr(VI) ions by lignin samples within the time interval under analysis is best described by the

TABLE 4

Residual concentration of Cr(VI) ions in solutions
after sorption on lignin samples

Initial concentration of Cr(VI) ions, mg/L	Residual concentration of Cr(VI) ions, mg/L		
	HL	HL-1	HL-3
0.05	0.04	0.02	0.03
0.10	0.09	0.08	0.09
0.15	0.09	0.08	0.08
0.20	0.07	0.07	0.07
0.25	0.05	0.07	0.06
0.30	0.12	0.07	0.05
0.40	0.07	0.07	0.06
0.50	0.09	0.11	0.08
0.60	0.12	0.17	0.16
0.80	0.29	0.33	0.33
1.00	0.58	0.62	0.61

model of pseudo-first order, which is confirmed by the corresponding correlation coefficients.

The linear dependences obtained from the experimental data on the basis of the pseudo-second order equation are shown in Fig. 6. These dependences show relative changes in sorption capacity with time (t/A_t). The presented linear dependences are described by the equations of straight lines: $y = 5.6868x + 87.898$ (HL sample), $y = 4.9x + 35.679$ (HL-1), $y = 4.043x + 41.8395$ (HL-3). The constants for this chemical model were determined from the equations of the straight lines (see Table 3).

Changes in the residual concentration of Cr(VI) ions after sorption on lignin samples for different initial concentrations are listed in Table 4. Sorption capacities of lignin samples under investigation were calculated from the presented data, and the dependences on initial concentrations of Cr(VI) ions were plotted (Fig. 7). One can see that there are no substantial changes in the dependences of Cr(VI) ion sorption by lignin samples under investigation. The maximal values of sorption capacity are within the range of 0.56−0.62 mg/g.

CONCLUSION

The sorption properties of hydrolytic lignin obtained from sunflower husk were studied with respect to Cr(VI) ions.

It was established that the highest values of sorption capacity observed within Cr(VI) ion concentration range from 0.05 to 1.0 mg/L are characteristic of non-modified hydrolytic lignin (0.59−
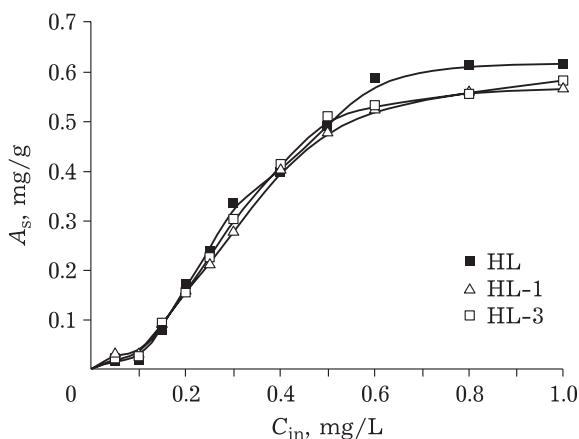

Fig. 7. Dependence of the sorption capacity of hydrolytic lignin from sunflower husk on the initial concentration of Cr(VI) ions in solution (sorption time 30 min).

0.62 mg/L). For the samples of hydrolytic lignin after alkaline treatment, almost no differences in sorption capacity are observed, and the maximal values of sorption capacity are 0.56−0.58 mg/g.

Investigation of the kinetic regularities of sorption revealed that the time within which the sorption equilibrium is achieved is equal to 30 min, and the highest values of sorption capacity are characteristic of the sample of hydrolytic lignin treated with a 3 % solution of NaOH (HL-3), which may be due to the better developed surface of the sample. It is demonstrated that the sorption of Cr(VI) ions by lignin samples HL, HL-1 and HL-3 within the analyzed time interval is better described by the model of pseudo-first order with correlation coefficients 0.989, 0.998 and 0.994, respectively.

So, sorbents based on hydrolytic lignin may be used for additional sorption purification of chromium-containing waste waters with the concentration of Cr(VI) ions up to 1 mg/L. It is economically reasonable to use non-modified hydrolytic lignin in view of its lower cost.

Acknowledgements

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