Chemistry of Natural Compounds, Vol. 42, No. 4, 2006

SORPTION OF CERTAIN HEAVY-METAL IONS BY HYDROLYZED LIGNIN AND ITS DERIVATIVES

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UDC 547.99.992

The ability to form intermolecular coordination of lignin macromolecules and metal ions through both ionic and coordinative metal—ligand bonds was shown by studying the sorption activity of hydrolyzed lignin from cotton seed husks (HLCSH) and its aminated derivatives. The studied lignins exhibited high sorption activity for metal ions over the whole range of concentrations used. The heavy-metal ions fell in the following order of decreasing lignin sorption activity: Fe > Pb > Cu > Cd > Zn.

Key words: hydrolyzed lignin, hydrolyzed lignin derivatives, sorption.

Hydrolyzed lignin is a cheap sorbent whose sorption properties must be studied. We reported previously that AGL-1 (84.76 m^2/g) and AGL-5 (90.08 m^2/g) have the highest specific surface area among aminated hydrolyzed lignins of cotton seed husks (HLCSH) [1]. Because the specific surface area is one of the factors that determines the sorption capacity of solids, we selected these samples in order to study their sorption activity for the heavy-metal ions Pb, Cu, Fe, Cd, and Zn.

The sorbates were 0.5, 1.0, 3.0, and 5.0% solutions of the salts $Pb(CH_3COO)_2$, $FeSO_4$, $CuSO_4$, $Cd(NO_3)_2$, and $ZnCl_2$. The sorption capacity of the lignins was determined from the content of metal ions in the filtrates after sorption on samples of the produced lignins.

Acute and chronic poisoning are observed as a reulst of the toxicity of Pb ions and their ability to accumulate in organisms. The maximum permissible concentration (MPC) of Pb is 0.03 mg/L. It is classified as a second class dangerous substance [2]. Model experiments on the sorption of Pb ions by certain derivatives of HLCSH were carried out under laboratory conditions (Table 1).

Table 1 shows that the sorption activity of AGL-1 is greater than that of starting HLCSH and AGL-5. This can be explained by the high content of carboxylic groups in this sample. The IR spectra of lignins treated with $Pb(CH_3COO)_2$ solutions showed that intermolecular coordination of lignin macromolecules can form with Pb ions through both ionic and coordinative metal—ligand bonds.

Carboxylate ions (CH_3COO^-) in the IR spectrum of $Pb(CH_3COO)_2$ are characterized by absorption bands at 1543 and 1486 cm^{-1} [3]. The IR spectra of HLCSH, AGL-1, and AGL-5 before and after sorption of Pb ions showed that a band at 1600 cm^{-1} due to COO^- stretching disappeared and new bands at 1541, 1543, 1562, 1614, and 1618 cm^{-1} and at 1373, 1390, and 1405 cm^{-1} appeared. These can be assigned to asymmetric and symmetric vibrations of carboxylate ions in the studied samples. The observed frequencies of the carboxylate stretches indicate that ionic metal—ligand complexes were formed [4-6].

The frequencies of the hydroxyl stretches provided additional information about the Pb-containing lignins. The observed shift of the absorption maximum due to OH stretches, mainly in the low-frequency region up to 175 cm^{-1} (with the exception of samples No. 7 and 8), indicated that H-bonds had formed in the Pb-containing lignins.

Thus, the study of characteristic frequencies in IR spectra of HLCSH and its aminated derivatives before and after sorption of Pb ions showed that intermolecular ionic metal—ligand coordination of lignin macromolecules with Pb ions had occurred. The main reaction centers in the studied lignins were hydroxyl and carboxylic groups.

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TABLE 1. Sorption Activity of HLCSH, AGL-1 and AGL-5 for Pb^{2+} Ions

$Pb(CH_3COO)_2$ conc., %	Sorption capacity, %		
	HLCSH	AGL-1	AGL-5
0.5	98.0	99.4	99.7
1.0	81.0	96.0	98.0
3.0	86.67	91.67	86.67
5.0	74.0	80.0	74.0

TABLE 2. Sorption Activity of HLCSH, AGL-1 and AGL-5 for Fe^{2+} Ions

$FeSO_4$ conc., %	Sorption capacity, %		
	HLCSH	AGL-1	AGL-5
0.5	99.90	99.88	99.99
1.0	99.36	99.93	99.93
3.0	99.75	99.94	99.81
5.0	99.95	99.96	99.92

TABLE 3. Sorption Activity of HLCSH, AGL-1 and AGL-5 for Cu^{2+} Ions

$CuSO_4$ conc., %	Sorption capacity, %		
	HLCSH	AGL-1	AGL-5
0.5	99.76	99.96	99.92
1.0	91.0	98.8	96.60
3.0	79.3	84.17	82.67
5.0	74.8	80.2	77.20

Sorption of Fe Ions. Soluble iron (Fe) salts exhibit a general toxic effect. Compounds of trivalent (oxidized) Fe have an inflammatory effect on the gastrointestinal tract. The MPC of Fe in water of aquifers is 0.33 mg/mL. It is classified as a third class dangerous substance [2]. Analogous model experiments were carried out to study the sorption of Fe ions (Table 2).

Table 2 shows that the sorption capacity of HLCSH and its aminated derivatives remained high over the whole range of $FeSO_4$ concentrations studied. A study of the IR spectra and the nature of Fe sorption by the investigated lignins showed that absorption bands characterizing hydroxyl stretching shifted mainly to the low-frequency region. This experimental fact indicates that H-bonds formed in the investigated lignins after sorption of Fe ions. Furthermore, the observed frequencies of carboxylate stretches (1617, 1618, 1620, 1622, 1623 cm^{-1}) in the spectra of the investigated lignins after sorption were supposed of the formation of ionic metal—ligand complexes.

In all spectra of the studied lignins and those of the starting HLCSH, AGL-1, and AGL-5, absorption bands were observed at 1270-1274 cm^{-1} that also characterize absorption by symmetric carboxylate vibrations. This fact may indicate that a coordinative bond formed between the stereochemically free electron pair of Fe^{2+} and the O atom of the carbonyl group [7-9].

Thus, based on the IR spectral study of characteristic frequencies of the industrial lignins and their derivatives before and after sorption of Fe ions, intermolecular coordination of lignin macromolecules with Fe ions may form through both ionic and coordinative metal—ligand bonds.

Sorption of Cu and Cd Ions. The sorption activity of starting HLCSH and its aminated derivatives was studied for Cu and Cd ions.

TABLE 4. Sorption Activity of HLCSH, AGL-1 and AGL-5 for Cd^{2+} Ions

$Cd(NO_3)_2$ conc., %	Sorption capacity, %		
	HLCSH	AGL-1	AGL-5
0.5	93.94	98.27	98.93
1.0	83.93	91.07	91.07
3.0	65.28	79.37	79.37
5.0	71.43	57.15	57.15

TABLE 5. Sorption Activity of HLCSH, AGL-1 and AGL-5 for Zn^{2+} Ions

$ZnCl_2$ conc., %	Sorption capacity, %		
	HLCSH	AGL-1	AGL-5
0.5	75.0	84.5	85.0
1.0	63.75	75.71	67.5
3.0	51.67	70.48	73.3
5.0	30.0	56.57	57.0

Table 3 shows that HLCSH has a high sorption activity for dilute solutions of $CuSO_4$. As the Cu concentration increases, the sorption capacity of HLCSH decreases. In other words, HLCSH sorbs well Cu ions from its dilute solutions. An analogous picture was observed for sorption of Pb ions by HLCSH and its derivatives (Table 1).

Table 3 also indicates that the aminated derivatives of HLCSH, like the starting lignin, had a high sorption activity for dilute solutions of $CuSO_4$. As the Cu concentration increased, the sorption capacity of the investigated lignins decreased slightly. A sorption capacity that remains above 70% for a 5% salt solution can then be used as a factor determining the practical use of the investigated lignins.

The sorption activity for Cd ions was studied under analogous conditions (Table 4). Soluble forms of Cd compounds are known to be mainly its inorganic salts. The MPC of Cd in water of aquifers is 0.0013 mg/L. Cadmium is classified as a second class dangerous substances [2].

The sorption activity of the investigated lignins for Zn ions was studied under analogous conditions (Table 5). It should be noted that Zn occurs in water mainly as the ionic species in cyanide and tartrate complexes and sometimes in insoluble forms such as the hydroxide, carbonate, sulfide, etc. Many Zn compounds, primarily the sulfate and chloride, are toxic. However, Zn is an active microelement that promotes growth and normal development of organisms. The MPC of Zn is 1.03 mg/mL. Zinc is classified as a third class dangerous substances [2].

Thus, the study of the sorption activity of HLCSH and its aminated derivatives (AGL-1 and AGL-5) established that it has a high sorption capacity for certain metal ions over the whole range of studied concentrations. The sorption activity of the lignins for the studied heavy-metal ions decreases in the order Fe > Pb > Cu > Cd > Zn.

EXPERIMENTAL

Hydrolyzed lignin of cotton seed husks was washed with hot distilled water until the washings were neutral, dried, sieved through a 0.25-mesh sieve, and used without further characterization.

The concentrations of Fe, Pb, Cu, Cd, and Zn in filtrates obtained after sorption on lignins were determined by a volumetric method at OAO Analit-servis.

Aminated HLCSH were prepared as before [1].

IR spectra of lignin samples after sorption of metal ions were recorded on a Perkin—Elmer System 2000 (Sweden) Fourier—IR spectrometer with resolution 4 cm^{-1}, scan rate 0.2 cm/s, and 500 scans. Lignin samples were prepared as pressed KBr disks.

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