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New Approach to the Realisation of Adsorption Properties of Lignin: Preparation of Sulphur Sorbents for Heavy Metal Ions

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Abstract

This paper proposes a new approach to the development of new sorption materials designed for extraction of compounds of high toxic heavy metals from wastewater, pollution by which is of global environmental problem. To obtain new sorbents it is proposed to use large-tonnage wastes of wood chemistry, *i.e.*, lignin, organochlorine residues from epichlorohydrin production and the waste of processing of high sulphur crude oils and natural gas, elemental sulphur, which allows simultaneously solving the problems of waste disposal and wastewater treatment. The availability of sorption materials using lignin previously subjected to chlorine water was demonstrated. Sorbents containing 2.4–12.5 % of sulphur are formed in 91–93 % yields by the interaction between the product with different degrees of chlorination and sodium disulphide in hydrazine alkaline system. Their maximum opportunity for heavy metal removal (Ni, Zn, Cd, Pb, Hg, Cu, Co) from model solutions with initial metal ion concentration in solution of 5000 mg/L was explored. High sorption activity of the resulting materials was detected for all the studied metals. Sorbents of a new type were also prepared when using chlorinated lignin (chlorine content is 5.7 %), sodium polysulphide (Na_2S_n , $n = 1.5\text{--}4.0$) and wastes from epichlorohydrin production, the main component of which is 1,2,3-trichloropropane (86.2 %). The materials obtained herewith contain from 18.3 to 65.0 % of sulphur and generally show higher sorption activity toward the studied metals than sorbents obtained without the use of organochlorine residues.

Key words: heavy metals, adsorption, lignin, organochlorine residues

INTRODUCTION

One of the global environmental problems of modern civilization is related to environmental pollution by heavy metal compounds [1, 2]. Large amounts of wastewater containing highly toxic compounds of heavy metals are formed in processes of manufacture and application of metal-containing catalysts and in other spheres of human activities when obtaining metals and their compounds, application and the use of galvanic coatings [3–5]. Adsorption occupies a

special place among various methods of treatment of wastewater from toxic components allowing creation of flexible highly effective easy automated treatment systems [6]. However, the development of sorption technologies in the solution of environmental problems is restrained by the absence of available highly effective, convenient in application sorbents; therefore, studies in this area are primarily aimed at the development of new or modification of known sorption materials [7].

From the viewpoint of the rational use of natural resources, utilization of wastes of other industrial productions is a promising area upon creation of new adsorbents of heavy metal compounds [8–11].

Lignin is the most important large-tonnage waste of the wood chemical industry [12]. Its industrial processing covers only a small portion of the produced volume [13, 14]. Considering the spatial structure of lignin that is a natural cross-linked polymer [15] it is promising for preparation of efficient sorption materials. Currently, the opportunity to produce activated coal by lignin pyrolysis has been studied in some detail [16]. However, activated coal that removes well organic components is insufficiently active toward sorption of heavy metal ions [6]. This is driven by the fact that heavy metal ions relating to thiol poisons [4] most easily generate by the donor-acceptor mechanism strong surface complex with sorbents containing a sulphur atom [17] that are absent in carbon materials. In these regard, attempts were made to prepare sulphur-containing sorbents using lignin [18]. For this purpose, polycondensation of 1,2,3-trichloropropane with sodium polysulphide and thiourea was carried out at a temperature of 60 °C. In this process, lignin almost does not form chemical bonds with a polysulphide polymer ensuring the required dispersity of the obtained sorbent. Quantitative characteristics of sorption capacity are not given in [18], it was only noted that the sorbent efficiently removed gold, platinum, and mercury from aqueous solutions at low concentrations of these metals.

The proposed paper presents a new approach to preparation of sulphur sorbents based on

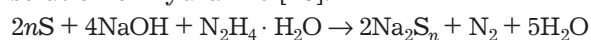
lignin. For this purpose, lignin is preliminarily subjected to the action of chlorine water, and the resulting chlorolignin is used to prepare sorbents. There are data in the literature [19] about preparation of sulphur materials using large-tonnage industrial wastes that are hydrolysis lignin, sulphur, and chloroaliphatic compounds. The resulting product containing 4.2–31.7 % of sulphur was recommended by the authors [19] as a modifying agent for bitumen. The sorption ability of heavy metal ions was not noted.

EXPERIMENTAL

Two types of sulphur sorption materials based on chlorinated lignin were obtained during studies. Their preparation includes the following stages that are carried out in a single reaction vessel without isolation of intermediates.

Preparation of sodium polysulphide

Preparation of Na₂S_n is based on the reaction of elemental sulphur with an aqueous alkaline solution of hydrazine [20]:



The value of *n* in the resulting polysulphide is defined by the molar ratio of S/NaOH. At S/NaOH ratio is 1 : 1, Na₂S₂ is preferably formed, at 3 : 2 – Na₂S₃, at 2 : 1 – Na₂S₄, at 1.5 : 1 – Na₂S_{1.5} (a mixture of Na₂S and Na₂S₂). Dissolution of sulphur in an aqueous alkaline solution of hydrazine in the presence of alkali (water/hydrazine hydrate mass ratio equal to 20 : (1–3)) is carried out at a temperature of 45–60 °C, afterwards, the solution is stirred for 3 h at this temperature.

TABLE 1

Synthesis of sorbent **I** from chlorolignin and sodium disulphide

Products	Masses of reactants, g			Chlorine content in chlorolignin, %	Product yield, g (%)	Content in product*, %	
	Chlorolignin	NaOH	S			S	Cl
Ia	10.0	0.3	0.24	2.6	9.1 (91)	2.42	Absent
Ib	10.0	0.6	0.51	5.7	9.3 (93)	5.48	Traces
Ic	10.0	0.8	0.64	7.1	9.2 (92)	7.0	~0.5
Id	10.0	1.6	1.28	14.1	9.3 (93)	12.5	2.3

* The contents were determined by the microanalytic method.

TABLE 2

Synthesis of sorbent **II** from chlorolignin, organochlorine waste and sodium polysulphide (Na_2S_n)

Products	n	Mass of reagent ^a , g			Product yield, g	Content ^b , %	
		S	Chlorolignin	Waste fraction		S	Cl
IIa	2	5.0	10.0	8.0	20.0	26.2	4.8
IIb	3	7.5	10.0	8.0	19.3	39.1	3.6
IIc	4	10.0	10.0	8.0	18.2	65.0	7.2
IIId	1.5	3.75	10.0	8.0	16.6	18.3	13.5
IIe	2	5.0	12.0	8.0	21.3	19.1	4.6
IIf	2	5.0	8.0	8.0	18.2	29.3	4.8
IIg	2	5.0	6.0	8.0	14.2	28.1	5.6

^a $m\text{NaOH} = 6.25 \text{ g}$.^b Chlorine and sulphur contents in samples were determined by standard microanalytic techniques.

Preparation of sulphided lignin

Chlorolignin is prepared from hydrolysis lignin by the action of chlorine water saturated with chlorine [19]. To synthesize sorbents chlorolignin samples with various chlorine contents are used (Table 1). Chlorolignin from the calculation $\text{Na}_2\text{S}_2/\text{Cl} = 1 : 2$ is added to a solution of Na_2S_2 with stirring at a temperature of 40°C , that is 1 mol of Na_2S_2 is required for 2 mol of chlorine. The mixture is stirred for 2.5 h at 40°C , the resulting product (sorbent **I**) is filtered off and dried. Four samples of sorbents (**Ia–d**) are obtained in such a way; their yields and sulphur contents in the samples are presented in Table 1.

Sorbent preparation using sodium polysulphide, chlorolignin, and epichlorohydrin production wastes

Chlorolignin with chlorine content of 5.7 % was used for preparation of sorbents in this series (sorbent **II**). The 1,2,3-trichloropropane fraction of epichlorohydrin production wastes with 1,2,3-trichloropropane content of 86.2 mass %, epichlorohydrin of 6.5 mass %, dichloropropanols of 6.4 mass %, the rest of 0.9 mass % was used as organochlorine waste. Organochlorine wastes are obtained directly from epichlorohydrin production setup and used without additional treatment. Sodium polysulphides (Na_2S_n , $n = 1.5\text{--}4.0$) are used as sulphiding agents.

Chlorolignin is added to a solution of Na_2S_n at a temperature of 45°C and organochlorine waste

is simultaneously added dropwise at a mass ratio of chlorolignin/organochlorine waste of $(5\text{--}4) : 4$ so that a ratio of total chlorine/sulphur in polysulphide would be $2 : n$. The reaction mixture is stirred for 6 h at 45°C , cooled; a dark-brown product is filtered off and dried in vacuum. Seven samples of sorbents are obtained in such a way, their yields and sulphur contents in them are indicated in Table 2. Four samples (**IIa–d**) that differ by the size of n and, as a result, sulphur content are used for the study of sorption activity in this series of sorbents.

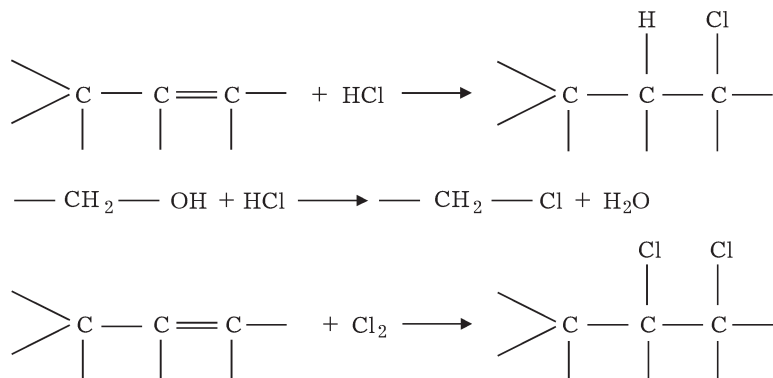
Sorption activity studies

Models of salt solutions with metal content of 5000 mg/L are used to study sorption activity. A sample weight of a sorbent (0.5 g) is shaken with 50 mL of a model of a solution for 3 h

TABLE 3

Sorption characteristics of sorbents **I** and **II**

Products	Sorption of metal cations (A), mg/g						
	Ni^{+2}	Zn^{+2}	Cd^{+2}	Pb^{+2}	Hg^{+2}	Cu^{+2}	Co^{+2}
Ia	280	315	340	269	312	189	262
Ib	352	423	435	338	467	408	323
Ic	418	379	462	376	425	411	311
Id	360	290	418	324	437	117	258
IIa	452	423	335	338	367	408	446
IIb	387	404	445	417	436	378	452
IIc	304	326	443	404	428	397	372
IIId	436	412	297	386	304	378	417



Scheme 1.

using S-3.02M shaker at a temperature of 20 °C. The residual concentration of metal ions is determined photometrically [21] using KFK-3 ZOM3 photocolormeter. The value of absorption (A) is determined by conventional calculation using the formula [11]

$$A = (C_0 - C_f)V/m$$

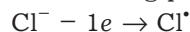
where C_0 is the initial concentration of metal in the initial solution of 5000 mg/L; C_f is the final concentration defined photometrically (mg/L); V is the volume of the studied solution of 0.05 L; m is the mass of the used adsorbent of 0.5 g.

Data on sorption for sorbents of structures **I** and **II** are given in Table 3.

RESULTS AND DISCUSSION

The preliminary stage of lignin activation by its chlorination is used to prepare sulphur-containing sorbents. Judging by the complexity of the structure of a lignin molecule, there are several sites of the introduction of chlorine during chlorination: various areas of propane fragments with the formation of $\text{Cl}-\text{C}(sp^3)$ bonds and aromatic rings, during chlorination

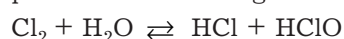
of which $\text{Cl}-\text{C}(sp^2)$ bonds are formed [14]. A chlorine atom is inactive in nucleophilic substitution reactions during the action of polysulphide anions in the latter case. Lignin chlorination can be carried out electrochemically (uses of chlorine directly formed at the anode during NaCl electrolysis) or by the action of aqueous chlorine solution (chlorine water) [14]. It is obvious that in the first case, chlorine atoms formed during electrochemical reactions are chlorinating particles:



The latter are also chlorine molecules that are obtained during combining two atoms:

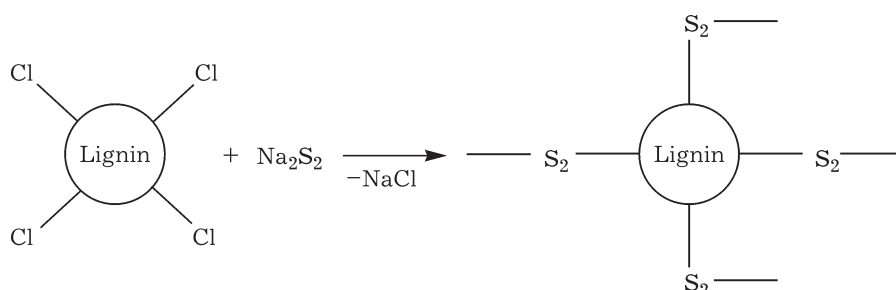


Molecules of Cl_2 , as well as the products of its interaction with water act as chlorinating particles when using chlorine water:

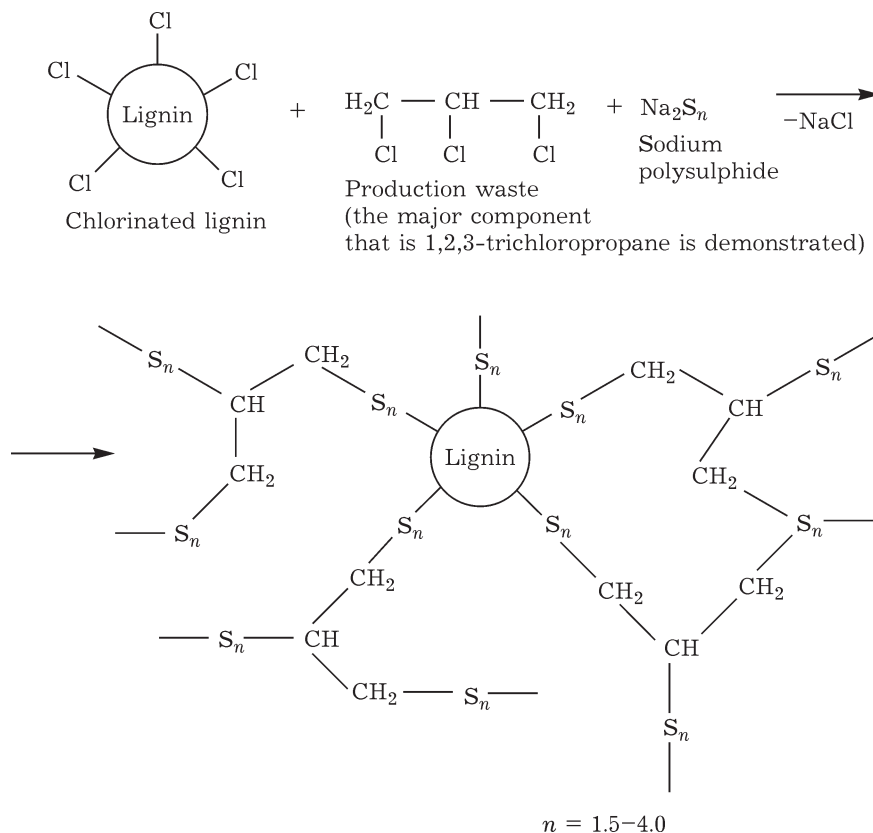


Chlorine molecules chlorinate aromatic rings only in the presence of Lewis acid catalysts, while Cl_2 и HCl contribute to the introduction of chlorine into propane lignin fragments (Scheme 1).

Therefore, at low degrees of lignin chlorination by chlorine water, $\text{Cl}-\text{C}(sp^3)$ bonds



Scheme 2.



Scheme 3.

are preferably formed, in which chlorine atoms can be during the action of nucleophiles S_n^{2-} . Almost complete chlorine substitution in chlorolignin at its content up to 5.7 % serves as a confirmation of this (see Table 1).

Chlorination into aromatic rings happens at deeper chlorination with chlorine water (action of Cl^+ atoms at the moment of formation), which is confirmed by the presence of residual chlorine in chlorolignin sulphidation products (see Table 1). Chlorolignin obtained by electrochemical chlorination with the maximum chlorine content of 30 % is used for sulphidation [22], only 15–17 % is substituted by sulphur during sulphidation with polysulphides.

Therefore, chlorolignin sulphidation products that are sorbents **Ia–d** are formed by Scheme 2.

Cross-linking of chlorolignin particles and the formation of the sorbent as brown powders happen during polycondensation.

Aliphatic chlorohydrocarbons participate in the formation of sorbents **IIa–g** in polycondensation with Na_2S_n when organochlorine wastes are additionally used. This process is

demonstrated in Scheme 3 on an example of 1,2,3-trichloropropane (major waste component).

The formation of a network polymer contributes to overlapping of chlorine atoms in some fragments of a trichloropropane chain, which hinders their substitution during the action of sodium polysulphide (presence of residual chlorine (see Table 2)).

Thus, sulphur-containing solid products that demonstrated high sorption activities toward heavy metal ions on model systems can be obtained using chlorolignin (see Table 3).

Sorption activity of sulphur-containing sorbents is defined by the effect of many factors: sulphur content, sorbent porosity, solution pH value, sulphur distribution on the metal surface, *etc.*

For this reason, Table 3 data are hard to interpret; however, it is obvious that efficient sulphur-containing sorbents can be obtained using chlorolignin.

Efficient extraction of metals by obtained sorbents is defined by an opportunity for the complex coordination interaction of sulphur atoms with metal ions:



The presence of oxygen atoms in lignin creates additional conditions for complexation and contributes to strengthening of Me–sorbent bonds, which has been repeatedly noted for sulphur-containing ligand–metal systems [23].

CONCLUSION

Sulphur sorbents obtained from production wastes (lignin, chloroaliphatic residues, and sulphur) are efficient toward heavy metal cations, distinguished by the availability of raw materials for their production and have high sorption capacities. It should be expected that the obtained sorbents will be selective only to heavy metal ions (thiol poisons) and therefore can be used for purifying saline waste water containing Na⁺, K⁺, Ca⁺, and Mg⁺ ions, *etc.*

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