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Novel Type of Sorbents Based on Sodium Polysulphide from the Wastes of Epichlorohydrin Production for Extracting Heavy Metal Compounds

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Abstract

A method was developed for obtaining granulated sulphur-containing sorbents with the use of wastes from epichlorohydrin production containing about 76 % of 1,2,3-trichloropropane was developed. The interaction between the wastes and sodium polysulphide is carried out in the presence of petroleum coke particles playing the role of polycondensation centres. The sorbents obtained are capable of extracting metals from aqueous solutions to exhibit the following sorption capacity (mg/g): Zn up to 74, Cd up to 31, Hg up to 152, Cu up to 25. The sorption mechanism is under discussion.

Key words: organochlorine wastes, processing, sorbents, heavy metals, wastewater purification

INTRODUCTION

Among the wastes of production activities, heavy metals (Zn, Cd, Hg, Cu, Pb, etc.) and organochlorine residues of the chemical industry occupy a highly important place. The compounds of heavy metals (chemical elements those exhibit a density greater than 4.5 g/cm³ in the form of elementary substances) belong to a series of thiol poisons, *i. e.* the substances those can block sulphur-containing groups in proteins, whereas organochlorine toxicants belong to nerve poison and exhibit carcinogenic activities [1].

Well-known method for processing organochlorine residues *via* complete destructive chlorination to form CCl₄ in recent years is less and less used. This could be connected with the fact that CCl₄ was mainly used in production of Freon species those were found to be hazardous with respect to the ozone layer [2]. As a conse-

quence, searching for efficient ways to process organochlorine waste remains a major problem in modern chlorine industry. The production of epichlorohydrin, an important intermediate product in manufacturing epoxy resins and synthetic glycerin, is based on the substitutional chlorination of propylene and chlorohydrination of allyl chloride with accompanying by the formation of a great amount of chlorinated organic wastes [3]. Earlier, a method was proposed for processing such wastes into organosulphur products and materials – thiokols, valuable flotation reagents, ligands for complexation and reagents for the sulphurization of catalysts [4, 5].

An important property of organosulphur compounds consists in their ability to form stable coordination compounds with heavy metal ions. The possibility of such interaction could be explained with using the principle of hard

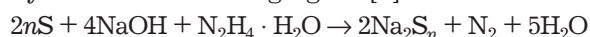
and soft acids and bases by Pearson, where-with soft acids (heavy metal cations) would preferably coordinate with soft bases (sulphur atoms) [6]. Low molecular mass organic sulphur compounds use to form complexes with many transition metals which can be applied in catalytic systems [7], in chemical analysis [8], and in other fields. Sulphur-containing polymers also exhibit the ability of complex formation [9]. There are data available from the literature concerning the adsorption capacity of polyethylene monosulphide with respect to silver ions [10] and obtaining the sorbent with the use of lignin and polymeric sulphides formed from 1,2,3-trichloropropane [11]. However, the most of widely used organosulphur polymers (polyarylene sulphides and thiokols) cannot be used as an adsorbent due to the features of their structure (steric shielding of sulphur atoms in polyarylene sulphides) and the rubbery state of thiokols.

We have proposed a method for obtaining solid granulated sulphur-containing sorbents with the use of wastes from epichlorohydrin production, and studied the ability of the sorbents to extract the compounds of Zn, Cd, Hg and Cu from model solutions.

EXPERIMENTAL

The sorbents were obtained using waste the fractions of organochlorine obtaining, whose main component is presented by 1,2,3-trichlo-

ropropane. The wastes taken directly from a plant for epichlorohydrin production exhibited the following componential composition (mass %): 1,2,3-trichloropropane, 76.6, dichloropropanols 17.4, 1,2-dichloropropane 2.0, dichloropropenes 2.1, other products – 1.9. The mixture of organochlorine components was entered into polycondensation with sodium polysulphide with no pre-treatment the components. Sodium polysulphide was obtained via dissolving elemental sulphur in an aqueous solution of sodium hydroxide in the presence of hydrazine hydrate as a reducing agent [4]:



As it was noted in [4], the preferential formation of polysulphide Na_2S_n with a preset value of n is determined by a molar ratio S/NaOH. When the ratio is equal to 1 : 1 disulphide Na_2S_2 is preferably formed, whereas at the ratio of 3 : 2, the formation of Na_2S_3 is observed, and at the ratio of 2 : 1 there is Na_2S_4 formed.

In order to perform the formation of granules in the course of polycondensation, to a polysulphide solution obtained were introduced polycondensation centres presented by finely grinded petroleum coke (with the grain diameter $d \leq 0.15$ mm). It should be noted that the in manufacturing the electrode petroleum coke the particles with the size less than 6 mm can not be used for the targeted purpose, thus they in fact represent the wastes of commercial petroleum coke production. The latter represents a rather

TABLE 1

Synthesis conditions and characteristics of sorbents obtained (process temperature 50 °C)

Sample No.	Starting reagents, g				n	Sorbent yield, g	Grain size, mm	Content, %	
	S	NaOH	Petroleum coke	Organochlorine waste ^a				S	Residual Cl
1	8.0	5.0	2.5	10.8	4	13.8	~5	54.0	9.2
2	6.0	5.0	2.5	10.8	3	11.8	~1.5	43.2	13.8
3	4.0	5.0	2.5	10.8	2	10.3	~2	38.6	14.2
4	16.0	10.0	4.0	22.0	4	24.0	~3	60.2	7.5
5	8.0	5.0	2.0	9.8 ^b	4	11.2	~1.5	65.4	4.2
6	4.0	2.5	1.0	4.0	4	6.0	~1–1.5	54.0	8.8
7	6.0	5.0	2.5	6.0 ^c	3	11.2	~3	40.5	3.6

^aWaste fraction consumption was calculated from the content of main component (1,2,3-trichloropropane).

^bPure 1,2,3-trichloropropane was used.

^cFraction was supplemented with 10 % of CH_2Cl_2 .

TABLE 2

Adsorption characteristics of the sorbents obtained

Sample No.	Absorption of I ₂ , %	Absorption of methyl orange, mg/g	Activity with respect to metal cations, mg/g (pH 3)			
			Zn	Cd*	Hg	Cu*
1	16.4	186.0	65	30	136	15
2	9.0	326.0	38	24	97	19
3	8.3	33.0	25	10	72	12
4	12.6	118.0	48	28	116	19
5	15.2	211.0	60	30	132	20
6	12.8	117.0	52	30	95	19
7	16.8	318.0	74	31	152	25
Petroleum coke	14.0	116.2	56	26	108	15

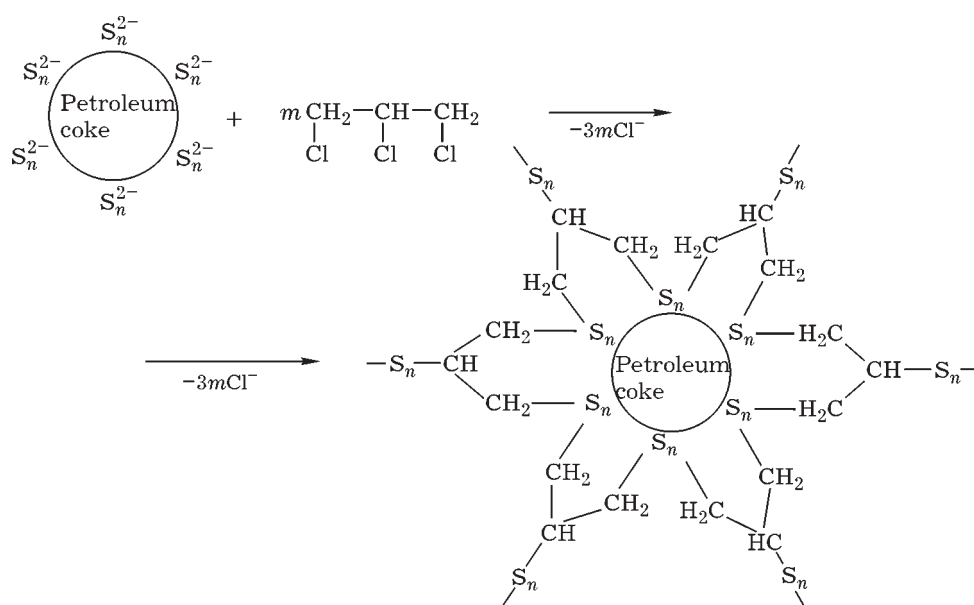
* Adsorption procedure was performed at metal ion concentration in the initial solution equal to 1 mg/L.

porous material with good absorption properties [12]. The mentioned substance being introduced in the solution of sodium polysulphide, the anions of S_n^{2-} are partially adsorbed on the surface of petroleum coke particles, and the polycondensation takes place with the participation of both adsorbed anions and anions remaining in solution. After the process completion, the adsorbent was filtered off, washed with water, alcohol, ether to dry it then under vacuum for 8 h.

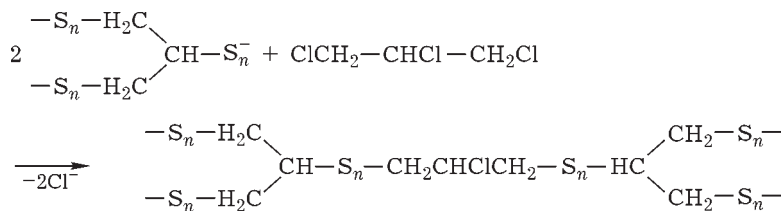
As the result, sufficiently homogeneous granules are formed whose size depends on the amount of petroleum coke used, the "sulphidity" level of an anion (n), the hydrodynamic

conditions and other factors, to range within 1.5–5 mm (Table 1).

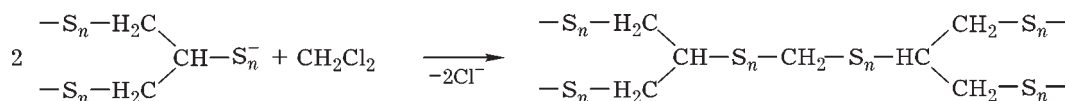
The porous structure of the sorbents obtained was investigated according to a standard technique described in [13], via studying the efficiency of iodine absorption from the solution (microporosity) as well as the absorption of methyl orange (macroporosity). In addition, we investigated the efficiency of extraction from model solutions with respect to the compounds of Zn, Cd, Hg and Cu (Table 2). For this purpose, a weighed portion of the sorbent (0.2 g) was shaken with 20 mL of a metal salt solution with a certain concentration during a certain time. The



Scheme 1.



Scheme 2.



Scheme 3.

residual concentration of metal in the solution was determined by means of photocolorimetric technique with the use of dithizone [14, 15].

RESULTS AND DISCUSSION

The polycondensation of sodium polysulphide with organochlorine wastes containing 1,2,3-trichloropropane results in obtaining a cross-linked polymer that forms the granules of a sorbent together with the particles of petroleum coke. Scheme 1 demonstrates the structure of such granules.

In the course of forming a spatial network of polysulphide polymer, some chlorine atoms appear spatially shielded with respect to attacking by polysulphide anions even in the 1,2,3-trichloropropane, which favours saving the residual chlorine within the sorbent granules (see Table 1). With increasing the length of the polysulphide chain, the polymer becomes more "loose", thereby the content of residual chlorine and the sorbent microporosity level exhibit a decrease. However, the macroporosity level according to methyl orange absorption varies in a more complicated manner, reaching the highest value for trisulphide polymer, whereas for $n = 2$ this parameter abruptly drops down to an abnormally low value. To all appearance, the maximum porosity at $n = 3$ could be caused by an active participation of 1,2,3-trichloropropane as a bifunctional monomer, which promotes "moving apart" the polymer layers (Scheme 2).

This results in increasing the residual content of chlorine. The "moving apart" of the polymer layers could also occur due to the par-

ticipation of other, in particular bifunctional, mixture components (dichloropropanols, 1,2-dichloropropane, *etc.*). In this connection, of particular interest is an experiment connected with obtaining sorbent sample No. 7 (see Tables 1, 2), wherein dichloromethane was added to the fraction of wastes in an amount of 10 mass % with respect to 1,2,3-trichloropropane for performing the polycondensation procedure. The resulting sorbent exhibited a low content of residual chlorine, high microporosity and medium macroporosity (Scheme 3).

Data concerning the n value, micro- and macroporosity of the sorbents obtained satisfactorily correlate with the sorption activity with respect to metal ions (see Table 2). At least, the maximum activity is demonstrated by a sorbent having the highest micro- and macroporosity.

It should be noted that for all the cations under consideration, the highest sorption capacity was exhibited in the case of solutions with pH 3. Perhaps, decreasing the pH value

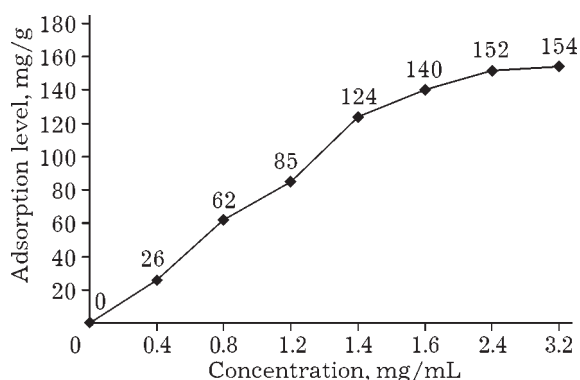
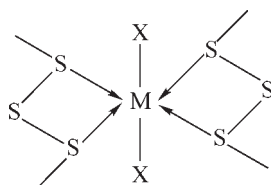


Fig. 1. Mercury sorption isotherm by sample No. 7.

results in the fact that the atoms of sulphur are protonated in the pores and channels, which prevents the latter from the penetration of metal ions therein. Increasing the pH value promotes enhancing the hydrolysis of the salts of cations under investigation; thereby the hydrolyzed species are adsorbed to a worse extent. At pH > 4.5, and high metal concentration values in solution (>2.0 mg/mL) we observed precipitating hydroxides.

The sorption process was not accompanied by changing the pH value of the solution, which could indicate a complex coordination mechanism of the sorption process. The sorption isotherm obtained for the extraction of mercury ions in the form of $\text{Hg}(\text{NO}_3)_2$ (Fig. 1) exhibits a distinctive pattern corresponding to the Langmuir isotherm. This indicates the fact that there occurs a monolayer adsorption on the active centres being in a good agreement with the complex coordination mechanism:



M = Zn, Cd, Hg, Cu;
X = Cl, NO_3

A complete saturation of the sorbent is observed after 3–5 h of sorption procedure depending on the nature of a cation and the structure of a sorbent.

CONCLUSION

With the use of organochlorine waste products from manufacturing epichlorohydrin jointly with available reagents (sulphur, caustic soda, hydrazine hydrate, petroleum coke) employing a stan-

dard reactor equipment one can obtain granulated sulphur-containing sorbents, whose properties are determined by the ratio between the reagents, by the composition of waste products used and by the hydrodynamic regime of the process.

The sorbents obtained can efficiently recover the compounds of zinc, cadmium, mercury and copper from aqueous solutions.

Thus, the method developed for obtaining sorbents from waste products can solve an equally important environmental problem such as wastewater purification from heavy metal compounds for a number of metal processing factories.

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