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## Recycling Spent Sulphur-Containing Sorbents Obtained from Sodium Polysulphide and Organochlorine Wastes

V. A. GRABELNYKH<sup>1</sup>, E. P. LEVANOVA<sup>1</sup>, A. V. REDINOVA<sup>2</sup>, N. V. RUSSAVSKAYA<sup>2</sup> and N. A. KORCHEVIN<sup>2</sup>

<sup>1</sup>Favorsky Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Favorskogo 1, Irkutsk 664033 (Russia)

E-mail: venk@irioch.irk.ru

<sup>2</sup>Irkutsk State Railway Engineering University, Ul. Chernyshevskogo 15, Irkutsk 664074 (Russia)

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### Abstract

By means of reducing or thermal cracking, spent sulphur-containing sorbents obtained from waste organochlorine products can be converted into valuable organosulphur products such as 1,2-dithiol-3-thione, or 1,2,3-tris(methylsulphonyl)propane. The metal contained in the sorbent in both cases is transformed into corresponding sulphide and could be used to produce the metal in the usual way.

**Key words:** sulphur-containing sorbents, processing, 1,2-dithiol-3-thione and 1,2,3-tris(methylsulphonyl)propane

### INTRODUCTION

The most important method of wastewater purifying from highly toxic heavy metal compounds consists in an adsorption extraction by solid sorbents [1, 2]. Sorbents used in practice, need a number of requirements to provide the technological application thereof such as a high sorption capacity, low cost, high mechanical strength, fire safety, the potentiality of easy recovery and reuse. The sorbents used can not simultaneously meet all the requirements for materials of this kind, so many research centers perform extensive work for the modification of known and the development of new types of adsorbents.

In order to remove heavy metal ions from aqueous solutions it is promising to create polymer sulphur-containing sorbents, whose adsorption capabilities are associated with the ability of these ions to form strong coordinate bonds with sulphur atoms. The authors of [3]

presented a new type of sorbents prepared from sodium polysulphide and organochlorine waste from the production of epichlorohydrin. Performing the reaction of polycondensation between sodium polysulphide and organochlorine compounds from industrial waste products on the surface of petroleum coke particles allows one to obtain an adsorbent in the form of granules having a diameter ranging from 2 to 5 mm, which facilitates the use in metal recovery processes. The sorbents obtained in such a way exhibit a high sorption capacity with respect to the major toxicant ions (Zn, Cd, Hg, Cu). The production thereof is based on the use of available reagents and industrial wastes being carried out using a standard reactor and auxiliary equipment.

The adsorbents exhibit a high mechanical strength; they are inert with respect to organic solvents and oils. Because of this, they could be used in the process of purifying metal-containing wastewaters. However, the sorption of

TABLE 1

Desorption of zinc from the surface of the sorbent obtained from  $\text{Na}_2\text{S}_4$ . Weighed sample portion 0.2 g, initial zinc content in the sample portion 10 mg, sulphur content in the sorbent 54 %

Desorbing solutions	Zn <sup>2+</sup> concentration in the resulting solution, mg/mL	Mass of recovered zinc, mg	Extraction level, %
H <sub>2</sub> O (80 °C)	0.18	3.6	36
HCl (conc.)	0.38	7.6	76
HCl (1 : 1)	0.325	6.5	65
HCl (1 : 2)	0.27	5.4	54
HCl (1 : 5)	0.25	5.0	50
Thiourea (10 %)	0.22	4.4	44

metal ions on the surface and in the pores that occurs *via* a complex-coordination mechanism predetermines a strong binding between ions and the active centers of the sorbent, which should hinder metal desorption and the regeneration of the sorbent. Taking into account that all the sorbents were prepared using wastes, it could be appropriate and cost-efficient to use them once in the wastewater treatment process with subsequent qualified recycling the spent sorbents. The purpose of this investigation consisted in studying the possibilities of the complete isolation of the metals under recovering from spent sorbents to obtain valuable organosulphur products those are of interest as flotation reagents and extraction agents.

## EXPERIMENTAL

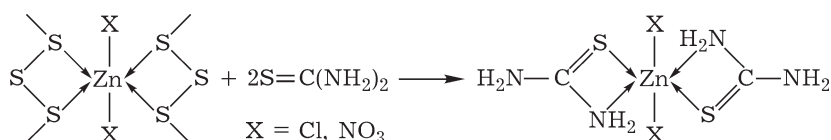
NMR spectra were registered using a Bruker DPX-400 spectrometer (400.13 MHz) in  $\text{CDCl}_3$  solutions, TMS was used as an internal standard. Mass spectra were registered using a Shimadzu GCMS-QP5050A gas chromatograph-mass spectrometer (column SPB-5,  $60000 \times 0.25$  mm), quadrupole mass analyzer, electron ionization, electron energy 70 eV, ion source temperature equal to 190 °C, detected mass range 34–650 Da). The content of  $\text{Zn}^{2+}$

ions in the solution was determined photocolometrically [4] using a MKM-02 microcolorimeter.

Previously we studied the possibility of metal desorption from the sorbent under consideration using hot water (80 °C), a solution of hydrochloric acid (concentrated acid, water-diluted acid at a ratio of 1 : 1, 1 : 2, 1 : 5), thiourea solution (10 %). A weighted portion of sorbent (0.2 g) saturated with zinc (50 mg/g) was shaken with 20 mL of a desorption solution during 1 h. Data concerning zinc extraction from the surface of the sorbent are presented in Table 1.

It is evident that a considerable desorption level is achieved only in the case of concentrated hydrochloric acid. However, this value is not the maximum one. The solution of the thiourea was used as a desorption agent basing on data concerning possible forming complex compounds thereof with the salts of a number of metals, including zinc [5]. Table 1 demonstrates that thiourea as a desorption agent is inefficient. To all appearance, this is caused by the presence of a greater number of  $\text{Me}-\text{S}$  bonds with sufficient strength in the coordination compounds on the sorbent surface, as to compare with the complexes formed by thiourea (Scheme 1).

Thus, it has been experimentally demonstrated that sulphur-containing polymeric sor-



Scheme 1. Transformation coordinate complex on the surface of the adsorbent [3] in the complex with thiourea.

bents saturated with heavy metal ions are extremely difficult to undergo desorption.

Taking into account the data published concerning the reactivity of polysulphide oligomers in redox systems [6] and the data on thermal decomposition thereof [7], we considered two possible ways to utilize waste sorbents containing heavy metals.

The base-reductive cleavage of waste sorbents was carried out with the use of hydrazine hydrate - KOH system.

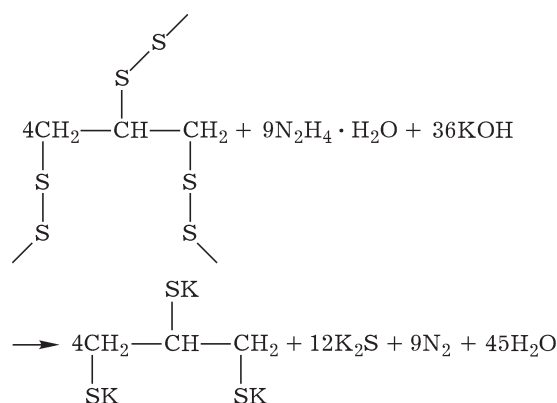
To a solution of 6 g of KOH in 50 mL of hydrazine hydrate were introduced 4.0 g of sorbent containing 50 mg/g of zinc, the solution was stirred at 60–65 °C during 2 h. The mixture was filtered through filter paper. The filter was washed with hot water, dried, and then, without separating the precipitate, was boiled with 100 mL of concentrated nitric acid to dissolve it completely. The solution was filtered to determine photocolometrically the content of zinc therein (194 mg). The experimental data demonstrated an almost complete zinc conversion into zinc sulphide ZnS that under the action of nitric acid converted into zinc nitrate  $Zn(NO_3)_2$ . The filtrate after the separation of zinc sulphide was treated with methyl iodide, wherewith 1,2,3-tris(methylsulphanyl)propane **I** was obtained and characterized. The yield of compound **I** from 4.0 g of the sorbent was equal to 1.6 g. The structure of compound **I** is confirmed by means of  $^1H$  NMR ( $CDCl_3$ ),  $\delta$ , ppm: 2.04 s ( $SCH_3$  at CH), 2.06 s ( $SCH_3$  at  $CH_2$ ), 2.79 m (CH and  $CH_2$  protons) and by means of gas chromatography-mass spectrometry,  $m/z$  182 ( $M^+$ ). The schematic diagram of the process is considered in the section "Results and discussion".

The thermal decomposition of the sorbent saturated with zinc ions was carried out in a distillation flask under vacuum (20 mmHg) in the flow of an inert carrier gas. The thermolytic products were recrystallized from ethanol. The yield of product 1,2-dithiol-3-thione **II** from the sorbent was equal to 1.2 g from 4.0 g of the sorbent. The structure of compound **II** was confirmed by means of  $^1H$  NMR ( $CDCl_3$ ),  $\delta$ , ppm: 8.35 d (CCHC), 7.18 d (CH-S),  $^3J = 5.5$  Hz, and by means of GC-MS,  $m/z = 134$  ( $M^+$ ). The physicochemical properties correspond to data from [8]. The vat residue was dissolved in boil-

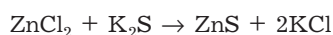
ing nitric acid to determine the content of zinc. From 4.0 g of the saturated sorbent after dissolving the distillation residue we obtained a solution containing 203 mg of zinc according to photocolometric data.

## RESULTS AND DISCUSSION

The base-reductive cleavage of polysulphide polymer involved in the structure of the sorbent occurs *via* breaking S-S bonds. For the fragment formed with the participation of the main component of organochlorine wastes [3], the process could be presented by the following scheme:

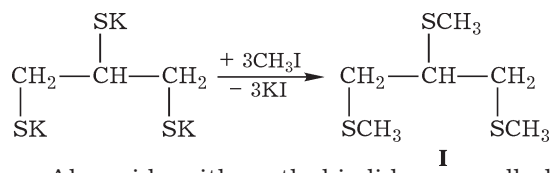


The resulting potassium sulphide reacts with the metal salt to form zinc sulphide:



In the course of the reaction, the ZnS and petcoke present in the sorbent form a precipitate. As demonstrated above, one can determine the content of zinc in this precipitate.

In the course of methyl iodide treating the filtrate obtained after the separation of the solid phase, one observes the formation of 1,2,3-tris(methylsulphanyl)propane **I**, the substance that can serve as an efficient ligand for the complexation, and an efficient metals extraction agent and flotation agent for metals:



Alongside with methyl iodide as an alkylating agent one could employ also other alkyl halides including those containing functional substituents. Excess potassium sulphide with an

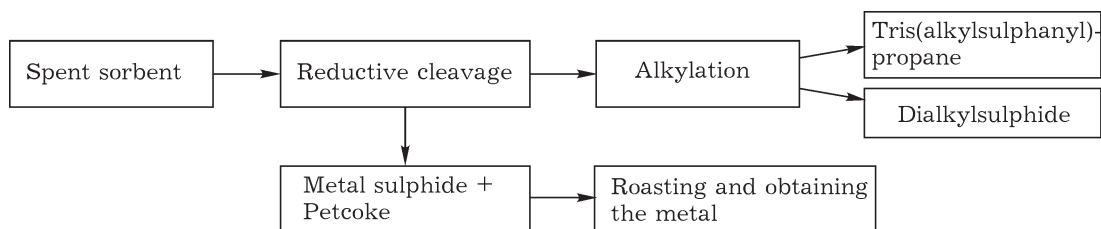


Fig. 1. Schematic diagram of utilizing the spent sorbent.

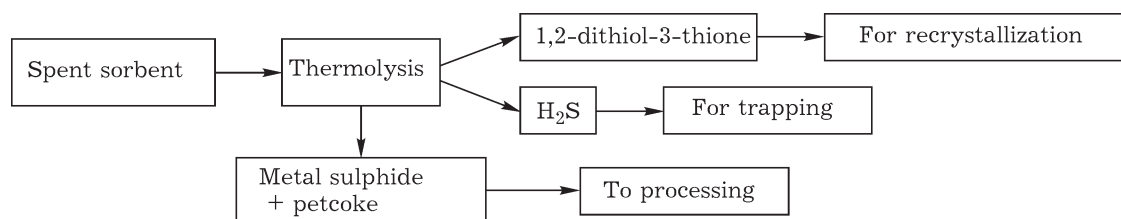
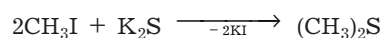


Fig. 2. Schematic diagram of thermal processing the sorbent.

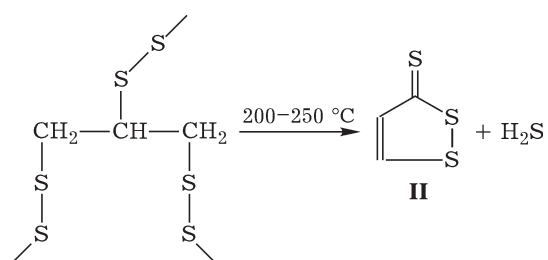
alkylating agent results in producing a corresponding organic sulphide:



The resulting dimethyl sulphide could be used to obtain DMSO, a paramount solvent in the organic chemistry. Application could be found also by other sulphides obtained via replacing an alkylating agent.

Figure 1 demonstrates a diagram of utilizing the spent sorbent using the process of base-reductive cleavage.

The thermal cleavage of sulphur presented for the main fragment of the oligomer occurs through the following scheme:



The metal sorbed together with hydrogen sulphide and sulphur forms sulphide that remains still in distillation flask alongside with petcoke. The resulting excess hydrogen sulphide can be caught by alkali to use for producing sodium polysulphide. The 1,2-dithiol-3-thione **II** obtained in the course of thermolysis is well

known; this substance finds application as an anticorrosive and antiwear additives for oils [9].

Figure 2 demonstrates a schematic flow diagram of the thermal processing of the sorbent.

## CONCLUSION

Spent sulphur-containing sorbents are not subject to desorption and regeneration, but the application thereof for wastewater treatment could be quite appropriate. After working in the adsorption set-up they can be utilized in a qualified manner *via* the isolation of metal sulphide with obtaining valuable products such as 1,2,3-tris(methylsulphanyl)propane, or 1,2-dithiol-3-thione. The presence of petroleum coke in the sorbent provides the facilitation of both reductive and thermal destruction of the polymer in a sorbent. The use of this sorbent would promote the utilization of organochlorine wastes, purification of metal-containing wastewater, complete metal regeneration and obtaining valuable organosulphur products.

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