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Ureasulfonamide Polymeric Sorbent for Selective Mercury Extraction

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Summary. A new polymeric resin with sulfonamide pendant functions has been prepared for the selective extraction of mercuric ions. This polystyrene sulfonamide urea resin with a 3.5 mmol/g total nitrogen content is able to selectively sorb mercury from aqueous solutions. The mercury sorption capacity of the resin is around 1.60 mmol/g under non-buffered conditions. The experiments performed under identical conditions with some metal ions reveal that Cd(II), Pb(II), Zn(II), and Fe(III) ions are also extractable in low quantity (0.05–0.1 mmol/g). The sorbed mercury can be eluted by repeated treatment with hot acetic acid without hydrolysis of the amide groups.

Keywords. Sulfonamide; Metal complexes; Polymerizations.

Introduction

The use of polymer-bonded ligands in selective mercury removal has been the subject of many research articles [1, 2] and reviews [3, 4]. Because of the high toxicity of all mercury compounds, the extraction of mercuric ions from aqueous wastes and drinking water is of special environmental importance. Two common ligand types, sulfur and amide, are being used currently in the design of polymer sorbents for binding mercuric ions selectively.

The reactivity of sulfur compounds toward mercuric ions is the key principle behind anchoring thiol [5, 6] and thio ether [7] functions for laboratory or industrial levels of applications.

Since thiol and thioether functions react with other metal ions, the mercury-thiol interaction is not specific. There are many articles about some other sulfur containing polymer-supported ligands such as xanthate [8], thiourea [9], pyridine-based thiols [10], and dithiozone [11] in highly selective mercury removal. Another important ligating group for selective mercury binding is the amide group, which forms covalent mercury-amide linkages under ordinary conditions.

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In conjunction with this, we have demonstrated in previous studies that polyacrylamide grafted polymeric sorbents [12, 13] and cellulose-*g*-polyacrylamide [14] are specific to mercuric ions and useful in the removal of trace mercury from aqueous mixtures. Foreign ions, such as Zn(II), Cd(II), Pb(II), and Fe(III), do not interfere, and those ions are not extracted to any extent by the amide groups of these polymers.

In this study, urea sulfonamide groups have been incorporated into crosslinked polystyrene beads to have the physical advantages of bead polymers. For this purpose, chlorosulfonated polystyrene beads have been modified by a reaction with urea. The mercury uptake ability and regeneration conditions of the resulting resin have been investigated.

Results and Discussion

Urea functions have been incorporated into crosslinked polystyrene resin beads (420–560 μm) according to the reaction in Scheme 1 for the preparation of a mercury-selective polymer. The polymer with a 3.74 mmol/g chlorosulfonation degree (determined by chloride analysis), when reacted with an excess of urea in 1-methyl-2-pyrrolidone solvent, gives rise to the corresponding polymer with urea sulfonamide functions.

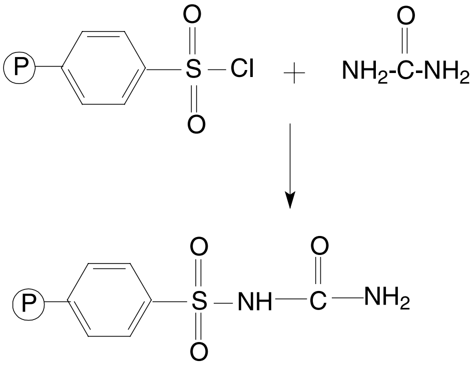
The total nitrogen content of the product was found as 3.5 mmol/g by *Kjeldahl* nitrogen analysis. Obviously, there must be an excess of the urea reagent because of the quantitative conversion.

Mercury Uptake

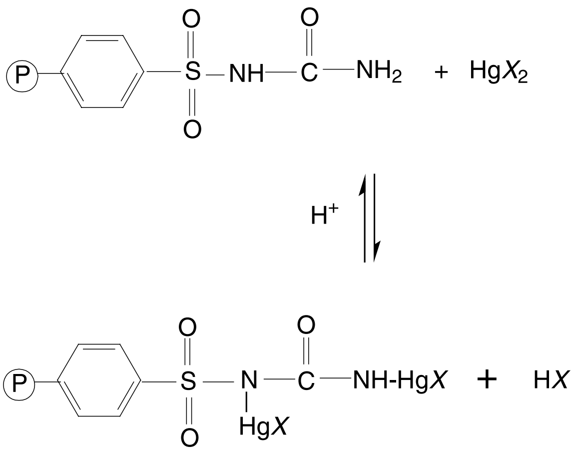
There exist two possible reaction sites, one sulfonamide group and one urea group, available for mercury binding.

Based on the basic reaction of mercuric ions with amide groups, yielding covalent mercury-amide linkages, mercury binding of the resin can be depicted as shown in Scheme 2.

In the mercury uptake experiments, we have deliberately used mercuric chloride because the Hg(II) ion has a reasonable affinity toward chloride ions. According to our experiences in previous studies [14], mercury uptake is somewhat higher when



Scheme 1



Scheme 2

Table 1. Metal uptake characteristics of the beads

Metal ion	Initial concentration	Resin capacity	Recovered metal
	M	mmol/g	mmol/g
Hg(II)	0.10	1.60	1.35
Hg(II)	0.05	1.58	1.30
Hg(II)	0.025	1.61	1.35
Cd(II)	0.150	0.05	–
Pb(II)	0.150	0.01	–
Zn(II)	0.150	0.04	–
Fe(III)	0.150	0.1	–

mercuric acetate is used. For this reason, in the present study $HgCl_2$ was used to determine the capacity of the polymeric sorbent under extreme conditions. The loading experiments indicate a mercury capacity of about 1.60 mmol/g in each case, and no significant capacity change is observed at different initial mercury concentrations (Table 1). The pH of $HgCl_2$ solutions remains almost constant in the 3.1–3.9 range through the extraction process.

In the experiments, we did not use buffer solutions because the use of buffer solutions is not practical under real application conditions.

To inspect mercury selectivity of the resin, metal extraction experiments have been repeated with Cd(II), Pb(II), Zn(II) and Fe(III) solutions. Very low sorption capacities (0.05–0.1 mmol/g) were found compared to mercury sorption capacity (Table 1). Therefore, overall results clearly indicate that mercury sorption is extremely selective.

Kinetics of the Mercury Sorption

To investigate the efficiency of the resin in the presence of trace quantities, we performed batch kinetic sorption experiments with highly diluted $HgCl_2$ solutions

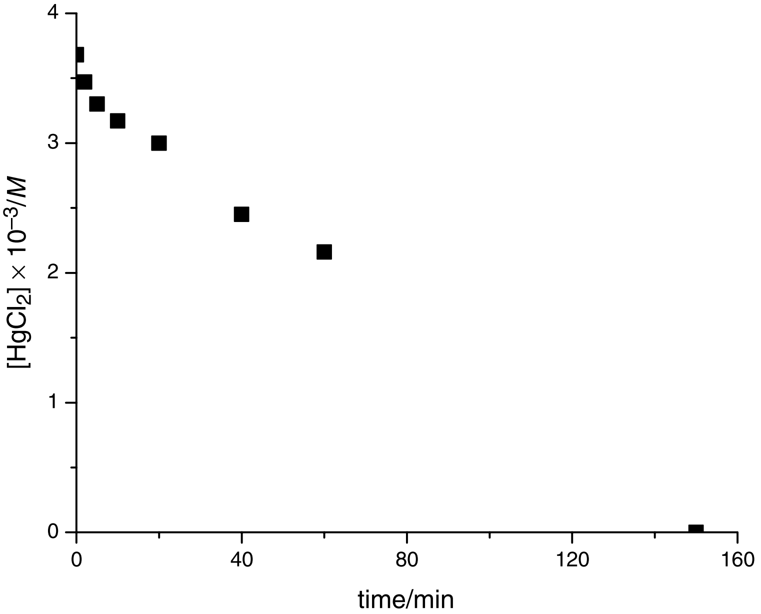


Fig. 1. Sorption-time plots of 0.1 g resin sample with 90 cm^3, 3.638×10^{-3} M $HgCl_2$ solution

(3.683×10^{-3} M). The concentration-time plot in Fig. 1 shows that within about 150 min of contact time, the Hg(II) concentration falls to zero.

The kinetics of the sorption obey second order kinetics ($k = 0.185/M \cdot s$ with a correlation factor of 0.990) as in the case of many metal complexations involving solid surfaces.

Splitting of the Sorbed Mercury

In the regeneration of mercury from loaded polymer, hot acetic acid was used as an appropriate agent. Mineral acids can be considered as extracting agents. However, strong acids would inevitably cause the hydrolysis of the urea groups. Therefore, mineral acids are not suitable in the regeneration process.

Although acetic acid is less effective and slow in regeneration, it does not cause any hydrolysis. When loaded samples are heated in glacial acetic acid at 80°C for 1 h, the amount of recovered mercury is around 1.35 mmol/g (Table 1), which is about 84% of the capacity of fresh polymer.

Conclusions

The studied resin, having urea and sulfonamide groups, shows a reasonable mercury selectivity over Zn(II), Cd(II), Pb(II), and Fe(III) ions. Under nonbuffered conditions, the mercury uptake capacity is around 1.60 mmol/g when Hg(II) concentrations are within the 0.05–0.1 M range. The recovery of mercury can be achieved by elution with acetic acid at 80°C without hydrolysis of the urea groups. The mercury sorption obeys second order kinetics. Although the mercury loading capacity is about half of the theoretical capacity because of the lesser hydrophilicity of the resin, it is still high enough and useful for the removal of mercury even at low concentrations.

Experimental

Materials: All the chemicals are analytical grade: styrene (Fluka), divinyl benzene (DVB) (Fluka), chlorosulfonic acid (Fluka), urea (E-merck).

Preparation of Spherical Beads of Crosslinked Styrene-DVB (10%) Copolymers
The copolymer was prepared according to the procedure described elsewhere [15]. The resulting spherical beads were sieved, and the 420–590 μm fraction was used for further modifications.

Chlorosulfonation of the Styrene-DVB Resin Beads
The reaction was performed by treatment of styrene-*DVB* spherical beads with chlorosulfonic acid as described before [15]. Chlorosulfonation degree was determined by boiling the product with a NaOH (10%) solution for 4 h. The chlorine content of the solution was determined by the mercuric thiocyanate method [16]. The chlorine analysis was found to be 3.74 mmol/g which corresponds to ~63.65% chlorosulfonation.

Modification of the Chlorosulfonated Resin with Urea
The chlorosulfonated polymer (10 g) was added portion wise to a stirred solution of urea (3 g, 0.05 mol) in 1-methyl-2-pyrrolidone (30 cm^3) at 0°C. The mixture was shaken with a continous shaker for 24 h at room temperature. Then, the reaction content was poured into water (600 cm^3), filtered, and washed with excess of water and methanol, respectively. The modified resin was dried under vacuum at room temperature for 24 h. The yield was 10.8 g. The total amine content was determined by *Kjeldahl* nitrogen method according to the literature [17] and found to be 3.5 mmol/g.

Determination of the Nitrogen Content
The nitrogen content of the final product was determined by *Kjeldahl* nitrogen analysis as follows. The polymer sample (0.5 g) was put into 20 cm^3 H_2SO_4 (80%) and refluxed for 6 h. After cooling, the mixture was diluted cautiously to 50 cm^3 and filtered. The filtrate was used in the *Kjeldahl* analysis. The consumption of 35 cm^3 0.1 M HCl for the neutralization of the evolved ammonia indicated 3.5 mmol as the total amide content.

Mercury Sorption Experiments
The determination of the mercury sorption capacity of the polymer was performed by the interaction of polymer samples with aqueous $HgCl_2$ solutions as follows. The resin sample (0.2 g) was added a Hg(II) solution (20 cm^3, 0.1 *M*). No buffer was used in these experiments. The mixture was shaken for 24 h at room temperature and filtered. The residual mercury concentration of the final solution was assayed by the colorimetric analysis of a 1 cm^3 filtrate, with diphenyl carbazide as the color reagent [18]. The final concentration of the residual liquor was 0.08 *M*. From the difference in the concentrations of the initial and final solutions, the sorbed mercury was calculated to be 1.60 mmol/g for the $HgCl_2$ solution.

Similar experiments were repeated under the same conditions with different initial mercury concentrations (0.025, 0.05, and 0.1 *M*). The sorbed amounts were calculated according to the residual mercury contents, as previously described. The relevant data are listed in Table 1.

Sorption Tests for Foreign Ions
The sorption capacities of the resin toward foreign ions [Zn(II), Cd(II), Pb(II), and Fe(III)] were examined by the simple contact of the aqueous solutions of those ions with 0.15 *M* initial concentra-

tions for 24 h. Residual metal analyses were performed by complexometric ethylenediaminetetraacetic acid titrations, as described in the literature [19]. The results are shown in Table 1.

Kinetics of Mercury Sorption

Batch kinetic experiments were performed with very dilute Hg solutions ($3.683\times10^{-3}\,M$). For this purpose, the polymeric sorbent (0.2 g) was wetted with distilled water (2 cm^3) and added to a solution of Hg (90 cm^3, $3.683\times10^{-3}\,M$ $HgCl_2$). The mixture was stirred magnetically and aliquots of the solutions (5 cm^3) were taken at appropriate time intervals for analysis of the residual Hg content by the method described above. The collected analytical data were used to produce the concentration-time plot in Fig. 1.

Regeneration of the Resin

A half-gram of the mercury-loaded sample was introduced to 10 cm^3 of glacial acetic acid at a constant temperature of 80°C, and the mixture was stirred for 1 h. The mixture was filtered, and 1 cm^3 of the filtrate was used for colorimetric mercuric analysis. The analysis gave mmol of Hg(II)/g of loaded polymer.

Acknowledgements

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