Thiol Containing Sulfonamide Based Polymeric Sorbent for Mercury Extraction

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ABSTRACT: A new polymeric resin with thiol pendant functions has been prepared for the extraction of mercuric ions. The thiol containing sulfonamide based resin with 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 1.70 mmol/g under non-buffered conditions. Experiments performed in identical conditions with several metal ions revealed that Cd(II), Pb(II), Zn(II), Fe(III), and Fe (II) ions also were extractable in quantities (1.0–1.65 mmol/g). The sorbed mercury can be eluted by repeated treatment with $4M$ HNO_3 without hydrolysis of the amide groups. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1879–1883, 2009

Key words: sulfonamide; metal complexes; thiol containing resin

INTRODUCTION

Waste waters containing heavy metal pollutants come from different industrial activities such as mining, power plants, plating facilities, and electrical equipment manufacturing. All heavy metals are toxic and non-biodegradable and should be separated from waste waters.

Mercury is a highly toxic metal that is very poisonous for living organisms even in trace concentration (ppb).

Approximately two thirds of the Hg in natural environments is of anthropogenic origin.[1] Burning of fossil fuels, such as petroleum, natural gas, and coal, is the most important contributor to the total environmental Hg budget, since they contain $\sim$ 0.2 ppm of Hg.[2] Mercury can be found in significant amounts in wastes from chloroalkali manufacturing plants, electrical and electronics manufacturing, and sulfide ore roasting operations.

Exposure to Hg can have toxic effects on reproduction, the central nervous system, liver, and kidneys, and cause sensory and psychological impairments.

Therefore, before the disposal of mercury containing industrial wastes their mercury content should be eliminated.

Mercury in industrial effluents and flue gas is usually recovered using chelating agents, which are not reusable after Hg is removed by distillation.[3] Alternative treatment methods are greatly needed to keep Hg out of the environment.

To minimize the adverse effects of Hg in the environment, it is desirable to find ways to capture it before it becomes a problem. Several techniques are available for this including precipitation, ion exchange and adsorption. Precipitation is effective within a narrow pH range and results in large volumes of Hg containing sludge, while ion exchange is effective only for wastes with low dissolved solids concentrations.

Adsorbents can be designed that are specific to Hg and whose volume is much less than an amorphous sludge.

Bailey et al.[4] reviewed several adsorbents and their applications for Hg removal and found that several natural materials were capable of adsorbing moderately high amounts of Hg.

The ability of a material to capture metals is controlled in part by the number of available functional groups used for binding metals. Functional groups with a known affinity for specific metals can be attached to other substances to create an effective adsorbent.[5]

The use of polymer-bonded ligands in selective mercury removal has been the subject of many research articles[6,7] and reviews.[8,9] 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[10,11] and thio ether[12] functions for laboratory or

Metal ion	Initial concentration (mmol/mL)	Resin capacity (mmol/g)	Recovered metal (mmol/g)
Hg(II)	0.10	1.70	1.30
Hg(II)	0.05	1.65	1.20
Hg(II)	0.025	1.63	1.25
Cd(II)	0.150	1.50	–
Pb(II)	0.150	1.45	–
Fe(III)	0.150	1.63	–
Fe(II)	0.150	1.00	–

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,[13] thiourea,[14] pyridine-based thiols,[15] and dithiozone[16] in highly selective mercury removal.

Amide containing polymers include an iminodiacetamide,[17] a dipyridylamide[18] and polythiourea on charcoal[19] are another important for binding highly selective Hg(II). Amide groups form covalent mercury–amide linkages under ordinary conditions. We described amide and sulfonamide containing polymers for selective removal of mercury from aqueous solution in previous studies.[20–25]

The thiol (–SH) group is known to form stable complexes with soft heavy metals of high polarizability such as Hg, Ag, Au, and to a lesser extent, Cd and Zn, while failing to coordinate well with the more abundant smaller, lighter metals such as Ca, Na, and Mg.[26]

In this study, a new polymeric resin with sulfonamide pendant thiol containing resin was prepared for the extraction of mercuric ions. Mercury sorption characteristics and regeneration conditions of the resulting resins were studied. Affinity of the resins for other metal ions such as Cd(II), Pb(II), Zn(II), and Fe(III) were also investigated.

EXPERIMENTAL

Materials

All the chemicals are analytical grade: Styrene (Fluka, Buchs, Switzerland), Divinyl benzene (Fluka), Chlorosulfonic acid (Fluka), thioaniline (E-Merck, Darmstadt, Germany), Mercury Chloride (E-Merck), and Diphenyl carbazide (Fluka).

Preparation of spherical beads of crosslinked styrene–10% DVB copolymers

The copolymer was prepared according to the procedure described elsewhere.[27] 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.[27]

Analysis of the chlorosulfonation degree was carried out by boiling 0.25 g of the polymer sample in 20 mL 10% NaOH solution for 4 h. After filtration and neutralization with HNO_3 solution ($2M$) the chloride content of the solution was determined by the mercuric thiocyanate method.[28] The chloride content was calculated as 4 mmol/g, which correspond to 70% chlorosulfonation.

Preparation of the thiol containing resin

The chlorosulfonated beads (10 g) were added portion wise to a stirred solution of thioaniline (6.2 g, 49.6 mmol) in 2-methyl pyrrolidone (50 mL) at 0°C. The mixture was shaken for 24 h at room temperature. The reaction content was poured into water (300 mL), filtered and washed with excess of water and acetone, respectively. The product was dried under vacuum at room temperature for 24 h. The yield was 15 g. The total nitrogen content was determined by Kjeldehal nitrogen method according to the literature[29] and found to be 3.5 mmol.

Mercury sorption experiments

The mercury uptake experiments were performed in non-buffered conditions. In these experiments, a
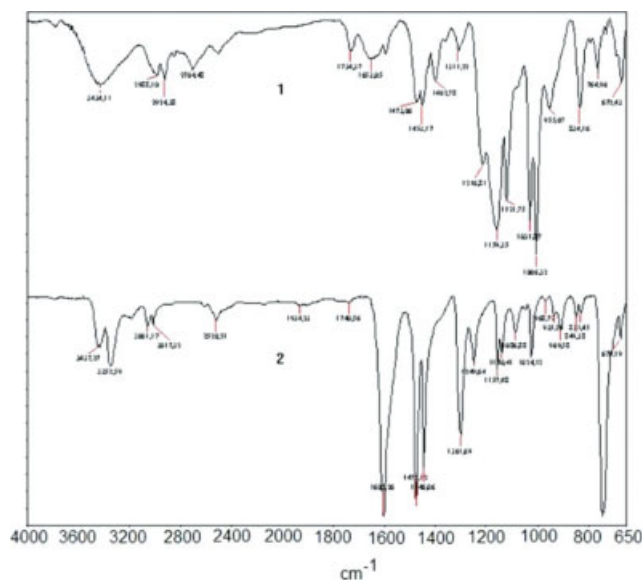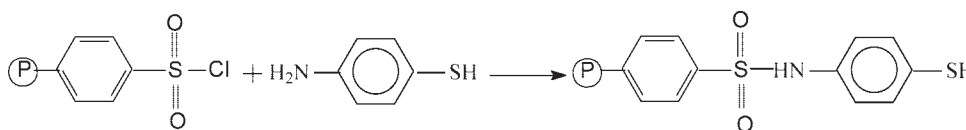

Figure 1 FT-IR Spectra of the resin (1) and thioaniline (2). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scheme 1 Preparation of the resin.

quantity (0.2 g) of the thiol containing resin was added to Hg (II) solution (20 mL, 0.1*M*). The mixture was shaken on a continuous shaker for 24 h and filtered. A sample (1 mL) of the supernatant solution was transferred to a volumetric flask and diluted to 100 mL with water.

The residual mercury concentration of the final solution was assayed by the colorimetric analysis of a 1 mL filtrate, with diphenyl carbazide as the color reagent.[30]

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 I.

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 mol/L initial concentrations for 24 h. Residual metal analyses were performed by complexometric ethylene diamine tetra acetic acid (EDTA) titrations, as described in the literature [31]. The results are shown in Table I.

Kinetics of mercury sorption

To test the efficiency of the sorbent for trace quantities of mercury, batch kinetic experiments were carried out with a much diluted Hg solution ($2 \times 10^{-4}M$).

For this purpose, the polymer resin sample (0.2 g) was wetted with distilled water (1 mL) and added to a solution of Hg (90 mL of $2 \times 10^{-4}M$ of HgCl$_2$ in 100 mL of water), and the mixture was stirred magnetically.

Variation in the mercury concentration was monitored by analysis of samples (5 mL) taken at appropriate time intervals. The data collected are pictured in Figure 1.

Regeneration of the resin

Mercury-loaded sample (0.1 g) was introduced to 10 mL of 4*M* HNO$_3$ at room temperature and the mixture was stirred for 24 h.

The mixture was filtered, and 1 mL of the filtrate was neutralized with NaOH. The neutralized solution was used for colorimetric mercuric analysis. Desorption capacity of the resin was found as 1.30 mmol/g.

RESULTS AND DISCUSSION

Thiol containing sulfonamide based resin have been prepared starting from crosslinked polystyrene resin beads (420–560 μm) according to the reaction pathways in Scheme 1. Crosslinked polystyrene resin was reacted with chlorosulfonic acid. The resin with a 4 mmol/g chlorosulfonation degree (determined by chloride analysis), when reacted with an excess of thioaniline in a NMP solvent, gives rise to the corresponding polymer with thiol sulfon amide functions according to the reaction in Scheme 1.

The total nitrogen content of the product was found as 3.5 mmol/g by Kjeldehal nitrogen analysis.

The resin was also characterized by FT-IR. In the Figure 1(2) N—H stretching vibrations at 3437, 3332 cm^{-1} and SH vibration peak at 851 cm^{-1} were observed for thioaniline. According to the Figure 1(1), a characteristic SH vibration peak at 851 cm^{-1} and S=O stretching vibrations of sulfonamide group were observed at 1379 and 1156 cm^{-1}, respectively, for the resin.

Mercury uptake

The thiol containing resin obtained was an efficient sorbent to remove mercury through the thiol groups.

On the basis of the basic reaction of the mercuric ions with thiol groups, which yielded covalent mercury–sulfur linkages, the mercury binding of the resin can be depicted as shown in Scheme 2.

Sulfur-containing ligands, which are usually considered soft bases, can strongly coordinate soft acids like Hg(II) ions. Additionally, monothio- mercury binding is more favorable than dithio-mercury binding for the resin according to the experimental results.
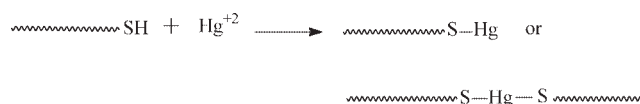
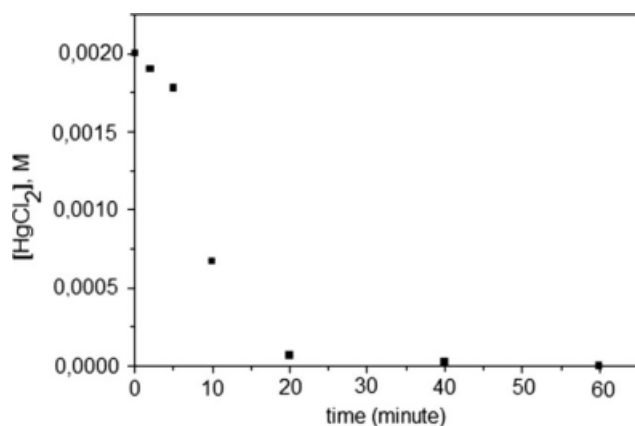**Scheme 2** Mercury binding mechanism.

Figure 2 Sorption time plots of 0.2 g resin sample with 90 mL of 2×10^{-4} M $HgCl_2$ solution at room temperature.

In the mercury uptake experiments, we deliberately used mercuric chloride because the Hg(II) ion has a reasonable affinity to chloride ions.[22]

The loading experiments indicated a mercury capacity of about 1.70 mmol/g in each case, and no significant change in capacity was observed at different initial mercury concentrations (Table I). The pH of $HgCl_2$ solutions remained almost constant, in the 3.1–3.9 range, throughout the extraction process. Buffer solutions in the experiments were not used because their use is not practical in real application conditions.

To inspect mercury efficiency of the resin, metal extraction experiments were repeated with Cd(II), Pb(II), Zn(II), and Fe(III) solutions. Each showed a sorption capacity (1.0–1.63 mmol/g).

Kinetics of the mercury sorption

To investigate the efficiency of the resins in the presence of trace quantities, batch kinetic sorption experiments were performed with highly diluted $HgCl_2$ solutions ($2 \times 10^{-4}M$). The concentration–time plots in Figure 2 shows that within about 60 min of contact time, the Hg(II) concentration falls to zero.

The kinetics of the sorption obey second order kinetics ($k = 177/M$ s with a correlation factor of 0.98) for the resin.

Splitting of the sorbed mercury

To be useful in metal ion recycling processes, metal ions chelated by resins should be easily eluted under appropriate conditions. Since chelating ligands are thiol groups, metal ions can be released by an acid treatment.[11]

In the regeneration of mercury from loaded polymer, $4M$ HNO_3 was used as an appropriate agent.

The mercury-loaded samples were contacted with $4M$ HNO_3 for 24 h at room temperature. The solution was neutralized with NaOH. The desorption capacity of the resin was found as around 1.30 mmol (76%). When the mercury-loading experiment was repeated five times with regenerated polymer, the observed loading capacity was 1.65 mmol for resin.

CONCLUSIONS

The resin produced was highly effective in removing mercury, and its format makes it of interest for technological use as a column-packing material. Under non-buffered conditions, the mercury uptake capacity was around 1.7 mmol/g.

To find any potential difference in the reactivities of the used and original polymer, the chelating polymer was filled in a small column and was loaded with Hg (II) and decomplexed with $4M$ HNO_3 solutions. This procedure was repeated five times, and the Hg (II) binding capacity was determined again. This inspection implies that, after five times of recycling, the mercury uptake capacity of the polymer becomes 1.65 mmol/g, which is the same as that of the original polymer.

To determine the possible interference from foreign ions on the mercury uptake, we first treated the polymeric sorbent with each of metal ions; Fe(III), Cd(II), and Pb(II) separately.

Since the resin has thiol function, it can sorb other metal ions easily.

The recovery of mercury can be achieved by elution with $4M$ HNO_3 at room temperature. The mercury sorption obeys second order kinetics. The sorbent is efficient for trace quantities of mercury, which may be interesting materials for the treatment of drinking and waste waters.

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