

Polymer-Supported Iminodiacetamides for Selective Mercury Extraction

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ABSTRACT: A new polymeric resin with iminodiacetamide functions has been prepared for the selective extraction of mercuric ions. This polystyrene sulfone amide-based resin with a 9.6 mmol g^{-1} amide content is able to selectively sorb mercury over many metal ions, including Cd(II), Zn(II), Fe(III), and Pb(II). Among these, Cd(II) and Zn(II) ions are not sorbed at all, and Fe(III) and Pb(II) ions show only trace absorptions (0.58 and 0.17 mmol/g , respectively) under the same conditions. The selectivity of the resin, its high mer-

cury loading capacity (4.23 mmol g^{-1}), and its ability to regenerate via acetic acid make it a promising material for the large-scale selective separation of mercuric ions from aqueous mixtures. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1316–1321, 2003

Key words: separation techniques; sorbent; metal–polymer complexes; crosslinking

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 superior reactivity of sulfur compounds toward mercuric ions is the key principle behind anchoring thiol^{5,6} and thioether⁷ functions for laboratory or industrial levels of applications. Thiol and thioether functions, however, are known to react also with many other metal ions. Therefore, the mercury–thiol interaction is not specific.

There are many articles describing the use of some other sulfur-containing polymer-supported ligands such as xanthate,⁸ thiourea,⁹ pyridine-based thiols,¹⁰ and dithiozone¹¹ in highly selective mercury removal. These materials do sorb other metal ions such as Cd(II) and Pb(II) in reasonable quantities.

Another important ligating group for selective mercury binding is the amide group, which forms covalent mercury–amide linkages under ordinary conditions. The amide group has less of a tendency to bind with other metal ions under the same conditions because of the weak electron-donating nature of the

amide group. As a result, the amide ligand is unique in its selective mercury uptake.

This phenomenon led us to use polymer-supported amides in selective mercury removal. In conjunction with this, we have been demonstrated in previous studies that crosslinked polyacrylamide¹² and cellulose-g-polyacrylamide¹³ 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, amide 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 in two steps by a reaction with ethylene diamine and 2-chloroacetamide. The mercury uptake ability and regeneration conditions of the resulting resin have been investigated.

The use of a polymer in a spherical bead shape might provide easy filtration of an aqueous solution after the mercury extraction process. The tertiary amine function, however, is expected to shift the reaction in favor of mercury binding by trapping the evolved hydrogen chloride.

EXPERIMENTAL

All the chemicals were analytical-grade commercial products: chlorosulfonic acid (Carlo Erba, Milan, Italy), divinyl benzene (DVB; E. Merck, Hohenbrunn, Germany), styrene (ST; Fluka, Buchs, Switzerland), ethylene diamine (E. Merck), HgCl_2 (E. Merck),

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$\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (E. Merck), $\text{Pb}(\text{NO}_3)_2$ (E. Merck), $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (E. Merck), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (E. Merck), and diphenyl carbazide (E. Merck). They were used as received.

Preparation of the chlorosulfonated ST-DVB beads

The preparation of the crosslinked ST-DVB (10%) beads and their chlorosulfonation were performed according to previously described procedures.¹⁴

Determination of the chlorosulfonation degree

A half-gram of the chlorosulfonated polymer was added to 20 mL of a 5M NaOH solution and refluxed for 2 h. The mixture was filtered and washed with 150 mL of distilled water. The filtrate and washings were transferred to a volumetric flask and diluted to 250 mL. The chloride content of the solution was assayed by the mercuric thiocyanate method.¹⁵ This analysis gave 3.5 mmol of chlorine/g of polymer, which corresponded to 63.2% chlorosulfonation of the phenyl rings of the styrenic units.

Reaction with ethylene diamine

Twenty grams of the chlorosulfonated polymer was added portionwise to a stirred solution of 18 mL (33.5 mmol) of ethylene diamine in 15 mL of 2-methyl pyrrolidinone at 0°C. The mixture was shaken for 3 h at room temperature, poured into 250 mL of water, and filtered. After being washed several times with water, the bead product was dried at 50°C for 8 h *in vacuo*. The yield was 22.0 g.

Determination of the conversion yield

The conversion yield of the aforementioned reaction product was assayed by the determination of the free amino group content of the product. For this purpose, 0.25 g of the reaction product was mixed with 5 mL of a 1M HCl solution. The mixture was stirred for 24 h at room temperature to neutralize the amino groups. The sulfone amide group did not hydrolyze in the acid solution. The mixture was filtered and washed with distilled water. The filtrate and washings were transferred to a volumetric flask and amounted to 100 mL. The residual acid concentration was determined by a titration of a 25-mL aliquot with a 0.1M NaOH solution. Therefore, 10.5 mL of the titer indicated 3.24 mmol of primary amino groups per gram of the polymer.

Reaction with chloroacetamide

Sixteen grams of the aforementioned polymer were added to a solution of 11.7 g (0.125 mol) of chloro-

acetamide in a mixture of 20 mL of triethylamine and 15 mL of 2-methyl pyrrolidinone. The reaction mixture was shaken at room temperature and heated at 60°C for 8 h. The reaction content was poured into 250 mL of distilled water and washed with an excess of water (6×50 mL). The vacuum-dried final product weighed 20.2 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 mL of H_2SO_4 (80.0%) and refluxed for 6 h. After cooling, the mixture was diluted cautiously to 50 mL and filtered. The filtrate was used in the Kjeldahl analysis. The consumption of 50.4 mL of 0.1M HCl for the neutralization of the evolved ammonia indicated 9.6 mmol as the total amide content.

Mercury sorption experiments

The determination of the mercury sorption capacity of the polymer possessing amide functions was performed by the interaction of polymer samples with aqueous HgCl_2 solutions as follows. The resin sample (0.24 g) was wetted with water and left to stand in 5 mL of distilled water for 24 h. To this mixture, 20 mL of a solution of $\text{Hg}(\text{II})$ (0.225 mol L^{-1}) was added (so that the concentration of the solution was 0.18 mol L^{-1}). 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-mL filtrate, with diphenyl carbazide as the color reagent.¹⁶ The final concentration of the residual liquor was 0.12M. From the difference in the concentrations of the initial and final solutions, the sorbed mercury was calculated to be 4.23 mmol g^{-1} for the HgCl_2 solution.

Similar experiments were repeated under the same conditions with different initial mercury concentrations (0.05, 0.1, 0.15, and 0.18M). 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 affinities of the resin toward foreign ions [$\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$, and $\text{Fe}(\text{III})$] were examined by the simple contact of the aqueous solutions of those ions with 0.15 mol L^{-1} initial concentrations for 24 h. Residual metal analyses were performed by complexometric ethylenediaminetetraacetic acid titrations, as described in the literature.¹⁷ The results are shown in Table II.

TABLE I
Mercury Sorption Characteristics of the Resin

Initial Hg(II) concentration (mol/L)	Mass increase (%)	Capacity of the resin (mmol/g)	Recovered Hg(II) ^a (mmol/g)	pH ^b
0.05	84.1	4.10	nd	4.0 (3.6)
0.10	89.8	4.17	nd	3.8 (3.7)
0.15	90.5	4.12	1.70	3.8 (3.7)
0.18	96.1	4.23	1.74	3.9 (3.6)

nd = no data.

^a In first regeneration with hot acetic acid.

^b Final pHs are given in parentheses.

Mercury sorption in the presence of Fe(III) ions

This was performed by the mercury loading experiment being repeated in the presence of Fe(III) ion as follows. Ten milliliters of 0.15 mol L^{-1} HgCl_2 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solutions were mixed and interacted with 0.235 g of the resin sample for 24 h at room temperature. The mixture was filtered, and 1 mL of the filtrate was treated with 5 mL of 0.3 mol L^{-1} KSCN and 5 mL of a dithiazone solution (2 g/50 mL CCl_4). The mixture was shaken vigorously in a separator funnel. For the analysis of the residual iron, 1 mL of the aqueous phase was taken and diluted to 100 mL. The absorption measurements at 460 nm^{15} gave a $1.14 \times 10^{-4} \text{ mol L}^{-1}$ Fe(III) concentration. This corresponds to a 0.137 mol L^{-1} Fe(III) concentration in the starting solution. This result indicates a 0.67 mmol Fe(III) sorption per gram of the polymer.

An analysis of the mercury in the extract phase was performed by the measurement of the absorbance of the mercury–dithiazone complex at 496 nm, as described in the literature.¹⁸ For this purpose, 0.5 mL of the extract phase was taken and diluted to 100 mL with CCl_4 . This analysis gave a $7.87 \times 10^{-2} \text{ mol L}^{-1}$ residual mercury concentration. This corresponded to 4.1 mmol of Hg(II)/g of polymer.

Kinetics of mercury sorption

Batch kinetic experiments were performed with extremely dilute HgCl_2 solutions ($5.39 \times 10^{-4} \text{ mol L}^{-1}$). One gram of the polymer sample was soaked in 10 mL of

distilled water and left to stand overnight for the thorough wetting of the polymer. To the mixture, 100 mL of a solution of HgCl_2 ($5.93 \times 10^{-4} \text{ mol L}^{-1}$) was added with continuous stirring by a magnetic stirring bar (at 300–350 rpm). The sorption kinetics were followed by monitoring of the residual mercury content by an analysis of 5-mL samples taken from the stirred mixture at 10-min time intervals. The mercury contents were assayed by the diphenyl carbazide method as previously described. The collected analytical data were used to produce the concentration–time plot in Figure 1.

Regeneration of the resin and recovery of the mercury

A half-gram of the mercury-loaded sample (a product of entry I) was introduced to 10 mL 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 mL of the filtrate was used for colorimetric mercuric analysis. The analysis gave 3.18 mmol of Hg(II)/g of loaded polymer.

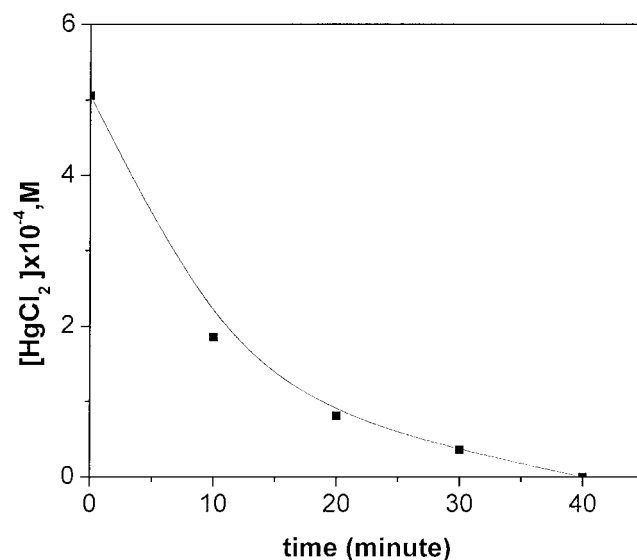
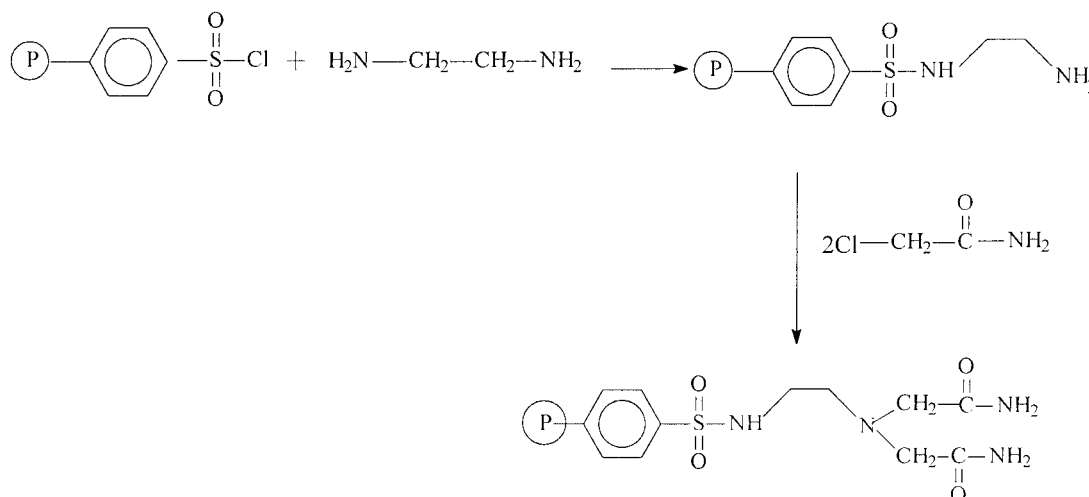


Figure 1 Concentration–time plot of a solution of HgCl_2 (100 mL, initial concentration = $5.05 \times 10^{-4} \text{ M}$) interacting with 1.150 g of a polymer resin.

TABLE II
Sorption of Foreign Ions by the Resin

Metal salt	Foreign ion concentration (mol/L)	Resin capacity for foreign ions (mmol/g)
HgCl_2	0.15	4.12
$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	0.15	0.0
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.15	0.0
$\text{Pb}(\text{NO}_3)_2$	0.15	0.17
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.15	0.68



Scheme 1

RESULTS AND DISCUSSION

Amide functions have been incorporated into crosslinked polystyrene resin beads (420–560 μm) according to the reaction pathways in Scheme 1 for the preparation of a mercury-selective polymer.

The polymer with a 3.5 mmol g^{-1} chlorosulfonation degree (determined by chloride analysis), when reacted with an excess of ethylene diamine in a DMF solvent, gives rise to the corresponding polymer with 2-aminoethyl sulfone amide functions. An analysis of the primary amine content by acid titration (3.24 mmol g^{-1}) implies quantitative conversion in this step. Obviously, there must be an excess of the ethylene diamine reagent because of the quantitative conversion. In other words, the side reaction yielding ethylene disulfone amide has been suppressed by excess ethylene diamine. In the last step, a reaction with a twofold excess of chloroacetamide at room temperature affords the final product with two carbon amide and one sulfone amide groups. The Kjeldahl nitrogen analysis of the product (9.6 mmol g^{-1}) reveals the full conversion of the primary amine groups.

The quantitative conversions in these reactions seem unlikely. However, they are not unexpected because the reaction of the crosslinked beads with external reagents takes place at the accessible sites of the polymer matrix. Therefore, except in the first step, successive modification steps must proceed with quantitative conversions because all the reacting groups remain accessible in the following steps.

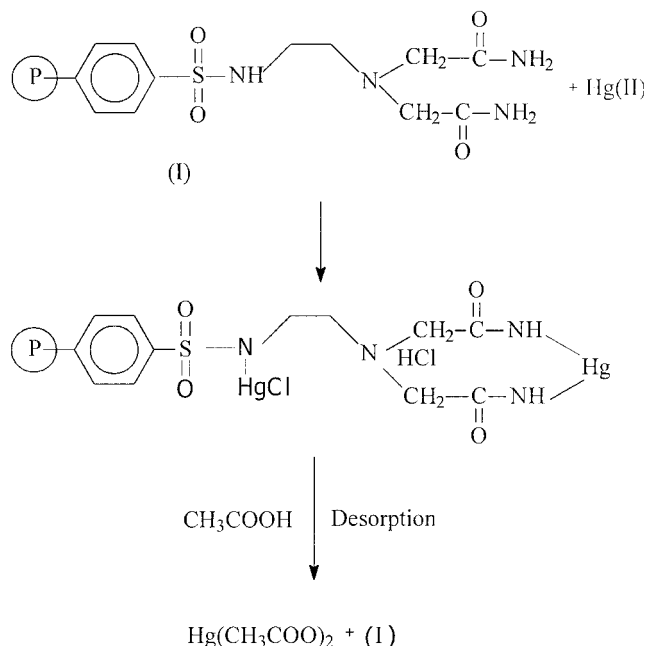
Mercury uptake

There exist three possible reaction sites, one sulfone amide group and two carbon amide groups, available for mercury binding.

Nitrogen analysis by the Kjeldahl method gives 9.6 mmol of nitrogen/g of polymer. This amount is slightly higher than the expected value, 9.50, calculated under the assumption of quantitative conversions in the second and third modification steps. The difference might be due to minor quaternization of the secondary amine function.

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,¹⁹ mercury uptake is somewhat higher when mercuric acetate is used. For this reason, in this study HgCl_2 was employed to determine the efficiency of the polymer sorbent under extreme conditions.

Regarding the structure of the resulting resin, there are three amide groups available for mercury binding. If mercury binding takes place and gives monoamido mercury group formation, the capacity of the resin will be $9.5 \times 0.75 = 7.12$ mmol/g . However, the loading experiments indicate a mercury capacity of about 4.1 mmol g^{-1} in each case, and no significant capacity change is observed at different mercury concentrations. This result reveals that mercury binding proceeds mostly via diamido mercury formation. This might be due to the vicinity of the amide functions, which make it easy to form diamido mercury moieties in the sorption. The tertiary amine function may also bring an additional contribution to the diamido mercury formation by trapping evolved hydrogen chloride. The pHs of HgCl_2 solutions remain almost constant in the 3.7–3.9 range throughout the extraction process. The mass percentage increases around 90% (Table I) confirm this proposal. Indeed, 4.23 mmol g^{-1} of mercury accounts for 0.85 g of elemental mercury/g of polymer. In the experiments, we did not use buffer



Scheme 2

solutions because the use of buffer solutions is not practical under real application conditions.

On the basis of these results, the mercury sorption process can be depicted simply, as shown in Scheme 2. The sulfone amide nitrogen must also be involved in the mercury uptake, although it is less nucleophilic than carbon amide groups. The theoretical capacity in that case should be half of the total nitrogen, that is, $9.5/2 = 4.75 \text{ mmol g}^{-1}$. The practical capacity, 4.23 mmol g^{-1} , is about 89% of the theoretical capacity for only diamido formation. This is due to the gradually increasing hydrophobicity of the resin as mercury binding continues.

Regeneration of the resin and recovery of the mercury

In the recovery of mercury from loaded polymer, hot acetic acid was chosen as an appropriate reagent. Mineral acids can be considered as re-extracting agents. However, strong acids would inevitably cause the hydrolysis of the amide linkages. For this reason, mineral acids are not suitable for the elution of mercury. Although acetic acid is less effective and slow in leaching, it does not cause any hydrolysis. Another advantage of acetic acid over mineral acids is its recyclability by repeated evaporation–condensation processes with a continuous extracting apparatus such as a Soxhlet extractor. Moreover, acetic acid is environmentally safe. When loaded samples are heated in glacial acetic acid at 80°C for 1 h, the amount of recovered mercury is around 1.74 mmol/g (Table I). If we assume all the mercury sorbed is in the diamido mercury form, this

amount will correspond to 3.18 mmol g^{-1} , which is about 75% of the capacity of fresh polymer. However, repeated regeneration gives almost a quantitative recovery of the mercury. The mercury-free polymer obtained in this way can be used in the next cycle. Although we have not studied the efficiency of the regenerated polymer, according to our previous experiences (with polyamide mercury extractions),¹² the polymer samples can be recycled and are reusable without a loss of activity.

Selectivity of the mercury uptake

For testing the selectivity of the polymer resin in mercury sorption, the experiments were repeated with some foreign metal ions commonly present in mercury minerals. The sorption tests with $\text{Pb}(\text{NO}_3)_2$, ZnCl_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{Cd}(\text{NO}_3)_2$ solutions (at 0.15 mol L^{-1} concentrations) indicate only small amounts of sorption for Fe(III) and Pb(II) ions (Table II).

No traces of Zn(II) and Cd(II) sorptions were detected. The 0.68-mmol Fe(III) and 0.17-mmol Pb(II) sorptions might be due to the precipitation of the metal hydroxides or double salt formation rather than true coordination. Obviously, the tertiary amino group is responsible for generating hydroxide ions. Indeed, when the loading experiment was repeated with mixed solutions of Hg(II) (0.15 mol L^{-1}) and Fe(III) (0.15 mol L^{-1}), although the mercury loading capacity remained constant, the ferric ion capacity was reduced to 0.58 mmol g^{-1} because the HgCl_2 solution was acidic (pH 3.7).

Kinetics of the mercury sorption

To examine the efficiency of the polymer for trace quantities, we performed kinetic experiments with extremely diluted HgCl_2 solutions (100 ppm mercury). The concentration–time plot in Figure 1 shows that within about 40 min of contact time, the Hg(II) concentration falls to zero.

Interestingly, the kinetics of the sorption obey first-order kinetics rather than second-order kinetics, and this reveals that the process is diffusion-controlled. The rate constant k is equal to $1.47 \times 10^{-3} \text{ s}^{-1}$ (correlation factor = 0.998). Although the kinetics of the mercury uptake are also a function of the stirring rate, this value obtained at moderate stirring rates (350–400 rpm) must indicate at least the order of the rate constant.

Diffusion onto the polymer surface determines the reaction rate. Of course, the diffusion of mercury through the polymer matrix is almost impossible because of the great hydrophobicity of the polymer, and the reaction takes place mainly on the outer surfaces of the bead particles. At slow stirring rates, the amount

of sorbed mercury is substantially lower than that observed at high stirring rates.

CONCLUSIONS

The studied resin, having carbon amide and sulfone amide groups, shows a reasonable mercury selectivity over Zn(II), Cd(II), Pb(II), and Fe(III) ions. Under non-buffered conditions, the mercury uptake capacity is around 4.1 mmol g^{-1} when Hg(II) concentrations are within the $0.05\text{--}0.18 \text{ mol L}^{-1}$ range. The recovery of mercury can be achieved by elution with acetic acid at 80°C without hydrolysis of the amide groups. The mercury sorption obeys first-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.

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