

Selective mercury uptake by polymer supported hydroxyethyl sulfonamides

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Available online 23 December 2007

Abstract

Hydroxyethyl sulfonamide function supported on styrene-divinyl benzene (9% mol/mol) bead resin is presented as mercury selective reagent. The resin product with 3.49 mmol g⁻¹ of 2-hydroxyethyl sulfonamide content removes reasonable quantities of mercuric ions (0.83–1.64 mmol g⁻¹) from aqueous solutions of HgCl₂, Hg (CH₃COO)₂ and Hg (NO₃)₂, in non-buffered conditions. Experiments showed that, the resin is able to extract mercury selectively, in the presence of foreign ions such as Zn(II), Cd(II), Fe(III), and Pb(II). Only negligible amount of sorption was detected for the case of Fe(III) (0.31 mmol g⁻¹).

The loaded resin can be regenerated by HCl solution (2 M) and mercuric ions can be recovered (99% in the first contact) without any hydrolysis. Having advantage of hydrolytic stability of the sulfonamide linkage, the resin presented shows no loss in the capacity after 20 sorption–desorption cycle.

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Keywords: Functional resin; Selective extraction; Selective mercury removal; Traces mercury

1. Introduction

Mercuric ions react with amides to form mono- or diamido-mercury compounds in ordinary conditions. The reaction takes place even in aqueous solutions at room temperature and mercury-amide bond is known to be mostly covalent. Chemistry of mercury-amide reaction is well known for more than a century [1]. This chemistry furnishes a method of selective mercury sorption, as described in our previous papers [2–4].

Although polymer supported thiols [5], thioethers [6] and thioamides [7] have been described as mercury selective sorbents, selectivity of those ligating groups are limited and appreciable quantities of foreign ions such as Pb(II), Zn(II), Cd(II) are also absorbed at the same time [8]. Recently a mercury selective resin with amine and thiol groups has been reported [9]. Whereas reaction of amides with mercuric ions is very selective, because the amide nitrogen is in lack of electron donating character and less prone to form coordinative bond with other transition metal ions. Although Cu(II) ion has been reported to give complexes by coordinating through amide nitrogen, such reactions generally take place in drastic conditions [10].

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This makes amide group unique in selective mercury binding. Based on this chemistry we have demonstrated that, nonfunctional crosslinked polyacrylamide is a powerful and selective sorbent for removal of mercuric ions from aqueous solutions [11]. This study revealed that hydrophilicity is crucial for efficient mercury binding. Amido-mercury compounds are hydrophobic in nature. For this reason during mercury sorption by crosslinked polyacrylamide hydrophobicity increases as the mercury binding proceeds and hydrophilic–lyophilic balance is reached when about 60% of the amide groups are utilized. Beyond this point the hydrophobicity does not allow binding of additional mercury and 40% of amide groups remain unreacted. For the same reason water insoluble polyamides such as natural wool and Nylon-6 show only negligible mercury sorptions (0.24 and 0.09 mmol g⁻¹, respectively) [12].

Continuing hydrophilicity seems to be essential to enhance percentage of mercury binding per amide group. Indeed crosslinked poly (4-vinyl pyridine) quaternized with chloroacetamide is excellent sorbent for mercury uptake and almost 100% of the amide groups are involved in mercury binding due to continuing hydrophilicity provided by the pyridinium groups, as reported before [13].

Those previous studies revealed that, water soluble polymers and their crosslinked analogues with carbonamide functions are efficient materials for removal of mercuric ions selectively from aqueous mixtures. Only drawback of these materials is low hydrolytic stability of the carbonamide functions involved. In order to avoid the hydrolysis, hot acetic acid has been used as proper reagent for desorption of the mercury from loaded polymer samples in recycling process. However hot acetic acid shows limited success and 65–75% of mercury can be recovered in the first contact. A complete stripping of the mercury can be achieved only by repeating the acid-leaching process for 3–4 times.

Sulfonamides, on the other hand are much more stable against acid–base hydrolyses and they show similar reactivity towards mercuric ions [14]. However sulfonamides, especially aromatic sulfonamides are highly hydrophobic which is not desirable for mercury sorption from aqueous solutions.

This study is targeted to prepare a polymer sorbent which can be regenerated by mineral acids by taking advantage of hydrolytic stability of the sulfonamide groups. For this purpose, in this study we have prepared polystyrene based resin having

2-hydroxyethyl sulfonamide functions. The hydroxyl group has been considered as hydrophilic group which is essential for mercury uptake from aqueous solutions. The structure and binding characteristics of the new polymer sorbent have been investigated to demonstrate the affinity and selectivity for mercury in the absence and presence of some foreign ions and regeneration of the sorbent with HCl solution has been studied using conventional analytical procedures.

2. Experimental

2.1. Materials

Styrene (E. Merck) and ethanolamine (E. Merck) were distilled before use. All the other chemicals were analytical grade commercial products; Divinyl benzene (Aldrich), Chlorosulfonic acid (Aldrich), HgCl₂ (E. Merck), Hg (NO₃)₂ (E. Merck), Mercuric(II) acetate, (E. Merck), *N,N*-diphenyl carbazide (Across Chemicals). They were used as purchased, unless otherwise stated.

2.2. Preparation of crosslinked poly (styrene-co-divinyl benzene) bead resin

Poly (styrene-co-divinyl benzene) (*poly(ST-DVB)*) was prepared by suspension copolymerization of styrene with divinyl benzene (DVB) in aqueous suspension according to a common procedure as described before [15]. Thus, 57.2 mL (0.5 mol) styrene, 7.0 mL (0.05 mol) DVB and 65 mL toluene (as porogen) were mixed and 1.8 g (7.5 × 10⁻³ mol) dibenzoyl peroxide was dissolved in this mixture, under nitrogen atmosphere.

A three necked 1 L flask with a nitrogen inlet, a dropping funnel and a reflux condenser was used as a reactor. First, 1.2 g. of Gum Arabic (suspension stabilizer), 2 g Na₂SO₄ and 400 mL of distilled water were added in the reactor and it was placed in a thermostated-oil bath. The aqueous mixture was stirred until clear solution was obtained. The mixture was heated to 85 °C and kept at this temperature. Nitrogen was flushed through the solution. The above organic mixture was added drop wise by means of the dropping funnel, under nitrogen stream. The mixture was stirred by magnetic bar for 8 h at constant temperature.

Then the reaction content was poured into 1 L of water and beaded product was collected by filtration. It was washed with excess of water and dried

at 70 °C for 24 h. The yield of pearl-like bead product was 54.6 g. The macro-porous product was fractionated by sieving and 210–560 μm size (71.3%) of fraction was used in the next step.

2.3. Chlorosulfonation of ST-DVB bead resin

Under fume cupboard, 150 mL CH_2Cl_2 is placed in a 1 L volume of flat bottom flask. 50 mL of chlorosulfonic acid was cautiously added to the flask while stirring. A calcium chloride guard tube was attached to the flask and left to stand overnight, at room temperature. The reaction content was filtered through a ground glass filter and washed with 70 mL CH_2Cl_2 . The brownish solid product was added portion wise to 1.5 L of ice–water under vigorous stirring. The mixture was filtered as quickly as possible. The product was washed with acetone (2×100 mL) and diethyl ether (75 mL). Then it was dried at room temperature under vacuum for 48 h.

2.4. Determination of the chlorosulfone content

This was carried out indirectly by analysis of the chloride ion content of the chlorosulfonated product. Thus, 0.75 g of the above product was mixed with 20 mL 10% NaOH solution and the mixture was refluxed for 150 min for hydrolysis of the chlorosulfone group, while stirring. The mixture was cooled, filtered and washed with distilled water. The filtrates and washings were combined and made up 50 mL in a volumetric flask. Thirty milliliters of this solution was neutralized with 1.5 mL of HNO_3 solution (65%). To this solution 40 mL of 0.1 M AgNO_3 solution was added and stirred for 5 min. White precipitate of AgCl was filtered, washed with water (3×10 mL), dried at 45 °C for 3 h and weighed (0.26 g). This amount corresponds to 4.03 mmol of chlorosulfone group per gram of the polymer.

2.5. Sulfamidation with ethanolamine

To a solution of 55 mL ethanolamine in 160 mL dimethyl formamide, there was added 60 g of the chlorosulfonated product. The mixture was shaken for 18 at room temperature on a shaker. The reaction content was filtered, washed with excess of water (3×250 mL), acetone (100 mL) and diethyl ether (50 mL). The sulfamidation product, after vacuum drying at 45 °C for 24 h weighed 66.0 g.

2.6. Determination of the sulfonamide content

This was assayed based on salt forming ability of the sulfonamide group with NaOH or KOH. For this purpose 1 g of the sulfonamidated polymer sample was introduced to 10 mL of methanolic KOH solution (10%). The mixture was shaken for overnight at room temperature and filtered. The residual KOH content of the methanol solution was determined by titration of 2 mL of the filtrate with 0.10246 M HCl solution in the presence of phenolphthalein as color indicator. 26.0 mL of the titer consumption, when compared to that of the mother methanolic KOH solution (32.8 mL per 2 mL) corresponds to a 3.49 mmol g^{-1} of sulfonamide content.

2.7. Swelling in water

In order to test hydrophilicity of hydroxyethyl-sulfonamide resin, a sample (0.2 g) was placed in a sintered glass funnel and soaked into distilled water. The sample was removed and outer surface of the sample was dried superficially by a soft paper. Final weight (0.444 g) of the swollen sample indicated an equilibrium swelling ratio of 222.0%.

2.8. Mercury loading tests

Mercury loading experiments were carried out using non-buffered solutions, in order to avoid interferences of the buffer components. Instead pH variations of the solutions were monitored to follow released protons while mercury binding.

The polymer sample (1 g) was soaked into 100 mL of Hg(II) solution (0.06 M). The resulting mixture was shaken for 16 h at room temperature and filtered. Final mercury concentration of the filtrate was determined by Atomic Absorption (AA) method after appropriate dilution of the analysis samples. Mercury sorption capacity of the polymer was assigned from the difference of initial and final mercury contents.

In order to inspect effect of counter ions, this experiment was repeated for aqueous solutions (100 mL) of $\text{Hg}(\text{CH}_3\text{COO})_2$, HgCl_2 and $\text{Hg}(\text{NO}_3)_2$ salts (0.06 M of each). The relevant data were listed in Table 1.

2.9. Effect of the concentration

Effect of the initial Hg(II) concentration on mercury uptake was studied by capacity measurements

Table 1

Mercury uptake and desorption characteristics of the hydroxyethyl sulfonamide resin

Mercuric salt	Initial conc. (M)	Loaded mercury (mmol g ⁻¹)	Recovered ^a mercury (mmol g ⁻¹)
Hg(CH ₃ COO) ₂	0.06	1.64	1.14
Hg(NO ₃) ₂	0.06	1.46	1.15
HgCl ₂	0.06	0.83	0.69

^a Per gram of loaded sample.

using Hg(NO₃)₂ solutions in various concentrations (0.01–0.06 M). This was carried out by interaction of 0.2 g of the polymer samples with 30 mL of Hg(NO₃)₂ solutions. The capacities were found based on analyses of the final solutions, as described above.

2.10. Effect of NaCl

Since Hg(II) has a great affinity towards chloride ions there is a competition between the sorbent and chloride ions in mercury in presence of NaCl. Accordingly mercury loading capacity of the sorbent must depend on the chloride ion concentration. To investigate effect of chloride ion concentration the mercury loading tests were carried out in presence of NaCl.

For this purpose a series of mixed HgCl₂–NaCl solutions were prepared in which concentration of HgCl₂ was kept constant (0.06 M) and NaCl concentration varied in 0.01–0.30 M range. The capacities and simultaneous pH changes were determined.

2.11. Effect of foreign ions

In order to investigate selectivity of the mercury sorption loading experiments were performed in presence of some foreign ions such as Pb(II), Zn(II), Cd(II) and Fe(III) which might present in mercury ores. For this purpose the polymer samples (1 g) were interacted with binary solutions (100 mL) of Hg(NO₃)₂ with Pb(NO₃)₂, Zn(NO₃)₂, Hg(NO₃)₂, Fe(NO₃)₃ (in 0.07–0.075 M range) for 24 h. Final concentrations of Hg(II) and foreign ions were determined by AA. The data collected were listed in Table 2.

2.12. Kinetics of mercury sorption

Kinetic experiments were performed by batch method using dilute Hg(CH₃COO)₂ solutions (80 ppm). For this purpose 1 g of the polymer sample was wetted with 20 mL water and left to stand

for 2 h. To this mixture 80 mL of 3.86×10^{-4} M Hg(CH₃COO)₂ solution was added under continuous stirring (350 rpm). The sorption kinetics was followed by monitoring residual mercury contents of the aliquots (5 mL) taken at appropriate time intervals (1–10 min). Variation of the mercury concentration with time was pictured in Fig. 2.

2.13. Recovery of mercury from loaded polymer sample

Mercury loaded samples were subjected to acid leaching to regenerate the polymer. Thus, 0.5 g of mercury loaded sample was placed in 25 mL of 2 M HCl solution and the mixture was shaken by continuous shaker, for 2 h at room temperature and filtered. Amounts of the mercury released were assigned by analysis of the filtrate. The relevant data were collected in Table 1.

3. Results and discussion

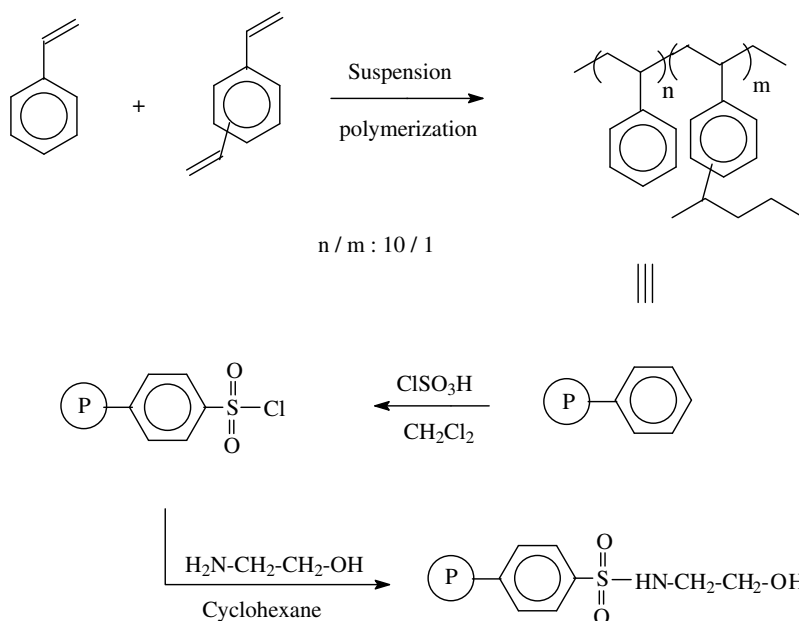
Sulfonamide group is a mercury selective ligand which binds Hg(II) with covalent linkage, as in the case for carbonamide groups. Advantage of the former is its reasonable hydrolytic stability against acid hydrolysis.

Since hydrophobicity of the ligating group is another limiting factor in mercury uptake, 2-hydroxyethyl sulfonamide functions were incorporated into crosslinked ST-DVB resin beads in two steps as depicted in Scheme 1. The hydroxyethyl function was chosen to impart hydrophilicity to the polymer structure.

Crosslinked ST-DVB resin was prepared in bead form by suspension copolymerization of styrene with DVB (9% mol/mol) and 210–560 μm size of fraction was chlorosulfonated by reaction with chlorosulfonic acid in CH₂Cl₂. Chlorine analysis (gravimetric method) of the resulting product gives 4.03 mmol chlorosulfone groups per gram, implying that 78.2% of the styrene units have been chlorosulfonated.

Table 2
Effect of the concentration on the capacity

Initial Hg (NO ₃) ₂ conc. (M)	Final mercury conc. (M)	Mercury uptake (mmol g ⁻¹)
0.01	3.34×10^{-4}	1.45
0.02	1.04×10^{-2}	1.44
0.04	3.04×10^{-2}	1.44
0.05	4.03×10^{-2}	1.46
0.06	5.05×10^{-2}	1.42



Scheme 1. Incorporation of hydroxyethyl sulfonamide function into poly (ST-DVB) resin beads.

The reaction with 2-hydroxyethylamine in the second step yields sulfonamide resin with 3.49 mmol 2-hydroxyethylsulfonamide function per gram. By assuming non-reacted chlorosulfonyl groups turned to be sulfonic acid (in final washing with water), this corresponds to 94.3% of conversion yield. In another words 73.7% of styrene units carry 2-hydroxyethylsulfonamide functions.

4. Mercury uptake

Mercury loading capacity of the hydroxyethyl sulfonamide resin depends on the counter anion accompanying the mercuric ions (Table 1). The highest capacity is observed in case of mercuric acetate (1.64 mmol g⁻¹). However this amount is far below the sulfonamide content (3.49 mmol g⁻¹). One possibility is binding of the mercury by forming diamido-mercury structures. In this case two amide groups are utilized to hold one mercuric ion.

However this possibility is unlikely, because the sulfonamide groups are almost at fixed positions in the crosslinked polymer matrix and too far from each other to come close to form diamido-mercury structures. Indeed FT-IR spectra (Fig. 1) contradict this assumption. Thus, IR spectrum of the polymer (Fig. 1a) shows two characteristic bands associated with N–H and O–H stretching vibrations at 3485 and 3250 cm⁻¹, respectively. After the mercury sorption (from mercuric acetate solution) intensity of the N–H stretching vibration band (Fig. 1b) decreases greatly, while O–H group is retaining almost unchanged. This implies that mercury binding occurs at the nitrogen atom of the sulfonamide group by simultaneous de-protonation as depicted in Scheme 2. Whereas no significant change is observed in intensity of the N–H plane bending vibration band at 1640 cm⁻¹, since this band is obscured by vibration band of carbonyl group of the acetate anion accompanying.

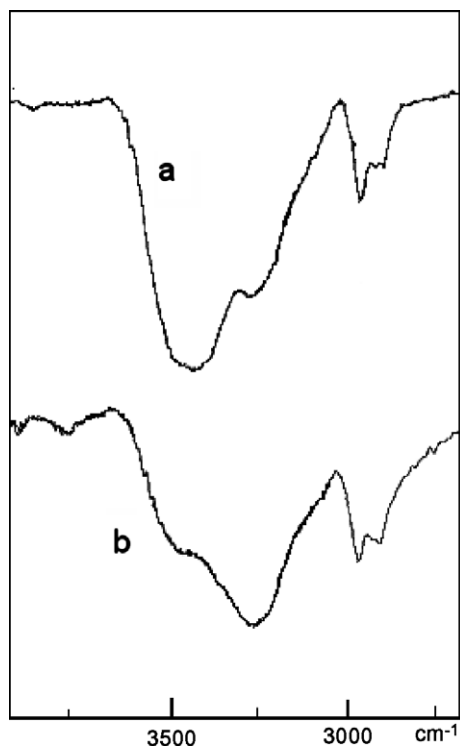
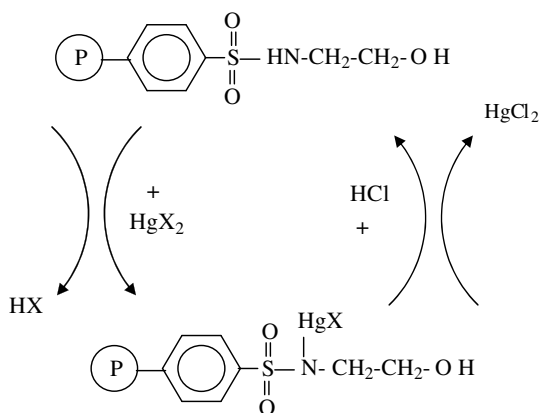


Fig. 1. FT-IR spectra of the mercury-free (a) and acetoxymercurated (b) 2-hydroxy-ethylsulfonamide polymer.

As a result, some portion of the sulfonamides remains untouched and mercury binding must occur mostly by forming mono-amido-mercury structures.

Based on this consideration it can be concluded that, ratio of the mercury binding capacity to the sulfonamide content is



$\text{X} : \text{Cl}^-, \text{NO}_3^-, \text{CH}_3\text{COO}^-$

Scheme 2. Sorption and desorption of mercuric ions from the resin.

$$1.64/3.49 = 0.47$$

In other words 47.0% of the sulfonamide groups take part in mercury binding and rest (53.0%) of this remains unreacted. This ratio is around 0.6 for the case of the polyacrylamide resins studied in our previous work (11). This is largely due to limited hydrophilicity induced by the hydroxethyl groups, in addition to hydrophobic nature of the sulfonamide group. Indeed, the equilibrium swelling ratio of the resin in water is modest (222% w/w₀) which reveals low hydrophilicity of the resin.

The capacity of the absorbent does not vary appreciably while in contact with $\text{Hg}(\text{NO}_3)_2$ or $\text{Hg}(\text{CH}_3\text{COO})_2$ solutions (Table 1). However, mercury sorption greatly reduces (down to 0.83 mmol g^{-1}) for the case of HgCl_2 . High mercury uptake from $\text{Hg}(\text{CH}_3\text{COO})_2$ solutions is due to weakness of acetic acid formed during the mercury binding (Scheme 2). Large difference in extractabilities from $\text{Hg}(\text{NO}_3)_2$ and HgCl_2 solutions is because of the high affinity of Hg to chloride anions.

Moreover the mercury loading capacity does not depend on the initial mercury concentration. Indeed, extracted quantities of $\text{Hg}(\text{II})$ from $\text{Hg}(\text{NO}_3)_2$ solutions (0.01–0.06 M) did not change practically and remained in $1.42\text{--}1.46 \text{ mmol g}^{-1}$ (Table 2). In another words, capacity of the resin is almost independent of the initial $\text{Hg}(\text{II})$ concentrations.

5. Effect of chloride ions

Presence of chloride ions is expected to affect mercury sorption process. Lower sorption capacity for HgCl_2 is because of its chloride anion. High affinity of mercury against chloride is well known in chemistry and this affinity furnishes an analytical method for determination of chloride ions [16]. Indeed mercury ties up chlorides tightly from aqueous solution of inorganic mixtures.

Due to this fact extractability of mercury in presence of NaCl seems to be important criteria to show efficiency of the polymeric sorbent in extracting from sea water.

To examine effect of chloride anion, mercury loading tests were repeated in various NaCl concentrations. The Fig. 2 shows that, there is a marked decrease in mercury uptake while the salt concentration rises. In 0.3 M NaCl extracted mercury is only 0.08 mmol g^{-1} , which is almost one tenth of the initial value. This reveals that, there is competition

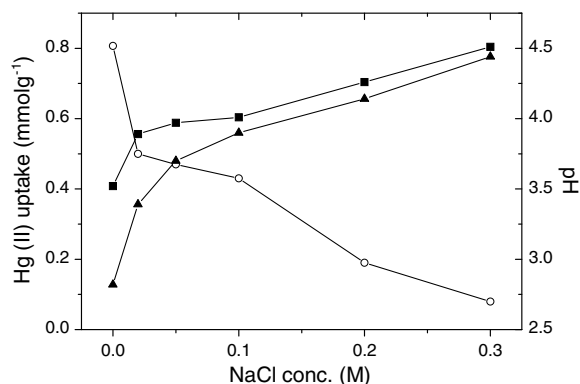
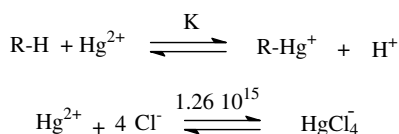


Fig. 2. Effect of NaCl concentration on the mercury uptake (○) and pH of the solutions at the beginning (■) and at the end (▲) of equilibrium sorption.



Scheme 3. Equilibrium of mercury sorption and complex formation with chloride ions.

between the sorbent and chloride ions in mercury binding.

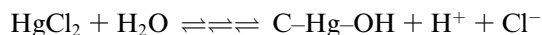
Chloride ions are known to form stable anionic complexes of mercury such as HgCl_3^- and HgCl_4^{2-} . Formation constants of these complexes are 1.6×10^{14} and 1.26×10^{15} , respectively [17]. Although our experiments were not conducted at constant ionic strengths, mercury binding constant of the sulfonamide resin can be estimated roughly based on this information. The competition between chloride ions and the resin in mercury binding can be depicted simply by the following equilibriums (Scheme 3).

Where, R–H denotes the resin. Activity constants of the R–H and R– Hg^+ components in solid phase can be taken unity. Using the results obtained for 0.3 M NaCl concentration ($[\text{HgCl}_4^-] = 0.0584 \text{ M}$, $\text{pH} = 4.2$, unbound $[\text{Cl}^-] = 0.0664 \text{ M}$), approximate

value of mercury binding constant of the resin was found to be $K = 1.3 \times 10^7$.

Nevertheless there is still a considerable mercury sorption (0.43 mmol g^{-1}) in 0.1 M NaCl, which is average salt concentration of the sea water. This means that the polymeric sorbent is expected to work fairly well for extraction of mercury from sea water.

The solution becomes more acidic during the mercury sorption (Fig. 2b, c) from NaCl solutions. This implies that, mercury binding occurs by simultaneous de-protonation of the sorbent, as depicted in Scheme 2. And mercury binding can take place in acidic region, at the pH's as low as 2.82. It is interesting to note that as the salt concentration increases the difference between initial and final pH levels come closer in accordance with decreasing mercury uptake. Apparently one important effect of the chloride ion is to suppress dissociation of HgCl_2 according to the following equilibrium



This is common almost for all the transition metal salts, so that their hydroxides tend to precipitate even in 5–7 pH ranges. This consideration is being established by the fact that, in the absence of the sorbent, as the salt concentration is increased the solution becomes less acidic and the initial pH values increase accordingly.

6. Effect of foreign metal ions

In order to probe the degree of selectivity of the Hg(II) uptake, the sorption experiments were carried out in presences of potentially contaminating foreign metal ions, such as Zn(II) , Cd(II) , Pb(II) and Fe(III) . In these experiments binary solutions of Hg(II) with the foreign metal ions were used and extractability of the mercury and accompanying metal ions were investigated. Table 3 shows that, presences of the foreign ions do not affect on mercury sorption and absorbed quantities of Hg(II) retain almost the same ($1.36\text{--}1.46 \text{ mmol g}^{-1}$).

Table 3
Effect of some foreign ions on mercury sorption capacity

Mixture	Foreign Ion conc. (M)	Hg(II) conc. (M)	Foreign ion sorbed (mmol g^{-1})	Mercury capacity (mmol g^{-1})
$\text{Hg}(\text{NO}_3)_2\text{--Pb}(\text{NO}_3)_2$	0.075	0.06	0.02	1.37
$\text{Hg}(\text{NO}_3)_2\text{--Zn}(\text{NO}_3)_2$	0.070	0.06	0.01	1.41
$\text{Hg}(\text{NO}_3)_2\text{--Cd}(\text{NO}_3)_2$	0.074	0.06	0.03	1.46
$\text{Hg}(\text{NO}_3)_2\text{--Fe}_2(\text{NO}_3)_3$	0.068	0.06	0.31	1.36

Among the foreign ions studied only ferric ion is absorbed simultaneously (0.31 mmol g^{-1}), while mercury capacity does not change practically. No significant sorption was detected for the other metal ions. These results indicate that mercury sorption is highly selective, at least in the presence of the foreign ions studied.

7. Kinetics of mercury uptake

To investigate efficiency of the polymeric sorbent, batch kinetic experiments were performed using highly dilute (80.24 ppm) Hg(II) solutions. A rapid decrease in Hg(II) concentration of the solution indicates fast mercury binding (Fig. 3). Linearity of $1/\text{conc.}$ -versus time plots indicated a second order kinetics with respect to Hg(II) concentration ($k = 14.2 \text{ M}^{-1} \text{ s}^{-1}$ with a correlation factor of 0.994). Overall process must be diffusion controlled. Almost 2/3 of the initial mercury content are removed in the first five minutes of contact time.

Fig. 3 shows that the mercury concentration falls down to zero levels in 30 min of contact time. The overall result shows that, the polymer supported 2-hydroxyethyl sulfonamide groups can be used successfully in removal of trace mercury.

8. Regeneration of the polymer sorbent

Mercury loaded polymer samples can be made mercury-free by treating with hydrochloric acid solutions (2 M). In this process the mercuric ions are eluted from the polymer and transferred to the acid solution. Overall result of the process is regen-

eration of the polymer sorbent and recovery of the mercury.

One gram of mercurated polymer, when soaked into 50 mL of 2 M HCl solution for 3 h, releases 1.14 mmol mercury. The data appears to be much less than the initially loaded quantity (1.64 mmol g^{-1}). However recovered mercury is based on per gram of loaded sample, but not based on mercury-free polymer.

If all the mercury is linked by mono-amido-mercury acetate form, mass increase per mole of $-\text{HgOOCH}_3$ fragment will be 259.6 g . Since the linking process occurs by replacing with one amide proton, true mass increase would be 258.6 g .

Mass increase by mercury sorption must be

$$1.64 \text{ mmol g}^{-1} \times 258.6 \text{ g mol}^{-1} \\ = 424.1 \text{ mg per gram of the resin.}$$

Then, upon loading weight of one g of the initial polymer would become; $1 + 0.4241 = 1.4241 \text{ g}$. This amount is $1.64/1.4241 \text{ g} = 1.1516 \text{ mmol g}^{-1}$ of the loaded polymer. Accordingly, percentage of mercury recovery would be $(1.14/1.1516) \times 100 = 99.0\%$.

This implies that, the mercury uptake occurs mostly by forming mono-amido-mercury structures and about 99% of the mercury can be recovered by leaching with 2 M HCl solution. Second acid treatment to remove rest of the mercury on the polymer, however gave no detectable mercury in the aqueous solution, probably because of its very low concentration.

Apparently such a high recovery of the sorbed mercury is not only due to acid strength of HCl but also due to the chloride anion accompanied.

Advantage of this polymer is supposed to be hydrolytic stability of the sulfonamide linkages involved. Such stability makes the polymer sorbent reusable soon after the acid treatment.

The regenerated polymer sorbent can be recycled many times without losing the mercury uptake capacity, which is sought for industrial level of separations. Simple washing with water is enough to remove acid residues and the material becomes ready for the next use.

To inspect stability and regenerability of the polymer sorbent, the mercury loading and stripping experiments were repeated 20 times and the capacity was checked in each five cycle. The results showed that, the capacity lies in $1.44\text{--}1.46 \text{ mmol g}^{-1}$ range (from $\text{Hg}(\text{NO}_3)_2$ solutions). That means the capac-

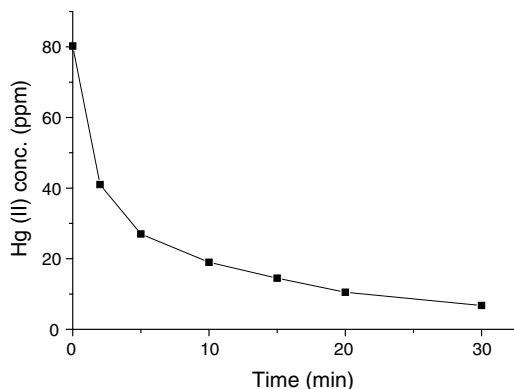


Fig. 3. Concentration-time plot of dilute ($4 \times 10^{-4} \text{ M}$) $\text{Hg}(\text{CH}_3\text{COO})_2$ solution (100 mL) while contacting with 1 g of the polymer sample.

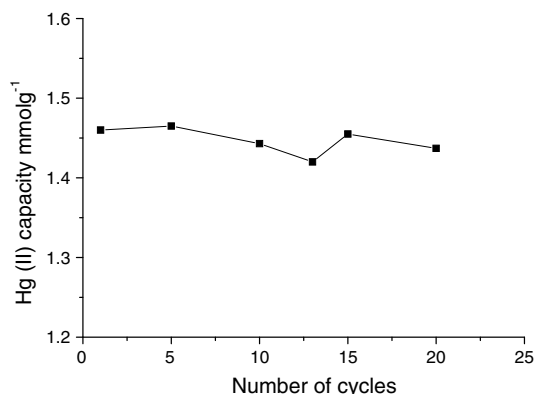


Fig. 4. Variation of the mercury uptake capacity by number of the recycling.

ity is almost the same of the initial capacity and remains constant (Fig. 4) up to 20 cycles. This can be considered as satisfactory for industrial applications.

9. Conclusion

Like carbon amides, polymer-bound sulfonamide group presented is also efficient in selective mercury uptake from aqueous mixtures with Zn(II), Cd(II), Pb(II) and Fe(III) ions. 47.0% of the sulfonamide functions are involved in mercury binding, probably due to moderate hydrophilicity induced by the hydroxyethyl groups. Overall results indicate that, hydrophilicity, pH and presence of chloride ions are the main factors governing the mercury uptake. No significant capacity change occurs in 0.01–0.06 M concentration range. Moreover the hydroxyethyl sulfonamide resin is also efficient for extraction in the dilute solutions of mercury.

Unlike carbon amide resins, this resin can be regenerated with 2 M HCl solution without hydrolysis of the sulfonamide groups and more than

99% of loaded mercury is recovered in the first contact. Since no significant capacity loss is detected after 20 times of recycling, this resin might be of interest for long term uses in continuous processes.

This study reveals that, the mercury capacity can be enhanced by incorporation of more hydrophilic groups into polymer supported sulfonamides.

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