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# Preparation of crosslinked quaternary amide–sulfonamide resin for removal of mercury ions from aqueous solutions

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## ABSTRACT

Cross-linked copolymer beads were prepared by suspension polymerization of styrene (0.90 mol) and divinyl benzene (DVB) (0.10 mol) mixtures. The resulting copolymer beads with sulfonamide-based quaternary amide functions were prepared in three steps: (1) by chlorosulfonation with chlorosulfonic acid; (2) by sulfonamidation reaction with N,N-dimethylethylenediamine; and (3) by quaternization reaction with chloroacetamide. The resulting polymer resin, which had a chloroacetamide content of 2.50 mmol/g, was effective in extracting mercury from aqueous solutions. The mercury sorption capacity was around 3.0 mmol/g in non-buffered conditions. Experiments performed in identical conditions with several metal ions revealed that Cd(II), Mg(II), Zn(II), and Fe(III) ions also were extractable in low quantities (0.2–0.8 mmol/g). The sorbed mercury could be eluted by repeated treatment with hot acetic acid without hydrolysis of the amide groups.

*Keywords:* Polymer modification; Sulfonamide; Mercury removal; Quaternization

## 1. Introduction

Mercury is one of the most toxic elements for plants and animals. Mercury can be found in significant amounts in wastes from chlorine-alkali manufacturing plants, electrical and electronics manufacturing, and sulfide ore roasting operations.

The major effects of mercury poisoning manifest as it can easily pass the blood–brain barrier and affect the fetal brain. Symptoms of mercury poisoning not only cause neuronal disorders, but also damage to the cardiovascular system, kidney, bones, etc. [1,2]. The permitted discharge limit of wastewater by US EPA for total mercury is 10 μg $L^{-1}$, and the limit for drinking water is 2 μg $L^{-1}$ [3]. Related limits established by the European Union are, however, 5 and 1 μg $L^{-1}$ for wastewater and drinking water, respectively.

Mercury can be removed from wastewater by several methods, such as chemical precipitation, membrane filtration, electro dialysis, ion exchange, solvent extraction, and adsorption. Adsorption ((bio)-adsorption/ion exchange) appears to be the most promising technique to remove mercury from aqueous solutions with mercury concentrations below 100 ppm [4,5].

Several materials such as clays, activated carbon, resins, and silica are modified with organic functional groups to improve the selectivity that have been studied for adsorption of mercury [6].

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The use of polymer-bonded ligands in selective mercury removal has been the subject of many research articles [7,8] and reviews [9,10].

Mercuric ions interact strongly with ligands containing nitrogen or sulfur donor atoms, including pyridine, poly(ethylenimine), thioether, thiourea, and phosphine sulfide. Recently, many of these polymers such as porous cellulose carrier modified with poly(ethyleneimine) [11], polystyrene beads with imidazolylazo functions [12], poly(4-vinylpyridine) hydrochloride resin [13], dithiocarbamate-incorporated monosize polystyrene [14], modified chloromethylated polystyrene-PAN [15], pyridine-based thiols [16], and N-chlorosulfonamide groups into polystyrene–divinylbenzene [17] were synthesized and used for the selective removal of mercury ions.

Nitrogen is the other important atom that has a great affinity for mercury ion. Especially, amide ligands tend to complex with mercury ion. Amide compounds readily react with mercuric ions under ordinary conditions to give mono or diamido mercury compounds. The mercury–amide linkage is believed to be covalent rather coordinative [18]. There are several studies that were conducted on removal of Hg(II) ions from aqueous media by polymers carrying pendant sulfur and nitrogen-containing ligands.

Cellulose-based sorbents have been studied by several research groups all around the world because of the excellent properties that cellulose serves. Poly (acrylamide) grafted onto cellulose synthesized by Bicak et al. has been demonstrated to be a very efficient selective sorbent for the removal of Hg(II) from aqueous solutions [19]. Also, other important nitrogen-containing sorbent such as polystyrene-supported amines [20] and immobilized N-methyl-D-glucamine [21] were described in the literature.

In this study, tertiary amine containing sulfonamide-based polymeric sorbent was prepared and quaternized with chloroacetamide. A new sorbent is efficient at removing mercury ions selectively. The conditions for regeneration of the resulting resin and for affinity of the sorbent for other metal ions such as Cd(II), Mg(II), Zn(II), and Fe(III) were also investigated.

## 2. Experimental setup

### 2.1. Materials

Styrene (Fluka), divinylbenzene (55% grade) (DVB), dibenzoyl peroxide (Fluka), gum arabic, chlorosulfonic acid (Fluka), triethyl amine (Fluka), diphenylcarbazide (E-Merck), mercury(II) chloride (E-Merck), iron(III) chloride (E-Merck), magnesium sulfate (E-Merck), zinc sulfate (E-Merck), cadmium nitrate (E-Merck), HCl (E-Merck), ethylenediamine tetra acetic acid (E-Merck), eriochrome black T (E-Merck), N,N-dimethylethylenediamine (Aldrich), chloroacetamide (Aldrich), dimethyl formamide (DMF), 2-methyl pyrrolidone (NMP), ethanol, and acetic acid.

### 2.2. Instruments

UV–vis spectrophotometer (Perkin Elmer, Lamda 25) and Thermo FT-IR (with ATR), scanning electron microscope (SEM) (FEI Quanta FEG 250).

### 2.3. Cross-linked poly(styrene–divinylbenzene) (PS) beads

Beads were prepared by the suspension polymerization of a mixtured styrene (54 mL, 0.48 mol) and DVB (55% grade, 10 mL, and 0.038 mol) in toluene (60 mL), using gum arabic as stabilizer, according to a previously described procedure [22]. The beads were sieved and the 420–590 μm size fractions were used for further reactions.

### 2.4. Chlorosulfonation of the beaded polymer

The beaded polymer was chlorosulfonated using chlorosulfonic acid as described in the literature [22] as follows: 10 g of cross-linked PS–DVB resin was interacted with 45 mL of chlorosulfonic acid at 0˚C for 2 h and at room temperature for 18 h. The reaction mixture was added slowly to ice–water mixture and was stirred at 0˚C for 20 min. Chlorosulfonated resin was filtered under vacuum and was washed with excess of cold water, acetone, and ether, respectively. The degree of chlorosulfonation was determined by analysis of the liberation of chloride ions. For these purpose, a polymer (0.2 g) sample was added to 10% NaOH (20 mL) and boiled for 4 h. After filtration and neutralization with $HNO_3$ (5 M), the chlorine content was determined by the mercuric thiocyanate method [23] and was found to be about 3.50 mmol/g which corresponds to ~61% chlorosulfonation.

### 2.5. Sulfonamidation reaction with chlorosulfonated polystyrene resin (CSPS) and N,N-dimethylethylenediamine (Resin 1)

Chlorosulfonated resin (10 g) was added portion wise to a stirred solution of N,N-dimethylethylenediamine (12 mL) (0.05 mol) in 2-methyl pyrrolidone (30 mL) at 0˚C. The mixture was shaken with a continuous shaker at room temperature. The reaction content was poured into water (1 L), filtered, and washed with excess water and methanol, respectively. The resin was dried under vacuum at room temperature for 24 h. The yield was 11.50 g.

### 2.6. Determination of sulfonamide content of the Resin 1

Sulfonamide content of the sorbent was determined titrimetrically. For this purpose, the sulfonaminated polymer sample (0.1057 g) was added to 10 mL of 0.5 M NaOH and continuously shaken for 24 h. After filtration, 5 mL of the filtrate was titrated with 0.5 M HCl solution. By comparison with the result for the unreacted solution, the sulfonamide content was found as 2.84 mmol/g.

### 2.7. Reaction of cross-linked tertiary amine-containing beads with chloroacetamide (Resin 2)

Four gram of tertiary amine-containing beads were soaked into a solution of 3 g (0.0321 mol) 2-chloroacetamide in 30 mL DMF. The mixture was shaken by a continuous shaker for 2d at room temperature, and then heated to 80˚C in a constant temperature bath for 48 h. Beads were filtered and washed with DMF, excess of water, and acetone, respectively. The vacuum dried sample weighed 4.7 g.

#### 2.7.1. Chloride analysis

The quaternization yield was followed by analysis of the chloride ions in the final product. Thus, 0.1 g of the quaternized beads was boiled in 9 mL of 10% NaOH solution for 3 h. Analysis of the chloride ion solution was performed by the mercuric thiocyanate method as described in the literature [23]. Chloride content of the sorbent was found to be 2.5 mmol/g.

### 2.8. Mercury and heavy metal uptake measurements of the resins

The mercury and heavy metal sorption capacities of the resins were determined by mixing weighed amount of polymer sample (0.2 g) with 20 mL aqueous $HgCl_2$ solution (0.074 M).

Similar experiments were repeated under the same conditions with different initial mercury concentrations (0.025 and 0.05 M). No buffer was used in these experiments. The sorbed amounts were calculated according to the residual mercury contents, as previously described. The relevant data are listed in Table 1. The mixtures was stirred for 24 h at room temperature and then separated by 0.45 μm filter membrane. The Hg(II) concentration was determined colorimetrically using diphenylcarbazide [24]. The mercury loading capacities were calculated from the initial and final Hg(II) contents of the solutions. The pH of mercury solutions remained almost constant, in the 3.1–3.9 range, throughout the extraction process. To inspect mercury efficiency of the resin, metal extraction experiments were repeated with Cd(II), Zn (II), Mg(II), and Fe(III) solutions (Table 1).

In order to examine the selectivity of Hg binding, sorption capacity measurements were also performed using Cd(II), Pb(II), Zn(II), and Fe(III) ion solutions (0.15 M initial concentrations). Analyses of the residual metal contents of the supernatant solutions were performed by a complexometric titration method using ethylenediamine tetra acetic acid (EDTA) solution (0.1 M).

### 2.9. Mercury sorption kinetics of the sorbent

In order to estimate efficiency of the Resin 2 for trace mercury, batch kinetic experiment was performed using high diluted $HgCl_2$ ($3.70 \times 10^{-4}$ M) solutions. For this purpose 0.2 g of sorbent was wetted with 1 mL of distilled water and added to a solution of Hg(II). The mixture was stirred with a magnetic stirring bar and aliquots of the solution (5 mL) were taken at appropriate time intervals for the analysis of the residual Hg(II) contents by the method as mentioned above.

### 2.10. Regeneration of the adsorbent

For desorption studies, mercury-loaded adsorbent was collected, gently washed with distilled water to remove any unabsorbed metal ions, and then every 0.1 g mercury-loaded adsorbent was left in contact with 10 mL of glacial acetic acid and stirred at 80˚C for 2 h. After cooling, the mixture was filtered and 2 mL of the filtrate was taken out for colorimetric analysis of the mercury ion.

## 3. Results and discussion

### 3.1. Preparation of the cross-linked polymeric sorbents

In this study, cross-linked polystyrene–DVB copolymer was prepared and the beads were modified with chlorosulfonic acid, N,N-dimethyl ethylenediamine, and chloroacetamide, respectively.

### 3.2. Preparation of CSPS resin

Cross-linked polystyrene–DVB copolymer was prepared using suspension polymerization method. The

Table 1
Metal uptake characteristics of the Resin 1

| Metal ion | Initial concentration (M) | Resin capacity (mmol/gresin) |
|---|---|---|
| Hg(II) | 0.074 | 2.00 |
| Hg(II) | 0.050 | 1.95 |
| Hg(II) | 0.025 | 1.83 |
| Cd(II) | 0.150 | 1.60 |
| Mg(II) | 0.150 | 2.20 |
| Zn(II) | 0.150 | 2.00 |
| Fe(III) | 0.150 | 2.20 |

polymer was chlorosulfonated using excess of chlorosulfonic acid at room temperature for 24 h.

Chloride analysis of the product in the fist step (3.50 mmol/g) revealed a degree of chlorosulfonation of ~61%.

### 3.3. Reaction with CSPS resin and N,N-dimethyl ethylenediamine (Resin 1)

Excess of N,N-dimethylethylenediamine was dissolved in NMP. Chlorosulfonated polystyrene resin was added portion wise at 0℃. The reaction was continued at 0℃ for 2 h and at room temperature for 24 h. The sulfonamide-based tertiary amine containing resin was filtered and washed with excess of water and methanol, respectively (Fig. 1). The Resin 1 was characterized by detection of sulfonamide content and was found as about 2.84 mmol/g.

### 3.4. Reaction of cross-linked amine-containing beads with chloroacetamide (Resin 2)

Reaction of cross-linked tertiary amine function Resin 1 in DMF with excess 2-chloroacetamide yielded a product with a chloride content of 2.50 mmol/g, corresponding to about 88% quaternization (Fig. 2).

Spectroscopic characterization of the resins were performed by FT-IR (Fig. 3). In the sulfamidation products for resin 1 and resin 2, S=O stretching vibrations of sulfonamide group appear at about 1,311 and 1,149 $cm^{-1}$. In addition, the sharp peak at about 1,685 $cm^{-1}$ corresponds to C=O stretching vibration of the amide group in the Resin 2.

The resins were also characterized using SEM method. It can also be seen in the SEM images that the shapes of the polystyrene beads (Fig. 4(a)) cracked, because of the exothermic chlorosulfonation reaction, sulfonamidation, and quaternization (Fig. 4(b)). As could be seen from the (Fig. 4(c)), a visible change of the surface morphology in the Hg(II) adsorbed Resin 2 demonstrated that the sorption of Hg(II) ions has taken place onto the sorbent.

### 3.5. Mercury uptake measurements

The mercury sorption capacities of the resins were determined by mixing weighed amount of polymer sample (0.2 g) with 20 mL aqueous Hg(II) solutions with different concentrations (0.074, 0.05, and 0.025).

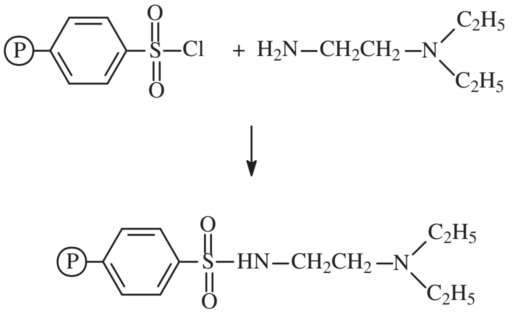

Fig. 1. Preparation of Resin 1.

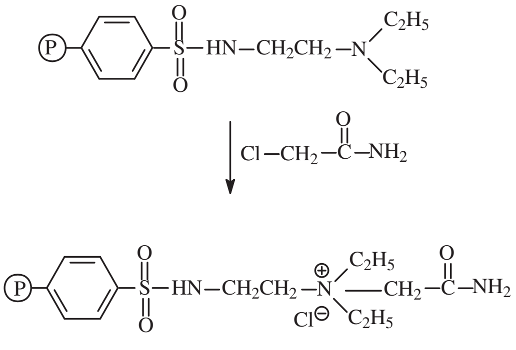

Fig. 2. Preparation of Resin 2.

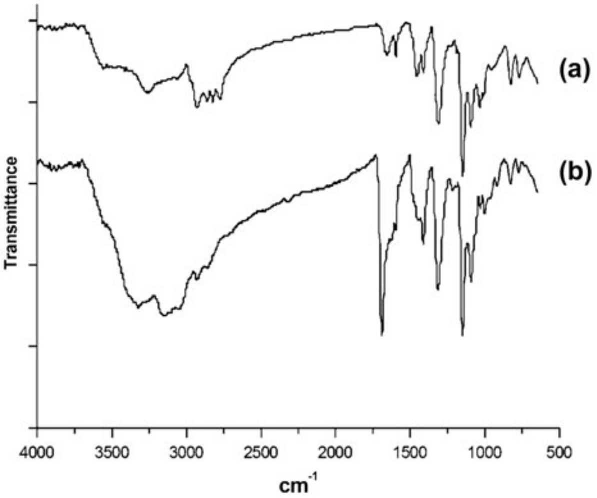

Fig. 3. FT-IR spectra of the Resin 1 (a) and Resin 2 (b).

The mixture was stirred for 24 h and then filtered. The Hg(II) concentrations were determined colorimetrically using diphenyl carbazide.

The mercury loading capacities were calculated from the initial and final Hg(II) contents of the solution.

### 3.6. Metal uptake of Resin 1

The sulfonamide-containing polymeric sorbent was an efficient sorbent to remove mercury. On the basis of the basic reaction of the mercuric ions with sulfonamide groups, this yielded covalent mercury–sulfonamide linkages [25].

The mercury binding of the polymer can be depicted as shown in Fig. 5.

The pH of mercury solutions remained almost constant, in the range of 3.1–3.9, throughout the extraction process. Buffer solutions were not used in the experiments because their use is not practical in real application conditions.

Resin 1 has sulfonamide and tertiary amine functions. Especially, amine function group removes heavy metal ions such as Cd(II), Mg(II), Zn (II), and Fe(III) as well as Hg(II) ion from aqueous solutions. All the metal uptake characteristics of Resin 1 were given in Table 1.

Resin 2 has sulfonamide and quaternary amine–amide functions. Based on the basic reaction of mercuric ions with amide and sulfonamide groups, yielding covalent mercury–amide and mercury–sulfonamide linkages, mercury binding of the resin can be shown in Fig. 6.

Mercury sorption of the resin has been studied in non-buffered conditions. Because the use of buffer is not practical in large-scale mercury extractions and the buffer components might be competitive in the mercury uptake, pH of the Hg(II) solutions are slightly acidic and remain almost constant in the range of 3.1–4.0 during the mercury extractions.

Aqueous solutions of the $HgCl_2$ were used in the mercury sorption experiments. The sorption capacity of the bead sample was estimated by the analysis of the excess $Hg^{2+}$ in the supernatant solutions. The overall $Hg^{2+}$ uptake capacity from 0.074 M $HgCl_2$ solution was 3.30 mmol/g.

In the 0.025–0.074 M initial mercury concentration range, loading capacity of the polymer did not change. To inspect selectivity of the quaternary resin, metal extraction experiments have been reported with Cd (II), Mg(II), Zn(II), and Fe(III).

Since, in ordinary conditions, the amide and sulfonamide groups are not capable of forming coordinative bonds with other transition metal ions, as a result of the reduced electron-donating character of the amide

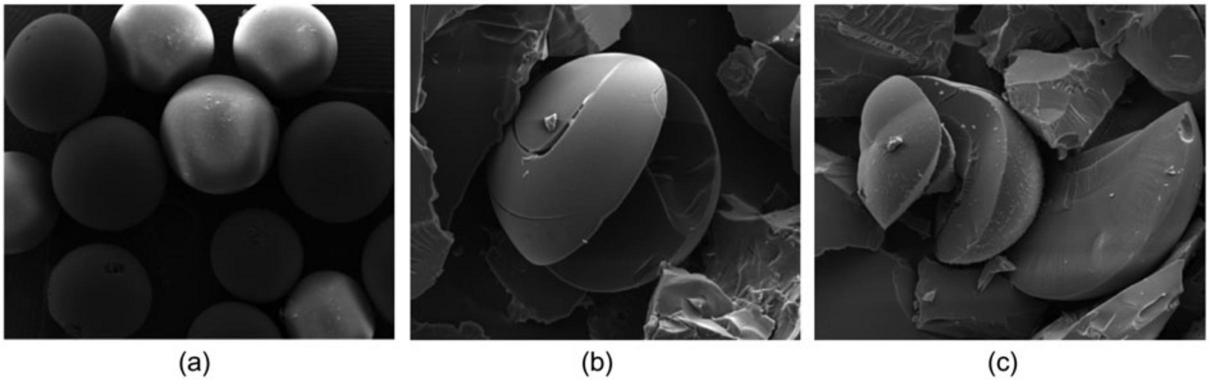

Fig. 4. SEM pictures of the PS Resin (a), Resin 2 (b), and mercury-loaded Resin 2 (c).

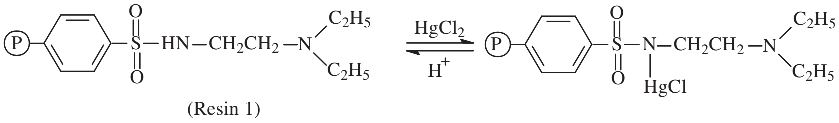

Fig. 5. Mercury uptake of Resin 1.

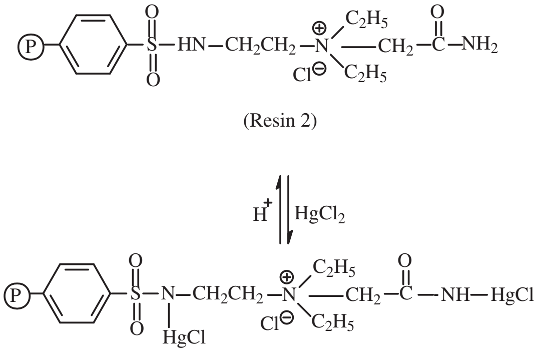

Fig. 6. Mercury uptake of the Resin 2.

nitrogen, the separation of $Hg^{2+}$ is expected to be highly selective. Other metal ions sorption capacities of the Resin 2 between 0.20 and 0.30 mmol $g^{-1}$ were observed (Table 2). Therefore, overall, the results clearly indicate that $Hg^{2+}$ sorption is extremely selective.

$Hg^{2+}$ sorption capacity of the resin was compared with other synthetic sorbents described in the literature [21,26–30] (Table 3). Sorption capacity of the resin is rather satisfactory.

### 3.7. Kinetics of the mercury sorption

To examine the efficiency of the Resin 2 for trace quantities, kinetic experiments were investigated with extremely diluted $HgCl_2$ solutions ($3.70 \times 10^{-4}$ M).

The kinetics of the mercury sorption depends on many factors, such as stirring rate and pH of the solution. To obtain information about kinetic profiles of the mercury sorption, we performed experiments by the batch method with low mercury concentrations under non-buffered conditions. The concentration–time plot in Fig. 7 shows that within about 1 h of contact time, the Hg(II) concentration falls to zero.

Table 2
Metal uptake characteristics of the Resin 2

| Metal ion | Initial concentration (M) | Resin capacity (mmol/g) | Recovered metal (mmol/g) |
|---|---|---|---|
| Hg(II) | 0.074 | 3.45 | 3.20 |
| Hg(II) | 0.050 | 3.30 | 3.01 |
| Hg(II) | 0.025 | 3.15 | – |
| Cd(II) | 0.150 | 0.32 | – |
| Mg(II) | 0.150 | 0.25 | – |
| Zn(II) | 0.150 | 0.30 | – |
| Fe(II) | 0.150 | 0.24 | – |

Table 3
Comparison of the sorption capacities of different adsorbents

| Adsorbent | Chelating ligand | Capacity (mmol/g) | Reference |
|---|---|---|---|
| Cross-linked polymethyl methacrylate | Ethylenediamine | 0.15 | [26] |
| Cross-linked poly(glycidyl methacrylate) | Amine-mercaptan | 3.10 | [27] |
| Polythioamides | Thioamides | 3.50 | [28] |
| Cross-linked polyhydroxyethyl methacrylate | Polyethyleneimine | 1.67 | [29] |
| Cellulose | Sulfonamide | 1.95 | [30] |
| Cross-linked poly(vinylbenzyl chloride) | N-methyl-D-glucamine | 1.35 | [21] |

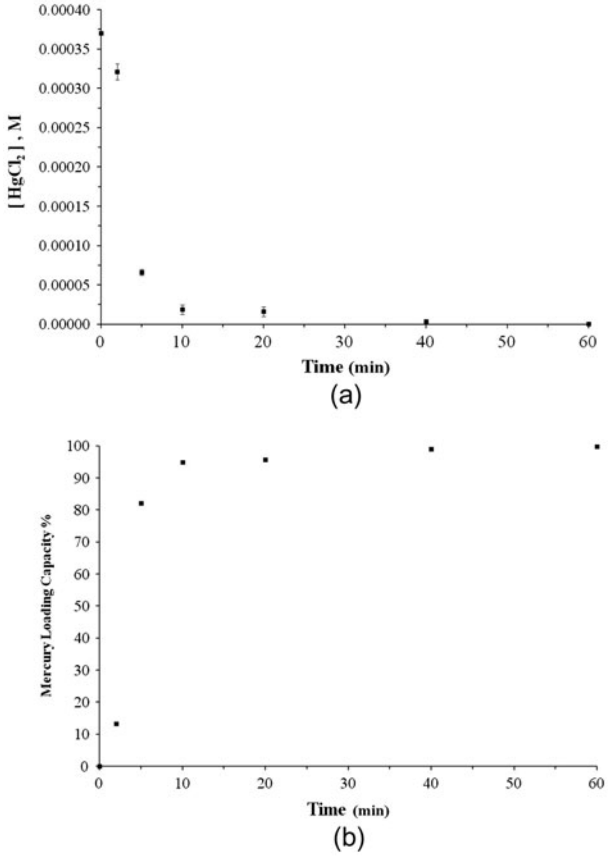

Fig. 7. Hg(II) adsorption kinetics of the Resin 2: (a) [$HgCl_2$] vs time (b) mercury loading capacity % vs. time; (error < 5%). The error bars indicate the concentration ranges from three tests.

The rate constant of adsorption was studied with the help of the pseudo-first-order rate expression of Lagergren model and the pseudo-second-order kinetic rate expression of Ho and McKay [31–33].

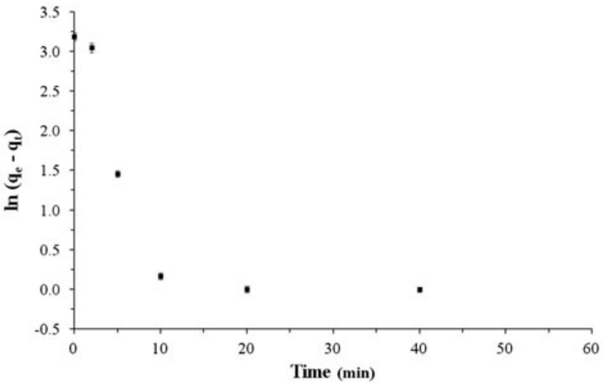

Fig. 8. The pseudo-first-order model plots of Hg(II) adsorbed by the Resin 2 (error < 5%). The error bars indicate the concentration ranges from three tests.

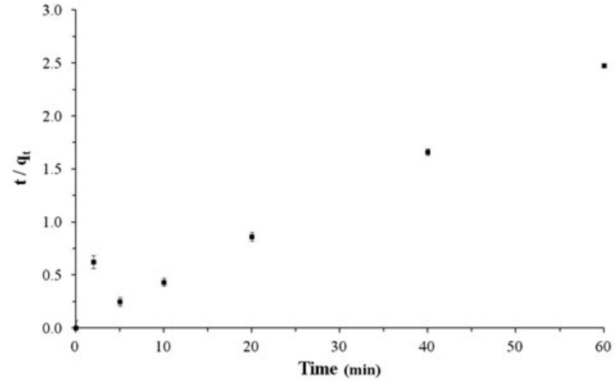

Fig. 9. The pseudo-second-order model plots of Hg(II) adsorbed by the Resin 2 (Error < 5%). The error bars indicate the concentration ranges from three tests.

The pseudo-first-order equation assumes that the adsorption rate decreases linearly as the adsorption capacity increases, which is suitable especially for low concentrations [33]. A linear form of this model is:

$$\ln(q_e - q_t) = \ln q_e - \left(\frac{k_1}{2.303}\right)t \tag{1}$$

where $q_t$ and $k_1$ are the amount of dye adsorbed at time $t$ (mmol/g) and the equilibrium rate constant of pseudo-first-order kinetics (1/min), respectively. The linear fitting of $\log(q_e - q_t)$ with the contact time ($t$) can be approximated as pseudo-first-order kinetics (Fig. 8). The low correlation coefficient values obtained for the pseudo-first-order model indicated that adsorption was not occurred exclusively onto one site per ion.

The pseudo-second-order kinetic model assumes that the rate limiting step is the interaction between two reagent particles [34].

Table 4
Parameters of the kinetic models of Hg(II) adsorption onto Resin 2

| Kinetic models | Parameters | Hg(II) |
|---|---|---|
| Pseudo-first order | $k_1$ (1/min) | 0.075 |
| | $q_{e,\text{calc.}}$ (mg/g) | 9.80 |
| | $q_{e,\text{exp}}$ (mg/g) | 44.0 |
| | $R^2$ | 0.570 |
| Pseudo-second order | $k_2$ (g/mg min) | 43.0 |
| | $q_e$ (mg/g) | 45.0 |
| | $q_{e,\text{exp}}$ (mg/g) | 44.0 |
| | $R^2$ | 0.9999 |

This model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where $k_2$ is the constant of pseudo-second-order rate (g/mg min), and $q_t$ is the adsorption amount at time $t$. Plotting $t/q_t$ vs. $t$, straight lines were obtained (Fig. 9).

Parameters of the kinetic models of Hg(II) adsorption onto Resin 2 are given in Table 4.

According to the data of Table 3, the pseudo-first-order kinetic model having a low value for $R^2$ does not present a good fit with experimental data. In contrast, in the case of pseudo-second-order kinetic model, the high values of correlation coefficients showed that the data fitted well to the pseudo-second-order rate kinetic model.

### *3.8. Regeneration of the Resin 2*

Mercury-loaded Resin 2 was regenerated by using glacial acetic acid. Regeneration capacity was found as about 3.0 mmol/g resin. According to these results, resin was regenerated efficiently.

## 4. Conclusion

The new sulfonamide-based resins were prepared starting from cross-linked CSPS. Resin 1 has sulfonamide and tertiary amine groups. In order to determine possible interference from foreign ions on the mercury uptake, we first treated the polymeric sorbent with each of metal ions; Fe(III), Cd(II), Mg(II), and Zn (II) separately. Hence, these experiments show that the mercury uptake by the polymeric sorbent is not selective. Under non-buffered conditions, the mercury uptake capacity is around2.00 mmol/g.

Resin 2 was prepared by quaternization of Resin 1 with chloroacetamide. The mercury sorption capacity was calculated as about 3.30 mmol/g and the resin, having carbon amide and sulfonamide groups, shows a reasonable mercury selectivity over Zn(II), Cd(II), Mg(II), and Fe(III) ions.

Since, in ordinary conditions, the amide and sulfonamide groups are not capable of forming coordinative bonds with other transition metal ions, as a result of the reduced electron-donating character of the amide nitrogen, the separation of mercury ions is very highly selective.

The recovery of mercury can be achieved by elution with acetic acid at 80°C without hydrolysis of the amide groups. Regenerability of these materials with acetic acid makes them attractive for large-scale applications.

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