Preparation of a novel chloromethylated polystyrene-2-mercapto-1,3,4-thiadiazole chelating resin and its adsorption properties and mechanism for separation and recovery of Hg(II) from aqueous solutions

Huihua Zhou, Jianjun Zheng, Hui Wang, Jianxin Wang, Xiaoguang Song, Yanmei Cao, Lei Fang, Yuping Feng and Chunhua Xiong

ABSTRACT

With an efficient methodology, a novel chloromethylated polystyrene-g-2-mercapto-1,3,4-thiadiazole chelating resin (MTR resin) was prepared via a one-step reaction. The structure of MTR resin was characterized by elements analysis, Fourier transform infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. Meanwhile, the adsorption properties of the resin for Hg(II) were investigated by batch and column experiments. The results showed that the resin possessed much better adsorption capability for Hg(II) than for other metal ions. The statically and the dynamic saturated adsorption capacities were 343.8 mg/g and 475.1 mg/g. The adsorption kinetic and equilibrium data were well fitted to the second-order model and the Langmuir isotherm model, respectively. Desorption of mercury from the resin can be achieved using 30 mL of 2 mol/L HCl-5% thiourea solution with a desorption ratio of 92.3%. Compared with other absorbents, MTR resin was greatly conserve natural resources and reduce the cost.

Key words | adsorption, chelating resin, chloromethylated polystyrene-g-2-mercapto-1,3,4-thiadiazole, desorption, mercury

INTRODUCTION

Water pollution of heavy metals is considered to be a serious menace to the environment, especially to human health in terms of their persistence, bio-magnification, non-degradation and toxicity (Mubarak et al. 2014). Mercury, as one of the important heavy metals, damages the nervous system in humans by Hg(II) accumulating in the vital organs of humans and animals through the environment and food chain (Yuan et al. 2011). It can be released to the environment from wastewater such as paper, oil refinery, pulp, chlor-alkali manufacturing (Verta et al. 2011), and battery manufacturing industries (Vinod et al. 2011). Hence, transition metal detection and removal for contaminated water seems to be particularly important for green environment.

In the mercury recovery progress from industrial effluents, various technologies have been applied to eliminate environmental pollution, such as solvent extraction (Nikoloski et al. 2014), reduction, coagulation (Xie et al. 2010), reverse osmosis (Emadzadeh et al. 2015; Nguyen et al. 2015), chemical precipitation (Vymazal et al. 2007), membrane separation (Goh et al. 2015), and ion exchange. Adsorption, by contrast, is deemed to be the most suitable method due to its low cost, high adsorption capacity, easy metal recovery and good reusability for the recovery of mercury in the case of low concentration (Aziz et al. 2008). Chelating resins, as a kind of adsorption material, have been widely used in the fields of analytical chemistry and...
separation chemistry thanks to its low cost, high adsorption capacity, good recovery, and excellent selectivity for some metals ions (Xiong et al. 2015). Recently, some authors have used different kinds of resins for the removal of Hg(II) such as functionalized cross-linked polystyrene resin and sulfamine modified absorbent (Qi et al. 2013; Zhang et al. 2014), but with low sorption capacity. Macroporous chloromethylated polystyrene beads (PS-Cl) are an ideal polymeric matrix with stable mechanical properties. The active chloromethyl group in PS-Cl can be easily converted into a number of new functional groups via special reactions (Guo et al. 2015). These structural characteristics are attractive for developing adsorbents for metal ions (Xiong et al. 2012). Chelating resins containing subgroups with sulfur or nitrogen atoms can be used in the selective removal of precious metals.

In this study, a new chelating resin with 2-mercaptop-1,3,4-thiadiazole containing nitrogen and sulfur as the functional group was synthesized and it was obtained by a substitution reaction inducing 2-mercaptop-1,3,4-thiadiazole onto PS-Cl. The synthetic resin was characterized by Fourier transform infrared (FTIR) spectroscopy, elemental analysis and thermogravimetric analysis (TGA). The adsorption capability for Hg(II) in the aqueous solution had been investigated by a series of batch and column experiments. To further understand the adsorption process, the adsorption kinetics, isotherms and the thermodynamic properties of the adsorption of Hg(II) on the synthetic resin were also determined. At the same time, the recovery of Hg(II) and reusability of the adsorbents were also exhaustively studied. The experimental results may develop a new pathway to the removal and recovery of Hg(II) from aqueous solutions and fit in with environmental protection.

**MATERIALS AND METHODS**

**Chemicals**

2-Mercapto-1,3,4-thiadiazole was purchased from Sinopharm Chemical Reagent Co., Ltd, China. Macroporous chloromethylated polystyrene beads (PS-Cl for short) with a degree of cross-linking of 8% DVB, a chlorine content of 19.15%, and a specific surface area of 43 m2/g were produced by Jiangsu Su Qing Water Treatment Engineering Group Co., Ltd. Metal standard solution of Hg(II) ion was provided by certified reference materials stock solution (1,000 μg/mL) of National Standard Materials Research Center. All reagents and solvents were of analytical reagent grade and were used without further purification.

**Apparatus**

The specific surface area and the mean pore size of the resins were determined on an Autosorb-1 automatic surface area and pore size analyzer. The elemental analysis was carried out using a Gmbh Vario EL III elemental analyzer. IR spectra and scanning electron micrographs for the samples were obtained from a Nicolet 380 FTIR spectrometer and a HITACHIS-3000N scanning electron microscope (SEM), respectively. TGA was performed using a Mettler TGA/DSC1 simultaneous thermal analyzer (with a temperature range of 50–1,000 °C, heating rate of 20 °C min⁻¹, and atmosphere of N₂). The sample was shaken in a DSHZ-300A temperature constant shaking machine. The water used in the present work was purified using a Mol research analysis type ultrapure water machine. A Mettler Toledo Delta 320 pH meter was used for pH measurement. The concentrations of metal ions were measured by inductively coupled plasma optical emission spectroscopy (ICP OES).

**Synthesis of resin**

20.0 mg of PS-Cl beads and 25 mL of dioxane were added to a 100 mL three-neck round-bottom flask which was equipped with a condenser, thermometer, and nitrogen gas inlet tube, swelling overnight. Then, a certain amount of 2-mercaptop-1,3,4-thiadiazole was added to the flask. After the system being swept with nitrogen to remove air, the reaction mixture was reacted by means of rotor stirring under a nitrogen atmosphere at 100 °C for 12 h. Once the reaction completed, the resin was carefully washed thoroughly with dioxane, deionized water and then with ethanol, acetone and ether. After that, the obtained resin was dried in a vacuum at 50 °C.

**Resin adsorption and desorption**

Batch adsorption experiments were performed in conical flasks containing 30 mL of adsorption solution and 15.0 mg of dried MTR resin. Adsorption of metal ions from aqueous solution to the adsorbents was studied at various pH (3–7) in acetic acid–sodium acetate (HAc–NaAc) employed as the buffer solution to control the pH of the solutions. Adsorption experiments were conducted in a shaker at 100 rpm at constant temperature (288–308 K) for 24 h. Aliquot samples were taken from the flask at appropriate time intervals as necessary. The residual concentration of the metal ions in the aqueous phases was determined by...
ICP. Adsorption isotherm studies were carried out with different initial Hg(II) concentrations (0.267 mg/mL–0.467 mg/mL Hg(II) solution). The kinetic experiments were carried out as the effect of contact time with time ranging from 1 to 30 h. The adsorption capacity (Q, mg/g) and distribution coefficient (D, mL/g) were calculated with the following formulas:

\[ Q = \frac{(C_0 - C_e)V}{m} \]  
\[ D = \frac{Q}{C_e} \]

where \( C_0 \) is the initial concentration in solution (mg/mL); \( C_e \) is the equilibrium concentration in solution (mg/mL); \( V \) is the volume of solution (mL); and \( m \) is the resin dry weight (g).

Desorption experiments were carried out following the completion of the adsorption experiments. After adsorption experiments, the resins were separated from the aqueous solution by filtration, washed with acetic acid–sodium acetate (HAc–NaAc), and eluted by the batch method using various concentrations of HCl-5% thiourea, HCl and HNO₃ at 298 k for 24 h. After that time, the concentration of Hg(II) was similarly analyzed as described above. After each adsorption–desorption cycle, the resin beads were washed and reconditioned for adsorption in the succeeding cycle. The desorption ratio (E) was calculated as follows:

\[ E(\%) = \frac{C_dV_d}{(C_0 - C_e)V} \times 100\% \]

where \( C_d \) is the concentration of the solutes in the desorption solutions, \( V_d \) is the volume of the desorption solution, and \( C_0, C_e, \) and \( V \) are the same as defined above.

Continuous packed bed studies were performed in a fixed-bed mini glass column (5 mm²50 cm long) with 100.0 mg of resin. The Acetal Resin (AR) in the column was presoaked for 24 h before the experiment. The Hg(II) solution concentration at a certain concentration and flow rate was passed continuously through the stationary bed of absorbent in down-flow mode. The experiment continued until a constant Hg(II) ion concentration was obtained. The column studies were performed at the optimum pH value determined from batch studies and at a constant temperature of 25 °C representative of environmentally relevant conditions.

**RESULTS AND DISCUSSION**

**Synthesis of AR resin**

The synthesis conditions, such as reaction solvents, molar ratio, and reaction temperatures were investigated, and the optimal synthesis conditions were determined according to N content (N%) and functional group conversion (FGC, %). According to the N content (DMF, 8.751%; toluene, 2.439%; 1,4-dioxane, 9.673%), it was obvious that 1, 4-dioxane is better than toluene and DMF at 100 °C for 12 h. That may be due to the swelling property and permeability of MTR resin are different in various solvents. Thus, 1, 4-dioxane was the most appropriate reaction solvent in this experiment. The study temperature of MT is in the range of 40–100 °C in accordance with the toluene boiling point of 110.8 °C. Based on the above results, the optimum conditions are as follows: toluene as the reaction solvent, a reaction temperature of 100 °C and a molar ratio of ATD to PS-Cl at 4:1 (Figure 1).

**Characterization of resins**

**FTIR spectral analysis of the resins**

In order to evaluate the structure of synthetic resin MTR, FTIR spectra were obtained and are shown in Figure 2. As
shows in Figure 2, absorption peak at 1,428 cm\(^{-1}\) and 1,507 cm\(^{-1}\) indicated the presence of the penta-heterocycles aromatic ring absorption peak at 885 cm\(^{-1}\) and 1,033 cm\(^{-1}\) indicated the presence of \(\text{C}=\text{C}\). By comparison with the curve of PS-Cl, the characteristic peak of \(\text{CH}_2\text{-Cl}\) at 673 cm\(^{-1}\) and 1,262 cm\(^{-1}\) significantly reduced to almost disappeared in the curve of MTR resin. In the spectra of MTR resin, a strong characteristic band of the penta-heterocycles aromatic ring peak at 1,066 cm\(^{-1}\) and 1,499 cm\(^{-1}\) appeared, which suggests the presence of the penta-heterocycles aromatic ring introduced to the modified polymer. It indicated that MT-SH has successfully replaced the chlorine in the C-Cl keys of chlorine atoms and chlorine on the ball.

**TGA analysis**

TGA curves for PS-Cl, MT, MTR and MTR-Hg are shown in Figure 3. The decomposition of PS-Cl was a two-step reaction. At the first step, from 25 °C to 235 °C, the PS-Cl weight loss rate was about 29.24 wt\%, because of the residual moisture evaporation and fracture chloromethyl bond. Secondly, from 425 °C to 835 °C with 69.77 wt\% weight loss ratio, which indicates that the skeleton structure of PS-Cl was broken. The remaining mass after heating was the char residue. MT began to decompose at 105 °C and the decomposition reached 99.7 wt\% at 95 °C. As for MTR, two weight losses were obtained. The first weight loss occurred from 25 °C to 505 °C and the weightlessness rate at about 42.37 wt\%. According to the optimal synthetic conditions of nitrogen content was 9.861 wt\%, the MT available in synthetic resin content of about 41.20 wt\%, it caused by the evaporation of the water and the decomposition of MT and the breaking of the covalent bond between PS-Cl and MT. In the second case, which occurs at about 505 °C, MTR did a further decomposition, and the weight loss rate reached 78.38 wt\% at 1,000 °C. The TGA curve of MTR-Hg exhibited similar to the curve of MTR. Compared to the weight loss rate of MTR, it is faster decomposition at the TGA curves for MTR after adsorption of Hg(II) than previous studies. Therefore, according to the infrared spectra in Figure 2 and the TGA in Figure 3, the proposed structure of the novel prepared resin is shown in Figure 4.

**Scanning electron microscope**

The morphologies and surface compositions of MTR before and after Hg(II) adsorption were characterized by SEM and shown in Figure 5. Apparently, the smooth surface of MTR turned thicker and coarser with granular flake material after adsorption of Hg(II), which suggested that the mercury was loaded on the surface of the resin.

**Effect of pH on Adsorption Capability for Hg(II), Zn(II), Cu(II), Ni(II), Cd(II), and Co(II)**

The pH of an aqueous solution is a very important factor for metal–chelate formation and in solid phase extraction processes. In view of it, the pH values of the model solutions, 30 mL of each and each containing 10 mg of Hg(II), Zn(II), Cu(II), Ni(II), Cd(II), and Co(II) metal ions, were tested on the range pH 3.0–7.0 using HAc–NaAc buffer solutions at 25 °C for 24 h. As the hydrolysis of metal ions at higher pH, the experiment set a maximum pH = 6.0. The results are
shown in Figure 6. It is obvious that the adsorption capacity of MTR for Hg(II) is far greater than for other metal ions, demonstrating that Hg(II) ion can be easily separated from these metal ions using AR. The highest adsorption capacity for Hg(II) was 343.8 mg/g at pH = 6.0 in the HAc – NaAc system, suggesting high selectivity and adsorption capacity for Hg(II). Therefore, pH = 6.0 was selected for subsequent studies.

**Effect of contact time and temperature**

The effect of the contact time on the adsorption of Hg(II) was tested on the time range 1–30 h under pH 6.0 at 288, 298, and 308 K. The change in the uptake of Hg(II) by the resin is shown in Figure 7. It is obtained that Hg(II) was adsorbed rapidly at different temperatures within a few hours (0–13 h), and then absorption increased slowly until the equilibrium state was reached at 21 h. After 21 h, the amount of Hg(II) adsorption did not increase with further post exposure. As is shown, the equilibrium adsorption capacity was found to increase within the range of reaction temperature (288–308 K), which implies that the adsorption of Hg(II) onto the adsorbent is endothermic at higher temperature. This effect suggests that the mechanism associated with Hg(II) adsorption onto MTR involves a temperature-dependent process.
Adsorption kinetics

There are several kinetics models which can examine the mechanism of the adsorption process from a liquid phase on MTR and interpret the experimental data. It can be described by the Lagergren first-order rate expression (Marczewski et al. 2010) and second-order kinetic model equation (Ho et al. 2001) that were followed by:

\[
\begin{align*}
\log (Q_e - Q_t) &= \log Q_1 - \frac{k_1}{2.303} t \\
\frac{t}{Q_t} &= \frac{1}{k_2 Q_2^2} + \frac{t}{Q_2}
\end{align*}
\]

(4) \hspace{1cm} (5)

where \(Q_e\) and \(Q_1\) are the amounts of Hg(II) adsorbed on the adsorbent at equilibrium and at various time (mg/g), \(Q_1\) and \(Q_2\) are the calculated adsorption capacities of the Lagergren first-order model and the second-order model (mg/g), respectively, and \(k_1\) and \(k_2\) are the rate constants of the Lagergren first-order model (min\(^{-1}\)) and the second-order model mL/(min·mg). The fitting validity of these models is traditionally checked by the linear plots of \(\log (Q_e - Q_t)\) versus \(t\) and \(t/Q_t\) versus \(t\), respectively.

As shown in Table 1, the correlation coefficient \(R_2^2\) for the second-order model is better than the correlation coefficient \(R_1^2\) for the Lagergren first-order model. Moreover, the experimental–calculated capacity of the second-order
model produces good fittings which indicated that the interactions would follow the second-order kinetics. This meant that the second-order model can describe the Hg(II)/MTR adsorption system studied in our work, and the rate-controlling step of the adsorption process is governed by chemisorption.

### Adsorption isotherms

To further explore the adsorption mechanism, we used Langmuir (Langmuir et al. 1918) and Freundlich (Shafqat et al. 2014) isotherm models to analyze the equilibrium data for the experiments carried out at different temperatures under pH 6.0. About 15.0 mg of adsorbent was added in a range of 0.267 mg/mL to 0.467 mg/mL Hg(II) solutions. Langmuir and Freundlich equations are widely used in equilibrium-based isotherm models. The linear form of the Langmuir isotherm was represented by the following equation:

\[
\frac{C_e}{Q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o}
\]

where \(Q_o\) is the maximal adsorption capacity (mg/g), \(Q_e\) is the equilibrium Hg(II) concentration on the adsorbent (mg/g), and \(K_L\) is the Langmuir constant. \(K_F\) is the Freundlich constant and \(n\) is an empirical constant related to the magnitude of the adsorption driving force. The linear Langmuir and Freundlich plots can be obtained by plotting \(C_e/Q_e\) versus \(C_e\) and \(\log Q_e\) versus \(\log C_e\), respectively. The data in Table 2 present the results along with associated correlation coefficients \(R^2\). They reveal that the adsorption of Hg(II) onto MTR resin fitted better to the Langmuir model than the Freundlich model at investigated temperatures. Those results indicated that the adsorption of Hg(II) onto MTR resin was a monolayer type – a layer of metal ions on the adsorbent surface appeared. The increase of the \(Q_o\) value with increasing temperature signified that the process needed thermal energy (endothermic) and that there was a chemical interaction between the adsorbent and the adsorbate.

### Thermodynamic parameters

The temperature of this adsorption experiment was varied to study the thermodynamic feasibility of the adsorption process. Adsorption of 10 mg/30 mL Hg(II) was performed (with 15.0 mg adsorbent dose) at 288, 298, and 308 K. Solution pH was maintained at 6.0. Thermodynamic parameters such as the Gibbs free energy (\(\Delta G\)), enthalpy (\(\Delta H\)), and entropy (\(\Delta S\)) for the adsorption process can be determined by using following equations (Liu et al. 2014):

\[
\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]

\[
\Delta G = \Delta H - T\Delta S
\]

where \(R\) is the gas constant and \(T\) is the absolute temperature as mentioned in the Arrhenius equation. \(K\) is the distribution coefficient of the adsorbate \((Q_o/C_e)\). The plot of \(\ln K\) versus \(1/T\) gives a straight line from which \(\Delta H\) and \(\Delta S\) are calculated based on the slope and intercept of the linear form. The negative value of \(\Delta G\) \((-6.64 \text{ kJ/mol to } -8.11 \text{ kJ/mol})\) confirms the spontaneity of the adsorption process with increasing temperature and a positive value.

### Table 1 | Kinetics model constants for adsorption of Hg(II) by MTR

<table>
<thead>
<tr>
<th>(T (K))</th>
<th>(Q_o) (exp) (mg/g)</th>
<th>First-order kinetics (k_1 \text{ (h}^{-1})</th>
<th>(Q_1) (mg/g) (R^2)</th>
<th>Second-order kinetics (k_2 \text{ (g/(mg·h))})</th>
<th>(Q_2) (mg/g) (R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>297.1</td>
<td>0.351</td>
<td>287.2</td>
<td>0.9604</td>
<td>3.82 \times 10^{-4}</td>
</tr>
<tr>
<td>298</td>
<td>343.8</td>
<td>0.433</td>
<td>323.5</td>
<td>0.9662</td>
<td>4.79 \times 10^{-4}</td>
</tr>
<tr>
<td>308</td>
<td>356.6</td>
<td>0.571</td>
<td>336.9</td>
<td>0.9571</td>
<td>6.10 \times 10^{-4}</td>
</tr>
</tbody>
</table>

### Table 2 | Parameters for adsorption isotherms of Hg(II) by MTR resin

<table>
<thead>
<tr>
<th>(T(K))</th>
<th>(Q_0) (mg/g)</th>
<th>(K_L) (mL/mg)</th>
<th>(R^2)</th>
<th>(n)</th>
<th>(K_F) ((mg/g) (mg/mL) (^{1/n}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>358.7</td>
<td>35.3</td>
<td>0.9609</td>
<td>7.07</td>
<td>453.3</td>
<td>0.8025</td>
</tr>
<tr>
<td>298</td>
<td>391.9</td>
<td>48.2</td>
<td>0.9718</td>
<td>6.92</td>
<td>486.7</td>
<td>0.8390</td>
</tr>
<tr>
<td>308</td>
<td>421.2</td>
<td>62.6</td>
<td>0.9871</td>
<td>6.57</td>
<td>506.1</td>
<td>0.8339</td>
</tr>
</tbody>
</table>

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of \( \Delta H \) (14.49 kJ/mol) suggests that the adsorption was endothermic in nature. In addition, the value of \( \Delta S \) (734 kJ/mol) was found to be positive due to the exchange of the metal ions with more mobile ions present on the exchanger, which would cause increase in the entropy, during the adsorption process (Jia et al. 2014).

**Desorption and regeneration studies**

Whether an adsorbent is economically attractive in the removal of metal ions from aqueous solution depends not only on the adsorptive capacity, but also on how well the adsorbent can be regenerated and recycled. For repeated usage of an adsorbent, adsorbed metal ions should be easily desorbed under suitable conditions. In this work, desorption of the adsorbed mercury ions from MTR were studied. The results are shown in Table 3. It was found that 2.0 mol/l HCl-5 wt% thiourea solution provided effectiveness of the desorption of Hg(II) from MTR resin. The amount of adsorption of Hg(II) was not significantly changed up to 5 cycles and the desorption efficiencies were above 91.3%. Therefore, the adsorbent material could be successfully applied for the recovery of Hg(II) from aqueous solutions.

**Dynamic adsorption and desorption**

Batch experimental data are frequently difficult to apply directly to fixed-bed adsorption because isotherms are unable to give accurate data for a dynamically operated column. The fixed-bed column operation allows more efficient utilization of the adsorptive capacity than the batch process. The total adsorption quantity of Hg(II) \( Q \) (mg/g) in the column can be calculated from the following equation (Barrow et al. 2012):

\[
Q = \int_0^V \frac{(C_0 - C_i)}{m} \, dV
\]

where \( C_0 \) and \( C_i \) are metal ion concentrations in the influent and effluent, respectively. \( m \) is the total weight of the adsorbent loaded in the column, and \( V \) is the volume of metal solution passed through the column. The capacity value \( Q \) was obtained by graphical integration to be 473.9 mg/g. Successful design of a column sorption process requires prediction of the concentration time profile or breakthrough curve for the effluent. Traditionally, the Thomas model is used to fulfill the purpose. The model has the following form (Schulze-Halberg et al. 2013):

\[
\ln \left( \frac{C_0}{C_e} - 1 \right) = \frac{K_T q m}{\theta} - \frac{K_T C_0}{\theta} V
\]

where \( K_T \) is the Thomas rate constant mL/(min·mg), \( q \) is the volumetric flow rate (mL/min), and \( m \) is the mass of the resin (g). The kinetics coefficient \( K_T \) and the adsorption capacity \( Q \) of the column can be determined from a plot of \( \ln \left( [C_0/C_e] - 1 \right) \) versus 1/q at a certain flow rate. The theoretical predictions based on the model parameters were compared with the observed data as shown in Table 4. It is shown that the experimental data were well fitted by the Thomas model with a high \( R^2 \) value. Under the same flow rate, with the increase of Hg(II) ion concentration, resin for metal ions adsorption rate increases, shorter time of arrival in penetrating point, the outflow curve slope increases, \( K_T \) value decreases, the saturated adsorption quantity increases, but easy to lead to breakthrough point in advance, column efficiency decline. Choose for both adsorption column efficiency and utilization, the concentration of 0.1 mg/mL is appropriate.

With respect to the dynamic desorption of Hg(II) from MTR resin, the 2.0 mol/L HCl-5 wt% thiourea eluent was

<table>
<thead>
<tr>
<th>Eluent</th>
<th>Concentration (mol/l)</th>
<th>Desorption rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl-5%thiourea</td>
<td>0.5</td>
<td>88.9</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>98.3</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>99.1</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>100</td>
</tr>
<tr>
<td>HNO₃</td>
<td>1.0</td>
<td>56.7</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>63.4</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>67.9</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>71.8</td>
</tr>
<tr>
<td>HCl</td>
<td>1.0</td>
<td>36.5</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>43.5</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>53.4</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>58.3</td>
</tr>
</tbody>
</table>

**Table 4** | Thomas adsorption model parameters of Hg(II) by MTR

<table>
<thead>
<tr>
<th>Resin</th>
<th>( C_o ) (mg/mL)</th>
<th>( \theta ) (mL/min)</th>
<th>( K_T ) (mL/min·mg/l)</th>
<th>( Q_1 ) (mg/g)</th>
<th>( Q_2 ) (mg/g)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTR</td>
<td>0.10</td>
<td>0.1</td>
<td>0.113</td>
<td>361.8</td>
<td>356.1</td>
<td>0.980</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.2</td>
<td>0.127</td>
<td>351.6</td>
<td>348.5</td>
<td>0.973</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.1</td>
<td>0.151</td>
<td>361.8</td>
<td>356.1</td>
<td>0.979</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.1</td>
<td>0.157</td>
<td>367.4</td>
<td>371.3</td>
<td>0.959</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>0.1</td>
<td>0.160</td>
<td>473.9</td>
<td>475.1</td>
<td>0.962</td>
</tr>
</tbody>
</table>
employed. The desorption curve was plotted with the effluent concentration ($C_e$) versus elution volume ($V$) from the column at a flow rate of 0.1 mL/min. As shown in Figure 8, a sharp increase of Hg(II) concentration at the beginning of acid elution was observed, the total volume of eluent was 30 mL, after which further desorption was negligible. Therefore, the 2.0 mol/L HCl – 5 wt% thiourea eluent could help in easy handling and removal of Hg(II).

The dynamic adsorption of resin after regeneration

The MTR resin regeneration after with the initial concentration of 0.1 mg/mL, the flow rate of 0.1 mL/min column for dynamic adsorption. The regenerated resin adsorption efficiency (eta) is defined as the following equation:

$$\eta(\%) = \frac{Q_0}{Q_n} \times 100\%$$

(12)

where $Q_0$ is the resin column for the first time the dynamic adsorption capacity (mg/g); $Q_n$ is the resin column regeneration after the dynamic adsorption capacity (mg/g); $n = 0, 1, 2, 3$.

By Figure 9, it can be concluded that resin for Hg(II) adsorption breakthrough point slightly ahead of time, but after three dynamic regeneration adsorption efficiency reach 95.1%, which shows the resin regeneration, still have better adsorption ability, can be repeated in the actual use, save resources, reduce the cost.

CONCLUSIONS

In this research, a novel chloromethylated polystyrene-2-mercapto-1,3,4-thiadiazole chelating resin which has N donor atoms and S donor atoms has been synthesized. FTIR, elemental, TGA and SEM results indicate that the immobilization of MT onto PS-Cl is accomplished. Furthermore, the results of the present investigation show that MTR resin is a potentially useful adsorbent for the separation of Hg(II) ions from mixed solution. The kinetics of adsorption of Hg(II) on MTR resin are complex and while the results are tested with models based on the Lagergren first-order and pseudo-second-order, close conformity could be obtained with pseudo-second-order mechanism. It is evident from the experimental data that the adsorption of Hg(II) ions onto MTR resin fitted well with Langmuir isotherm model than Freundlich isotherm models. The adsorption process is endothermic and spontaneous at ambient higher temperatures. Complete desorption of Hg(II) was achieved by using 5 wt% thiourea – 2.0 mol/L HCl solution, and the regenerated adsorbents could be reused with little loss of adsorption capacity. Finally, the MTR resin could provide a potential application for an efficient process of Hg(II) recovery from aqueous solutions.

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