J. Iran. Chem. Soc., Vol. 7, No. 3, September 2010, pp. 791-798.

JOURNAL OF THE
Iranian
Chemical Society

Readily Prepared Polystyrene-Bound Pyridine-2,6-dicarboxylate and Its Application for Removal of Mercury Ions

M.R. Iravani, S. Tangestaninejad*, M.H. Habibi and V. Mirkhani
Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran

(Received 20 September 2009, Accepted 4 February 2010)

Commercially available chloromethylated polystyrene (cross-linked with 2% divinylbenzene) was used to prepare novel and stable polymer supported pyridine-2,6-dicarboxylate. This polymer was found to accelerate the selective removal of Hg(II) from aqueous solutions containing different amounts of Hg(II) (10-100 ppm). Adsorption rate was high at the beginning and then equilibrium was reached in about 25 min. Maximum Hg(II) adsorption capacity of the resin was about 41.5 mg/g of the dry polymer. The Hg(II) adsorption ability increased with the increase in pH, in the range where the solubility of the Hg(II) was not affected by pH. More than 95% of the adsorbed Hg(II) was desorbed in 15 min by using 0.1 M HNO_3 as an elution agent. The regeneration of this resin by strong acid was feasible and desorption ratio was very high (up to 96%).

Keywords: Polystyrene, Polymer supported, Pyridine dicarboxylate, Mercury ion removal

INTRODUCTION

Contamination of water by heavy metal ions is increasingly becoming serious ecological and health problems due to their toxic effects even at very low concentrations [1]. Mercury is one of the most dangerous heavy metals. Inorganic and organic mercury compounds may be present in natural water and can be concentrated in various organisms like fish [2]. Mercury metal itself is also toxic. It is well-known that mercury(II) compounds are converted into more dangerous methylmercury species by aquatic organisms [3]. This poisonous compound concentrates in the blood and has an immediate and permanent effect on the brain and central nervous system [4]. Accordingly, mercury must be removed or reduced to very low levels in wastewater generated in industries such as metal smelting and caustic-chlorine production in mercury cells, metal processing, plating and metal finishing. These effluents require chemical treatment before they can be discharged.

A number of different technologies have been developed to recover mercury from wastewater [5-8]. Adsorption has been reported to be a promising technique for the removal of heavy metal ions [9]. Certain polymer sorbents consist of a metal chelate forming agent which interacts specifically with the heavy metal ions, and a carrier matrix which may be an inorganic material (*e.g.* activated carbon, alumina, silica, or glass) or polymeric microspheres [10]. One approach for the removal of mercury ions has been the use of cross-linked polymers modified with ligands of varying ionic affinities. 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], a resin incorporating imidazolylazo function in a polystyrene bed [12], poly(4-vinylpyridine) hydrochloride resin [13], polymer-

---

*Corresponding author. E-mail: stanges@sci.ui.ac.ir

supported thiacrown([14] aneS_4 and [17]aneS_5) [14], dithiocarbamate-incorporated monosize polystyrene [15], modified chloromethylated polystyrene-PAN [16], 6-mercaptopurinylazo resin on polystyrene-divinylbenzene [17], *N*-chlorosulfonamide groups into polystyrene-divinylbenzene and polyacrylamide onto functionalized polystyrene-divinylbenzene [18], grafted acrylate esters from cross-linked polystyrene beads [19], poly(2-hydroxyethyl methacrylate) gel beads modified with poly(ethyleneimine) [20], polystyrene-supported amines [21], immobilized *N*-methyl-*D*-glucamine [22] and polymeric thiacalix[4]arenas [23] were synthesized and used for the selective removal of mercury ions. In this study, we report a convenient method for the synthesis of a new resin containing pyridine-2,6-dicarboxylic acid (PDC) on chloromethylated polystyrene (CMP) for the removal of mercury(II) in environmental samples.

EXPERIMENTAL

Materials and Reagents

Chloromethylated polystyrene (CMP), N,N-dimethyl formamide (DMF), ethanol, chloroform, nitric acid, sodium acetate, mercury(II) acetate, 4,4′-bis(dimethylamino) thiobenzophenone (TMK) and pyridine-2,6-dicarboxylic were prepared from Merck Chem. Co. (Germany) and Aldrich Chem. Co. (USA) and used without further purification. Deionized water was used for the preparation of all solutions.

Apparatus

A Shimadzu UV-VIS spectrophotometer (Model UV160) was used for absorbance measurements. Elemental analyses were performed with a Perkin-Elmer 2400 Microanalyser. The adjustment of pH was done with a Metrohm pH meter (Model 827). FT-IR spectra (KBr pellets) was recorded on a Shimadzu (IRPrestige-21) spectrophotometer and thermogravimetric analysis was done on Mettler TA4000 (Model TG 50).

Preparation of Resin (PDC-CMP)

To a solution of PDC (0.5 g) in DMF (40 ml) was added CMP (4 g). The mixture was vigorously stirred and refluxed in DMF for 24 h. After cooling, the resin was collected by filtration, washed thoroughly with DMF, water, ethanol and chloroform, successively, and dried in vacuum at room temperature for several hours. The IR spectra of the reactants and products were recorded. Elemental analysis and TG analysis of the resin were performed.

Stability of the Resin

A 500 mg portion of the resin was stirred with 100 ml of 1-12 M HNO_3 and 1-12 M NaOH for 7 days, then filtered off and the exchange capacity for mercury(II) was determined.

Removal of Hg(II) by PDC-CMP

The Hg(II) solutions were prepared by dissolving $Hg(CH_3CO_2)_2$ (pH < 7) in deionized water. Adsorption of Hg(II) from aqueous solutions was investigated in batch experiments. The effect of the Hg(II) initial concentration and pH of the medium on the adsorption rate and capacity were studied. An aqueous solution of Hg(II) (20 ml, containing different amounts of Hg(II) in the range of 10-100 mg l^{-1}) was incubated with 100 mg of PDC-CMP resin at pH 5.5 and stirred at room temperature. After equilibration, the resins were filtered and washed with deionized water, and the filtrates were analyzed for determination of the remaining Hg(II). The IR spectra of the resin before and after the reaction with Hg(II) ions was recorded.

Mercury(II) Ion Capacity as a Function of pH

A batch technique was used, taking metal ion in excess of the resin. Capacities were determined in pH range of 1.0-8.0 (adjusted with HCl and NaOH). A 100 mg of the resin was taken in a beaker and mercury(II) ion solution (excess) was added. A 0.2 M sodium acetate buffer was used to adjust the pH of the solution to the desired level. The mercury(II) concentration was determined spectrophotometrically.

Determination of Mercury(II) Concentration

Thio-Michler's Ketone, 4,4′-bis(dimethylamino) thiobenzophenone (TMK), is a useful reagent for the sensitive spectrophotometric determination of silver and mercury [24]. In the reaction of mercury(II) ions with TMK, the ions are reduced to Hg(I) and then complexed. The color change has been recommended for the selective and sensitive spectrophotometric determination of mercury [25].

To a weakly acidic sample solution containing about 20 µg of Hg(II) in 10 ml, were added 2 ml acetate buffer (pH 3.9: obtained by dissolving 5 g $CH_3CO_2Na.3H_2O$ in 11.5 ml of glacial acetic acid and in 100 ml of water), 2.5 ml DMF and 2.5 ml TMK solution (0.001 M in DMF, 28.5 mg TMK in 100 ml). The solution was diluted with water to 25 ml, and the absorbance of the solution was measured after 10 min at 560 nm.

Equilibrium Time

To determine the equilibrium time for the adsorption of mercury(II) ions on the resin, at pH 5.5, the absorbed metal ions were determined at regular time intervals.

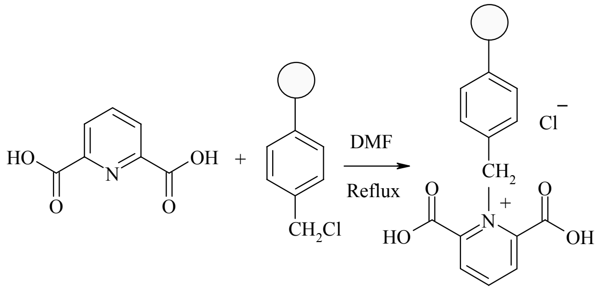
Regeneration of the Resin

To a 500 mg of the resin loaded with Hg(II) ions, was added 50 ml of HNO_3 0.1 M and the amount of Hg(II) ions desorbed in 15 min was measured.

RESULTS AND DISCUSSION

Synthesis of Resin (PDC-CMP)

In the past decade, metal coordinated polymers constructed by multi-carboxylate ligands have attracted extensive interest in virtue of their structural diversities and potential application in catalysis, ion exchange and adsorption [26,27]. In this respect, researchers have focused on transitional metal coordination polymers with all kinds of multi-carboxylate ligands, such as benzene-1,2,4,5-tetracarboxylate, benzene-1,3,5-tricarboxylate and pyridine-2,6-dicarboxylate [28-30]. In this study, we attempted to develop a new metal-chelating sorbent system in which chloromethylated polystyrene microspheres carrying pyridine-2,6-dicarboxylate were functional groups. We selected pyridine-2,6-dicarboxylate as a metal-chelate forming ligand because it forms very stable chelates with many metal ions [31]. To put it briefly, the chloromethylated polystyrene was functionalized with pyridine-2,6-dicarboxylate (Scheme 1).



Scheme 1

Chloromethylated polystyrene, (cross-linked with 2% divinylbenzene, 4-5% Cl content, 1.14-1.40 mmol g^{-1} Cl), was treated with an appropriate quantity of pyridine-2,6-dicarboxylic acid in refluxing DMF for 24 h. The resulting PDC-CMP resin was characterized by elemental analysis and IR spectroscopy. The nitrogen content of this resin was 1.24%. According to this value, the degree of pyridine-2,6-dicarboxylate, which was introduced into the polymer composition, was 0.886 mmol g^{-1} of support. This shows that only 63-77% of the total chlorine was substituted by pyridine-2,6-dicarboxylic acid.

The comparison of the IR spectra of CMP and PDC-CMP clearly indicated that the pyridine-2,6-dicarboxylic acid had been successfully introduced to the chloromethylated polystyrene (Fig. 1). In order to examine the thermal stability of CMP and PDC-CMP resin, differential thermal gravimetric (DTG) were carried out between 30 and 700 °C. These DTG curve also shows that pyridine-2,6-dicarboxylate group was bonded to polystyrene and the PDC-CMP resin a thermal stability up to 383 °C (Fig. 2).

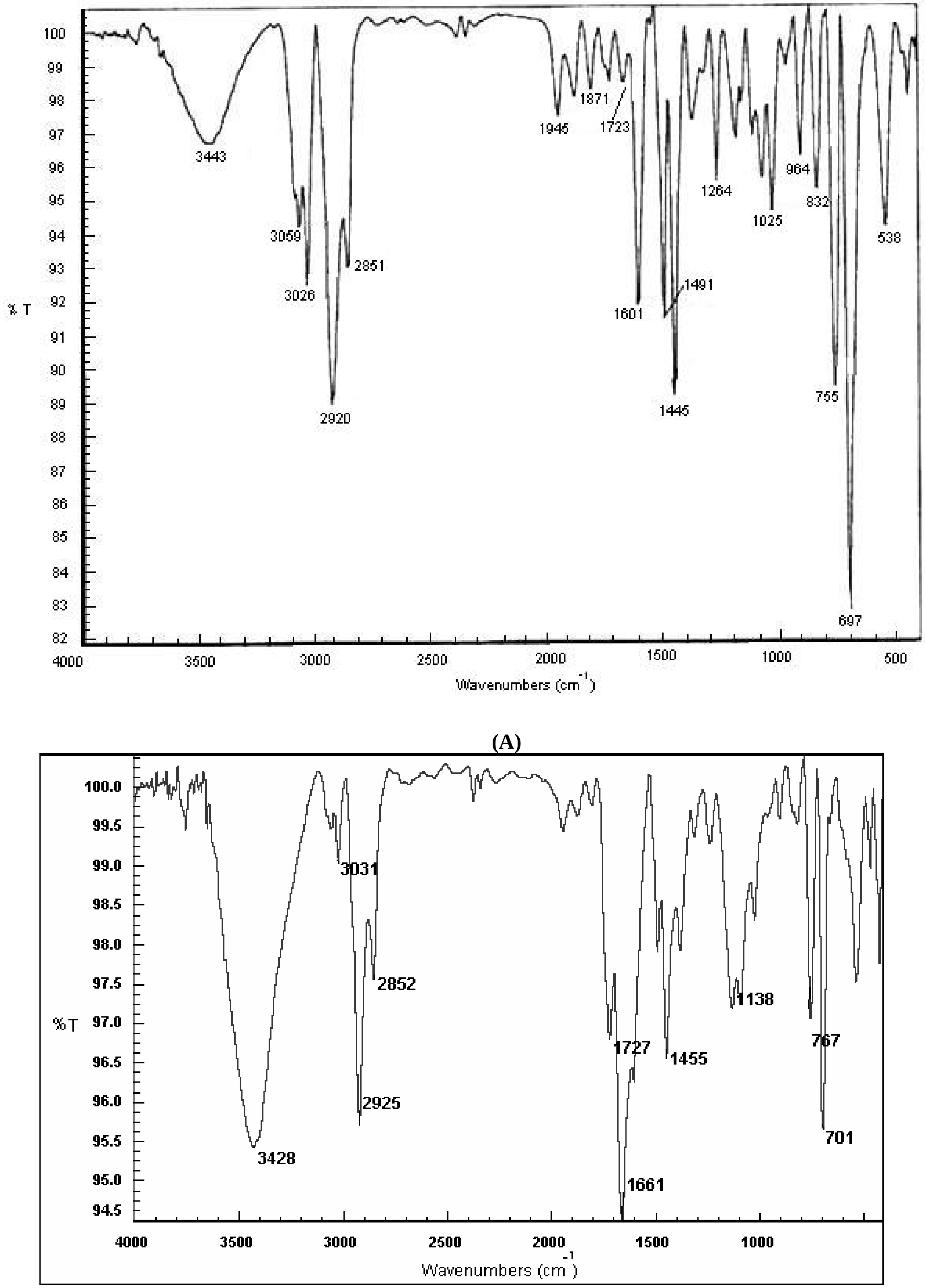
Adsorption of Hg(II) Ions

Scheme 2 shows the reaction between the PDC-CMP resin and mercury(II) ions, which is known in organic chemistry as mercuration reaction.

Spectrophotometric determination of mercury(II) ions with TMK. A plot of standard adsorption of mercury(II) ions with TMK is presented in Fig. 3 which shows that there is a linear relation between absorbance and mercury(II)-TMK complex.

Adsorption rate. Figure 4 shows the adsorption rates of Hg(II) on the resin from aqueous solutions containing different amounts of Hg(II) (in the range of 10-100 mg l^{-1}) at a constant pH of 5.5. As can be seen, mercury adsorption capacity increases with time during the first 25 min and then levels off according to the equilibrium adsorption capacity. In addition, adsorption of Hg(II) was quite fast especially when Hg(II) concentration was high.

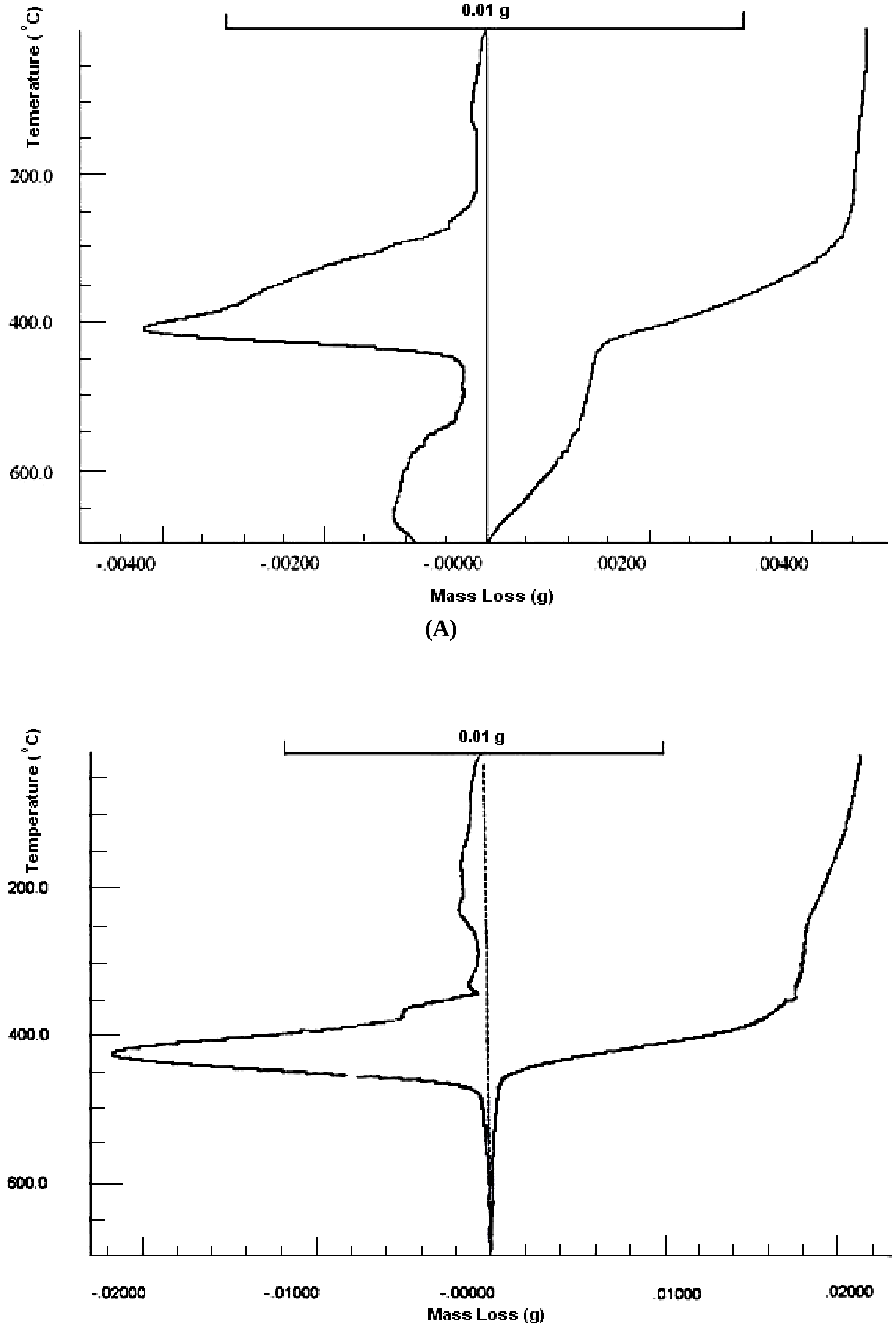
Effect of initial concentration of Hg(II). In Fig. 5, the effect of initial concentration of Hg(II) on the adsorption capacity of the resin has been shown. Hg(II) adsorption capacity of the resin increases initially with the increasing concentration of Hg(II) and then reaches a plateau at Hg(II)



(A)

(B)

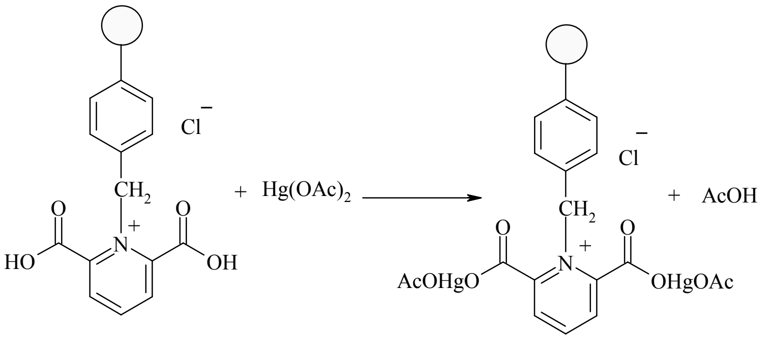
Fig. 1. FT-IR spectra of: (A) Chloromethylated polystyrene; and (B) polystyrene-bound pyridine-2,6-dicarboxylic acid.



(A)

(B)

Fig. 2. DTG curve of: (A) chloromethylated polystyrene; and (B) polystyrene-bound pyridine-2,6-dicarboxylic acid.



Scheme 2

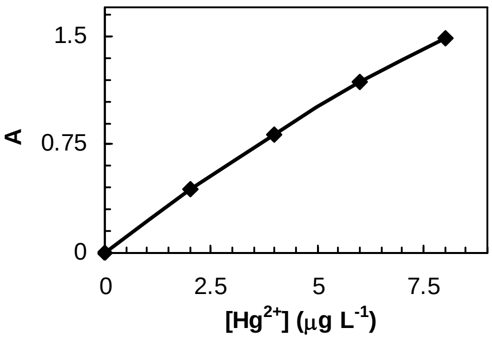


Fig. 3. Calibration plot of the absorbance of Hg(II)-TMK complex versus concentration of mercury ion.

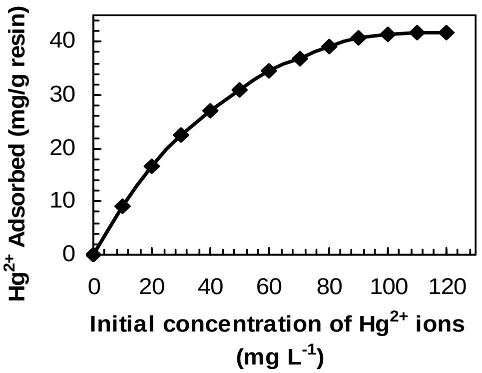


Fig. 5. Adsorption capacity of Hg(II) into resin.

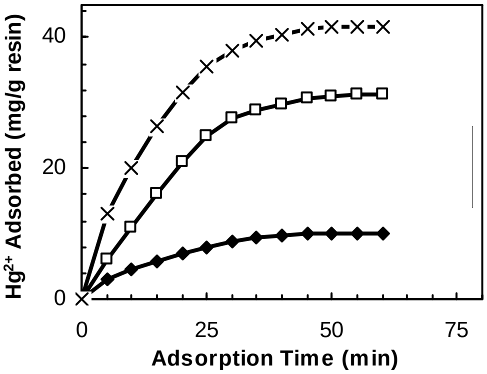


Fig. 4. Adsorption rates of Hg(II) on the resin: (◆) 10 mg l^{-1}, (□) 50 mg l^{-1}, (-×-) 100 mg l^{-1}.

concentration of 50 mg l^{-1}, which represents saturation of the active binding sites of the carboxylate functional groups (which are available for Hg(II) on the microsphere). The maximum Hg(II) adsorption capacity is 41.5 mg/g.

Effect of pH. Adsorption of heavy metal ions by resins is strongly dependent on pH [32]. In the absence of complexing chemical substances, the precipitation of the heavy metal ions is affected by the concentration. Precipitation of mercury ions becomes significant at pH 8.0. The theoretical and the experimental precipitation curves show that precipitation above this pH also depends on the concentration of Hg(II) in the medium [33]. In this study, we repeated the batch adsorption studies at different pHs in the range 1.0-8.0.

Figure 6 shows the effect of pH on the specific adsorption (*i.e.*, adsorption by chelating with the carboxylate groups attached on the polystyrene microspheres) of Hg(II).

As can be seen in Fig. 6, adsorption of Hg(II) increased with the increase in pH and then reached almost a plateau value around pH 6.

Regeneration

Desorption of the adsorbed Hg(II) ions from the resin was

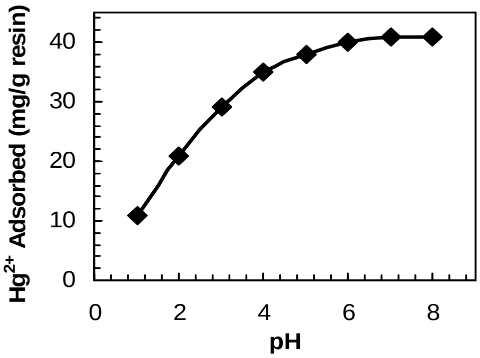


Fig. 6. Effect of pH on the adsorption of Hg(II) on the resin.

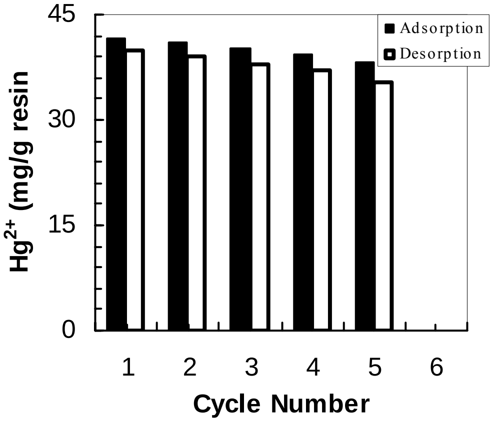


Fig. 7. Adsorption-desorption of Hg(II) ions

studied in a batch experimental set-up. The resin loaded (at pH 7.0) with Hg(II) ions was placed within the desorption medium containing 0.1 M HNO_3 and the amount of Hg(II) ions desorbed in 15 min was measured. The desorption ratio was then calculated by using the difference. Figure 7 shows the results of desorption studies.

The results indicated that the regeneration of the resin by strong acid was feasible. Desorption ratio was very high (up to 96%). It is obvious that chelate-forming interactions between incorporated carboxylate groups and Hg(II) ions are weaker with decreasing pH. The adsorption capacity of the recycled resin can still be maintained at 95% level at the fifth cycle.

CONCLUSIONS

Polystyrene carrying carboxylates group was used for adsorption-desorption of Hg(II) ions from aqueous solution under different experimental conditions. High adsorption rates were observed at the beginning of the adsorption process. The maximum Hg(II) adsorption capacity of pyridine-2,6-dicarboxylate-incorporated microspheres was 41.5 mg/g resin. Adsorption amounts of Hg(II) ions increased with increasing pH.

ACKNOWLEDGEMENTS

We are thankful to the Isfahan University Research Council for the partial support of this work.

REFERENCES

[1] S. Rapsomanikis, P.J. Craig, Anal. Chim. Acta 248 (1991) 563.
[2] J.E. Fergusson, The Heavy Elements: Chemistry, Environmental Impact and Health Effect, Pergamon Press, Oxford, 1990, p. 157.
[3] H. Emteborg, E. Bulska, W. Frech, D.C. Baxter, J. Anal. At. Spectrom. 7 (1992) 405.
[4] E.P.C. Lai, B. Wong, B.V.A. Vandemoot, Talanta 40 (1993) 1097.
[5] J.H. Pavlish, E.A. Sondreal, M.D. Mann, E.S. Olson, K.C. Galbreath, D.L. Laudal, S.A. Benson, Fuel Process. Technol. 82 (2003) 89.
[6] W.J. O'Dowd, R.A. Hargis, E.J. Granite, H.W. Pennline, Fuel Process. Technol. 85 (2004) 533.
[7] J. Barron-Zambrano, S. Laborie, P. Viers, M. Rakib, G. Durand, J. Membr. Sci. 229 (2004) 179.
[8] M.M. Matlock, B.S. Howerton, D.A. Atwood, J. Hazard. Mater. 84 (2001) 73.
[9] A.G. Howard, M.H. Arbab-Zavar, Talanta 26 (1979) 895.
[10] Y.K. Lee, K.J. Whang, K. Ueno, Talanta 22 (1975) 535.
[11] R.R. Navarro, K. Sumi, N. Fujii, M. Matsumura, Water Res. 30 (1996) 2488.
[12] D. Das, A.K. Das, C. Sinha, Talanta 48 (1999) 1013.
[13] B.L. Rivas, H.A. Maturana, M. Luna, J. Appl. Polym. Sci. 74 (1999) 1557.
[14] T.F. Baumann, J.G. Reynolds, G.A. Fox, React. Funct. Polym. 44 (2000) 111.
[15] A. Denizli, K. Kesenci, Y. Arica, E. Piskin, React.

Funct. Polym. 44 (2000) 235.
[16] M.A.H. Hafez, I.M.M. Kenawy, M.A. Akl, R.R. Lashein, Talanta 53 (2001) 749.
[17] B.C. Mondal, D. Das, A.K. Das, Anal. Chim. Acta 450 (2001) 223.
[18] H. Bulbul Sonmez, B.F. Senkal, D.C. Sherrington, N. Bicak, React. Funct. Polym. 55 (2003) 1.
[19] A. Denizli, S. Senel, G. Alsancak, N. Tuzmen, R. Say, React. Funct. Polym. 55 (2003) 121.
[20] H. Bulbul Sonmez, N. Bicak, React. Funct. Polym. 61 (2004) 33.
[21] X. Zhu, S.D. Alexandratos, Ind. Eng. Chem. Res. 44 (2005) 8605.
[22] X. Zhu, S.D. Alexandratos, Ind. Eng. Chem. Res. 44 (2005) 7490.
[23] B. Tabakci, A.D. Beduk, M. Tabakci, M. Yilmaz, React. Funct. Polym. 66 (2006) 379.
[24] K.L. Cheng, B.L. Goydish, Microchem. J. 10 (1966) 158.
[25] G. Ackermann, H. Roder, Talanta 24 (1977) 99.
[26] B. Chen, M. Eddaoudi, S.T. Hyde, M. O'Keeffe, O.M. Yaghi, Science 291 (2001) 1021.
[27] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage, Science 295 (2002) 469.
[28] L. Pan, N.W. Zheng, Y. Wu, S. Han, R. Yang, X.Y. Huang, J. Li, Inorg. Chem. 40 (2001) 828.
[29] R. Murugavel, D. Krishnanurthy, M. Sathiyendiran, J. Chem. Soc., Dalton Trans. (2002) 34.
[30] M.J. Plater, M.R. St, J. Foreman, R.A. Howie, J.M.S. Skakle, A.M.Z. Slawin, Inorg. Chim. Acta 315 (2001) 126.
[31] E.W. Lee, Y.J. Kim, D.Y. Jung, Inorg. Chem. 41 (2002) 501.
[32] Y.Konishi, S. Asai, Y. Midoh, M. Oku, Sep. Sci. Tech. 28 (1993) 1691.
[33] B.E. Reed, M.R. Matsumoto, Sep. Sci. Tech. 28 (1993) 2179.