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Adsorption and Separation of Mercury: Sorption-Desorption of Hg^{2+} with Cross-Linked Graft Copolymer of Acrylic Acid and its Application in the Metal Ion Separation Process

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A selective and reliable method has been developed for the extraction and separation of mercuric ion with cross-linked graft copolymer of acrylic acid based on sorption-desorption studies. The graft copolymer acts as an ion exchanger. The physico-chemical properties of the exchanger, and optimum pH, time, and temperature for Hg^{2+} adsorption were determined. Metal ion adsorption kinetics, isotherms, and thermodynamics have been studied. A plausible mechanism for mercury ion extraction has been suggested. Mercuric ion has been separated quantitatively from various synthetic mixtures containing metal ions (Ni^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+}).

Keywords adsorption; graft copolymer; Hg^{2+}; ion-exchange; separation

INTRODUCTION

The elemental form of mercury is toxic (1), but methyl mercury (CH_3Hg^+) produced by aerobic microorganism causes serious health hazards as they bind the thionol (−SH) group in proteins leading to neurological diseases and kidney failure (1). Several industries (such as mercury batteries and Hg vapor lamp), pesticides, and fungicides are major sources of mercury (1) in our environment. Global input of mercury (1) is approximately 10^{10} g per year. The permissible limit of mercury is 1 ppb (parts per billion) in drinking water (1). Many methods (1) such as solvent extraction, ion-exchange, and physical adsorption are available for removing mercury ion. However, mercury ion adsorption onto solid polymer surface (2,3) (solid phase extraction, SPE) is now considered one of the most promising techniques due to its cost effectiveness, eco-friendliness, and rapidness. At present several researchers (4–7) are engaged in synthesizing suitable polymers having selective mercury ion binding capacity. The cross-linked poly acrylic acid (1) is reported to be a good extractor for Hg^{2+}. However, the physico-chemical properties and selectivity of the cross-linked poly acrylic acid may be improved further by graft copolymerization.

In the present work, a novel procedure for extraction and separation of mercuric ion by cross-linked graft copolymer of acrylic from polyvinyl alcohol has been developed. Under the sorption conditions, kinetic, and thermodynamic parameters are evaluated. Different adsorption isotherms have been studied and possible mechanism of metal ion binding has been discussed.

EXPERIMENTAL

Chemicals and Reagents

Poly(vinyl alcohol) (Burgoyne Burbidges, Mumbai, India), viscosity average molecular weight = 16100, degree of hydrolysis = 98.5–99.0 mol%, viscosity = 30 cps) was used. Acrylic acid (Sisco Research Laboratories Pvt. Ltd., Mumbai, India) was purified before use. Ceric ammonium sulfate (Himedia Laboratories Pvt. Ltd. Mumbai, India), glutaraldehyde (S.d fine chem. Ltd, Mumbai, India mercury nitrate (Merck, Mumbai, India), and sulfuric acid (Merck, Mumbai, India), 98%, Sp. gr. = 1.84, Mol. Wt. = 98.08) were used as received.

Equipments

Fourier transform infrared (FTIR) spectra of the polymer were recorded on Shimadzu FTIR (Model No. 8400s) using KBr pellets. Thermal analysis was conducted using a Stantum Red Craft Thermal Analyzer (STA-780) in air at a rate of 10°C/min. The amount of metal ion in the solution was measured using atomic absorption spectrophotometer (AAS, Shimadzu, AA 6300) and complexometrically. An Elico L1-120 *p*H meter, thermostat, and chromatographic column (i.d. = 0.8 cm) were used.

Synthesis of Cross-Linked Graft Copolymer

Graft co-polymerization was carried out in a two-necked round-bottomed flask at 70°C. A definite amount of PVA (0.5 g) was mixed with AA (5 mL) monomer and stirred for 15 min at room temperature. Water (20 mL),

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concentrated sulfuric acid (2 mL), and CAS (0.2 g) were then added and stirred. Nitrogen atmosphere was maintained throughout the reaction period. After two hours, copolymerization was arrested by hydroquinone and the copolymer was precipitated by using nonsolvent acetone. The precipitated polymer was separated by filtration and washed several time with 1:10 H_2SO_4 (v/v). The homopolymers PVA and PAA were separated by prolonged (24 h) extraction with cold water in a Soxhlet apparatus. The purified polymer was dried to a constant weight. The isolated copolymer was dissolved in 20 mL hot water. Glutaraldehyde (0.19 g) was then mixed with constant stirring to crosslink the grafted product. The cross-linked graft-copolymer was precipitated by cooling the reaction mixture. Finally, the sample was extracted with acetone for 72 h to dissolve all other impurities. The colorless product was dried under vacuum at 100°C for 72 h to a constant weight. The yield was 5.59 g, which indicated the little loss of monomer. The dried solid was grounded and screened through a set of sieves for the particles of the size ranged between 0.15 to 0.20 mm for conducting experiments. The formation of cross-link between the graft copolymer of acrylic acid onto PVA is confirmed through spectral (FTIR), thermal (TGA and DTA) and chemical analysis following the procedure as reported earlier (8). The novelty of the preparative path is quantitative conversion of monomer to cross-linked graft copolymer.

Sorption and Desorption Procedure

Adsorption by batch method was carried out with suitable mechanical agitation (90–100 rpm) and temperature (5 to 40°C). To determine the retention of mercury ion, 0.013 g of prepared polymer (X-AA-g-PVA) was taken into a 100 mL beaker with 10 mL metal solution. The concentration of mercuric ion in aqueous solution was kept within 200 to 1200 mg/L (ppm). The pH of the solution was maintained at 4.8. One ml solution of the sample was withdrawn each time from the reaction mixture by a syringe at a gap of fixed time interval and analyzed for kinetic study. For isothermal study, the system was agitated for 60 min and then filtered for the analysis of residual metal ion complexometrically. The selectivity of the prepared resin among various metal ions (Hg^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+}; commonly found in electroplating waste) was determined by batch method. Resin sample (0.013 g) was equilibrated for 60 min with 10 ml solution (2 mL of each metal ion solution, which contained 0.001 mole metal ion). The adsorbed metal ions were sequentially eluted (desorbed) with the selective striping agents. Finally the resin washed with 0.01 M HNO_3 several times to remove potential interfering compounds and loosely retained molecules.

Treatment of Data

All the experiments were performed at least in triplicate at room temperature (27°C). The adsorption capacity (Q, mg/g), percentage of recovery (R), degree of grafting (G) and cross-link density (q) was calculated from the following relations (1).

$$Q = \text{Metal adsorbed (mg)}/\text{Adsorbent added (g)} \quad (1)$$

$$R = \text{Metal ion eluted (g)} \times 100/\text{Metal ion originally bound to polymer (g)} \quad (2)$$

$$G = \text{Polymer grafted (g)}/\text{PVA added (g)} \quad (3)$$

$$q = M_0/M_c \quad (4)$$

Where M_0 = molecular weight of the repeating unit, M_c = average molecular mass between consecutive cross-link (1).

RESULTS AND DISCUSSION

Physical and Chemical Characteristic

The physicochemical characteristics of the synthesized polymer (X-AA-g-PVA) are given in Table 1. The surface

TABLE 1
Some physico-chemical characteristics of the synthesized polymer

Parameters	Values	Measurement process (1)
Bulk density (g/cm^3)	1.40	Specific gravity bottle (1)
Particle size (mm)	0.20	Screening (1)
Surface area (m^2/g)	84.20	Methylene blue adsorption (1)
Exchange capacity (meq H^+/g)	3.80	Volumetric method (1)
Average molecular weight between two consecutive crosslink (g/mol)	1335.60	Swelling studies (1)
Crosslink density	0.053	Swelling studies (1)
IPDT (°C)	190	Thermogravimetric analysis (15)
Pore size (A^0)	67.73	Swelling studies (1)
Degree of grafting (g)	12.00	Chemical method (1)

area of the cross-linked polymer was determined by methylene blue adsorption method (1) and was found to be 84.2 m^2/g. The exchange capacity of the exchanger (3.8 meq.H^+/g) is superior to the literature value of commercially available many cation exchangers (1) such as SRS-100 (1.85), VERSATIC-10 (2.11), and uncross-linked (9) AA-g-PVA (3.6). The average molecular weight between two consecutive cross-link, cross-link density, pore size of the material and IPDT (integral procedure decomposition) were 1335.6 g/mol, 0.053, 67.73 A^0, and 190°C respectively. Both the molecular weight and the thermal stability (IPDT) are improved in the present polymer compared to previously reported (6) un-grafted but cross-linked PAA.

Influence of pH on Mercuric Ion Adsorption

The results of Hg^{2+} adsorption at various pH (2.6–5.4) are shown in Fig. 1. The adsorption capacity of the polymer was increased with pH from 2.6 to 4.8 and the then levels off with the further increase of pH. The optimum pH was found to be 4.8 and the rest of the experiment was done at this condition. The mercury ion goes to the exchange site mainly through ion exchange process (Eq. 5). The presence of exchangeable H^+ (exchange capacity = 3.8 meq · H^+/g) favors the ion exchange process. The absence of a sharp peak at 1722 cm^{-1} and appearance of a new peak at 1596 cm^{-1} in the FTIR spectrum of mercury adsorbed exchanger (spectrum is not shown) clearly indicates the presence of carboxylate anion (10) in the metal loaded sample. At low pH (<4.8) the equilibrium shifts towards left due to desorption. As a result, less amount of Hg^{2+} was adsorbed at pH 2.5. While at relatively higher pH (>4.8), the mercuric ion undergoes hydrolysis and interferes the exchange process. As a result the adsorption capacity levels off at pH beyond 4.8. Here it may be mentioned that due to the large size of a cross-linked polymer chain (R), the carboxylate anion ($RCOO^-$) probably becomes soft base, which in turn binds soft acid (Hg^{2+}) preferably.

$$2\,RCOO^-H^+\ (Resin) + Hg^{2+}\ (aq) = (RCOO)_2Hg\ (solid) + 2\,H^+\ (aq) \quad (5)$$

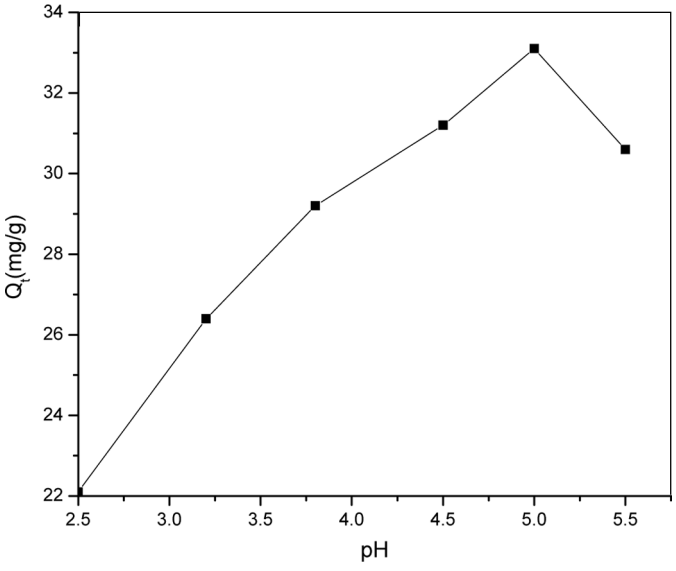

FIG. 1. Adsorption of Hg^{2+} at different pH. (Sorbent dose = 1.3 g/L, Sorbate dose = 200 mg/L, Time = 1 h, Temperature = 27°C, RSD for each dot = 2–3%; Replicate time = 40–50 min.).

Effect of Sorbate Dose on Metal Adsorption

The effect of the sorbate dose (Mercuric ion concentration) on adsorption, keeping the other conditions (pH = 4.8, temperature = 27°C, sorbent dose = 1.3 g/L and time = 1 h) fixed, was studied. It was observed that the mercuric ion uptake capacity of the sorbent increases sharply with the increase of metal ion concentration. The mercury ion retention capacity of the resin (X-AA-g-PVA) was 0.175 mmol/g at low level of sorbate (200 ppm) and became 0.740 mmol/g at 1000 ppm of mercury. The maximum uptake capacity was reported (5) to be 0.650 mmol/g at the similar experimental condition. So the present polymer is more suitable for mercury ion extraction compound to the previously reported one (5,6).

Selective Sorption of Hg^{2+} in the Competitive Condition

In this group of experiments, the competitive sorption of nickel, cadmium, mercury, lead, and zinc ions into the polymer were investigated. These experiments were performed at a constant pH (4.8), temperature (27°C), sorbent dose (1.3 g/L), and time (1 h) with the solution containing 0.001 mole of each metal ion. The selectivity (11) (S) of the polymer for the metal (M_1) ion with respect to the competitive metal (M_2) ions was determined according to the relationship:

$$S = \log K_d(M_1) - \log K_d(M_2) \quad (6)$$

where the distribution coefficients (K_d) of metal ions between the sorbent phase and sorption medium at equilibrium, was calculated by using the expression:

$$K_d = \text{metal ion (mg) adsorbed per g of polymer/ metal ion (mg) present per mL of solution} \quad (7)$$

The selectivity of the polymer for Hg^{2+} with respect to Ni^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} are 0.17, 0.24, 0.04 and 0.03 respectively. The positive values of selectivity (11) indicate that the prepared material binds preferably Hg^{2+} in the presence of Ni^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} ions. Higher soft

acid character of Hg^{2+} compared to Ni^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} makes the polymer (soft base) more selective towards the mercuric ion compound to the reported (5–6) earlier.

Effect of Contact Time, Adsorption-Desorption Kinetics, and Transport Mechanism

Figure 2 shows the amount of Hg^{2+} adsorbed (Q_t, mg/g) at various contact time, t (min). The results have indicated that ~90% adsorption took place in 32 min, and the time required to, reach the equilibrium is 60 min that is much less than the reported values of commercially available carboxylic resins (5). The rapid adsorption in the initial part may be attributed to the availability of the negatively charged surface of the sorbent ($RCOO^-$). The slow adsorption in the later part may be due to electrostatic hindrance between the adsorbed positively charged sorbate and available cationic sorbate in solution, and the slow pore diffusion of the solution into the bulk of the adsorbent. The similar types of results were observed by Denizil et al. (12) in the case of poly (2-hydroxy ethyl methacrylate-methacryloyl amido histidine) membranes.

The time-dependent experimental adsorption data (Fig. 2) are used to fit various kinetic models by linear regression plots. The equations (13,14) used for fitting the data are: First-order, pseudo-first order, second-order, pseudo-second order, Bhattacharya-Venkobachor, power function, and simple Elovich models. The present kinetic data could be best described by the first order model: $\times \ln(C/C_o) = k_1 t$ (C_o and C denote concentration of lead ion at $t = 0$ and $t = t$ respectively; k_1 refers first order rate constant, min^{-1}). The plot of $-\ln(C/C_o)$ against t gives rise to a straight line with very good correlation coefficient ($R^2 = 0.990$, 0.995 and 0.999 at 5, 27, and 40°C respectively). Desorption of Hg^{+2} with the eluent 0.05 M H_2SO_4 took place rapidly. The quantitative (>99%) desorption was achieved within an hour.

The Weber and Morris plot (13,14) of log Q_t versus 0.5 log t is found to be linear ($R^2 > 0.95$) over the range of contact time, which implied that intra-particle diffusion was the rate limiting step during adsorptin of Hg(II) from water. Here the quantity Q_e and Q_t represent metal ion adsorption capacity (mg/g) at equilibrium and time t.

Adsorption Isotherm and Energy

Five isotherms (13,14) (Langmuir, Freundlich, Redlich, Toth, and Temkin) were used for fitting the experimental data (Fig. 3) obtained at 5, 27, and 40°C (pH 4.8, time = 1 h, sorbate dose = 1.3 g/L). The isotherm data have been analyzed using the linear equation of various models. Among isotherms, the order of fitting the experimental data at 27°C is Temkin($R^2 = 0.994$) > Redlich-Peterson($R^2 = 0.990$) > Langmuir($R^2 = 0.975$) > Freundlich($R^2 = 0.954$) > Dubinn–Redushkevick ($R^2 = 0.850$). Here R represents the correlation coefficient. In order to distinguish between physical and chemical adsorption, the isotherm data (Fig. 3) was subjected to the Dubinn-Redushkevich (DR) isotherm model (13,14). The magnitude of E_{DR} (mean free energy of adsorption) obtained from DR isotherm is useful for estimating the type of adsorption (8). In the present case, the values were observed in range 25–50 KJ/mol, which indicates that the adsorption of Hg^{2+} takes place by the ion exchange process (Eq. 5).

Effect of Temperature and Adsorption Thermodynamics

The effect of temperature on Hg^{2+} adsorption is shown in (Figs. 2 and 3). The adsorption capacity increases with the increasing temperature from 5 to 40°C and

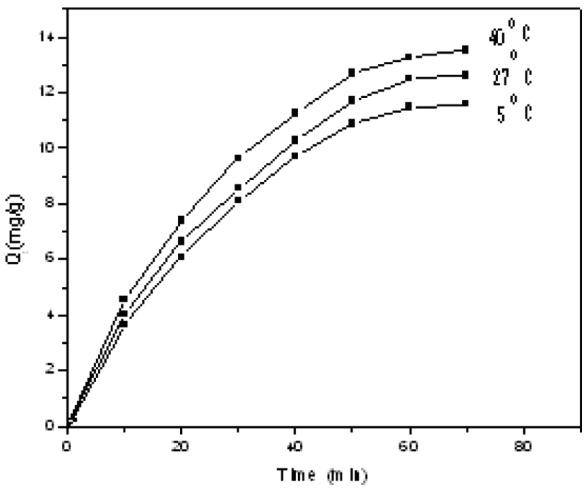

FIG. 2. Variation of Hg^{2+} adsorption with time. (Sorbent dose = 1.3 mg/L, *p*H = 4.8, Time = 1 h, Sorbate dose = 200 mg/L).

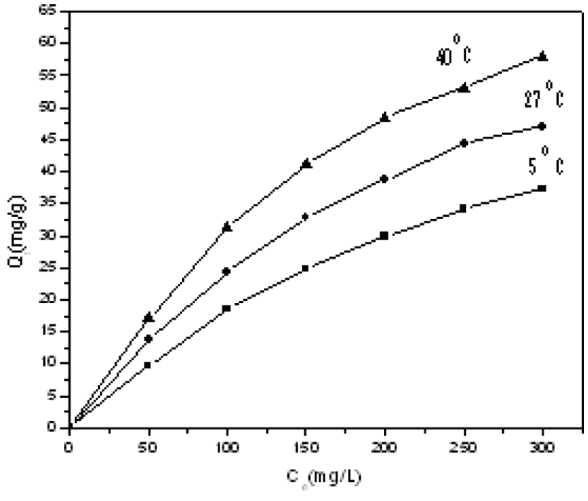

FIG. 3. Adsorption isotherm of Hg^{2++}. (Sorbent dose = 1.3 mg/L, *p*H = 4.8, Time = 1 h, Sorbate dose = 200 mg/L).

then decreases with further increase of temperature. The adsorption and desorption occurred through the ion exchange process (Eq. 5). The initial increase of temperature favors the adsorption, while increase of temperature above 40°C accelerates the desorption process.

Thermodynamic parameters such as free energy change (G^0), enthalpy changes (ΔH^0), and entropy change (ΔS^0) was calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of adsorption process. The Van't Hoff equation (8) (Eq. 6) could be used for the estimation of thermodynamic parameters (ΔH^0 and ΔS^0), and G^0 may be calculated through Eq. (7).

$$\ln(Q_e/C_e) = (\Delta S^0/R) - \Delta H^0/RT \quad (6)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

The value of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot of $\ln(Q_e/C_e)$ verses $1/T$. The negative values of (G^0 confirm the spontaneous nature and feasibility of the sorption process. The enthalpy change (ΔH^0) is found to be +14.80 KJ/mol, which indicates the endothermic nature of adsorption process. The positive entropy change (ΔS^0) for the adsorption indicated the increase of number of species in the system through the release of H^+ ion during adsorption (Eq. 5). Theoretical treatment supports the ion exchange mechanism.

Method of Hg^{2+} Separation and its Analytical Application

Ion exchanger was loaded in a chromatography column (i.d.0.8 cm) to achieve a bed height of 8 cm and washed with 2 M HCl. The mixture containing metal ion (10 mL) was passed through the column at a flow rate 1 mL/min. After extraction, the metal ions were eluted with suitable eluents and the amount of metal ions was determined by AAS, with a detection limit in the ppb range.

It was possible to separate Hg^{2+} from several metal ions present in binary mixture by using selective stripping agents. Each binary mixture was prepared by mixing an aliquot of standard solution of Hg^{2+} (2.20 mg/L) and one of the diverse metal ions at desired pH (A to D, Table 2). At pH 4.8, Pb^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} were co-extracted quantitatively along with Hg^{2+} from their respective binary mixtures. Hg^{2+} was eluted first from the column with the help of 0.05 M H_2SO_4 (in the case of mixture A), and then Pb^{2+} was desorbed with 0.01 M HNO_3. Similarly other diverse metal ions were separated from Hg^{2+} using different eluents as shown in Table 2 (B to D). Required volume of each eluents for complete separation is given in the table. After recovery, metal ions were determined complexometrically. The relative standard deviation (RSD) values indicate that the present method is much improved than reported earlier (1).

In order to asses the analytical application, the proposed method was applied to separate Hg^{2+} from the multicomponent synthetic mixture (E to F, Table 2) containing mercury with different metal ions commonly associated with electroplating waste and belong in the same analytical group. A clean separation of Hg^{2+} from ternary synthetic mixture (E) is exhibited by a representative elution curve (Fig. 4). The metal ions Zn^{2+}, Cd^{2+}, and Hg^{2+} were co-extracted quantitatively from the mixture E at pH 4.8. The Zn^{2+} ion was eluted first with 0.005 M

TABLE 2
Separation of Hg^{2+} from synthetic metal ion mixtures

Mixture	Cations	Added (mg)	Recovered (mg)	RSD (%)	Eluent (M) (mL)
A	Hg^{2+}	2.20	2.18	3.80	0.050 H_2SO_4 (60)
	Pb^{2+}	2.15	2.14	3.22	0.010 HNO_3 (50)
B	Hg^{2+}	2.20	2.19	1.98	0.050 H_2SO_4 (60)
	Ni^{2+}	2.15	2.13	1.52	0.005 H_2SO_4 (40)
C	Hg^{2+}	2.20	2.19	1.98	0.050 H_2SO_4 (60)
	Zn^{2+}	2.63	2.61	2.18	0.005 H_2SO_4 (45)
D	Hg^{2+}	2.20	2.18	2.02	0.050 H_2SO_4 (60)
	Cd^{2+}	1.80	1.79	2.78	0.005 H_2SO_4 (50)
E	Hg^{2+}	2.20	2.19	1.98	0.050 H_2SO_4 (60)
	Cd^{2+}	1.80	1.79	2.78	0.005 HNO_3 (50)
	Zn^{2+}	2.63	2.61	2.18	0.005 H_2SO_4 (45)
F	Hg^{2+}	2.20	2.18	1.98	0.050 H_2SO_4 (60)
	Pb^{2+}	2.15	2.14	3.22	0.010 HNO_3 (50)
	Ni^{2+}	2.15	2.13	1.52	0.005 H_2SO_4 (45)

[Column: internal diameter 0.08 cm, bed height 8 cm, flow rate 1 mL/min, pH 4.8, temp. 27°C].

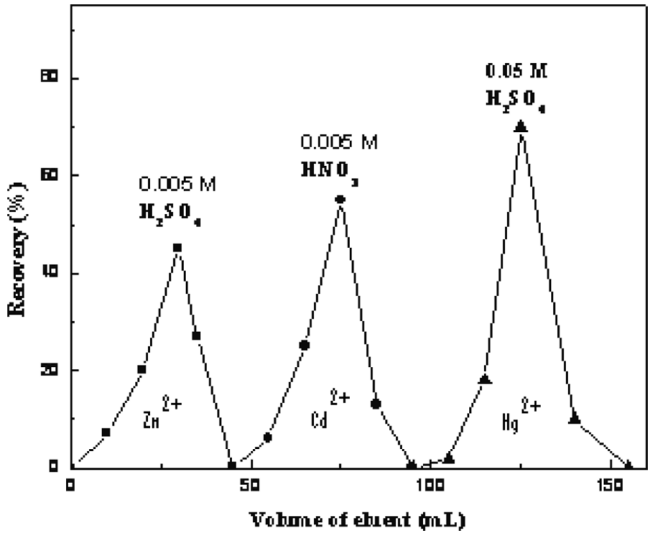

FIG. 4. Elution (desorption) profile of Zn^{2+}, Cd^{2+} and Hg^{2+} mixture.

H_2SO_4 (RSD = 2.18%), followed by Cd^{2+}(with 0.005 M HNO_3, RSD = 2.78%) and Hg^{2+}(with 0.05 M H_2SO_4, RSD = 1.98%). The results show a high degree of effectiveness and novelty of the prepared method (Elution curves are not overlapped).

CONCLUSION

The synthetic routes are simple and quantitative. The synthesized resin acts as cation exchanger with high exchange capacity. It has good chemical and thermal stability. Exchange bed could be used more than 35 cycles with little loss of exchange capacity. The developed technique could be applied for the selective extraction and separation of mercuric ion from real samples. The proposed method is highly efficient, cost-effective, simple, and rapid. The cross-linked AA-g-PVA has significantly higher mercury ion uptake capacity and selectivity than that of uncross-linked AA-g-PVA and commercially available carboxylic resins. The adsorption and desorption of mercuric ion took place mainly by the ion-exchange process. The adsorption process follows the first order kinetics and Temkin adsorption isotherm.

NOMENCLATURE

PVA	Polyvinyl alcohol
PAA	Polyacrylic acid
CAS	Ceric ammonium sulfate
Sorbate	Mercuric ion
Sorbent	Cross-linked graft copolymer
X-AA-g-PVA	Cross-linked graft copolymer of AA from PVA
AA-g-PVA	Uncross-linked graft copolymer of AA from PVA

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