SEPARATION AND PRECONCENTRATION OF TRACE AMOUNTS OF CADMIUM(II) AND MERCURY(II) IONS ON ROSANILINE-GRAFTED POLYURETHANE FOAM

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SUMMARY

Rosaniline-grafted polyurethane foam (Ros-PUF) has been synthesized, by coupling polyether polyol, rosaniline, and toluene diisocyanate, and characterized, by use of UV–visible and IR spectroscopy and thermogravimetric analysis. The Ros-PUF was used as a new sorbent for extraction of trace amounts of Cd(II) and Hg(II) from water by batch and column techniques. Cd(II) and Hg(II) were completely separated from 2–6 M HCl solution containing 1 M KSCN in 10–20 min. The kinetics and thermodynamics of sorption of the metal ions by Ros-PUF were studied. The average values of ΔH, ΔS, and ΔG for sorption of Cd(II) and Hg(II) by Ros-PUF were −54.38 kJ mol^{-1}, 159 J K^{-1} mol^{-1}, and –4.87 kJ mol^{-1}, respectively. The Dubinin–Radushkevich equation was used to explain the equilibrium isotherm. The sorption capacities of Ros-PUF were 0.12 and 0. 08 mmol g^{-1} for Cd(II) and Hg(II), respectively. The method has been successfully used to preconcentrate and remove Cd(II) and Hg(II) from tap water. Preconcentration factors were ~100 and recoveries were between 86.6 and 100% (average $RSD \approx 5.74$).

INTRODUCTION

Heavy metals such as cadmium(II) and mercury(II) are widely distributed throughout the environment as a result of soil erosion and of a broad range of industrial and agricultural processes. Inhalation of cadmium fumes produces emphysema then bronchitis. Mercury poisoning results in severe nausea, vomiting, and abdominal pain; kidney damage is also reported. The determination of low levels of Cd(II) and Hg(II) in environmental

samples and inexpensive removal of the species from water are very important.

Polyurethane foam (PUF) is an excellent sorbent which separates and preconcentrates metal ions relatively quickly compared with other solid sorbents [1–4]. PUF has been used in batch or dynamic techniques for collection of a variety of chemical compounds, especially those, e.g. Cd(II) and Hg(II), with harmful effects on humans, animals, and plants [5–12]. PUF to which organic reagents or functional groups are chemically bonded is also used but such material can suffer from poor selectivity and leaching of the reagents. There is, therefore, continued interest in the synthesis of new resins with high stability, high sorption capacity for metal ions, and good flexibility under the working conditions used. There have recently been many reports of the use of chelating matrices such as Nile blue A (oxanine dye) and methylene blue (thiazine dye) grafted on to PUF [13,14].

The preparation of rosaniline grafted polyurethane foam (Ros-PUF) by coupling polyether polyol, rosaniline (triphenyl methane dye), and toluene diisocyanate is the subject of this paper. The material has been characterised by use of UV–visible and IR spectroscopy and thermogravimetric analysis (TGA). Ros-PUF was found to be very suitable for separation and preconcentration of cadmium and mercury. Kinetic and thermodynamic equilibrium data have been obtained and the analytical applicability of Ros-PUF for collection of Cd(II) and Hg(II) from tap water has been tested.

MATERIAL AND METHODS

Reagents and Materials

All reagents used were of analytical reagent grade. Standard cadmium solution (1 mg mL^{-1}) was prepared by dissolving 0.1631 g $CdCl_2$, dried at 110°C, in distilled water containing 2 mL conc. HCl and diluting the solution with water to 100 mL. Standard mercury solution (1 mg mL^{-1}) was prepared by dissolving 0.1713 g $Hg(NO_3)_2.H_2O$ in distilled water containing 1 mL conc. HNO_3 and diluting the solution with water to 100 mL.

Synthesis of Rosaniline-Grafted Polyurethane Foam

A procedure described elsewhere [13,14] was used to synthesize Ros-PUF by mixing 20 g polyether polyol, 1 g distilled water, 0.04 g dime-

thyleneethanolamine, 0.04 g stannous octoate, 0.25 g polyether polysiloxane, and 0.1 g of rosaniline. This mixture was stirred to complete homogeneity then 13 g toluene diisocyanate was added gradually and the mixture was finally poured into box. The Ros-PUF was washed with 0.1 M HCl then distilled water and acetone and dried at room temperature.

Apparatus

All spectrophotometric measurements were performed by use of a Milton Roy Spectronic 501 and Shimadzu UV-1601 infrared and UV–visible spectrophotometers. Glass columns of approximately 15 cm × 1.5 cm i.d. were used for chromatographic separations.

General Procedures

Investigation of Sorption

Separation of Cd(II) and Hg(II) was performed by a batch technique at 25°C except where otherwise specified. Ros-PUF (0.2 g) was mixed with the tested metal ion solution (1.6 μg mL^{-1}, 25 mL) in a shaker thermostatted at the desired temperature and adjusted to the desired shaking speed. After fixed intervals samples of the solution were withdrawn and the concentrations of Cd(II) and Hg(II) ions were determined spectrophotometrically. Distribution coefficients (K_d) and percentage uptake (%E) were calculated by use of eqs (1) and (2):

$$K_d = \frac{C_0 - C}{C} \times \frac{V}{M} \qquad (1)$$

$$\%E = \frac{C_0 - C}{C_0} \times 100 \qquad (2)$$

where C_0 and C are the initial and final concentrations, respectively, of metal ions in solution, V is the volume of solution and M is the mass of Ros-PUF.

Chromatographic Separations

To study preconcentration, breakthrough capacities, chromatographic behaviour, and separation of the metal ions, a compact column of 15 cm×1.5 cm i.d. was packed with 1 g Ros-PUF by a procedure described elsewhere [5]. Solutions were passed through the column at a flow rate of 3 mL min^{-1}.

RESULTS AND DISCUSSION

Characterization of Rosaniline Grafted Foam

Rosaniline is also known as basic fuschin and basic violet 14. Its molecular formula is $C_{20}H_{20}N_3Cl$, its melting point 250°C, and its molecular weight 337.8 g mol^{-1}. Its molecular structure is:
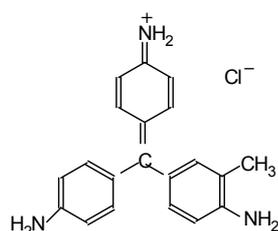
The UV–visible spectrum of Ros-PUF was compared with that of untreated foam. Two additional peaks at 325 and 400 nm were present in the Ros-PUF spectrum as a result of the reaction of PUF with rosaniline. The colour of rosaniline solution is violet-red whereas that of Ros-PUF is orange, changing to purple and yellow in acid and alkaline media, respectively (Table I). Infrared spectra of untreated foam and Ros-PUF were acquired by use of the thin-film technique. The results showed that bands at 3354.4 and 1715.2 cm^{-1} characteristic of the NH and C=O groups of the untreated foam were shifted to 3388.9 and 1699.7 cm^{-1} and the intensity of the absorption band at 2274.4 cm^{-1}, characteristic of isocyanate (–NCO)

Table I

Comparison of untreated PUF and Ros-PUF

Property	Untreated PUF	Ros-PUF
Colour	White	Orange changed to purple in acidic medium and yellow in alkaline medium
Density (kg m^{-3})	35.5	60.5
UV–visible spectra	Main UV band at 280 nm	New peaks appear at 325 and 400 nm
IR spectra	Bands at 3354.4 and 1715.2 cm^{-1}	Shift to 3388.9 and 1699.7 cm^{-1}
TGA weight loss (%)	1.7, 38.8, 52.8, and 7.2	3.7, 40.6, 44.6, and 11.1
TGA endothermic peaks	322.6 and 374.7°C	286.5 and 371.8°C

group, had decreased. These results indicate that an amide (–CONH–) group is formed by coupling of the NH$_2$ group of the reagent with the NCO group of PUF. An additional band was observed at 1011.5 cm^{-1}.

Thermogravimetric analysis of the untreated foam showed that thermal decomposition began at 172°C. Weight losses of 1.7, 38.3, 52.8, and 7.2% were recorded at 233, 337, 396, and >400°C, respectively, and three endothermic peaks appeared at 315.6, 322.6, and 374.7°C. TGA of Ros-PUF showed that thermal decomposition began at 193.5°C. Weight losses of 3.7, 40.6, 44.6, and 11.1% were observed at 233, 337, 400, and >400°C, respectively and two endothermic peaks occurred at 286.5 and 371.8°C. The TGA curves from untreated foam and from Ros-PUF showed that the reagent had reacted with the foam matrix. Ros-PUF was more thermally stable than other chelating resins.

The chemical stability of Ros-PUF was studied. Leaching of rosaniline from Ros-PUF with different solvents in batch mode was tested. Cubes of Ros-PUF (0.2 g) were mixed with the solvent tested (25 mL) in a 100-mL flask and shaken for 30 min. Rosaniline was not detected in the solvents. These results were indicative of the good chemical stability of Ros-PUF in the presence 1–6 M H$_2$SO$_4$, 1–6 M HCl, ethanol, isopropanol, butanol, chloroform, carbon tetrachloride, and acetone. Ros-PUF was stable for several months if stored in a polyethylene bag. The resin was also completely stable throughout 20 metal-uptake–elution cycles.

The densities of the untreated foam and of Ros-PUF were measured. The values obtained were 35.3 and 60.5 kg m^{-3}, respectively. These results indicate that the Ros-PUF is denser and has more cross-linking than the untreated foam, because of the additional bonds between the rosaniline and groups in the PUF.

The capacity of the Ros-PUF was calculated. The values obtained for Cd(II) and Hg(II), by use of a batch technique, were 0.12 and 0.08 mmol g^{-1} Ros-PUF. The capacity sequence Cd(II) > Hg(II) is a consequence of the radii of these ions. These results are indicative of the advantageous properties of Ros-PUF compared with unloaded and loaded PUF [5–10].

Preconcentration and Separation of Cadmium(II) and Mercury(II)

Effect of pH and Acidity on the Sorption of Cd(II) and Hg(II)

The effect of pH and acidity on the sorption of the anionic complexes [Cd(SCN)$_4$]$^{2-}$ and [Hg(SCN)$_4$]$^{2-}$ by untreated PUF and by Ros-

PUF were examined. When percentage uptake (%*E*) of Cd(II) and Hg(II) was plotted against pH the results showed that the metal ions tested were completely separated from 2–6 M HCl and that %*E* decreased with increasing pH. Also, the uptake of metal ions by Ros-PUF was greater than by untreated PUF (Fig. 1), confirming Ros-PUF was more efficient than untreated PUF. Values of the separation factor (α, $= K_{d(Cd)}/K_{d(Hg)}$) were calculated for the tested metal ions and showed that the selectivity sequence was in the order Hg(II) > Cd(II) in the pH range 2–6.
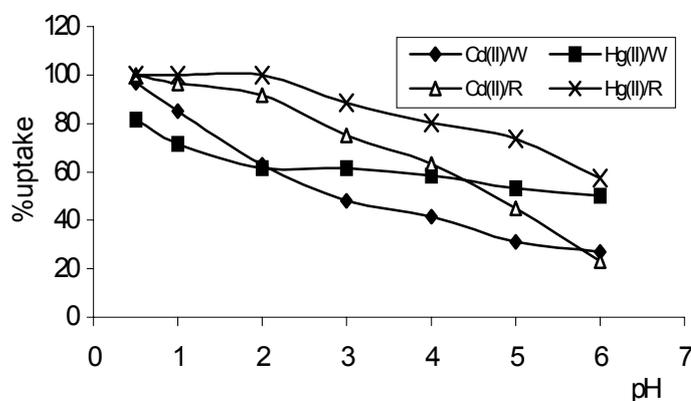

Fig. 1

Effect of pH on the sorption of Cd(II) and Hg(II) by untreated PUF (W) and by Ros-PUF (R)
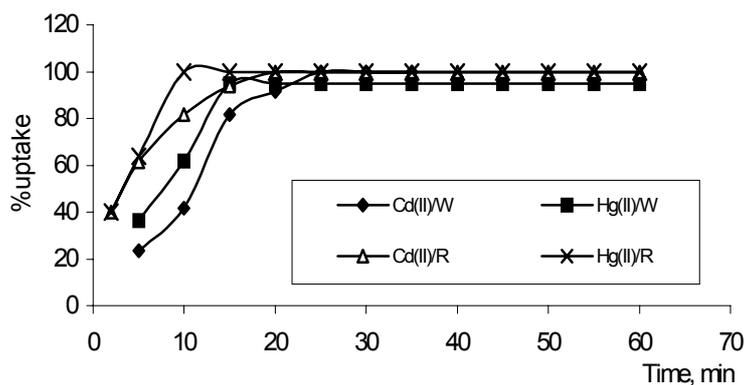

Fig. 2

Effect of shaking time on the sorption of Cd(II) and Hg(II) by untreated PUF (W) and Ros-PUF (R)

Kinetic Study

The effect of shaking time on the sorption of Cd(II) and Hg(II) by untreated PUF and Ros-PUF was studied. The results obtained showed the time required for sorption equilibrium was 10 and 20 min, respectively (Fig. 2). The times required for 50% adsorption of cadmium and mercury ions ($t_{1/2}$) were calculated [3] from Fig. 2 and found to be 4.8 and 7.5 min, respectively. This rapid extraction is because of application of the Ros-PUF in a batch technique; the results show Ros-PUF sorbent is relatively fast and efficient compared with other resins [1–4].

Sorption of metal ions by PUF might involve three steps – bulk transport of solute in solution, film transfer involving diffusion of solute through a hypothetical film boundary layer, and diffusion of the solute within the pore volumes of the adsorbent and along pore-wall surfaces to the active adsorption sites [15–17]. The Morris–Weber and Reichenberg equations (eqs 3 and 4) were used to study the particle diffusion mechanism of sorption of Cd(II) and Hg(II) by Ros-PUF.

$$Q_t = k_M \sqrt{t} \qquad\qquad (3)$$

$$Bt = -0.4977 - \ln(1 - F) \qquad\qquad (4)$$

where Q_t is the amount of metal ions sorbed after time t, k_M is the rate constant of interparticle transport and the value of Bt is a mathematical
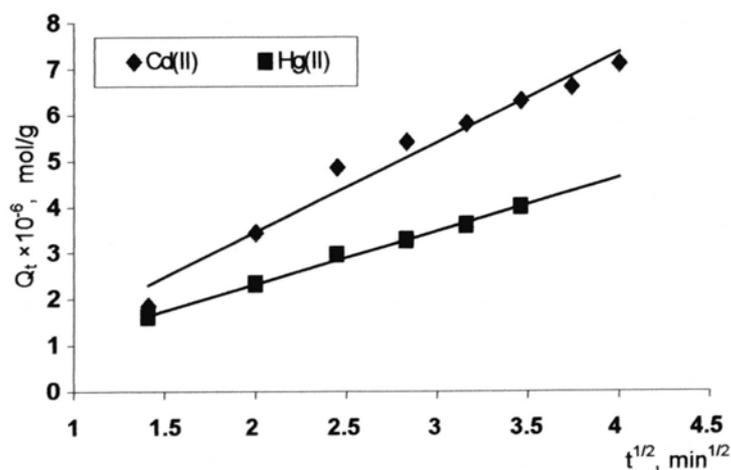

Fig. 3

Plot of Q_t against $t^{1/2}$ for sorption of Cd(II) and Hg(II) by Ros-PUF
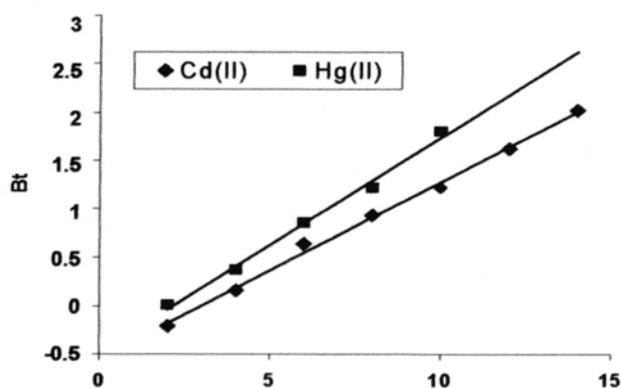
Fig. 4

Plot of *Bt* against *t* for sorption of Cd(II) and Hg(II) by Ros-PUF

function of F ($F = Q_t/Q_e$). The data obtained show that plots of $\sqrt{t}$ and Bt against t are linear but do not pass through the origin; k_M values of 1.79 and 1.21 μmol g^{-1} min$^{-1/2}$ were obtained for sorption of Cd(II) and Hg(II), respectively (Figs 3 and 4). According to these results, the rate of diffusion is rapid. Differences might be because of the presence of different sized pores in Ros-PUF.

Effect of Metal Ion Concentrations

The uptake of the different metal ions by Ros-PUF was determined as a function of the concentration of metal ion in the aqueous solution. The isotherms obtained were indicative of a good linear relationship over relatively wide range of ion concentrations (Fig. 5).

To describe the sorption equilibrium the Dubinin–Radushkevich isotherm model (eq. 5) was tested with the experimental data.

$$\ln Q_C = \ln K_{DR} - \beta\varepsilon^2 \ \text{ and } \ \varepsilon = RT\ln\left(1 + \frac{1}{C_{eq}}\right) \tag{5}$$

where Q_C is the amount of metal ions sorbed per unit mass of Ros-PUF, C_{eq} is the amount of metal ions adsorbed at equilibrium, and K_{DR}, ε, and β are constants. The linear plot of ln Q_C against ε^2 is shown in Fig. 6. The values of β for sorption of Cd(II) and Hg(II) ions, computed from the slope, are -2.43×10^{-4} and -1.25×10^{-3} kJ^2 mol^{-2}, respectively. The value of the sorption energy (activation energy, E), can be correlated with β

($E = 1/\sqrt{-2\beta}$). The values of E obtained were 45.5 and 20.0 kJ mol^{-1} for Cd(II) and Hg(II) ions, respectively, indicating that the rate of sorption is relatively fast.
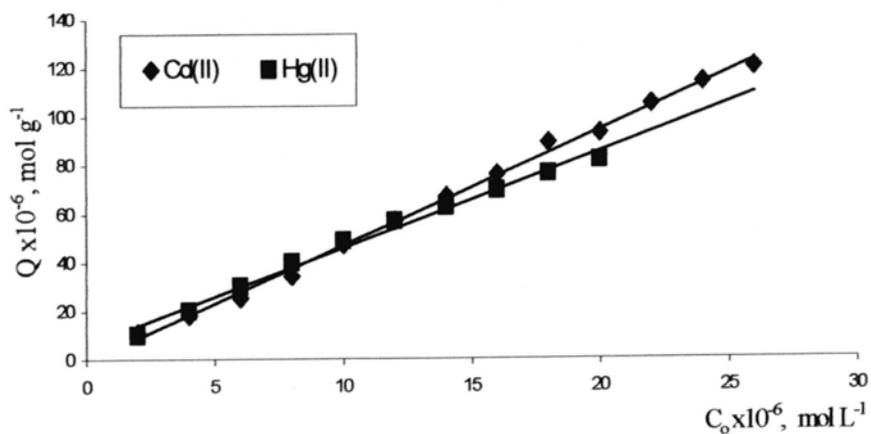

Fig. 5

Extraction isotherm curve for sorption of Cd(II) and Hg(II) from aqueous solution using Ros-PUF
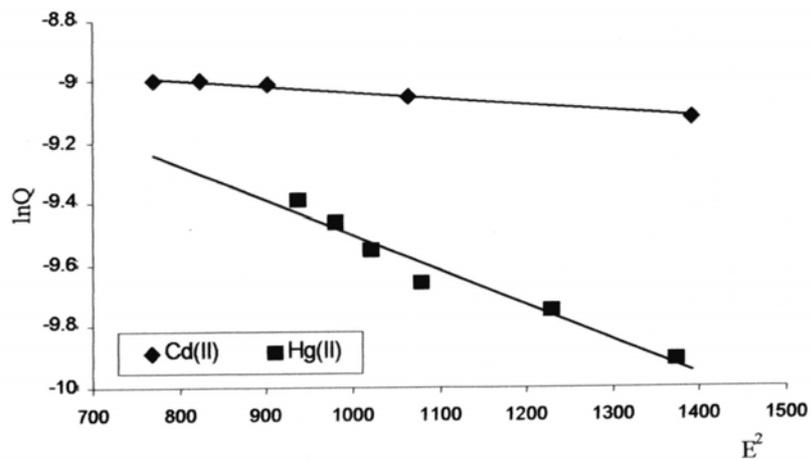

Fig. 6

Dubinin–Radushkevich (D–R) plot for sorption of Cd(II) and Hg(II) by Ros-PUF

Thermodynamic Investigations

The dependence on temperature of sorption of Cd(II) and Hg(II) ions by Ros-PUF was evaluated by use of eqs (6) and (7):

$$\log K_{C} = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \qquad (6)$$

$$\Delta G = \Delta H - T\Delta S \qquad (7)$$

where ΔH, ΔS, ΔG, T, R, and K_{C} are the enthalpy, entropy, Gibbs free energy, absolute temperature, gas constant (8.314 J mol^{-1}), and equilibrium constant, respectively. Plots of log K_{C} against $1/T$ give numerical values of ΔH and ΔS from the slope and intercept, respectively. Values of ΔG, ΔH, and ΔS at different temperatures for sorption of Cd(II) and Hg(II) are given in Table II. Average values of ΔG, ΔH, and ΔS for sorption of Cd(II) and Hg(II) by Ros-PUF were -4.87 kJ mol^{-1}, -54.38 kJ mol^{-1}, and 159 J K^{-1} mol^{-1}, respectively. The negative values of ΔG are evidence of the spontaneous nature of the sorption process and the negative values of ΔH show the chemisorption process was exothermic. The positive change in the entropy might be indicative of rapid adsorption of Cd(II) and Hg(II) by Ros-PUF.

Table II

Thermodynamic data for sorption of Cd(II) and Hg(II) ions by Ros-PUF at different temperatures

Temp. (K)	Distribution coefficient, K_d (mL g^{-1})		Gibbs free energy, ΔG (kJ mol^{-1})		Enthalpy, ΔH (kJ mol^{-1})		Entropy, ΔS (J K^{-1} mol^{-1})	
	Cd(II)	Hg(II)	Cd(II)	Hg(II)	Cd(II)	Hg(II)	Cd(II)	Hg(II)
303	1125.0	1958.8	-5.50	-6.89			191	127
308	916.3	1958.8	-5.06	-6.89	-63.27	-45.48	189	125
313	291.3	1125.0	-2.21	-5.68			195	127
323	187.5	1011.3	-1.11	-5.62			192	123

Breakthrough Capacity

Extraction of the metal ions from aqueous solution with Ros-PUF columns was studied. Solutions of Cd(II) or Hg(II) thiocyanate complexes (2 mg L^{-1}, 100 mL) were percolated at 3 mL min^{-1} through columns containing 1 g Ros-PUF. Saturation of each Ros-PUF column was reached after passage of 50–55 mL (Fig. 7).
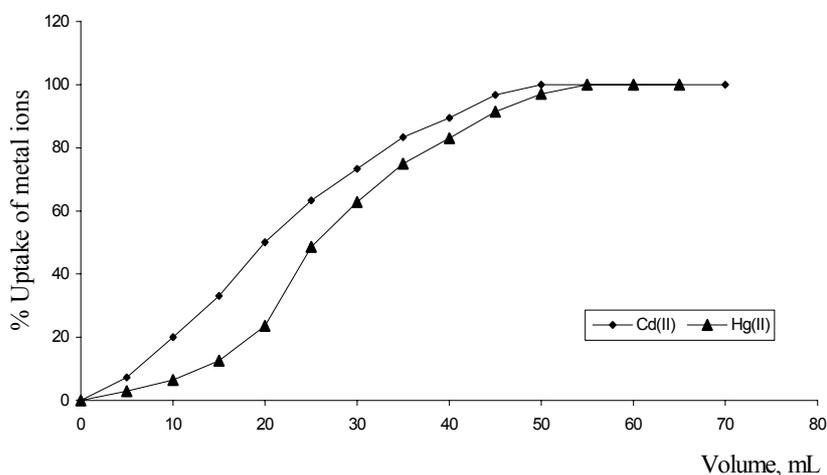
Fig. 7

Breakthrough curve for extraction of Cd(II) and Hg(II) from aqueous solution using Ros-PUF

The height equivalent to a theoretical plate (*HETP*) was calculated from the breakthrough capacity curve by use of the equation:

$$HETP = \frac{L(V_{50} - \overline{V})^2}{V_{50}\overline{V}}$$ (8)

where $\overline{V}$ is the volume at which the effluent has a concentration 0.1587 of the initial concentration. *HETP* values obtained by use of this equation were 1.92 and 5.11 mm for Cd(II) and Hg(II), respectively.

Effect of Eluting Agent Flow Rate

Elution of the metal ions from the Ros-PUF column was examined at different mobile phase flow rates. The Cd(II) ion was eluted from the Ros-PUF column by use 0.1 M HCl at different flow rates (1–10 mL min⁻¹). The chromatogram obtained indicated that Cd(II) could be completely eluted in the first 50 mL. Curves were usually symmetrical with relatively sharp peaks. *HETP* values were obtained from the elution curves by use of the Glueckauf (Eq. 9) and Van Deemter (Eq. 10) equations:

$$HETP = \frac{L}{16}\frac{W^2}{V_R^2}$$ (9)

$$HETP = A + \frac{B}{U} + CU \tag{10}$$

where N is the number of theoretical plates, V_R is volume of mobile phase at peak maximum, W is the width of the peak, and L is the length of the foam bed. Good column efficiency, i.e. a low value of $HETP$, was important if good separations were to be achieved. The $HETP$ value was found to be 0.71 mm at a flow rate of 2 mL min^{-1} (Fig. 8).
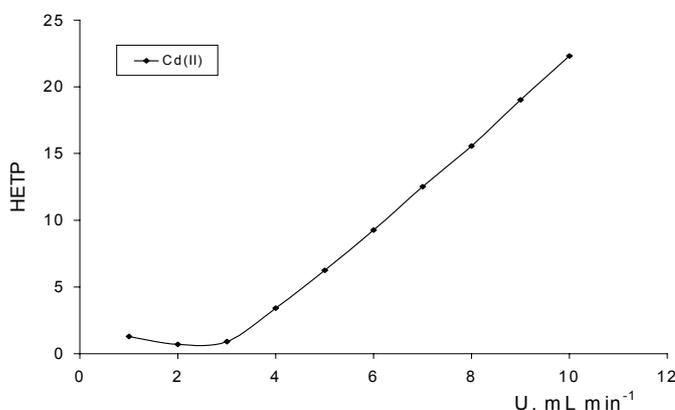

Fig. 8

Effect of flow rate on the height equivalent to a theoretical plate for Cd(II) using Ros-PUF

The ideal flow rate can be also calculated from the equation:

$$U = \sqrt{B/C} \tag{11}$$

where the constants B (molecular diffusion) and C (related to resistance to mass transfer) could be calculated from the Van Deemter equation. The value of U obtained by use of eq. (11) was 1.77 mL min^{-1}, which confirmed the value obtained from the elution curve.

Analytical Application

The validity of this method for separation and preconcentration of Cd(II) and Hg(II) from tap water was investigated using a column packed with 1 g Ros-PUF. Tap water (pH 7.8, TDS 550 mg L^{-1}, Na 43 mg L^{-1}, K 0.1 mg L^{-1}, Ca 44 mg L^{-1}, Mg 26 mg L^{-1}, Fe 0.01 mg L^{-1}, Mn 0.009 mg L^{-1}, Zn 0.1 mg L^{-1}, Cu 0.01 mg L^{-1}, CO$_3$ 12 mg L^{-1}, HCO$_3$ 39 mg L^{-1}, and Cl

67.8 mg L^{-1}) was spiked with each metal ion (50 μg L^{-1}) and passed through Ros-PUF at 3 mL min^{-1}.

Separation of Cd(II) and Hg(II)

The effect of thiocyanate concentration on extraction of Cd(II) and Hg(II) thiocyanate complexes with Ros-PUF was examined. Cd(II) was completely extracted from a concentration of 50% KSCN and Hg(II) was completely extracted from a concentration of 20% KSCN, showing that separation of a mixture of Cd(II) and Hg(II) (from 20% KSCN at pH~3) could be achieved by use of the Ros-PUF column. Cd(II) remained in the original solution and Hg(II) was retained on the column. Hg(II) was reco-vered with 0.1 M HCl at a flow rate 2 mL min^{-1}.

In another procedure 50% KSCN solution was added to a mixture of these ions and separation was performed by passing the solution through a Ros-PUF column. Cd(II) and Hg(II) were eluted using 0.1 M and 2 M HCl, respectively, at 2 mL min^{-1}. Figure 9 shows the data obtained. This tech-nique enables selective determination of each metal ion from the other ion in a mixture.
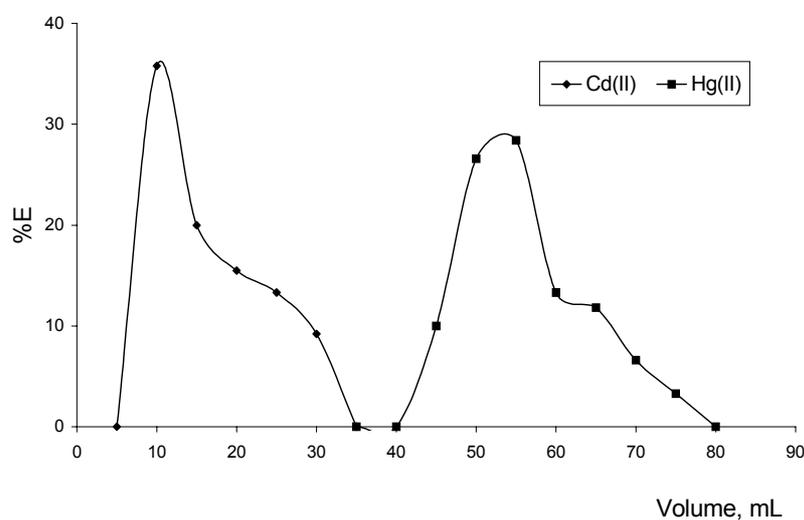
Fig. 9

Separation of Cd(II) and Hg(II) from aqueous solution on a Ros-PUF column by elution with 0.1 M HCl and 2 M HCl, respectively

Preconcentration of Metal Ions from Tap Water

The performance of the Ros-PUF column in the preconcentration of Cd(II) and Hg(II) from different volumes (25–1000 mL) of tap water was studied. Cd(II) and Hg(II) were eluted from the Ros-PUF column with recoveries of 86.6–100% at a flow rate of 2 mL min^{-1}. The results, summarized in Table III, show that the metal ions can be sensitively concentrated from large volumes of dilute aqueous solutions by use of columns packed with Ros-PUF. These values are in a good agreement with previously determined values for these metal ions. The preconcentration factor was estimated to be 100 with average $RSD \approx 5.74$.

Table III

Preconcentration of Cd(II) and Hg(II) from tap water using Ros-PUF

Metal ion	Volume (mL)	Preconcentration factor, P	Amount added (µg)	Amount found (µg)	Recovery (%E)	RSD
Cd(II)	25	2.5	50	50	100	
	250	25	50	48.3	96.6	6.97
	1000	100	50	43.3	86.6	
Hg(II)	25	2.5	50	50	100	
	250	25	50	48.5	97.8	4.52
	1000	100	50	45.7	91.4	

Tap water composition: Na 43 mg L^{-1}; K 0.1 mg L^{-1}; Ca 44 mg L^{-1}; Mg 26 mg L^{-1}; Fe 0.09 mg L^{-1}; Mn 0.009 mg L^{-1}; Zn 0.1 mg L^{-1}; TDS 550 mg L^{-1}; CO$_3$ 12 mg L^{-1}; Cl 67.8 mg L^{-1}, and pH 7.8

Mechanism of Sorption of Metal Ions by Rosaniline Grafted Polyurethane Foam

Possible mechanisms previously proposed for sorption of metal ions by untreated polyurethane foam (polyether type) are surface sorption [11,18], etherlike solvent extraction [11,19], anion exchange [16], cation chelation [17,20,21], and ion association [7]. The presence of anion-exchange sites arises because of the tendency of both the nitrogen atom of the urethane linkage and the oxygen atom of the ether to accept protons from the acidic medium to give:
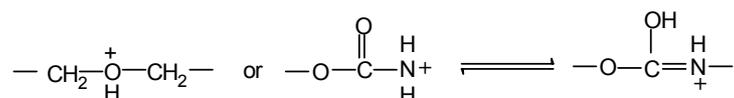
In this work the results obtained from determination of the effect of pH and acidity on the extraction of anionic complexes, $[Cd(SCN)_4]^{2-}$ and $[Hg(SCN)_4]^{2-}$ by use of Ros-PUF shows that metal ions were completely separated from 2–6 M HCl and that uptake decreased with increasing pH. Also, plots of log K_d against pH showed the dependence to be linear with a negative slope (log K_d = constant $- n \times$ pH, Fig. 10). The colour of Ros-PUF was orange; this changed to purple in acid medium. By using the Dubinin–Radushkevich isotherm model to describe the sorption equilibrium it was found that sorption of the metal ions was by chemisorption with an average value of the activation energy of 32.75 kJ mol^{-1}. Study of the variation of sorption with temperature yielded negative values of ΔH and ΔG, indicative of the exothermic and spontaneous nature of the sorption of metal ions by Ros-PUF. From these findings and others reported (for example, the free amino (NH$_2$) groups of untreated PUF are highly reactive toward diazotization [12,22,23]), we can show that partial hydrolysis of amide, urethane, and isocyanate groups to free amino groups occurs in concentrated acid solution. One might also reasonably suggest that sorption of metal ion complexes by Ros-PUF might proceed via both weak anion exchange and an ion-association mechanism.
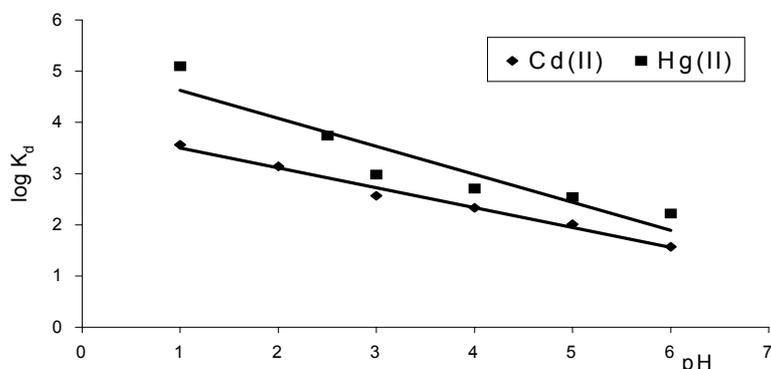

Fig. 10

Effect of pH on log K_d for sorption of Cd(II) and Hg(II) by Ros-PUF

CONCLUSION

This paper describes the preparation of a new polymeric extractor, polyurethane foam with a reagent, rosaniline, incorporated into the struc-

ture by covalent bonding. This new extractor (rosaniline-grafted polyure-thane foam) was used to extract, preconcentrate, and separate Cd(II) and Hg(II) ions from aqueous solutions. Characterization of the Ros-PUF indicated that it is more dense and stable than the untreated polyurethane foam, because of the additional bonding between the rosaniline and other groups in the polyurethane foam matrix. Experiments indicated that the reagent was not leached from the Ros-PUF and the stable chelate-forming resin matrix could be recycled many times without affecting its efficiency. Negative values of ΔG indicate the spontaneous nature of sorption of the tested metal ions. Negative values of ΔH indicate sorption of Cd(II) and Hg(II) by Ros-PUF was exothermic. Our study indicates Ros-PUF can be used to extract and remove Cd(II) and Hg(II) from wastewater and drinking water.

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