ION EXCHANGE LETTERS

Use of neutral red modified strong acid cation exchange resin for separation of heavy metal ions

Mu. Naushad[*], Ritesh Mitra and Jagdish Raghuvanshi

Chemistry laboratory, SRM-IST, SRM University, Modinagar, India
[*]Corresponding author: shad81@rediffmail.com

ABSTRACT

The potential of neutral red modified strong acid cation-exchange resin for separation of heavy metal pollutants has been explored. The distribution coefficients (Kd) of twelve metal ions in nitric acid and hydrochloric acid systems have been studied. On the basis of Kd values, some analytically important binary separations Al^{3+} from Fe^{3+}, Zn^{2+} from Fe^{3+}, Cu^{2+} from Fe^{3+}, and Ni^{2+} from Fe^{3+} have been achieved. The practical applicability of the modified material has been demonstrated in the analysis of a synthetic mixture for selective separation of Fe^{3+}.

Keywords: metal ions; distribution coefficients; separation

INTRODUCTION

The increasing level of heavy metals in the environment represents a serious threat to human health, living resources and ecological systems. These metals when present in the water more than acceptable limit are injurious to the health[1]. So, it is very important to remove these metals from the water before it is supplied to any useful purpose. It has led to environmental awareness and a need to develop analytical methods for selective separation of heavy metal ions. Many classical physical methods viz-fractional precipitation, distillation and ion-exchange have long been in use for the separation and purification of chemical compounds. Ion-exchange is one of the best methods for separation of metal ions. The potential of chelating ion-exchange resins for separation of metal ions has been very well established[2–5]. Azothiopyrine disulphonic acid[5] has been incorporated into an anion-exchange resin and the product has been used for uptake of mercury, copper, and cadmium from aqueous solutions. Similar use of pyrogallol sulfonic acid[7] enabled the separation and enrichment of Mo(VI), and Fe^{3+}. Dowex 1-X8 containing adsorbed sulphonated azo dyes[8] has been found useful for separation of copper and nickel. In this work the potential of the neutral red modified strong acid cation-exchange resin has been further explored for separation of heavy metal ions.

EXPERIMENTAL

Reagents

Amberlite IR-120 resin (H^+ form, see Figure 1) was obtained from BDH (India), neutral red (see Figure 2) was from E. Merck (Germany) and di-sodium salt of EDTA (A.R, S.D. fine Chem., India), nitric acid and hydrochloric acid (AR, BDH, India) and other reagents were of AR grade. Eriochrome Black-T, PAN and xylenol orange were used as indicators. A 0.01 M solution of the di-sodium salt of ethylene di-amine tetra-acetic acid (EDTA) was used for titration.

Preparation of modified resin

0.4 g Amberlite IR-120 resin (H^+ form) was treated with 40 mL of a 1000 ppm solution of neutral red solution at pH 3.0 for 24 hr with intermittent shaking[9]. Excess reagent was removed by washing of the resin with demineralized water and the resin was finally dried in an oven at $50 \pm 2°C$ to remove moisture.

Bulk modified resin was prepared under same experimental conditions[9].

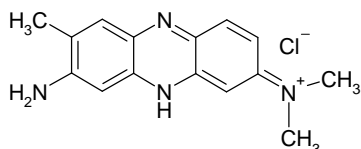
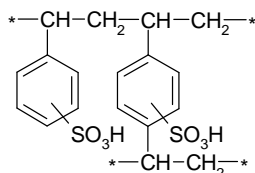**Figure 1** *Structure of neutral red*

Figure 2 *Structure of Amberlite IR-120*

Distribution Studies

The distribution coefficient (Kd) values of various metal ions on modified resin were determined by batch methods in various solvents systems. 0.4 g modified resin beads were equilibrated with 40mL metal ion solution in a 250 mL Erlenmeyer flask at 25± 2 ∘C. The amount of metal ion in the solution before and after equilibration was determined by titrating against 0.01M EDTA. Kd values of the metal ions were calculated by using the following formula (1).

$$K_d = \frac{I-F}{F} \times \frac{V}{M} \ [mL \cdot g^{-1}] \qquad (1)$$

Where, *I* is the initial amount of metal ion in the solution phase, *F* the final amount of metal ion in the solution phase, *V* the volume of solution (mL) and *M* is the amount of exchanger (g).

Separations

Quantitative separation of metal ions

Quantitative separations of some important metal ions of analytical utility were achieved on modified resin columns. 2.0 g modified resin was packed into a glass column of height 35 cm and internal diameter of 0.6 cm with a glass wool support at the end. The column was washed 2–3 times with demineralized water. 2.0 mL binary mixture of the metal ions to be separated was poured on to the top of the column and left to flow through the column at 0.5 mL·min^{-1} until the level of the sample solution was just above the resin surface. The column was then rinsed with a limited quantity of demineralized water, which was recycled through the column to ensure complete

adsorption of metal ions. Elution was performed at a constant flow of 0.5 mL·min^{-1} with appropriate mobile phases (Table I). The eluted metal ion fractions were analyzed titrimetrically against 0.01 M di-sodium EDTA solution.

Selective separation of metal ions from a synthetic mixture

For selective separation, a mixture of the metal ions Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+} and Fe^{3+} was poured on to the top of the column and left to flow through the column at 0.5 mL·min^{-1} until the level of the sample solution was just above the resin surface. The sample was recycled through the column to ensure complete adsorption of the metal ions. The mixture of metal ions Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+} and Al^{3+} was eluted first, together, by use of 0.01 M HNO_3. Fe^{3+} which was strongly retained by the resin was eluted later with 0.01 M HNO_3 (Table II).

RESULTS AND DISCUSSION

Neutral red has replaceable chloride ion and Amberlite IR-120 resin has replaceable hydrogen ions. It can be concluded that neutral red, which contains two aromatic rings, was attached to the polystyrene skeleton by physical adsorption, π–π dispersion forces arising from the aromatic nature of the resin and neutral red seem to be responsible for this adsorption. The presence of two nitrogen donor atoms of the neutral red facilitates its selective interaction with metal ions

To investigate the utility of the neutral red modified strong acid cation-exchange resin for separation of metal ions, distribution studies were performed with twelve metal ions using 0.01 M nitric acid and 0.01 M hydrochloric acid as mobile phases (Table I).

Table I *Distribution coefficient (K_d) values of different metal ions on neutral red modified Amberlite IR-120 cation exchange resin column in two different solvent systems*

Metal ions	0.01 M Nitric Acid	0.01 M Hydrochloric Acid
Mg^{2+}	860	1196
Ca^{2+}	980	1312
Sr^{2+}	1200	2305
Ba^{2+}	1593	2375
Pb^{2+}	2525	1800
Cd^{2+}	624	1228
Hg^{2+}	870	1200
Zn^{2+}	1259	2204
Ni^{2+}	1102	1195
Cu^{2+}	1220	1350
Al^{3+}	913	1205
Fe^{3+}	21000	22728

Table II *Quantitative separation of metal ions from a binary mixture using neutral red modified Amberlite IR-120 cation exchange resin column*

Sample No.	Metal ions	Amount loaded[a] [mg]	Amount found[a] [mg]	Recovery [%]	Error [%]	Volume of eluent [mL]	Eluent used
1	Al^{3+}	1.35	1.32	97.77	-2.23	45	
	Fe^{3+}	2.79	2.68	96.05	-3.95	55	
2	Zn^{2+}	3.27	3.24	99.08	-0.92	50	
	Fe^{3+}	2.79	2.68	96.05	-3.95	55	0.01 M
3	Cu^{2+}	3.18	3.08	96.85	-3.15	50	Nitric acid
	Fe^{3+}	2.79	2.68	96.05	-3.95	55	
4	Ni^{2+}	2.93	2.83	96.58	-3.42	45	
	Fe^{3+}	2.79	2.68	96.05	-3.95	55	

[a] Average of three replicate determinations

Table III *Selective separation of Fe^{3+} from a synthetic mixture of Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+} and Fe^{3+} on a column of neutral red modified Amberlite IR-120 cation exchange resin*

Sample No.	Separations achieved	Amount loaded[a] [mg]	Amount found[a] [mg]	Recovery [%]	Error [%]	Volume of eluent [mL]	Eluent used
1		2.79	2.68	96.05	-3.95	55	
2	Fe^{3+}	5.58	5.50	98.57	-1.43	60	0.01 M Nitric acid
3		8.37	8.32	99.40	-0.60	65	

[a] Average of three replicate determinations

It is clear from the Table I that modified resin has different selectivity for metal ions. It is interesting to note that all metal ions have high Kd values in 0.01 M hydrochloric acid than that of 0.01 M nitric acid except Pb^{2+}. On the basis of the different Kd values, several binary separations of analytical importance viz-Al^{3+} from Fe^{3+}, Zn^{2+} from Fe^{3+}, Cu^{2+} from Fe^{3+}, and Ni^{2+} from Fe^{3+} were achieved on the column of neutral red modified strong acid cation-exchange resin (Table II).

The elution of the metal ions did not occur at the same rate. The elution of metal ions through the column depends on metal–ligand stability. The metal ions which are weakly retained by the resin eluted first and strongly retained metal ions eluted at last (Figure 4a-d).
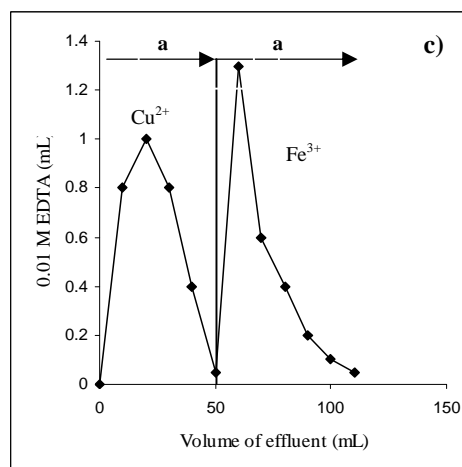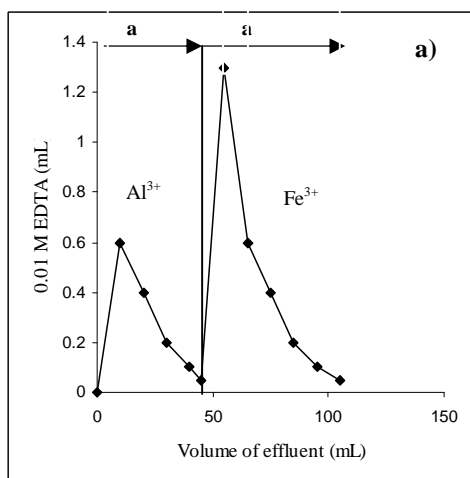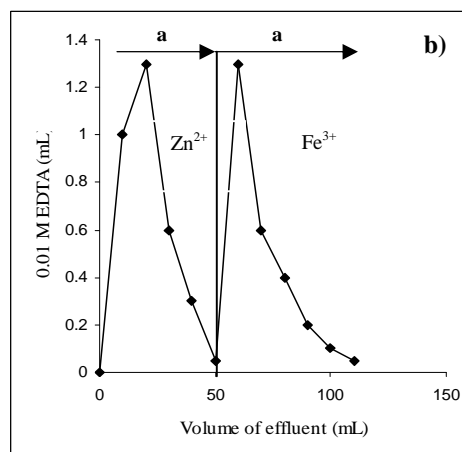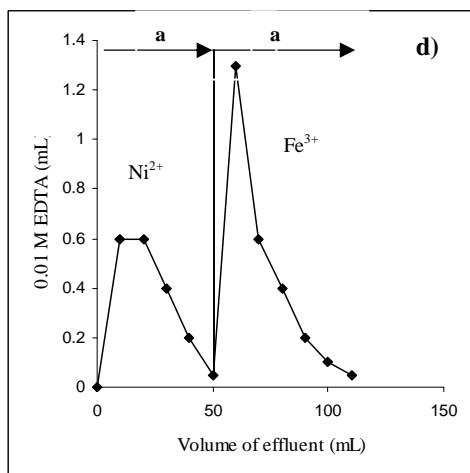
Figure 3a-d *Chromatograms of binary separations of metal ions on a column of neutral red modified Amberlite IR-120 cation-exchange resin, a= 0.01M HNO$_3$*

The high Kd values for Fe^{3+} in both solvent systems were because of the formation of a more stable metal-modified resin complex. The high Kd values of Fe^{3+} enabled its selective separation[10-12] from a synthetic mixture of Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+}. The metal ions Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+} and Al^{3+} were eluted first collectively as a mixture using 0.01 M HNO_3 solution as an eluant and Fe^{3+}, which was strongly retained by the resin was eluted later with the same eluent (Table III).

Conclusion
The neutral red modified amberlite IR-120, a strong acid cation-exchange resin can prove to be a potential material for the separation of metal ions.

Acknowledgement
The authors are highly thankful to the Dean and HOD (Sc. & Humanities), SRM-IST, SRM University for providing all necessary facilities.

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