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USE OF NAPHTHOL BLUE–BLACK-MODIFIED AMBERLITE IRA-400 ANION-EXCHANGE RESIN FOR SEPARATION OF HEAVY METAL IONS

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SUMMARY

The potential of naphthol blue–black-modified Amberlite IRA-400 anion-exchange resin for separation of heavy metal pollutants has been explored. The distribution coefficients (K_d) of metal ions in several acidic solvent systems have been studied. The effect of the dissociation constant of the solvent on the distribution coefficient of metal ions has also been investigated. On the basis of K_d values, some analytically important binary separations (Al^{3+} from Co^{2+}, Zn^{2+} from Ni^{2+}, Zn^{2+} from Co^{2+}, Ba^{2+} from Cd^{2+}, Ca^{2+} from Co^{2+}, Zn^{2+} from Zr^{4+}, Al^{3+} from Zr^{4+}, Pb^{2+} from Co^{2+}, and Zn^{2+} from La^{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 Zr^{4+}.

INTRODUCTION

The continual release of metal contaminants into the natural environment from waste streams, atmospheric emissions, combustion of fossil fuels, and urban habitation has led to environmental awareness and a need to develop analytical methods for selective separation of heavy metal ions. For separation and purification of chemical compounds, classical physical methods, for example fractional precipitation, distillation, and ion-exchange have long been in use. Ion-exchange is, perhaps, one of the best methods for separation of metal ions. It is a natural phenomenon and in nature is observed in inanimate soils, sands, and rocks, and in living organisms. The potential of chelating ion-exchange resins for separation of metal ions has been very well established [1–4]. Dowex 1-X8 containing adsorbed sulphonated azo dyes [5] has been found useful for separation of copper and nickel. Azothiopyrine disulphonic acid [6] has been incorporated into an anion-exchange resin and the product has been used for uptake of mercury, copper, and cadmium from aqueous solutions. Nabi et al. synthesized a variety of chelate-forming resins by incorporating complexing agents such as bromophenol blue [7], eriochrome black T [8], Congo red [9], alizarin red [10], crystal violet [11], toluidine blue [12], and naphthol blue–black [13].

In this work the potential of the naphthol blue–black-modified anion-exchange resin Amberlite IRA-400 has been further explored for separation of heavy metal ions.

EXPERIMENTAL

Reagents and Chemicals

Amberlite IRA-400 (Cl^-) resin (mesh size 20–50), formic acid, nitric acid, sulphuric acid, and perchloric acid were all AR from BDH, India. the disodium salt of EDTA was AR from S.D. Fine Chemicals, India, and naphthol blue–black was AR from CDH, India. Other reagents were also of AR grade. Ethanol solutions (1%) of 1-[1-hydroxy-2-naphtholazo]-5-nitro-2-naphthol-4-sulphonic acid sodium salt (eriochrome black-T) and 1-[2-pyridyl azo]-2 naphthol (PAN), and a 1% aqueous solution of *o*-cresolsulphonaphthalein 3′,3″-bis[methylimino diacetic acid sodium salt] (xylenol orange) were used as indicators in titrations of metal ions.

Preparation of Modified Resin

Anion-exchange resin (0.4 g) was treated with 40 mL of a 1000 ppm solution of naphthol blue–black at pH 6 (Elico-10 pH meter; India) for 24 h with intermittent shaking. Excess reagent was removed by washing of the resin with demineralized water and the resin was finally dried in an oven at 50 ± 2°C to remove moisture. Bulk modified resin was prepared under same experimental conditions [13].

Distribution Studies

Exchanger in the H^+ form (0.4 g) was treated with 40 mL of a solution of the metal ion of interest in the desired solvent, in an Erlenmeyer flask. The mixture was shaken for 4 h at 25 ± 2°C in a NSW (India) temperature-controlled incubator–shaker. The amount of metal ion in the solution before and after treatment was determined by titration against a

0.01 M standard solution of the disodium salt of EDTA. The K_d values may be expressed as:

$$K_\mathrm{d} = \frac{\text{milliequivalents metal ions g}^{-1}\text{ ion-exchanger}}{\text{milliequivalents metal ions mL}^{-1}\text{ solution}}$$

or

$$K_\mathrm{d} = \frac{I - F}{F} \times \frac{V}{M}\ \text{mL g}^{-1} \qquad (1)$$

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

Separations

Quantitative Separation of Metal Ions

For quantitative separations of some metal ions of analytical interest, 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 then 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 analysed titrimetrically against 0.01 M disodium EDTA solution.

Selective Separation of Metal Ions From a Synthetic Mixture

For selective separation, a mixture of the metal ions Zr^{4+} (1.82–9.12 mg), Zn^{2+} (1.31 mg), Cu^{2+} (1.27 mg), Fe^{3+} (1.12 mg), Ni^{2+} (1.18 mg), and Cd^{2+} (2.25 mg) 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 metal ions Zn^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, and Cd^{2+} were eluted first, together, by use of 0.1 M HNO_3. Zr^{4+}, which was strongly retained by the resin, was later eluted with 0.1 M $HClO_4$ (Table II).

Table I

Binary separations on naphthol blue–black-modified Amberlite IRA-400 resin

Binary mixture	Amount loaded (mg)	Amount found[a] (mg)	Recovery (%)	Error (%)	Volume of eluent for complete elution (mL)	Mobile phase
Al^{3+}	1.35	1.33	98.52	−1.48	40	0.2 M H_2SO_4
Co^{2+}	2.69	2.64	98.14	−0.68	50	0.1 M H_2SO_4
Zn^{2+}	3.29	3.30	100.30	+0.30	45	0.1 M $HClO_4$
Ni^{2+}	2.93	2.91	99.31	−0.69	50	0.1 M $HClO_4$
Zn^{2+}	3.29	3.30	100.30	+0.30	45	0.1 M $HClO_4$
Co^{2+}	2.95	2.93	99.32	−0.68	50	0.1 M H_2SO_4
Ba^{2+}	6.87	6.86	100.88	+0.88	65	0.2 M H_2SO_4
Cd^{2+}	5.62	5.60	99.64	−0.36	60	0.1 M $HClO_4$
Ca^{2+}	2.00	2.01	100.50	+0.50	40	0.1 M HNO_3
Co^{2+}	2.95	2.93	99.32	−0.68	50	0.1 M H_2SO_4
Zn^{2+}	3.29	3.30	100.30	+0.30	45	0.1 M $HClO_4$
Zr^{4+}	4.56	4.52	99.12	−0.88	60	0.1 M $HClO_4$
Al^{3+}	1.35	1.33	98.52	−1.48	40	0.2 M H_2SO_4
Zr^{4+}	4.56	4.52	99.12	−0.88	60	0.1 M $HClO_4$
Pb^{2+}	10.36	10.31	99.51	−0.49	70	0.1 M HNO_3
Co^{2+}	2.95	2.93	99.32	−0.68	50	0.1 M H_2SO_4
Zn^{2+}	3.29	3.30	100.30	+0.30	45	0.1 M $HClO_4$
La^{3+}	6.95	6.92	99.56	−0.44	60	0.2 M H_2SO_4

[a] Average from three replicate determinations

Table II

Selective separation of Zr^{4+} from a synthetic mixture of Zn^{2+} (1.31 mg), Cu^{2+} (1.27 mg), Fe^{3+} (1.12 mg), Ni^{2+} (1.18 mg), and Cd^{2+} (2.25 mg) on a column of naphthol blue–black-modified Amberlite IRA-400 resin

Amount loaded (mg)	Amount found[a] (mg)	Recovery (%)	Error (%)	Volume of mobile phase (0.1 M $HClO_4$) used (mL)
1.82	1.81	99.45	−0.55	45
4.56	4.54	99.56	−0.44	50
7.29	7.24	99.31	−0.69	60
9.12	9.00	98.68	−1.32	80

[a] Average from three replicate determinations

RESULTS AND DISCUSSION

In preliminary studies both anion-exchange (Amberlite IRA-400) and cation-exchange (IR-120) resins were tested for adsorption of naphthol blue–black, but adsorption occurred on IRA-400 only. It may be concluded that the naphthol blue–black was attached to the polystyrene skeleton by chemical adsorption. The presence of N-donor atoms and SO_3^{2-} groups on the naphthol blue–black (Fig. 1) facilitates its selective interaction with metal ions.

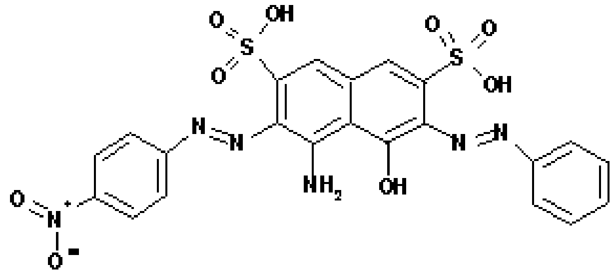

Fig. 1

The structure of naphthol blue–black dye

To investigate the utility of the material for separation of metal ions, distribution studies were performed with fifteen metal ions using different mobile phases (Table III). It is apparent from the table that naphthol blue–black-modified resin has different selectivity for metal ions, possibly because of the formation of metal complexes with different stability constants. Alkaline earth metal ions usually have lower K_d values than transition metal ions. It was interesting to note that uptake of metal ions is related to the acid dissociation constant of the solvents. The extent of ion uptake increases with the increasing acid dissociation constant. On the basis of the different K_d values several binary separations of analytical importance (Al^{3+} from Co^{2+}, Zn^{2+} from Ni^{2+}, Zn^{2+} from Co^{2+}, Ba^{2+} from Cd^{2+}, Ca^{2+} from Co^{2+}, Zn^{2+} from Zr^{4+}, Al^{3+} from Zr^{4+}, Pb^{2+} from Co^{2+}, and Zn^{2+} from La^{3+}) were achieved on the column of naphthol blue–black-modified IRA-400 anion-exchange resin (Table I).

Elution of the metal ions did not occur at the same rate. The ease of elution of ions through the column depends on metal–ligand stability. Metal ions weakly retained by the resin eluted first and strongly retained metal ions eluted last, as expected (Fig. 2).

Table III

Distribution coefficients (K_d) of metal ions in different mobile phases on naphthol blue–black-modified Amberlite IRA-400 (Cl^-) resin

Metal ion	0.1 M Formic acid	0.1 M Nitric acid	0.1 M Sulphuric acid	0.2 M Sulphuric acid	0.1 M Perchloric acid
Mg^{2+}	56	55	44	30	28
Ca^{2+}	42	38	38	36	32
Sr^{2+}	38	30	30	30	30
Ba^{2+}	34	22	18	10	6
Pb^{2+}	51	40	32	30	20
Cd^{2+}	298	180	120	110	82
Zn^{2+}	32	20	20	18	12
Ni^{2+}	406	300	300	290	284
Cu^{2+}	418	298	240	218	180
Co^{2+}	525	298	260	260	260
Cr^{3+}	490	360	360	294	288
Al^{3+}	49	40	32	18	18
Fe^{3+}	136	136	98	90	90
Zr^{4+}	45600	45000	38300	35342	35100
La^{3+}	20500	20000	18500	16080	15728

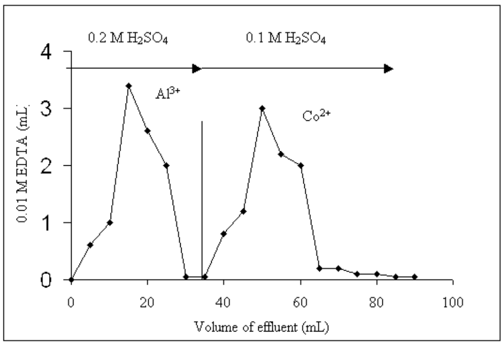

Fig. 2

Elution profiles of binary separations of metal ions on naphthol blue–black-modified Amberlite IRA-400 resin. Separation of Al^{3+} from Co^{2+}

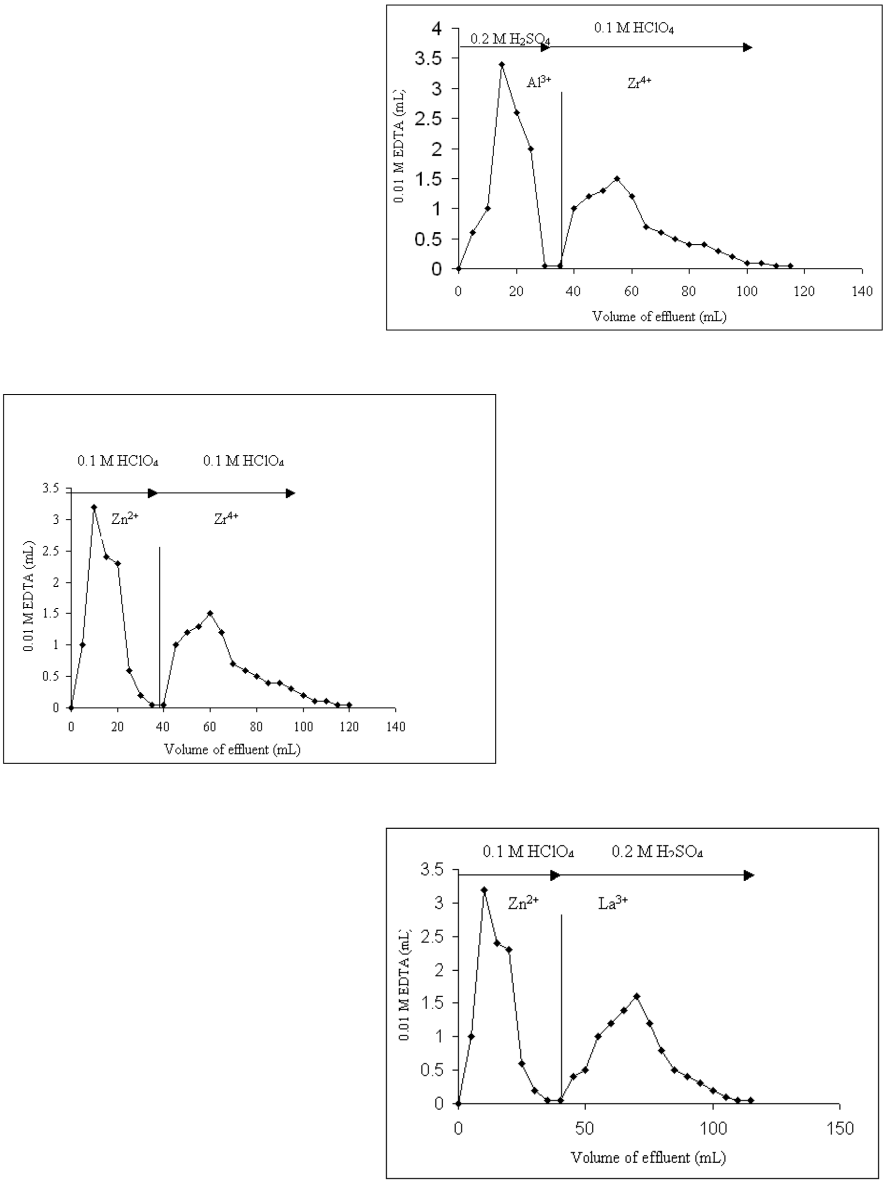

Fig. 2 (continued)

Elution profiles of binary separations of metal ions on naphthol blue–black-modified Amberlite IRA-400 resin. From the top: separation of Al^{3+} from Zr^{4+}, Zn^{2+} from Zr^{4+}, and Zn^{2+} from La^{3+}

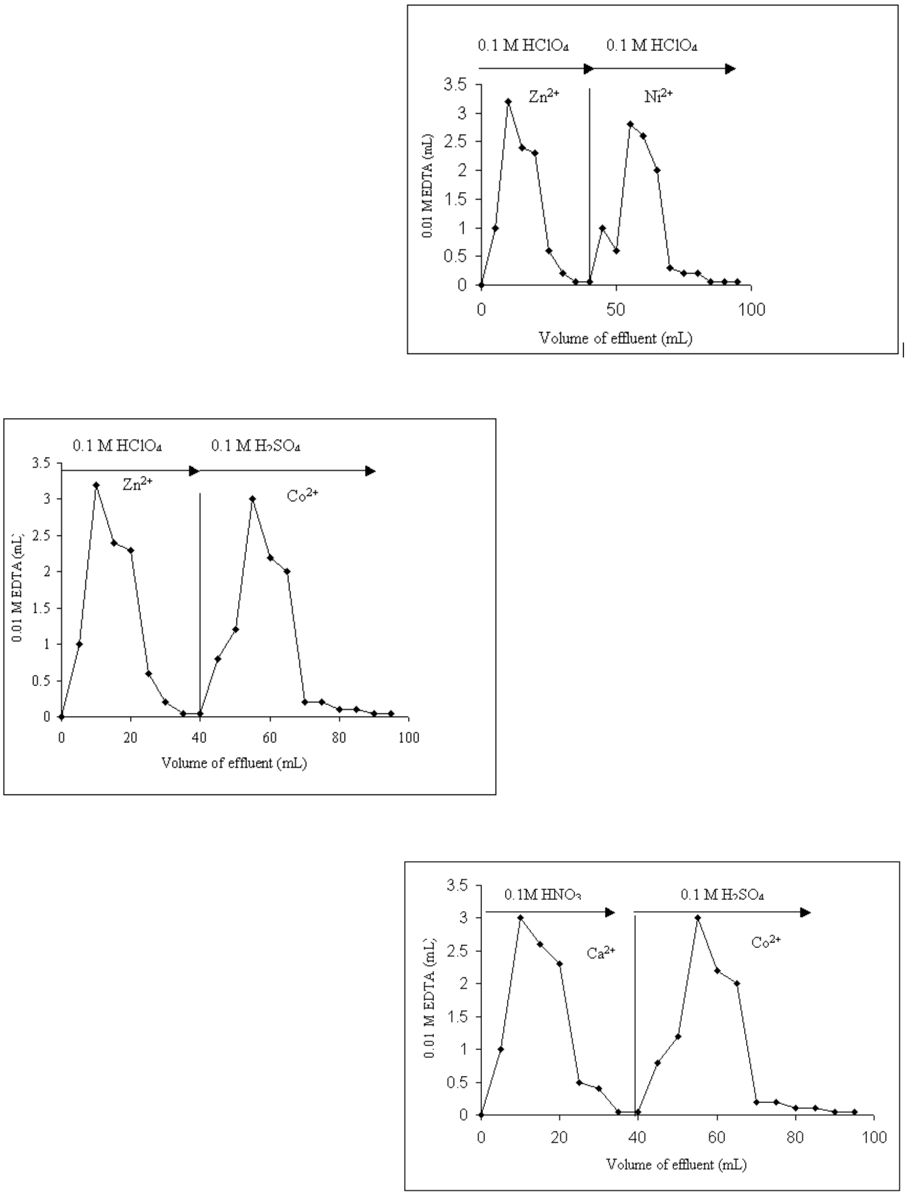

Fig. 2 (continued)

Elution profiles of binary separations of metal ions on naphthol blue–black-modified Amberlite IRA-400 resin. From the top: separation of Zn^{2+} from Ni^{2+}, Zn^{2+} from Co^{2+}, and Ca^{2+} from Co^{2+}

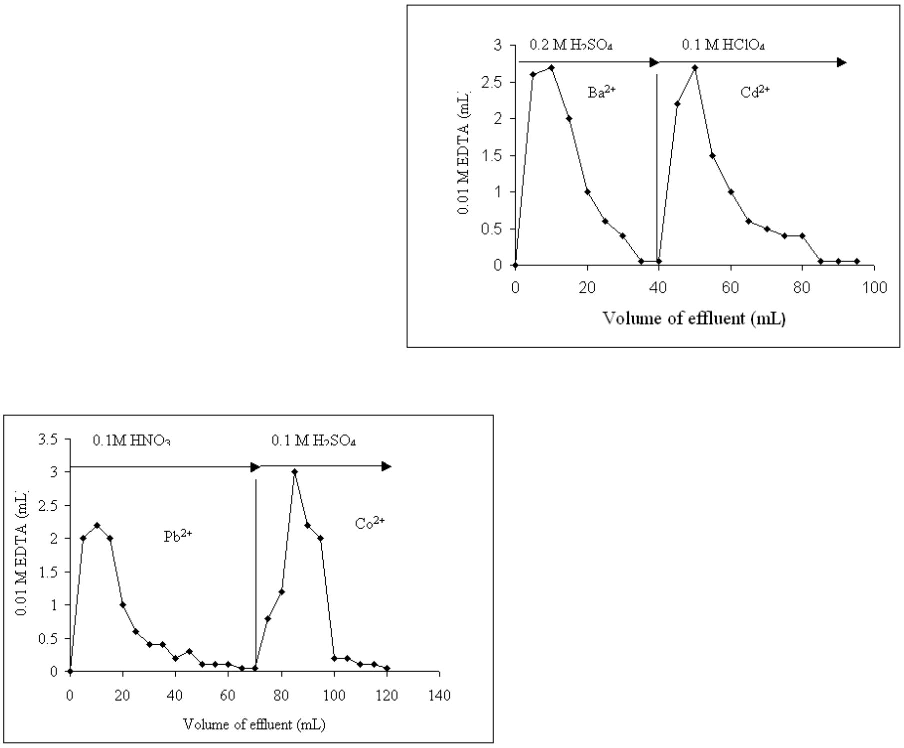

Fig. 2 (continued)

Elution profiles of binary separations of metal ions on naphthol blue–black-modified Amberlite IRA-400 resin. From the top: separation of Ba^{2+} from Cd^{2+} and Pb^{2+} from Co^{2+}

The exceptionally high K_d values for Zr^{4+} with all mobile phases were because of the formation of a more stable metal naphthol blue–black complex. The high K_d values of Zr^{4+} enabled its selective separation from a synthetic mixture of Zr^{4+}, Zn^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, and Cd^{2+}. The metal ions were first eluted together, as mixture, with 0.1 M HNO_3 solution and Zr^{4+}, which was strongly retained by the resin, was eluted later with 0.1 M $HClO_4$ (Table II).

CONCLUSIONS

IRA-400 anion-exchange resin modified with naphthol blue–black has been used for separation of metal ions of analytical importance. It is probable that the practical utility of the material can be further explored by use of a variety of solvent systems.

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