

Sorption studies on cresol red modified Amberlite IR400 (Cl⁻) resin: Binary and selective separation of Hg²⁺ ions

Amjad Mumtaz Khan^{*a}, Shalini Gautam^b & Sajad A Ganai^b

^aDepartment of Applied Chemistry, Z H College of Engineering & Technology

^bDepartment of Chemistry, Aligarh Muslim University, Aligarh 202 002, India
Email: amjad.mt.khan@gmail.com

Received 19 February 2008; revised 11 September 2008

Strong acid anion exchange resin Amberlite IR400 (Cl⁻) has been modified by sorption of cresol red. Equibration studies such as concentration, pH, time and temperature of the reagent on the adsorption of dye have been studied. The maximum uptake of cresol red was found to be 2.20 μmol per 0.3×10^3 g resin at pH 1.0. On the basis of K_d values in solvents having different polarity and dissociation constant, important binary separations of metal ions namely Pb²⁺, Bi³⁺, Mn²⁺, Zn²⁺, Ni²⁺, Sn⁴⁺, Hg²⁺, Mg²⁺, Zr⁴⁺, Ca²⁺, Ba²⁺ and Sr²⁺ have been achieved. To check the selectivity and the reproducibility of the method, separation of different amounts of Hg²⁺ has been achieved in a synthetic mixture containing Fe³⁺ (5.58 mg), Cu²⁺ (6.35 mg), Al³⁺ (2.69 mg) and Ni²⁺ (5.68 mg). The results show that the cresol red modified resin may be used for the removal of Hg²⁺ from industrial and domestic wastes. Results also indicate that the modified resin may also be suitable as a packing material in column chromatography for pre-concentration and recovery of some metal ions from industrial effluents and wastewater.

Keywords: Sorption, Cresol red, Amberlite IR400 (Cl⁻), Mercury separation, Anion exchange resin

Recently, incorporating chelating agents has modified the nature of ion exchange resin. These modified resins often show a definite selectivity towards certain ion or groups of ions. Such modified resins are prepared by immobilization of chelating agents on various supports. Aromatic complexing agents with sulphonate acid group when treated with exchange resin have been found useful for separation of metal ions. The selectivity of these modified resins depends upon the nature of the functional group of the ligand. Ion exchange is often used for removing certain ions from a solution replacing it by another ion *viz.* removal of phosphate ions, which interfere with standard quantitative inorganic analysis¹. For quantitative estimation the replacement of alkali metal ions by H⁺, is readily determined²⁻⁵. Industrial application of ion-exchange resins in water softening, metal recovery from waste treatment of electroplating solutions has been explored⁶⁻⁸.

Ion exchange materials occur in definite forms *viz.* H⁺, Na⁺, Cl⁻ and NO₃⁻ etc. The utility of the modified resins has prompted the researchers to search for new chelate forming resin beads and to check their selectivity towards the metal ions. The potential of chelating ion exchanger resins for the separation and

pre-concentration of metal has been firmly established⁹⁻¹³. These chelate forming groups are usually prepared by incorporation of complexing groups on the ion exchange resin. The resin beads adsorb metal ion and give the characteristic colour of the complex. It is possible to detect even traces because of surface area of beads. Griesbach and Hieses¹⁴ described the preparation of a chelating resin by chemical reaction and studied about fifteen adsorbents. Dowex1X-8 containing adsorbed sulphonated azo dyes¹⁵ has been found useful to separate copper and nickel ions. Azothiopyrene disulphonic acid¹⁶ has been incorporated to an anion exchange resin and the product has been used for the uptake of Hg²⁺, Cu²⁺ and Cd²⁺ ions from aqueous solutions. Similar use of pyrogallol sulphonate acid¹⁷ enabled the separation and enrichment of Mo⁶⁺ and Fe³⁺ ions. The incorporation of thiol¹⁸ functional group shows high selectivity towards heavy metal ions. Nabi *et al.*¹⁹⁻²⁴ synthesized a variety of chelate forming resins by incorporating complexing agents such as bromophenol¹⁹, eriochrome black-T²⁰, congo red²¹, alizarin red²², crystal violet²³ and toluidine blue²⁴. Metal ions can be selected for separation on the basis of distribution coefficients (K_d). It is also possible to separate trace quantity of a metal from a macro

amount of another metal ion. The resin sorbed with different chelating agents may show marked selectivity towards a particular metal ion. It is for this reason, effort have been made to develop new chelate form of exchange resin and to find their specificity for the detection, determination and separation of metal ions as well as anions

The present work has been undertaken as an effort to develop the new modified ion exchange resin using a new chelating agent. The strong acid anion exchanger resin Amberlite IR400 (Cl^-) has been modified by adsorption of cresol red. The analytical application of the material has been explored.

Experimental Procedure

Apparatus

A Genesis's spectronic 20D (USA made) UV-visible spectrophotometer, L1-10T digital pH meter (Elico, India), electronic balance (Varbal, India) and shaker cum incubator (MSW, India) with a stainless body and an electrical oven (NSW, India) were used.

Test solutions

0.1 M solution of NaOH, 2.0 M and 0.1 M solutions of HCl, 0.1 M, 0.2 M and 1.0 M solutions of CH_3COONa and 0.01 M solution of EDTA were prepared in demineralized water.

Reagents and chemicals

Amberlite IR400 (Cl^-) resin (mesh size 16-45, 8% by wt) in the protonated form was obtained from Merck (India) Ltd. and the disodium salt of EDTA from S.D fines Chemicals (India). Ethanolic solution (1%) of 1-(1-hydroxy-2-naphtholazo)-5 nitro-2-naphthol-4-sulphuric acid sodium salt (Erichrome Black-T) and 1-(2-pyridylazol) 2-naphthol (PAN), aqueous solution of (1%) of *o*-cresol sulphonaphthalein-3, cresol-red dye, [S.D fines Chemicals (India)], chloride and nitrate salts of metal ion etc. were prepared in distilled water. All other reagents used were of analytical grade reagents.

Preparation of modified resin

The modified cresol red resin was prepared by treating Amberlite IR400 (Cl^-) resin with aqueous solution of cresol red for 24 h at pH 1.0. The resin was washed several times with demineralized water to remove access reagent from the supernatant liquid. The sorbed resin was finally dried in an oven at 60°C to remove moisture.

Adsorption isotherm

(i) Effect of reagent concentration

To study the sorption of cresol red under static conditions, 0.3 g of resin in Cl^- form was equilibrated with 30 mL cresol red solution of different concentration (74-198 $\mu\text{mol/L}$) in a temperature controlled electronic shaker incubator at constant pH 1.0 for 2 h. The equilibrium concentration of the reagent was then determined spectrophotometrically at 435 nm.

(ii) Effect of time

The equilibrium time for sorption of cresol red on the resin was established by performing a series of adsorption experiments at constant pH 1.0. A constant mass of Amberlite IR400 (Cl^-) was stirred with known volume of an aqueous solution of cresol red (30 mL) for 1-6 h. The amount of cresol red adsorbed on the resin was determined by analyzing the supernatant solution every hour spectrophotometrically at 435 nm.

(iii) Effect of pH

To determine the effect of pH on the sorption of cresol red, 0.3 g of resin was shaken continuously with 30 mL of 198 $\mu\text{mol/L}$ cresol red solution for 2 h. The pH of solutions was adjusted by adding an appropriate acid, base or buffer solution of the desired pH. The equilibrium concentration of the reagent in the supernatant liquid was determined spectrophotometrically in the pH range 1.0 to 8.0 at wavelength 435 nm and between pH 9.0 to 10, the absorbance were recorded at 575 nm.

(iv) Effect of temperature

The optimum temperature for adsorption of cresol red on the resin was established by performing a series of adsorption experiment at pH 1.0. A fixed mass 0.3 g of Amberlite IRA400 (Cl^-) was stirred for 2 h with aqueous solution of cresol red 30 mL in the temperature range $25 - 70^\circ\text{C}$ in a water bath. The amount of cresol red taken up by the resin was determined by analyzing the supernatant solution spectrophotometrically at 435 nm.

Distribution coefficient (K_d) of metal ions

The modified resin beads (0.3 g) was loaded with 1.0 mL of 0.1 M metal ion solution and 29 mL of the appropriate solvent in 250 mL Erlenmeyer flask. The mixture was shaken continuously in a shaker incubator at 25°C for 2 h. The amount of cation in the solution before and after equilibrium was determined

by standard procedures. K_d value of each metal ion was calculated by using the formula

$$K_d = \frac{I-F}{F} \times 100$$

where I = volume of EDTA (mL) used for complete titration of the metal ion solution before treatment with the resin, F = volume of EDTA (mL) used after the treatment of the metal ion solution with the resin i.e. (amount of metal ion left in the solution after equilibrium with resin) and $I-F$ = amount of metal ion in the resin phase.

Quantitative separation of metal ions

The separations of metal ions were carried out by elution technique. Modified resin (1.5 g) was packed into a glass column, which was 1 feet long and 8 mm internal diameter having a glass wool support at the end. It was washed 2-3 times with DMW. 2.0 mL of binary mixture of the metal ion which is to be separated was poured on the top of the column and the solution was allowed to flow gently. The column was rinsed with demineralized water. The elution technique was carried out at a constant flow rate of 0.5 mL per min using appropriate eluting reagent. The eluted metal ion fractions were determined titrimetrically using a 0.01 M disodium salt of EDTA solution as a titrant. The selective binary separations of bismuth, mercury, zirconium and tin metal ions from other metal ions have been achieved.

Results and Discussion

Ion exchange resin with a large surface area and a macro porous structure are treated with a variety of complexing agents to enhance their selectivity to achieve separation and recovery of metal ions. It is with this aim, the resin has been modified by the incorporation of cresol red. Cresol red, which has three aromatic rings, is probably responsible to interact with the resin matrix (styrene-divinyl benzene copolymer) owing to the presence of hydroxyl group and $-\text{SO}_3\text{Na}$ group, which interact selectively with metal ions. It is imperative to presume that the dye cresol red, which contains three aromatic rings, may be attached to the poly(styrene-divinylbenzene) skeleton probably by physical adsorption and π - π dispersion forces arising from the aromatic nature of the resin and the dye is responsible for this adsorption.

Both Amberlite IRA400 (Cl^-) and Amberlite IR-120(H^+) were tried for adsorption of various chelating agents. It was observed that only Amberlite IRA400 (Cl^-) adsorb cresol red, the colour of the resin beads gets changed from light yellow to red. The IRA400 (Cl^-) resin has been found to exhibit sorption or desorption of cresol red at pH 1.0 with the concentration of the dye 198 $\mu\text{mol/L}$. The hydrophobic nature of styrene divinyl benzene copolymer matrix of Amberlite IRA400 (Cl^-) resin appears to be an excellent sorbent for cresol red. The IRA400 (Cl^-) resin beads show different colour at different pH ranging from 1 -10 i.e. (a) pH 1 to 3, orange red; (b) pH 4 – 6, reddish brown; (c) pH 7 – 8, purple d and (d) pH 9 and 10, dark purple.

The time required to attain equilibrium for the adsorption of cresol red on the resin was found to be 2 h and adsorption was constant at pH 1.0. Therefore, an equilibrium time of 2 h was chosen for adsorption studies throughout all these experiments. The adsorption behaviour of cresol red on the resin was almost linear and followed Langmuir adsorption isotherm. It was observed from the distribution coefficient values given in Tables 1 and 2 that cresol red has different selectivity for metal ions possibly because of the formation of metal complexes with different stability constants. The type of solvents used was based on the acid dissociation constant and polarity factor, which affect the ease of complexation. Adsorption studies of different metal ions in different solvent systems revealed many interesting features. It was found that almost all the metal ions exhibit low K_d values in solvent systems studied except mercury and bismuth, which show exceptionally high value of K_d . This differential behaviour makes it possible to separate mercury and bismuth ions from other metal ions. It is clear from Table 1 that methanol is the only solvent in which the K_d value for both Hg^{2+} and Bi^{3+} metal ions is zero, otherwise for all other metal ions the values are high. Thus, it consequently enhance the selectivity and separation possibility. On the basis of differences in K_d values several binary, ternary separations of metal ions were performed by selecting appropriate eluting reagents. The quantitative separations of metal ions Mn^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , from Bi^{3+} and of Ni^{2+} , Pb^{2+} , Sn^{4+} , Zn^{2+} from Zr^{4+} and Mg^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Zn^{2+} , Mn^{2+} , from Hg^{2+} are performed (Table 3). To check the selectivity and the reproducibility of the method, separation of different

Table 1 — Distribution coefficients of metal ions in different solvent systems on Amberlite IRA400 resin treated with cresol red

Metal ion	Distribution coefficient for solvent systems						
	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇
Mg ²⁺	00	2.2	18.3	1.8	1.6	11.7	22.4
Ca ²⁺	2.7	0.8	5.4	1.7	13.5	16.8	00
Sr ²⁺	13.8	0.9	4.1	10.4	00	15.0	24.4
Ba ²⁺	19.8	1.8	00	21.8	1.8	9.1	0.9
Hg ²⁺	155	216.6	00	56.5	233.3	135.5	157
Pb ²⁺	24.5	0.9	8.3	00	2.7	5.5	23.5
Mn ²⁺	00	0.9	8.8	0.9	00	0.9	1.9
Zn ²⁺	1.7	1.7	9.2	14.4	1.9	00	7.6
Cd ²⁺	00	5.4	00	8.5	-	6.0	3.8
Cu ²⁺	0.9	8.0	1.8	7.8	42.5	0.9	9.0
Al ³⁺	0.9	17.1	1.0	70	11.4	00	15.3
Fe ³⁺	0.9	10.4	6.0	56.3	17.2	3.7	0.9
Ni ²⁺	9.8	1.9	2.9	00	36.6	0.9	0.9
Co ²⁺	9.3	9.1	3.0	4.7	33.3	7.5	26.2
Sn ⁴⁺	50.0	4.1	100	116.6	-	83.3	22.2
Ag ⁺	16.6	-	-	-	1.9	-	-
Zr ⁴⁺	0.8	68	18.0	18.0	22.2	122	70
Th ⁴⁺	15.3	-	7.6	7.6	-	27.7	60
Ce ³⁺	8.3	17.3	-	-	358.3	188.8	0.9
Bi ³⁺	377.5	200	00	00	126.6	33.3	122.2

S₁ 0.1 M Acetonitrile S₂ 0.1 M DMSO S₃ 0.1 M Methanol S₄ 0.1 M FormamideS₅ 0.1 M Acetone S₆ 0.1 M Acetic acid S₇ 0.1 M Formic acid

Table 2 — Distribution coefficients of metal ions between solvent systems based on acid dissociation constant and Amberlite IRA 400 resin treated with cresol red

Metal ion	Distribution coefficient for solvent systems							
	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈
Mg ²⁺	11.5	00	15.2	25.2	0.8	00	6.0	2.1
Ca ²⁺	0.9	2.0	5.1	15.0	00	17.1	5.7	-
Sr ²⁺	16.4	1.9	12.3	10.3	4.7	3.0	1.9	-
Ba ²⁺	22.3	2.9	26.9	6.3	46.4	17.7	0.9	-
Hg ²⁺	24.4	17.7	300	183.3	256.6	1285	129.1	17.6
Pb ²⁺	20.0	1.8	9.8	3.7	19.1	11.1	5.7	2.3
Mn ²⁺	2.9	00	2.8	7.5	37.3	00	2.8	16.4
Zn ²⁺	00	00	-	7.5	4.6	5.4	12.7	-
Cd ²⁺	1.8	25.5	00	8.1	00	2.0	7.8	-
Cu ²⁺	1.9	3.8	6.0	5.8	11.1	5.1	5.2	546.6
Al ³⁺	9.1	12.5	53.0	11	14.2	12.7	46.6	-
Fe ³⁺	21.4	26.5	177.7	1	3.2	6.5	16.6	00
Ni ²⁺	1.9	13.5	00	00	40	2.2	4.9	00
Co ²⁺	3.8	85	209.0	3.9	43.3	11.7	3.8	-
Sn ⁴⁺	-	-	-	37.5	11.1	128.5	33.3	-
Ag ⁺	11.1	-	-	50	-	-	420.8	-
Zr ⁴⁺	425	23.8	193.3	-	-	31.3	-	-
Th ⁴⁺	193	00	422	-	5.0	46.6	76.6	-
Ce ³⁺	500	7.1	-	90.4	-	1.1	25.7	-
Bi ³⁺	621	76.6	70	177.7	128.5	151.2	135.5	-

S₁ 0.1 M Boric acid S₂ 0.1 M Succinic acid S₃ 0.1 M Tartaric acidS₄ 0.1 M 0.1 M Phenol S₅ 0.1 M TCA S₆ 0.1 M 0.01 M Nitric acidS₇ 0.1 M Formic acid S₈ 0.1 M Disodiumtetraborate

Table 3 — Binary separation of metal ions on cresol red modified Amberlite IRA400 (Cl⁻) anion exchange resin column

Binary mixtures	Amount loaded (mg)	Amount recovered (mg)	Recovery(%)	Volume of eluent (mL)	Eluent used
Bi ³⁺	20.9	14.2	67.94	70	0.1 M Formamide
Pb ²⁺	20.7	17.3	83.57	70	0.1 M Methanol
Bi ³⁺	20.9	16.3	77.96	70	0.1 M Acetonitrile
Mn ²⁺	5.49	4.39	79.96	70	0.01 M Nitric acid
Bi ³⁺	20.9	18.6	88.99	90	0.1 M Boric acid
Zn ²⁺	6.53	6.53	100.00	90	0.01 M Nitric acid
Bi ³⁺	20.9	17.4	83.25	80	0.1 M Boric acid
Ni ²⁺	5.87	4.34	73.93	80	0.01 M Nitric acid
Bi ³⁺	20.9	13.3	63.63	80	0.1 M Boric acid
Co ²⁺	5.89	4.71	79.96	80	0.01 M Nitric acid
Sn ⁴⁺	11.86	5.45	45.95	80	0.1 M Formamide
Ni ²⁺	5.87	5.75	97.95	80	0.01 M Nitric acid
Sn ⁴⁺	11.86	8.53	71.92	80	0.1 M Formamide
Pb ²⁺	20.7	15.7	75.84	80	0.1 M Nitric acid
Zr ⁴⁺	9.12	8.21	90.02	70	0.1 M Boric acid
Zn ²⁺	6.53	6.01	92.03	70	0.01 M Nitric acid
Hg ²⁺	20.05	8.8	43.89	80	0.01 M Nitric acid
Mg ²⁺	2.43	2.43	100.00	100	0.1 M Nitric acid
Hg ²⁺	20.05	18.4	91.77	70	0.1 M Formic acid
Ca ²⁺	4.01	4.01	100.00	70	0.01 M Nitric acid
Hg ²⁺	20.05	18.0	89.77	80	0.1 M Formic acid
Ba ²⁺	13.73	11.81	86.01	80	0.01 M Nitric acid
Hg ²⁺	20.05	14.0	69.82	70	0.1 M DMSO
Sr ²⁺	8.76	8.45	96.46	80	0.01 M Methanol
Hg ²⁺	20.05	15.6	77.80	80	0.01M Nitric acid
Zn ²⁺	6.53	6.53	100.00	80	0.1 M Nitric acid
Hg ²⁺	20.05	12.2	60.84	70	0.01 M Nitric acid
Mn ²⁺	5.49	5.49	100.00	80	0.1 M Nitric acid

Table 4-Selective separation of different amounts of Hg²⁺ from mixture containing: Cu²⁺ =6.35 mg, Al³⁺ = 2.69 mg, Fe³⁺ = 5.58 mg and Ni²⁺ = 5.68 mg. Eluent used: 0.1 M Nitric acid

S. No	Amount loaded (mg)	Amount found (mg)	Recovery (%)	Volume of eluent, (mL)
1	20.05	15.99	79.75	160
2	40.11	25.68	64.02	160
3	60.15	36.47	60.63	180
4	80.20	56.58	70.54	200

amounts of Hg²⁺ ions have been achieved from a synthetic mixture consisting of Hg²⁺ Fe³⁺ (5.58 mg), Cu²⁺ (6.35 mg), Al³⁺ (2.69 mg) and Ni²⁺ (5.68 mg). The results are presented in Table 4.

Conclusion

The results of the study prove that the cresol red modified Amberlite IR400 (Cl⁻) resin can successfully be used for the selective separation of different amounts of Hg²⁺ from a synthetic mixtures consisting of metal ions viz. Fe³⁺, Cu²⁺, Al³⁺ and Ni²⁺ ions. The resin has the potential for the removal of Hg²⁺ ions from industrial wastes and domestic water discharge.

Anion exchange resin sorbed with cresol red can be successfully utilized as a packing material in column chromatography and for preconcentration and recovery of Hg²⁺ ions from industrial effluents and wastewater.

Acknowledgement

The authors are grateful to the Chairman, Department of Chemistry for providing research facilities.

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