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Column chromatographic separation of some toxic heavy metal ions on an acidic cation exchange resin sorbed with an azo dye

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ABSTRACT

Chromatographic separations of some toxic heavy metals on acidic cation exchange resin (Amberlite IR-120) resin modified with methyl red dye were studied. The effect of pH, concentration and time was determined by standard methods to optimise the standard conditions for maximum sorption. The distribution coefficient (Kd values) of different metal ions were calculated in different solvent systems to explore the possibilities of separation of metal ions. Some binary separations of analytical interest could be achieved using columns packed with this material.

KEYWORDS

AmberliteIR 120;
Methyl red;
Distribution coefficient;
Binary;
Mobile phase.

INTRODUCTION

Recently, as waste volumes have grown to a great extent, it has become necessary to remove heavy metals from processed effluents. Some of these metals are relatively valuable, making it economical to recover them. During the last 20 years, several new ion-exchange resins have been developed that are selective for heavy metals. Recently, recovery has become widely recognized as a way to reduce waste treatment costs. Now a days due to increasing environmental problems from excessive and indiscriminate industrialization, we need a lot of effort for the removal of heavy metals from industrial effluents and waste water. The potential of chelating ion-exchange resins for separation and preconcentration of metal ions has been firmly established for this purpose[1-5] Ion exchange resins are widely used in different separation, purification and decontamination processes. The most common examples are water softening and water purification. In many cases ion exchange resins were introduced in such processes as a more flexible alternative to the use of natural or artificial zeolites.

Keeping in view, the chromatographic separation of some toxic heavy metal ions on acidic cation exchange resin sorbed with an azo dye, the present studies were undertaken with the objectives to study the effect of pH and concentration on the adsorption of the dye on the regenerated IR-120 cation exchange resin sorbed with an azo dye and and to determine the distribution coefficients (K_d values) of different metal ions on the treated resin. Finally on the basis of difference in K_d values, achieve binary separation of some heavy metal ions.

MATERIALS AND METHODS

Chemicals standards and glasswares

All the chemicals and the standards used in the present study were obtained from E.Merck, Spectrochem and Loba Chemie, India while the IR 120 Amberlite resin was procured from BDH, UK. The glassware utilized was of corning or borosil make.

Regeneration of amberlite IR-120 resin

Fifty grams of cation exchange resin (Amberlite IR-120) was taken in 0.1N HCl solution in a 100mL conical flask, shaken for 2-3 hrs. and allowed to stand over night. The supernatant was discarded and the exchanger was washed several times with distilled water to make it free of chloride ions. The chloride ions were checked by $AgNO_3$ solution. When the supernatant was free of chloride ions, the exchanger was made to pass through the filter paper and allowed to dry in open in the presence of air.

Preparation of methyl red dye solution

A hundred milligrams of methyl red dye was dissolved in 5mL methanol and diluted to 100mL with distilled water to prepare 1000ppm solution of the dye.

Preparation of modified amberlite IR-120 resin

About 40g of cation exchange resin (Amberlite IR-120) in H^+ form was treated with 25mL methyl red solution (1000ppm) in a 100mL conical flask by shaking it for 3-4 hrs on an orbital shaker and allowing the mixture to stand over night. The upper layer of the methyl red solution was decanted and the treated resin was washed several times with demineralized water to remove excess reagent. The resin with adsorbed methyl red was taken on a filter paper and finally dried in air to remove the moisture. The colour of Amberlite IR-120 resin changed from golden yellow to maroon red.

Preparation of indicators

One percent ethanolic solution of the indicators, Eriochrome Black T (EBT), 1-[2-pyridylazo]-2-naphthol (PAN) and Xylenol orange (XO) were prepared for end point determination during titration of the metal ions.

Preparation of standard solution of metal ions

A 0.1M solution of Na_2EDTA was prepared by dissolving the required amount of salt in demineralized water for titration.

Determination of λ_{max}

The stock solution of the dye was diluted to 100ppm and subjected to visible scanning (range from 350-800nm) by using UV-VIS Spectrophotometer. The maximum absorption of the compound was found to be 528.2nm which was taken as λ_{max} for methyl red for further analysis.

Ion exchange capacity

The ion exchange capacity of both treated and untreated Amberlite IR-120 resin was determined by column method. One gram of ion exchanger was loaded on a column supported with glass wool. The hydrogen ions were eluted by passing 0.1M solution of calcium chloride. The hydrogen ions in the effluent were determined after titrating gainst standard NaOH solution.

Effect of pH

In order to determine the effect of pH on the adsorption of methyl red, 1g Amberlite IR-120 resin was shaken continuously with 20mL methyl red solution of different pH (adjusted by adding appropriate acid, base, or buffer) for 3-4 hrs. The equilibrium concentration of the reagent in the supernatant liquid was determined spectrophotometrically at 528.2nm (Figure 1).

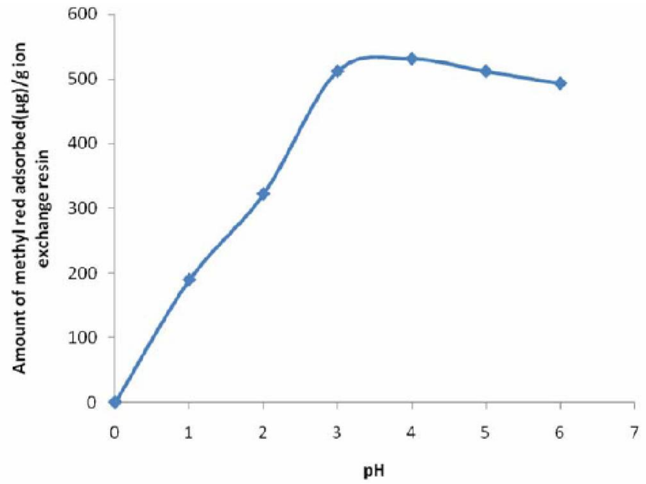

Figure 1 : Effect of pH on the amount of methyl red dye adsorbed by amberlite IR-120 resin

Effect of time

The equilibration time for adsorption of methyl red by the resin was established by performing a series of adsorption experiments at constant pH 4.0. A constant mass (1g) of Amberlite IR-120 was stirred with an aqueous solution of methyl red (50mL) for different times.

The amount of methyl red taken up by the resin was determined by analyzing the supernatant solution spectrophotometrically at 528.2nm (Figure 2).

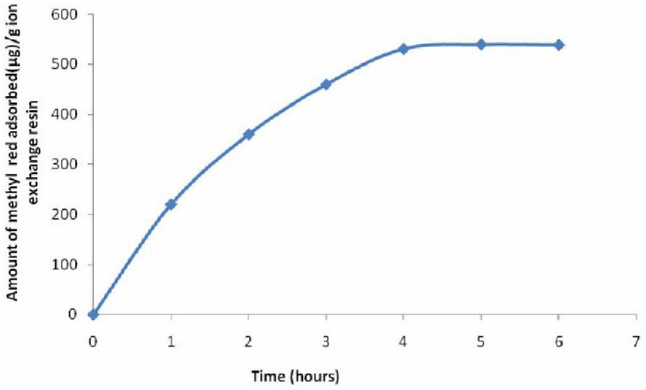

Figure 2 : Effect of equilibration time on the amount of methyl red dye adsorbed by Amberlite IR-120

Effect of reagent concentration

The sorption of methyl red dye under static conditions, in the protonated form (1g) was studied by equilibrating the exchanger in H^+ form with methyl red solutions of different concentration (20ppm, 50ppm, 75ppm, 100ppm, 125ppm, 150ppm) on an electronic shaker at constant pH 4.0 for 3-4 hrs. The equilibrium concentration of the reagent was then determined spectrometrically at 528.8 nm. The adsorption isotherm is shown in Figure 3.

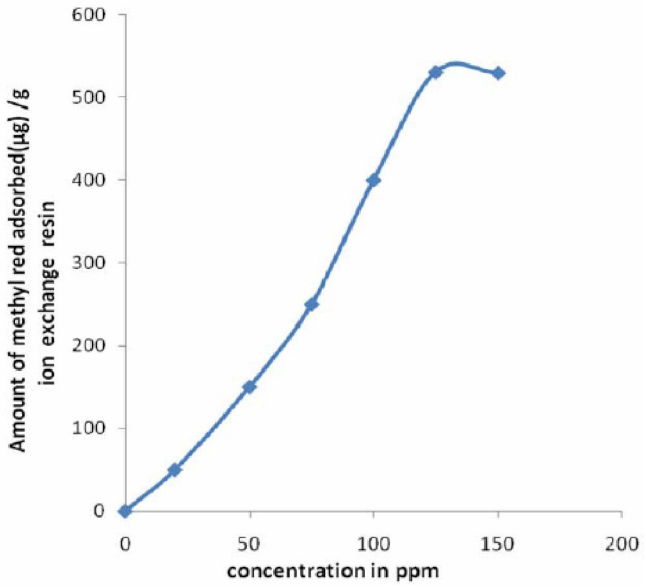

Figure 3 : Effect of methyl red concentration on the amount of dye adsorbed by Amberlite IR-120 resin

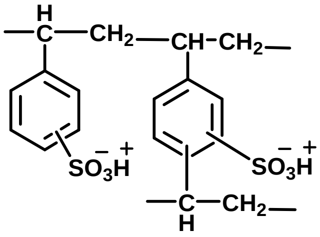

Figure 4.1 : Amberlite IR-120 resin

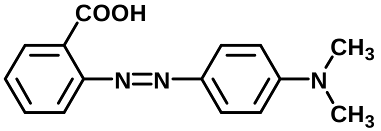

Figure 4.2 : Methyl red dye

TABLE 1 : Solvent systems used for determination of distribution coefficients of metal ions

Solvent system	Composition	Notation
0.5M Sodium acetate	-	S_1
0.1M Citric acid	-	S_2
0.05M Acetic acid+0.5M Sodium acetate	1:1	S_3
0.05M Acetic acid+0.5M Sodium acetate	1:1	S_4

TABLE 2 : Distribution coefficients of metal ions in the different solvent systems

Metalation	Distribution coefficient mL/g			
	S_1	S_2	S_3	S_4
Ca^{2+}	12	0	35	7.69
Mg^{2+}	5.714	0	68.18	0
Zn^{2+}	0	0	48	0
Bi^{3+}	0	400	0	160
Hg^{2+}	10	0	25	13.636
Co^{2+}	27.272	0	118	19.04
Pb^{2+}	46.66	0	86.66	14.285
Cd^{2+}	20	0	100	9.0909
Cu^{2+}	12	50	10.526	14.2857

Where, S_1 = 0.5M Sodium acetate, S_2 = 0.1M Citric acid, S_3 = 0.05M Acetic acid+0.5M Sodium acetate, S_4 = 0.05M Acetic acid+1M Sodium acetate

Distribution coefficients (K_d) of metals ions

Distribution coefficient (K_d values) for metal ions in water systems was determined by the batch process. For this modified resin beads (0.4g) were taken with 1.0mL of 0.10 M metal ion solution and 39mL of an appropriate solvent in a 250mL conical flask. The solvent systems studied for determination of the K_d values are listed in TABLE 1. The mixture was shaken continuously on a shaker for 4 hrs. The amount of cation in solution before and after equilibration was determined by EDTA titrations using the standard method and an appropriate metal ion indicator.

For determination of Ca^{2+}, Mg^{2+} and Zn^{2+} Eriochrome Black T (EBT) was used as an indicator; for Cu^{2+},1-[2-pyridylazo]-2-naphthol (PAN) was used and the determination of Hg^{2+}, Co^{2+}, Pb^{2+}, Bi^{3+} and Cd^{2+} was done using Xylenol orange (XO) as an indicator.

The titrations were performed by taking 10mL of 0.1M metal ion solutions followed by the addition of appropriate buffer and indicator and titration with standardized Na$_2$EDTA solution. The K$_d$ value for each metal ion was then calculated by the use of the formula:

$$K_d = \frac{(\text{Amount of metal ion in resin(g)})/\text{mass of resin(g)}}{(\text{Amount of metal ion in solution(g)})/\text{volume of solution(mL)}}$$

The K$_d$ values for the metal ions in the different solvent systems are presented in the TABLE 2.

Quantitative separation of metal ions

Separation of the metal ions was performed by an elution technique. Modified resin Amberlite IR-120 resin (2g) treated with methyl red dye was packed onto a glass column of 50 cm, with a glass-wool support at the end, and washed 2-3 times with demineralised water. When the level of demineralised water remained just above the surface of the resin, the binary mixture (2.0mL) was poured on to the top of the column. Binary solutions of the metal ions were prepared by mixing 0.1M solution of each ion. The column was then rinsed with an appropriate mobile phase. The metal ions were then eluted with the mobile pha and on the basis of K$_d$ values (TABLE 2) the effluent was collected in 10mL fractions. The metal ion content of each 10mL fraction was determined titrimetrically using disodium salt of EDTA (0.01M) solution as titrant. The total volume of an eluent used for complete removal of particular metal ions and the quantities separated are given in TABLE 3.

RESULTS AND DISCUSSION

Ion-exchange resins with a large surface area and macroporous structure are treated with a number of complexing agents to enhance their selectivity for achieving separation and recovery of metal ions. Amberlite IR-120 (Figure 4.1) cation exchange resin was thus tested for adsorption of methyl red dye (Figure 4.2). Equilibrium conditions such as concentration of methyl red, pH and adsorption time were also studied. The styrene divinyl benzene coplymer, Amberlite 120 served to be an excellent sorbent for methyl red dye. The adsorption isotherm of methyl red was somewhat linear

TABLE 3 : Quantitative separations of metal ions on amberlite IR-120 resin treated with methyl red

Binary mixture	Amount fed(mg)	Amount eluted(mg)	(%) of metal ion eluted	Volume of eluent(ml)	Eluent used
Zn^{2+}	28.75	28.17	97.99	30	0.1M Citric acid
Bi^{3+}	48.50	47.035	96.80	40	0.05M Acetic acie+0.5M Sodium acetate
Mg^{2+}	20.35	20.06	96.81	30	0.05M Acetic acid+1M Sodium acetate
Ca^{2+}	11.09	10.85	97.83	50	0.05M Acetic acid+05M Sodium acetate
Mg^{2+}	20.35	20.30	99.60	40	0.05M Acetic acid+1M Sodium acetate
Bi^{3+}	48.50	46.84	96.57	50	0.1M Citric acid
Zn^{2+}	28.75	28.70	99.84	30	0.05M Acetic acid+1M Sodium acetate
Cd^{2+}	18.83	18.20	96.65	40	0.05M Acetic acid+0.5M Sodium acetate
Cd^{2+}	18.83	18.06	95.91	30	0.1M Citric acid
Cu^{2+}	24.96	23.14	98.910	40	0.05M Acetic acid+0.5M Sodium acetate
Co^{2+}	23.79	23.14	97.20	40	0.1M Citric acid
Bi^{3+}	48.50	45.46	93.73	50	0.05M Acetic acid+0.5M Sodium acetate

following Langmuir's adsorption isotherm (Figure 1). The maximum uptake of methyl red was 530μg/g at pH 4.0 (Figure 2) and the time required to reach equilibrium for adsorption of methyl red by the cation exchange resin was 4 hrs (Figure 3). Hence an equilibrium time of 4 hrs was chosen to ensure complete adsorption throughout the experiment.

The results obtained revealed that the two aromatic residues attached to the azo group in methyl red dye get held to Amberlite IR-120 by the II-II dispersion forces which arise from the aromatic nature of the resin. Moreover the presence of two nitrogen donar atoms as azo group in the dye in sp^2 hybridised state facilitate in the selective interaction with the metal ions.

The distribution coefficients of the metal ions are depicted in TABLE 2. From the TABLE it is evident that methyl red has differential selectivity for metal ions, possibly because of the formation of metal complexes with different stability constants. The elution is based on the stability constant of metal eluting ligand (eluent) complex, those having a high stability constant will be eluted fast. The type of solvent used also affects the ease of complexation.

The adsorption of different metal ions in four different solvent systems tried, revealed many interesting features. It was observed (TABLE 2) that almost all the metal ions except Bismuth (III) had low K_d values in 0.5M sodium acetate (S_1), possibly because of greater tendency of Bismuth (III) to complex with methyl red. The high K_d value for Cobalt (II) in 0.05M acetic acid-0.5M sodium acetate (S_3) made it possible to separate it from other metal ions. As evident from the TABLE 2, the K_d values of the metal ions decrease with increasing sodium acetate content except Bismuth (III) in the mixed acetic acid-sodium acetate system. Similar results on Amberlite IR-120 sorbed with cationic dyes have been reported[6-7].

It is interesting to note that the K_d values for most of the metal ions are high when 0.05M acetic acid-0.5M sodium acetate (S_3) are used as solvent as compared to other solvent systems. This behaviour of metal ions is probably due to the formation of their more stable metal complexes with methyl red. On the basis of the different K_d values six binary separations of metal ions could be achieved on columns packed with this material, by selecting appropriate mobile phases (TABLE 3). As evident from the TABLE, no significant tailing was observed and only small volumes of eluents were required to give compact chromatograms.

The exceptionally high K_d value of Bi^{3+} enables its separation from a mixture of Zn^{2+}, Mg^{2+} and Co^{2+}. In the binary separation of Mg and Ca, Mg eluted ahead of Ca with the suitable acetic acid and sodium acetate solution. Hence the column of Amberlite IR-120 resin adsorbed with methyl red dye can be used to separate Mg from Ca ions in dolomite ore.

Similarly, (0.1to 0.5%) Cd is present along with Zn in the ore Zinc blende (Spha lerite) ore and the mixture of acetic acid and sodium acetate can be utilized to recover Cd from the ore.

CONCLUSION

From the above studies it can be concluded that methyl red loaded Amberlite IR-120 resin has differential selectivity for metal ions. It can also be used successfully as a packing material in column chromatography and for preconcentration and recovery of metals from industrial effluents and waste water. The method can also be used for the determination of composition of alloys and separate some metal ions from ores.

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