Metal Ions Uptake by Chelating Resin Derived from o-Substituted Benzoic Acid and its Synthesis, Characterization and Properties

Pathik M. Shah,[1] *Ajay V. Shah,*[2] *Bhavna A. Shah**[1]

Summary: Chelating resin [AFM] was synthesized by condensation of Anthranilic acid, Formaldehyde with m-Cresol. The chelating resin was characterized by FTIR Spectra, Elemental Analysis and SEM Photographs. The thermal behavior of the resin was characterized by TGA. The thermodynamic parameters such as Activation Energy (E_a), Order of decomposition (n), Entropy of decomposition (S^*), Enthalpy (H^*) and Free energy (G^*) were calculated by Coats and Redfern method using TGA graph. The chelating behaviour of the prepared resin was studied out with using some metal ions [Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II)]. The sorption capacities of metal ions is found in the following order, Pb(II) < Zn(II) < Cd(II) < Cu(II) < Ni(II). The rate of half exchange was rapid $t_{1/2} < 20$ min for lead ion. The separation of binary mixtures [Cu(II) and Zn(II) in brass and Pb(II) and Cd(II)] was successfully carried out using K_d value.

Keywords: batch equilibrium; chelating resin; column chromatography; free energy; morphology

Introduction

Despite advances in instrumentation and microcomputer technology, the determination of trace elements in complex matrices remains one of the most challenging areas of analytical chemistry. Chelating ion chromatography is considered as a very powerful technique for trace and ultra trace ion analyses in complex matrices.[1] The presence of heavy metals in environment is a cause of concern due to their acute and long-term toxicity. Cadmium and mercury are the major hazardous metals present in the environmental wastewater. Thus removal of trace heavy metals from the environmental area have become of increasing interest and there is a strong need for a reliable analytical procedure that can be applied for determination and removal of these metals at very low concentration.[2] Since long, considerable interest has been developed in the synthesis of ion exchange resin having special properties and containing specific functional groups.

The selective sorption of certain elements in the presence of others, based on the different stabilities of the complexes formed by functional groups of the sorbents, had led to use of these materials for selective preconcentration and separation of metal ions present in environmental, biological or industrial matrices.

The choice of an effective chelating resin and its application in analytical methodology is indicated by the physicochemical properties like polarizability, selectivity, exchange capacity, kinetic, stability characteristics of the polymer. Akaiwa and kawamoto[3] discussed the advantages of having synergistic agent on a chelating resin to enhance the sensitivity and separation of trace metals. The concept of hard and soft acid and base[4,5] provides an important

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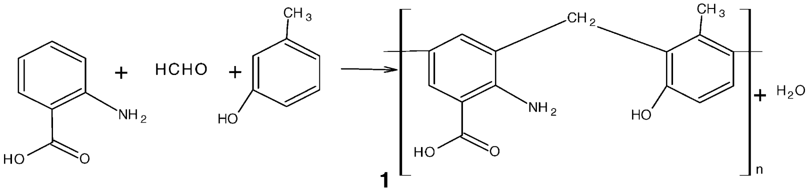
[1] Department of Chemistry, Veer Narmad South Gujarat University, Surat. India
E-mail: bhavna606@yahoo.co.in
[2] Science and Humanities Department, Polytechnic, Vidhyabharati trust, Umarakh, Bardoli, India

guideline for the selection of the methods. Usually O, N, S (sometime P) is present in the chelating resin which determines the ability to interact with the metal ions forming chelated ring. Functional groups of the chelating resin usually act as bases; oxygen containing functional groups are hard and sulfur containing functional groups are soft. Functional groups with basic nitrogen have an intermediate character.

The purpose of the present work is to explore the possibility of separation of Pb(II) ion from matrices by using AFM chelating resin. The sorption behavior of Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) on this resin was investigated at different pH values and at different concentrations. The quantitative separations of Pb(II)-Cd(II), Pb(II)- Zn(II) and Zn(II)-Cu(II) mixtures were achieved by the columns of the chelating resin. The separations are based on the affinity differences of these metal ions towards the chelating resin as a function of pH and tartaric acid electrolyte concentrations.

Preparation of AFM Resin

Anthranilic acid (13.7 g, 0.1 mole) was ground to fine powder and was taken in a 250 mL four-necked flask. It was fitted with a condenser, thermometer, stirrer and addition funnel containing 25 mL of DMF, which was added dropwise at room temperature. After the addition of DMF, 37% w/v (0.3 mole) 25 mL formaldehyde was added from the addition funnel with constant stirring. It was stirred for ½ h at room temperature. Then the solution of *m*-cresol (10.8 g, 0.1 mole) in 20 mL DMF was added from the addition funnel at the rate of 4 mL/min. The mixture was heated on water bath at 95 °C ± 5 °C temperature with constant stirring for about 3 h till soft jelly type material was obtained. The material converted to hard mass after curing in a sealed tube at 70 °C–75 °C for 2–3 h. The cured mass was then crushed to 20–50 mesh size particles and it was washed thoroughly with methanol and finally with hot double distilled water to remove the unreacted monomers. The resin was dried in vacuum oven at 100 °C.



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Experimental Part

Materials

All the reagents are of Analytical Grade and their purity is more than 98%. Anthranilic acid: (Loba Chem., Mumbai) purified by rectified spirit. Formaldehyde (37% w/v): (S.D. Fine Chem., Ltd. Mumbai.) was used as received. *m*-Cresol: (Loba Chem., Mumbai) purified by distillation. Metal ion solutions were prepared by dissolving appropriate amount of metal acetates in double distilled water and standardized by complexometric titration.

Apparatus and Procedure

The dry resin of 20–50 meshes size particles was used for characterization. An Infrared Spectrum of the synthesized resin was scanned in KBr pellets on "Shimadzu FTIR Spectrophotometer" model 8201 PC. The elemental analysis was carried out on "Carlo Erba Elemental Analyzer" model 1160. The surface analysis was done using Scanning Electron Microscopy (Philips XL30, Japan) at 100× and 500× magnifications. The optical photograph was taken on "SZX-12 Olympus, Japan". The thermogram of the resin sample was taken on "Mettler TA 4000" at constant heating rate of 100 °C/min in nitrogen atmosphere. The water swollen resin was regenerated with 0.1M HCl to obtain its H^+ form for further studies. The physico-chemical properties were studied according to literature methods.[6,7] The ion exchange properties such as rate of metal ion exchange, effect of pH on metal ion exchange capacity, effect of metal ions concentration and distribution coefficient in tartaric acid media were also studied.[8] All experiments were carried out according to earlier methods.[9] Batch equilibration method was adopted for the determination of metal ion uptake capacity of resin using different experimental variables such as metal ion concentration, pH and rate of exchange.[10,11]

$$\text{Exchange capacity} = \frac{\begin{bmatrix}\text{Vol. of metal ion soln. X}\\ \text{Molarity of metal ion soln.}\end{bmatrix} - \begin{bmatrix}\text{Vol. of EDTA soln. X}\\ \text{Molarity of EDTA soln.}\end{bmatrix}}{\text{Weight of resin sample} \quad \text{X} \quad {}^{\%\text{Solid}}/_{100}}$$

Rate of Exchange of Metal Ions

For this experiment, H^+ form of weighed (0.250 ± 0.001 g) dry resin sample was taken in different glass Stoppard bottles and equilibrated with buffer solutions of desired pH value for 24 h. After decanting buffer solution, 50 ml (0.05 M) metal ion solution of the same pH was added. The amount of unchelated metal ions was determined by complexometric titration at fixed time intervals.

Effect of pH on Metal Ion Exchange Capacity

To study the effect of pH on the metal ion uptake, it is necessary to buffer the resin and the solutions used. Buffer solutions of pH range 3.5–6.5 were prepared from 0.2 M acetic acid and 0.2 M sodium acetate solutions. A pH meter (Elico, model CL-44) was used to measure the pH value. Different sets of weighed (0.250 ± 0.001 g) dry resin were equilibrated with buffer in different Stoppard bottles for 24 h, so that resin attain desired pH value. After 24 h buffer solutions were decanted and 50 ml of 0.05 M metal ion solutions of varying pH from 3.5–6.5 were added. Metal ion solutions were equilibrated at room temperature for 24 h with intermittent shaking. After 24 h the solutions were decanted and metal ion concentration in the supernatant were measured by complexometric titration with 0.05 M EDTA solution using appropriate indicators. Blank experiments were also run simultaneously. The same method was followed through out the study to calculate the ion exchange capacity of the resin.

Effect of Metal Ion Concentration on Exchange Capacity

To study the effect of metal ion concentration on uptake of different metal ions by the resin, the weighed (0.250 ± 0.001 g) dry resin sets were equilibrated with acetate buffer at desired pH values (pH value of maximum exchange) for 24 h and then buffer solutions were decanted. Then the same resin were equilibrated with metal ion solutions (50 ml) of varying molar concentration i.e. 0.05 M, 0.1 M, 0.15 M, 0.20 M, 0.25 M and 0.30 M at the same pH value at room temperature for 24 h with intermittent shaking. After 24 h metal ion solutions were decanted and unchelated metal ions were estimated by complexometric titration.

K_d Value for Metal Ions in Presence of Electrolyte (Tartaric Acid) Solution

Measurement of distribution coefficient of metal ions over a wide range of conditions is a good way to avoid choosing eluting conditions for column separations by a strictly trial and error method. The distribution coefficient K_d of metal ion is defined as follow:

$$K_d = \frac{\text{mmole of metal ion on resin}}{\text{mmole of metal ion in solution}} \times \frac{\text{Vol. of metal ion solution}}{\text{Wt. of dry resin}}$$

Effect of different concentration and pH of electrolyte (tartaric acid) on metal ion uptake by the synthesized resin was studied. The weighed (0.250 ± 0.001 g) dry resin sample was suspended in 50 ml electrolyte solution of tartaric acid of different known concentrations i.e. 0.1 M, 0.2 M, 0.3 M, 0.5 M and 1.0 M. The pH of the suspension was adjusted to the desired value using acetate buffer and the resin was equilibrated for 24 h. To the suspension, 2.0 ml (5 mg/ml) of solutions of different metal ions under study were equilibrated for 24 h with intermittent shaking. After 24 h solutions were decanted and unsorbed metal ions were estimated.

Results and Discussion

Characterization of AFM Resin

The Chemical Stability was evaluated by measuring the change in sorption capacity for Cu(II) and after successive contact of resin with acidic and alkaline solutions in the various concentration ranges. As a result, sorption capacity of Cu(II) did not change in wide range after 20 cycles. The chelating resin was stable up to 5M in acidic solutions and up to 1M alkaline solutions. The yield of the reddish brown resin was 70%. The physical properties of AFM resin is shown in Table 1.

Infrared spectra shows strong broad band at 3400 cm^{-1} due the υ (O–H) stretching of phenolic group and carboxylic acid group and υ (N–H) stretching due to amino group. The weak band at 2924 cm^{-1} is due to the υ (C–H) stretching of methylene group. The medium strong band at 1718 cm^{-1} can be assigned to υ (C=O) stretching of ketonic group of acid. The medium strong band at 1615 cm^{-1} is due to bending of δ (N–H) and also due to υ (C=C) stretching of aromatic ring. The medium band at 1380 cm^{-1} is due to δ (C–H) bending of Ar–CH_3. The strong band at 1279 cm^{-1} is due to υ (C–N) stretching of Ar–NH_2. The medium broad band at 1159 cm^{-1} is due to υ (C–O) stretching of phenol. The medium band at 854 cm^{-1} is due to tetra substituted benzene ring. All these bands are observed in Figure 1.The results of elemental analysis are in good agreement with calculated values of % C, % H and % N as in Scheme 1. It should be 70.0%, 5.8% and 5.5% for C, H and N respectively. While the found values are 70.4%, 5.5% and 5.8% for C, H and N respectively.

SEM and Optical Photographs

Scanning Electron Micrographs and Optical Photographs are shown in Figure 2 (a), (b) and Figure 3 respectively which investigate the morphology of the reported resin sample. The morphology of the resin shows a fringed model of the crystalline-amorphous structure. The fringes represent transition state between the crystalline and amorphous phase. The resin exhibits more amorphous character with closed packed surface having more deep pits {Figure 2 (a)-100× and 2 (b)-500×} as compared to Anthranilic acid-Formaldehyde-Resorcinol [AFR] resin reported earlier.[9] The resin appeared to be reddish brown in colour.

Table 1.
Physical properties of AFM resin.

Properties	Value (SD)
% Moisture	8.6 ± 0.5
% Solid	91.4 ± 0.5
True density (dres) g/cm^3	1.15 ± 0.03
Apparent density (dcol) g/ml	0.6848 ± 0.0060
Void volume fraction	0.4045 ± 0.0050
Sodium exchange capacity mmol/g dry resin	6.24 ± 0.20
Concentration of fixed ionogenic group mmol/cm^3	6.5503 ± 0.2000
Volume capacity mmol/cm^3	3.71 ± 0.05

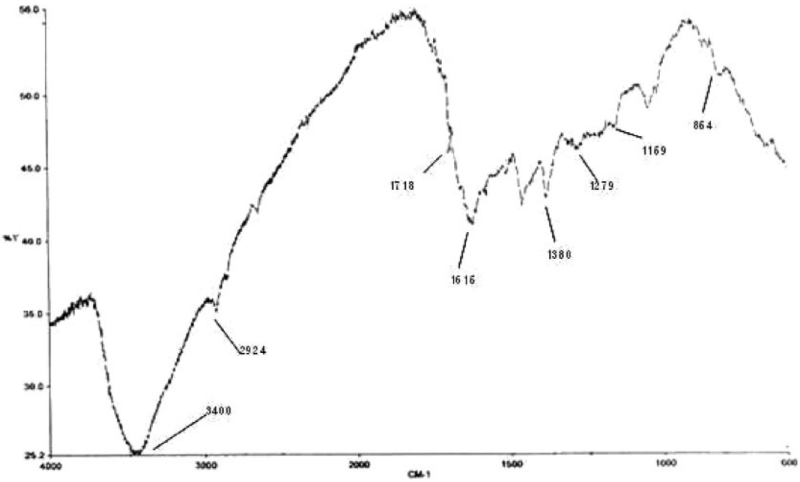

Figure 1.
FTIR of AFM resin.

Themogravimetric Analysis

The result of TGA reveals that the degradation of AFM resin takes place between 410 °C to 560 °C, which is shown in Figure 4. It involves single step degradation with weight loss of 52.7%. Broido,[12] Horowitz-Metzger[13] and Coats-Redfern[14] methods were used to estimate the Activation Energy (E_a) of thermal degradation. The values of Activation Energy calculated by all these methods are shown in Table 2. Intergal Produral Decomposition Temperature (IPDT) is calculated by Doyle's method.[15] IPDT expresses the overall thermal stability of the resin, which is 349 °C.

AFM resin contains non-polar $-CH_3$ group at meta position and it also contains bulky $-NH_2$ group. Due to their repulsive force, sufficient rigid structure cannot be obtained. This will produce more amorphous character in the polymeric resin. Hence it exhibits lower Activation Energy 20.4 KJ/mole of AFM resin compared to resorcinol containing amphoteric AFR resin,[9] which has 28.20 KJ/mole.

The thermal degradation of AFM resin exhibits second order reaction.[15] The

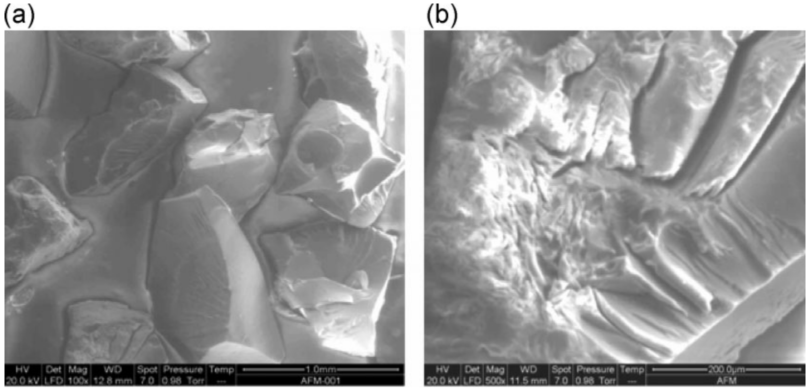

Figure 2.
SEM photographs of AFM resin at (a) 100× and (b) 500×.

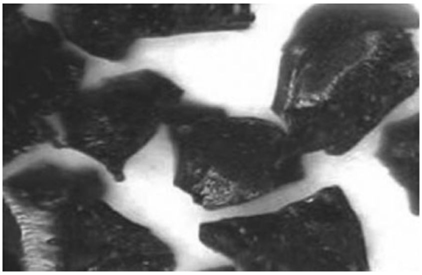

Figure 3.
Optical Photograph of AFM resin.

thermodynamic parameters such as Entropy change (S*), Enthalpy (H*) and Free Energy (G*) for degradation was calculated by Coats - Redfern methods,[14] which is shown in Table 2. Lower negative value of S* suggest more randomization in structure of AFM resin. The positive value of H* and G* of synthesized resin suggests that the degradation process was endothermic and slower one.

Rate of Exchange for Metal Ions

The role of physical core structure of resin is significant in the uptake of different metal ions by the resin copolymer. From the results, it is observed that the rate of exchange of metal ions is faster in beginning and then slows down. This happens due to elimination or exchange of ions from the solution to the surface of the resin. After the entire available site (group) of resin was occupied, it gives rise to slower rate of exchange.

Figure 5 shows the results of rate of exchange of metal ion on AFM resin. It is observed that half reaction time ($t_{1/2}$) for Cu(II) and Ni(II) is after 50 minutes, for Zn(II) is after 5 hours, for Pb(II) is after 20 minutes while for Cd(II) is after 2 hours.

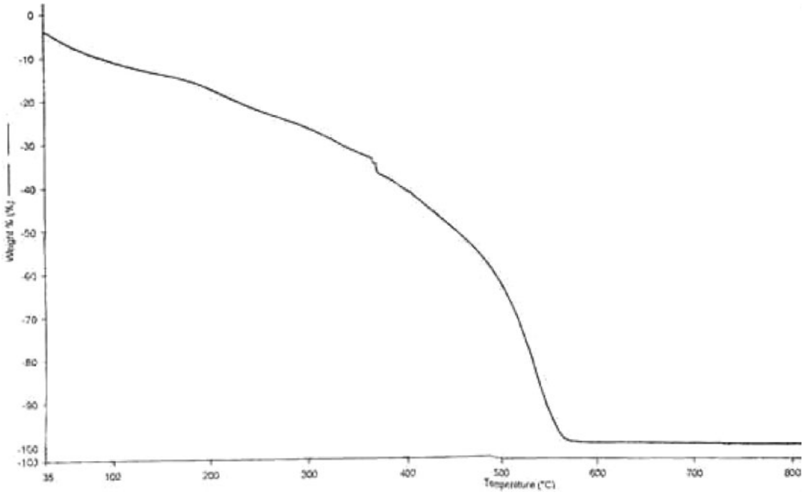

Figure 4.
TGA of AFM resin.

Table 2.
Thermodynamic parameters of AFM resin.

Properties	Broido method	Horowitz – Metzger method	Order of decomposition	Coats-Redfern method	IPDT °C
E_a (kJ/mol)	20.1	21.3		17.32	
S* (J/Kmol)	−100.34	−100.34	2	−105.07	349
H* (kJ/mol)	14.42	15.62		11.64	
G* (kJ/mol)	82.95	84.36		83.40	

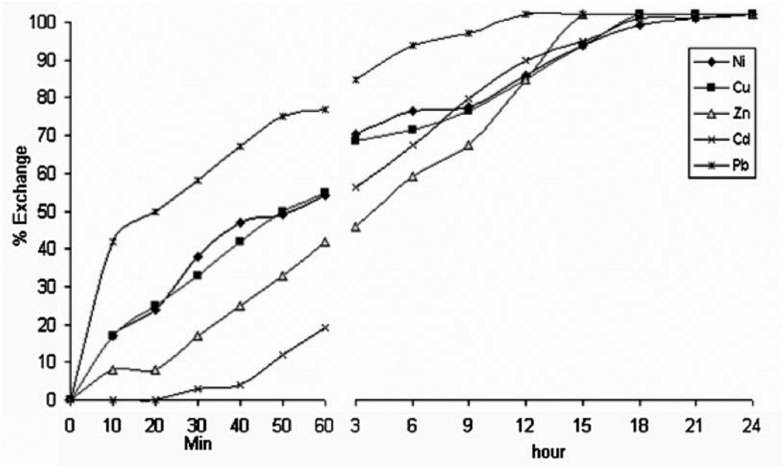

Figure 5.
Rate of exchange for metal ions exchange capacity on AFM resin.

Faster rate of $t_{1/2}$ was exhibited by Cu(II) than Zn(II). This is attributed to fact that the hydrated Cu(II) has smaller radii than hydrated Zn(II) and thus, have greater access to the surface.

Effect of pH on Metal Ion Exchange Capacity

At specific conditions of pH, resins are able to form chelate complexes with metal ions. The maximum exchange capacity for Cu(II) and Pb(II) is found to be at pH 6.0. For Ni(II) it is at pH 4.0 and for Cd(II) it is at pH 4.5, while ion exchange capacity of Zn(II) is independent of pH in the range of pH 3.5 to pH 6.5 which is shown in Figure 6. The exchange capacity is in the order of: Pb(II) < Zn(II) < Cd(II) < Cu(II) < Ni(II).

In the case of Cd(II) and Pb(II) purely electrostatic factors are responsible. The ion exchange capacity of Cd(II) is lower owing to the large size of its hydrated ion than that of Cu(II). The steric influence of the methyl group and amino group in AFM resin is probably responsible for their observed low binding capacities for metal ions.

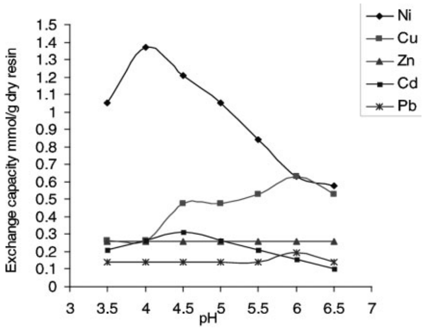

Figure 6.
Effect of pH on metal ion exchange capacity on AFM resin.

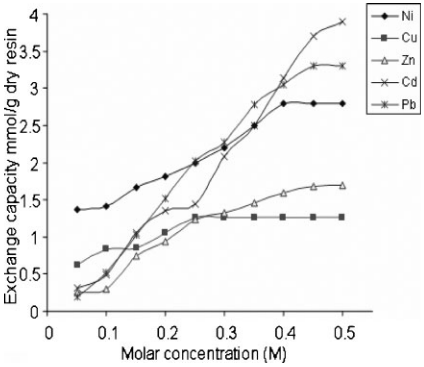

Figure 7.
Effect of concentration on metal ion exchange capacity on AFM resin.

Effect of Metal Ion Concentration on Exchange Capacity

The examination of data presented in Figure 7 reveals that the amount of sorption of metal ion increases with the increase in concentration of metal ions in solution. At lower concentration of metal ions the number of metal ions available in solution is less as compared to the available sites on the sorbent. However, at higher concentration the available sites of sorption remain same whereas more metal ions are available for sorption and subsequently the sorption becomes almost constant then after.

Effect of Electrolyte Concentration and pH on Distribution Coefficient (K_d) of Metal Ions

The difference in distribution coefficient value is caused by the competition between metal ions and counter ions from electrolyte solution for available exchange sites. Difference in K_d value of two or more metals are very useful for separation each of the metal ions from the solution. The value of distribution ratio for given pH and for a given concentration of electrolyte depends upon the nature and the stability of a chelate formation for particular metal ion. The data of K_d value shows a random trend for AFM resin.[9] The data of K_d value are shown in Table 3.

Chromatographic Column Separation of Binary Mixture

An ideal situation would be such that one K_d value is ten times greater than the K_d value for other ion, while the other approaches zero. The first eluting fractions of tartaric acid carry one metal ion, which has a smaller K_d value. The second metal ion can be eluted by changing the tartaric acid concentration to a level that has a lowest K_d value for second metal ion.

For the separation of binary mixture, 2 ml of 5 mg/ml of each metal ion solution

Table 3.
K_d value of metal ions on AFM resin in tartaric acid media at different pH.

Metal ion	Tartaric acid Conc.(M)	K_d value at different pH				
		3.0	3.5	4.0	5.0	6.0
Ni(II)	0.1	27.0	45.0	45.0	27.9	45.3
	0.2	69.0	27.0	27.0	9.0	9.0
	0.3	27.0	20.6	20.0	9.0	48.0
	0.5	150.0	60.3	39.6	–	9.0
	1.0	180.0	75.1	21.0	–	–
Cu(II)	0.1	90.0	90.5	54.0	39.0	150.0
	0.2	150.0	210.3	370.0	–	103.5
	0.3	90.0	215.9	51.3	100.2	75.8
	0.5	–	75.8	–	132.0	–
	1.0	–	–	–	–	–
Zn(II)	0.1	–	75.6	90.0	71.0	99.5
	0.2	99.5	75.0	100.0	90.0	–
	0.3	51.6	45.0	85.6	30.5	60.3
	0.5	30.4	18.2	45.0	12.3	–
	1.0	90.5	55.0	24.0	24.5	51.2
Cd(II)	0.1	200.0	75.0	18.0	66.8	60.0
	0.2	75.0	105.6	6.0	–	–
	0.3	150.0	15.0	48.3	70.3	–
	0.5	90.0	33.5	48.3	18.2	–
	1.0	100.2	100.2	12.0	75.6	–
Pb(II)	0.1	90.6	70.6	100.2	–	60.3
	0.2	150.0	240.0	200.3	140.0	130.0
	0.3	600.9	350.6	214.3	–	60.0
	0.5	–	300.0	90.5	33.6	75.5
	1.0	33.0	–	60.0	15.2	60.0

Table 4.
Separation of binary mixtures by AFM resin.

Metal Eluted	Eluent (Tartaric acid)		Recovery (%)	Fig. No.
	Conc.(M)	pH		
Pb(II)	1.0	3.5	94	8
Cd(II)	0.3	3.0	87	
Zn(II)	0.2	6.0	93	9
Cu(II)	1.0	3.0	89	
Pb(II)	0.1	5.0	92	10
Zn(II)	0.3	3.0	83	

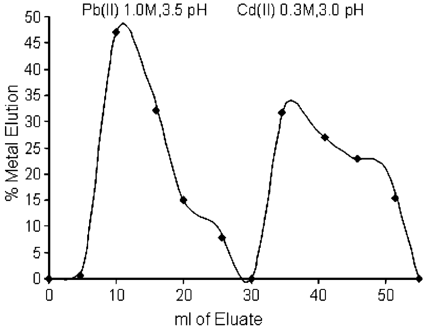

Figure 8.
Separation of Pb(II) and Cd(II) on AFM resin.

was taken. The chelating resin in H^+ form was packed into a chromatographic column to form a compact resin bed $\sim$ 15 cm high and 0.4 cm diameter. The solution was allowed to flow through automatic fraction collectors for the continuous determination of metal ion separation. Each fraction was analyzed individually for its constituent metal ion by complexometric titration. Percentage of metal ion recovery was examined with respect to volume of eluate.

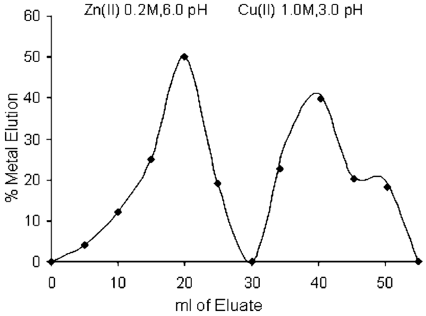

Figure 9.
Separation of Zn(II) and Cu(II) on AFM resin.

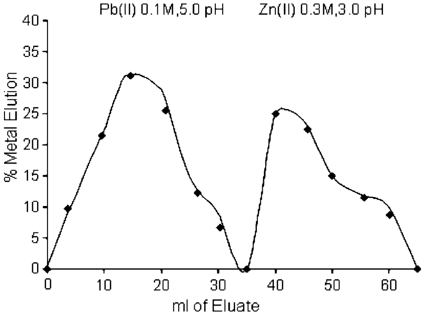

Figure 10.
Separation of Pb(II) and Zn(II) on AFM resin.

The separation of binary mixtures by AFM resin is summarized in Table 4, at different conditions. The plots of eluted volume versus % of metal ion elution are shown in Figure 8 to10. No cross contamination was observed for these separations. The recovery of metal ions is more than 80% in all cases. Synthesized resin was very useful for separation of metal ions particularly for heavy metal ions.

Conclusion

Preparation of AFM resin is simple condensation of monomers and less time consuming compared to resin containing 8-hydroxyquinoline.[16] The degradation of AFM resin is single step and second ordered. The steric influence of the methyl group and amino group in AFM resin is probably responsible for their observed low binding capacities for various metal ions. Thus, the interaction of this resin material with various metal ions in an aqueous environment may largely limit the binding sites, which are suitably, disposed in a conformationally favorable manner on surface layers. The data of K_d values shows a random trend[9] in certain cases. This shows that reported resin provides better selectivity for one metal ion in presence of the other metal ions. AFM resin is more selective towards Pb(II) than other metal ions. This makes clear separation of Pb(II) from transition metal ions.

Acknowledgements: We are thankful to Head, IIT, Mumbai for providing SEM. We are also thankful to Head, CDRI, Lucknow for providing spectral facility. We are thankful to Head, SICRAT, Vallabh Vidhyanagar, for providing Thermal Analysis.

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