ABSTRACT

Chromatographic column separations of metal ions from their binary mixtures [Zinc (II)-Lead (II), Cadmium (II)-Lead (II), and Cadmium (II)-Zinc (II)] were achieved in tartaric acid media at optimized (Kd) values with a synthesized chelating ion exchange resin (AFR) derived from anthranilic acid-formaldehyde-resorcinol. The physico-chemical properties of this resin were also studied. The studies of total ion exchange capacity, effect of pH, and concentration for different metal ions were carried out. AFR resin was characterized by FTIR and elemental analysis techniques. The kinetic parameters (Ea) have been evaluated from the thermogravimetric data and the morphology of the resin was examined by SEM technique.

INTRODUCTION

The analysis of trace elements in natural waters, wastewaters, and biological, industrial and geological samples in complex mixtures is the challenging problem in analytical chemistry. The heavy metals such as Pb, Cd and Hg etc. are toxic to most of the organisms. Therefore, its separation and detection is of prime importance. Ion exchange separation methods are also employed in numerous operations such as water softening and reduction of metal ions concentration. The early ion exchangers were silicates, fuller’s earth, and synthetic aluminum silicates, e.g., zeolites. Tree bark substrates [1] were reported to remove efficiently, the heavy metals from wastewater to...
below the product discharge limits. The exchange of calcium from soil to form calcium alumino silicates indicated the phenomenon of simple ion exchange. Chelating resins were also derived from naturally occurring compounds like guar [2] and guaran [3] by polymer grafting process.

A wide range of chelating ion exchange resins has been prepared from different monomers containing different functional groups such as 8-hydroxy quinoline, salicylic acid, and related monomers [4,5]. The physical properties, moisture content and alloy separation were carried out [6,7] using quinoline resins. Devi et al. [8] have prepared chelating ion exchange resin from hydroxamic acid with divinyl benzene and they studied the quantitative separation of lead-copper and cadmium-cobalt using column chromatography. Patel et al.[9] have prepared the terpolymer of salicylic acid /p-hydroxy benzoic acid and thiourea with trioxane in the presence of acid catalyst with different molar proportion of monomers. Samal et al. [10] has prepared resin from the diazonium salts of aniline with phenol/ resorcinol; coupled with formaldehyde in alkaline medium. They have studied the effect of alkali and alkaline earth metal ions uptake behaviour on resin. The optimum conditions for effective separation of Cu²⁺ from UO₂⁺² were also determined. The chelating behaviour of poly (8-hydroxyquino line 5,7-dimethylene) [11] and its cross-linked polymer derived by reaction with various amount of bisphenol-A towards some trivalent lanthanide ions such as La(III) and Gd(III) has been investigated by a static batch equilibration method.

Inoue et al. [12] have synthesized a new porous cation exchange resin having an open-celled monolith structure. This polymer is easier to pack it in a column and the ion exchange rate of this resin is much higher. Asem et al. [13] prepared chelate forming resins containing amino and thio groups. The interaction of this resin with Zn (II), Cd (II), and Hg (II) from their aqueous solutions was studied. Terpolymer resins [14] (4-HABF) were synthesized by the condensation of 4-hydroxy acetophenone and biuret with formaldehyde in the presence of acid catalyst and using varied molar ratios of reacting monomers. Chelating ion exchange properties of this resin have also been studied employing batch equilibrium method.

Ion exchange research has general application as quantitative removal and separation of transition and post transition metal ions. As sample of industrial effluents; wastewater, biological, and geological samples are often rich in transition metal ions, removal of these metals is an important task for industries. Although considerable works in this field have been reported, little work has been carried out on synthesis of chelating resin by Molecular imprinting. This process provides selective binding sites in synthetic polymeric matrix using a specific molecule (monomer) which is stable and exhibits good selectivity for the heavy metal ions.

Therefore, the purpose of this research is to develop a polymeric extractant for the selective chelation of ions of interest, present in the mixture. The AFR (anthranilic acid-formaldehyde-resorcinol) resin provides useful sequestering agents for removing and separating ions from binary mixtures. Thus, we have carried out the study on the synthesized AFR resin and explored its use in removal and separation of heavy metal ions.

**EXPERIMENTAL**

**Materials**

Anthranilic acid (Loba Chem., Mumbai) purified by rectified spirit. Formaldehyde (37%, S.D. Fine Chem., Ltd. Mumbai) was used as received. Resorcinol (Qualigens Fine Chem., Mumbai) purified by rectified spirit.

All the reagents were of the analytical grade and their purities were more than 98%. Metal solutions were prepared by dissolving appropriate amount of the acetates of the metals in double distilled water and standardized by EDTA titrations.

**Preparation of the AFR Resin**

Anthranilic acid (13.7 g, 0.1 mol) was ground to fine powder and was taken in to a 250 mL three necked flask. It was fitted with a condenser; thermometer, stirrer and addition funnel containing 20 mL of DMF. This was added dropwise at room temperature while stirring the solution. After the addition of DMF, 25 mL of formaline 37% (0.3 mol) was added from addition funnel along with constant stirring. The mixtuwer was stirred for 1 h then the solution of resorcinol (11.0 g, 0.1 mol) in 20 mL DMF was added from addition funnel at the rate
of 2 mL/min. The mixture was refluxed on water bath at 100 ± 5°C while stirring till soft jelly type of material was obtained. The cured mass was then crushed to 20-50 mesh size particles as needed and washed with 150 mL methanol and finally with 100 mL hot double distilled water to removed unreacted monomers. The resin was dried in vacuum oven at 120°C. The resin was non-melting and insoluble in H2O and most organic solvents.

Infrared spectra of the synthesized resin sample had been scanned in KBr pellets on Shimadzu FTIR spectrophotometer model 8201PC. The surface analysis was done using scanning electron microscopy (Philips XL30, Japan). The thermogram of the resin sample was taken on Mettler TA 4000 at constant heating rate of 10°C/min in N2 atmosphere. The elemental analysis was carried out on Carlo Erba Elemental Analyzer model 1160. The swollen resin was stored in 0.1M HCl to obtain its H+ form for the further studies.

The physicochemical properties, e.g., moisture content percentage, solid percentage, true density, apparent density, void volume fraction, concentration of fixed ionogenic group, sodium exchange capacity, salt splitting, and resin stability were studied according to literature methods [15,16]. The results are shown in Table 1. The adsorption properties such as effect of pH on metal ion exchange capacity, effect of concentration of different metal ions, and distribution coefficient Kd in tartaric acid media were also studied [17].

**Resin Stability**

The resin stability is usually expressed in terms of copper ion exchange capacity of the resin. To study the stability of the resin, 0.25 g H+ form of the moist exchanger was equilibrated at pH 5.0 with acetate buffer for 12 h. After decanting the buffer solution, the resin was equilibrated for 24 h with 25 mL of 0.1 M cupric acetate solution at pH 5.0. The copper exchange capacity of the resin was determined by estimating the amount of copper taken up by the resin. The metal was eluted with 1M HCl and the resin was regenerated. The same resin was used again for determination of copper exchange capacity. This procedure was repeated 20 times. The resin stability was determined in terms of copper exchange capacity by regenerating the resin for twenty times. Resin stability towards acids and bases was tested by leaving sample of resin in contact with 2 M hydrochloric acid for 7 days. After 4 days in 2 M hydrochloric acid, the solution was slightly yellow. The depth of color intensified gradually during these seven days.

**Swelling Studies**

The H+ form of dry resin (0.5 g) was equilibrated with 30 mL of distilled water for 4 days. The swollen resin was collected by filtration, adhering trace of water were removed by pressing with filter paper and sample was weighed. The swollen resin was dried in a vacuum for 24 h and weighed again. From the swollen and dry weight of the sample the equilibrium water content (EWC) was calculated using the following equation.

\[
EWC = \frac{\text{weight of wet resin} - \text{weight of dry resin}}{\text{weight of wet resin}}
\]

**Table 1.** Physico chemical properties of resin.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Results (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (%)</td>
<td>10.0 (±0.5)</td>
</tr>
<tr>
<td>solid (%)</td>
<td>90.0 (±0.5)</td>
</tr>
<tr>
<td>True density (g/mL)</td>
<td>1.112 (±0.020)</td>
</tr>
<tr>
<td>Apparent density (g/mL)</td>
<td>0.7010 (±0.0050)</td>
</tr>
<tr>
<td>Void volume fraction</td>
<td>0.3642 (±0.0050)</td>
</tr>
<tr>
<td>Concentration of fixed ionogenic group (mmol/ g dry resin)</td>
<td>6.1825 (±0.0050)</td>
</tr>
<tr>
<td>Sodium exchange capacity (mmol/ g dry resin)</td>
<td>6.1 (±0.2)</td>
</tr>
</tbody>
</table>

**Effect of pH on Exchange Capacity for Metal Ions**

To study the effect of pH on metal ion exchange, it is necessary to buffer the resin and the solutions used. Buffers were prepared by using sodium acetate and acetic acid. In case of nickel and cadmium, pH was adjusted by using ammonium chloride and ammonium hydroxide while in all other cases acetate buffers were used. Each 1.0 g of dry resin in H+ form was equilibrated
with different buffer solutions of varying pH in different flasks. Thus, the resin attained desired pH. After 12 h of equilibration period, the buffer solutions were decanted and 25 mL of 0.05 M metal ion solutions of varying pH from 3.5 to 6.5 were added. In all cases, metal acetate salts were used. Metal solutions were equilibrated for 24 h with intermittent shaking. After 24 h the solutions were decanted and 5 mL of metal ions were estimated by complexometric titration and metal ion capacity was calculated

\[
\text{Capacity of metal ion} = \left( \frac{\text{volume of metal ion soln}}{\text{normality of metal ion soln}} \right) \times \left( \frac{5 \text{ mL of EDTA}}{\text{normality of EDTA}} \right) \times \left( \frac{\text{weight of resin}}{\% \text{ solid/100}} \right)
\]

**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 solutions of metal acetate (25 mL) of varying concentration in the range 0.05 to 0.5 M were equilibrated with 0.25 g dry H+ form resin for 24 h. After 24 h of equilibration period solution were decanted and metal ions were estimated.

**Kd Values for Metal Ions in Presence of Electrolyte Solution (Tartaric Acid)**

Effect of different concentration of electrolyte on metal ion uptake by the synthesized resin was studied using following procedure. The dry H+ resin sample (0.25 g) having uniform particle size (20 to 50 mesh) was suspended in the electrolyte solution of tartaric acid (50 mL) of different known concentrations. 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 mL of (5 mg/mL) solution of the metal ions under study was added. The pH was again adjusted to desired value. The mixture was further equilibrated for 24 h and then filtered. The solid was washed with water. The filtrate and washings were combined and examined for the metal ion concentration.

\[
K_d = \frac{\text{mmol of metal ion on resin}}{\text{vol. of solution}} \times \frac{\text{mmol of metal ion in soln}}{\text{weight of dry resin}}
\]

**Packing of the Column**

A glass column (25 cm length and 0.5 cm i.d.) with porous frit at the bottom was filled with water and water was allowed to pass through the column in order to ascertain the support material free from air which would cause channeling effect. The slurry of H+ form of resin was poured along the walls of the column to form
compact resin bed. When slurry had been poured the outlet was opened and care was taken to keep water level above the top of the resin bed. This column (length 17.3 mL and 15 g resin) was used for different heavy metal ion separation. Tartaric acid of different concentration and pH was used as an eluting agent for different systems. For each column the optimized conditions of concentration and pH of eluting agent was known from the $K_d$ values. Separations of metal ions by selective elution on column were carried out for binary mixtures of equimolar concentration. The solution mixture was passed through the column at a flow rate of 0.5 mL/min. Elution was carried out at different pH and concentration of tartaric acid.

**RESULTS AND DISCUSSION**

**Spectral Characterization of Resin**
The strong broad band at 3429 cm$^{-1}$ is due to the $\nu$(O-H) stretching of phenolic group. The weak medium band at 2921 cm$^{-1}$ is due to the stretching $\nu$(C-H) of methylene group. The medium strong band at 1738 cm$^{-1}$ can be assigned to $\nu$(C=O) stretching of aromatic acid group. The medium strong band at 1614 cm$^{-1}$ is due to $\delta$(N-H) bending of R-NH$_2$. The strong band at 1261 cm$^{-1}$ is due to $\nu$(C-N) stretching of (Ar - NH$_2$). The medium broad band at 1193 cm$^{-1}$ is due to $\delta$(O-H) bending of phenol. The medium broad band at 868 cm$^{-1}$ is due to $\delta$(C-H) bending of tetra substituted benzene ring. The FTIR spectral data matches with the probable structure of the copolymerized monomers as shown in Scheme I confirms the polymerization. The FTIR of AFR resin is shown in Figure 1.

**Scanning Electron Micrographs**
Surface analysis has found to be of great use in understanding the surface features of the material. The morphology of the reported resin was investigated by scanning electron micrographs, which are shown in Figure 2.

<table>
<thead>
<tr>
<th>Table 2. Activation energy of degradation of AFR resin.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Energy of activation ($E_a$) (kJ/mol)</strong></td>
</tr>
<tr>
<td>Broido method</td>
</tr>
<tr>
<td>28.20</td>
</tr>
</tbody>
</table>

**Figure 2.** SEM of AFR at different magnifications: (a) 400× and (b) 500×.
The white bar at the bottom of the SEM micrographs represents the scale. The morphology of the resin polymer shows a fringed micelle model of the crystalline-amorphous structure. The fringes represent transition material between the crystalline and amorphous phases. This tends to draw attention away from the details of fine structure and gives little insight into the structure of large entities such as spherulites.

The SEM photographs exhibit such spherulites which are the aggregate of crystallites present along with some amorphous regions. The amorphous region shows secondary structural features such as corrugations and shallow pits.

**Themogravimetric Analysis**
The thermogram of the present resin sample is shown in Figure 3. The result of TGA reveals that the resin sample undergoes degradation in one step. It shows that the resin has good thermal stability. The degradation starts at 400°C, which extends up to 595°C involving 56% weight loss. The thermogravimetric analysis has proved to be useful analytical technique in evaluating kinetic parameter such as activation energy (E_a). Here, Broido [18] and Horowitz-Metzger [19] methods are used to estimate the activation energy of thermal degradation. For the typical calculation of E_a the relevant plots of 1000/T versus lnln1/y and ln 1/1-α versus θ are shown in Figures 4 and 5, respectively.

The straight lines are due to linear regression analysis of the experimental data. The value of activation energy calculated according to the Broido and Horowitz-Metzger methods are in good agreement, which are shown in Table 2.

**Elemental Analysis**
The results of elemental analysis are in good agreement with calculated values of %C, %H, and %N which is shown in Table 3 and are in good agreement with the structure represented in Scheme I.

**Resin Stability**
It was observed that up to 20 loadings acid washing cycles, sodium ion exchange capacities, and copper ion exchange capacities of reported resin did not change, suggesting that the resin exhibits appreciably better stability.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Calculated (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>64.68 (65.06)</td>
<td>5.00 (4.97)</td>
</tr>
</tbody>
</table>
Swelling Studies
The equilibrium water content (EWC) of resin is 9.6%.

Effect of pH on Metal Ions
Chelating ligand forms complexes with various metal ions at specific pH conditions. Wide difference in optimum pH conditions for two or more metal ions indicates selectivity and specificity of the chelating groups for different metal ions. Therefore, the synthesized resin was used to study the effect of variation in pH on chelating ability of the resin towards various metal ions. Ion exchange capacity versus pH for different metal ions at 0.05M concentration is shown in Figure 6. It reveals that maximum ion exchange capacity for Zn (II), Pb (II), Cu (II), Ni (II), and Cd (II) was at pHs 4.0, 5.5, 5.0, 4.0, and 5.5, respectively. It suggests that selectivity of metal ion is dependent on pH. For Ni (II) more acidic condition favoured the selectivity. The remaining metals had been selected at around pH 5.0 to 5.5. It is due to different tendency of chelate formation at different pH. This can be related to the difference in the stability of metal complexes formed on resin.

Effect of Concentration of Metal Ions on Exchange Capacity
The study of the effect of concentration of metal ion show that the uptake of metal ion by the resin increases in proportion to the concentration of metal ion in solution. Saturation occurred for Zn (II) and Cd(II) at 0.45 M, and for Pb (II), Cu (II), Ni (II) at 0.30, 0.25, and 0.40 M, respectively. This may be due to different selectivity at various concentrations which is shown in Figure 7.

Effect of Electrolyte Concentration and pH on Distribution Coefficient ($K_d$) Values of Metal Ions
The distribution coefficient ($K_d$) was determined by the batch equilibration method. The distribution of the different metals as the function of pH and concentration of electrolyte solution (tartaric acid) are presented in Table 4. The present investigation limits the distribution studies up to a certain pH for each metal ion to prevent the
Figure 10. $K_d$ vs. tartaric acid concentration at pH 4.0 for different metal ions.

Figure 11. $K_d$ vs. tartaric acid concentration at pH 5.0 for different metal ions.

Table 4. $K_d$ values of metal ions in tartaric acid media at various molarities and pH.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Conc. of tartaric acid (M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3.0</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>0.1</td>
<td>47.4</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>24.3</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>24.3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>49.8</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>72.0</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>0.1</td>
<td>44.4</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>70.5</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>150.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>70.2</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>0.1</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>48.6</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>232.8</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>62.7</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>28.5</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>0.1</td>
<td>236.7</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>631.5</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>33.0</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>16.5</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>175.8</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>0.1</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>55.6</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>
hydroxide formation of metal ion at higher pH. For heavy metals, Pb (II) showed higher K_d values, while Cd (II) showed lower K_d.

To achieve more clear separation of heavy metal ions in short time, maximum K_d value difference was selected for optimizing the condition of chromatography. 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 show a random trend [20] in certain cases, such as Pb (II) in 0.2 M tartaric acid, and also Zn (II) in 0.3 M tartaric acid. This may be due to amphoteric nature of the AFR resin.

The data of Table 4 are represented graphically to investigate the selectivity of different metal ions at a given pH for different concentration of tartaric acid. Figures 8-12 show that the reported resin provides better selectivity for one metal ion in presence of the other metal ions.

Chromatographic Column Separation of Binary Mixtures
The superior selectivity towards multivalent cations exhibited by chelating resin has been demonstrated in column experiments by using K_d values. The values of K_d are shown in Table 4.

In the case of the separation of zinc (II) from lead (II), cheated zinc (II) and lead (II) were separated by selective adsorption. Zinc (II) was eluted with 0.2 M tartaric acid solution of pH 4.0 because at the same condition lead (II) showed highest K_d value.

Therefore, first few fractions contained only zinc (II) and later with 0.3 M tartaric acid of pH 3.0 only lead (II) was eluted subsequently due to low K_d value at that condition. Recovery of zinc (II) was found to be 89% while for lead (II) it was 91%. No cross contamination was observed for this separation. Result is given in Figure 13.

Similarly, other binary mixtures were separated. In the case of separation of cadmium (II) from lead (II),
cadmium (II) was eluted with 0.2 M tartaric acid of pH 3.0. First few fractions contained only cadmium (II), later lead (II) was eluted with 0.5 M tartaric acid of pH 3.0. Recovery of cadmium (II) was found to be 87% while that of lead (II) was found to be 90%. Result is given in Figure 14.

Figure 15 shows the separation of cadmium (II) and zinc (II). Cadmium (II) was eluted with 0.3 M tartaric acid of pH 3.0 and later zinc (II) was eluted with 0.1 M tartaric acid of pH 3.5. Recoveries of cadmium (II) and zinc (II) were found to be 85 % and 88%, respectively.

CONCLUSION

The synthesis of this resin is a time saver. This is clearly seen from the fact that where other resin needs 42 h of refluxing, it can be synthesized in only 2 h. The resin shows lower percentage of moisture content compared to other reported resins, which indicates the high degree of cross-linking and has higher stability.

From the data it reveals that metal ion selectivity increase with atomic number of transition metal ions, selectivity is: Zn (II) > Cu (II) > Ni (II).

Similar result is obtain with post transition metal ions, with exchange capacity Pb(II) > Cd(II). This resin is also useful at high concentration of metal solution (0.25 to 0.45 M). Nickel (II) and Cadmium (II) have lower Kd values. Thus, this resin can be useful in ion exchange chromatography and for removal of toxic metals from river water.

From the result it is observed that there is considerable difference between the distribution coefficients of each metal ion at optimum condition which can be used in separation of heavy metal ions. Here three binary mixtures of Zn (II)-Pb (II), Cd (II)-Pb (II), and Cd (II)-Zn (II) were separated successfully using optimum condition of Kd values.

ACKNOWLEDGEMENT

We are thankful to Head of, IIT, Mumbai for providing SEM. We are also thankful to Head of, CDRI, Lucknow for providing spectral facility and to Head of, SICRAT, Vallabh Vidyanagar for providing thermal analysis.

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