

Selective Sorption of Heavy Metal Ions from Aqueous Solutions Using *m*-Cresol Based Chelating Resin and Its Analytical Applications

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ABSTRACT: Salicylic acid-Formaldehyde-*m*-Cresol (SFM) terpolymer had been synthesized in DMF media by conventional method. The resulting resin had been characterized by FTIR spectra, elemental and thermogravimetric analyses. The morphology of SFM resin had been studied by SEM and Optical photograph. Various parameters like rate of equilibration, effect of pH on ion exchange capacity and effect of concentration on ion exchange capacity had been studied. The maximum sorption capacities at 0.05M concentration for Ni(II) and Cu(II) were 0.7905 (pH-6.0) and 0.6315 (pH-5.5) mmol/g of dry resin respectively. The distribution coefficient (K_d) for five metal ions [Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II)] were determined in various concentration of tartaric acid electrolyte at different pH. The quantitative separations of heavy metal ions and transition metal ions from their admixtures [Cu(II)- Pb(II), Pb(II)- Zn(II), Ni(II)- Cd(II)] had been performed by using distribution coefficient (K_d).

KEY WORDS: Chelating resin, Adsorption, Cation exchange capacity, Distribution co-efficient (K_d), Heavy metals, Transition metals.

INTRODUCTION

Heavy metals are generally biorefractory, cannot be degraded or detoxified biologically and tend to accumulate in living organisms, thus causing diseases and disorders. Effluents discharged from major industries like chromoplasting, textile, leather tanning, electroplating, pigment and dyes, metallurgical, metal finishing, photography and wood-preserving industries contains

heavy metal ions which are very toxic. Due to its high toxicity and persistence, its disposal in landfill sites is considered as an environmental hazard because it may be leached into drinking water samples [1]. Some industrial processes result in the release of heavy metals into the aquatic ecosystem. This has led to increase concern about the effect of toxic heavy metals as environmental

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pollutants [2]. Cadmium is a metal of current toxicology concern. The principal toxic effects of cadmium are local irritation of the respiratory tract and renal damage. Zinc is an essential trace element for mammals, plants and lower form of organisms but in higher concentration, it is also toxic. Owing to their position in same group of the periodic table, selective separation of these metal ions from each other is a difficult task especially when present at trace levels [3].

Removal, separation and enrichment of trace metals in aqueous solutions play an important role for the analysis of wastewaters, industrial and geological samples, as well as for environmental remediation. In addition, there is also a growing interest to recover the precious metals due to both environmental and economical reasons [4]. The rapid development of electronic instrumentation has created powerful analytical tools but it can give erroneous result due to the presence of matrix elements. To obtain reliable data, the best course is to separate the analytes of interest from the matrix constituents and to determine them in isolated state. Thus, preconcentration and separation followed by analysis is mandatory, particularly when analyte is present at ng/cm^3 level. Solvent extraction and ion exchange resin are the two most common methodologies for the preconcentration and separation of trace elements from various matrices. Solvent extraction is ineffective due to requirement of large volume of solvent, which may create health problems. Solid phase extraction using chelating resins is the method of choice due to its high separation efficiency, good reproducibility of retention parameters and high sensitivity. They have found widespread applications in the enrichment of metals from various sources [5].

There is current interest in developing chelating matrices and exploring them for metal enrichment. It stems partly due to higher selectivity of chelating resins for metal ions, which is also tunable by pH control. The focus of current research in this area is on the development of matrices of higher capacities. This can be achieved by increasing the number of chelating sites on the matrices as well as their accessibility. Numerous chelating resins have been reported for their use in the separation of heavy metal ions. Chelating resin with S, O and N as donor atoms usually has excellent exchange properties for soft metal ion like mercury, cadmium, lead, platinum, palladium and noble metal ions [6].

The purpose of the present work is to explore the possibility of separation of heavy metal ions from aqueous solutions by using Salicylic acid- Formaldehyde-m-Cresol (SFM) chelating resin. The sorption behavior of Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) on the resin was investigated at different pH values and at its different concentrations. The quantitative separations of heavy metal and transition metal ions from their admixture [Cu(II)- Pb(II), Pb(II)- Zn(II), Ni(II)- Cd(II)] were achieved by columns chromatography technique. 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.

EXPERIMENTAL SECTION

Materials

All the reagents were of Analytical Grade and their purity were more than 98 %.

Salicylic 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 [7].

Preparation of the SFM Resin

Salicylic acid (13.8 g, 0.1 mole) was ground to fine powder and was taken in to a 250 mL four-necked flask. It was fitted with a condenser, thermometer, stirrer and addition funnel containing 20 mL of DMF, which was added dropwise at room temperature while stirring continuously. After the addition of DMF, 37% w/v 25mL formaldehyde (0.3 mole) was added from addition funnel with constant stirring. It was stirred for 1h at room temperature. Then the solution of m-cresol (10.8 g, 0.1 mole) in 20 mL DMF was added from addition funnel at the rate of 2 mL/min. The mixture was heated on water bath at $100\text{ }^\circ\text{C} \pm 6\text{ }^\circ\text{C}$ temperature with stirring for about 2-3 h till soft jelly type material was obtained. The material converted to hard mass after curing in a sealed tube at $70\text{--}75\text{ }^\circ\text{C}$ for 2-3 h. The cured mass was then crushed to 20-50 mesh size particles and it was washed with methanol and finally with hot double distilled water to remove unreacted monomers. The resin was dried in vacuum oven at $100\text{ }^\circ\text{C}$.

Apparatus and procedure

The dry resin of 20-50 mesh size particles were used for characterization. Infrared spectra of the synthesized resin had been scanned in KBr pellets on "Shimadzu FTIR Spectrophotometer" model 8201PC. The elemental analysis was carried out on Euro EA 3000 Elemental Analyser. The surface analysis was done using Scanning Electron Microscopy (Philips XL30, Japan) at 400× 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 10 °C / min in N₂ atmosphere. A pH meter (Elico, model CL-44) was used to measure the pH.

The water-swollen resin was regenerated with 0.1M HCl to obtain its H⁺ form for further studies. The physico-chemical properties like % moisture content, % solid, 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 [8]. 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 studied for all the metal ions [Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II)] [9]. All experiments were carried out according to earlier methods [10]. A batch equilibration method was adopted for the determination of the metal ion uptake capacity of resin using different experimental variable such as rate of exchange, metal ion concentration and pH.

Rate of exchange of metal ions

For this experiment, H⁺ form of accurately weighed (0.250 ± 0.001 g) dry resin sample was taken in different glass stopper bottles and equilibrated with buffer solutions of desired pH value for 24h. 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. To do this, buffer solutions of pH range 3.5-6.5 were

prepared from 0.2 M acetic acid and 0.2 M sodium acetate solutions. Different sets of weighed (0.250 ± 0.001 g) dry resin were equilibrated with buffer in different stopper 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 solutions were decanted and metal ion concentration in the supernatant were measured by complexometric titration with 0.05M EDTA solution using appropriate indicator. A blank experiment was also run simultaneously. The metal uptake was calculated by different method. The same method was followed through out the study to calculate the ion exchange capacity of the resin.

Exchange capacity =

$$\frac{\left[\frac{\text{Vol. of metal ion soln.} \times \text{Molarity of metal ion soln.}}{\text{Weight of resin sample} \times \frac{\% \text{Solid}}{100}} \right] - \left[\frac{\text{Vol. of EDTA soln.} \times \text{Molarity of EDTA soln.}}{\text{Weight of resin sample} \times \frac{\% \text{Solid}}{100}} \right]}{\text{Weight of resin sample} \times \frac{\% \text{Solid}}{100}}$$

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 accurately weighed (0.250 ± 0.001 g) dry resin sets were equilibrated with acetate buffer at desired pH values (pH value of highest exchange) for 24 h and then buffer solutions were decanted. Then the same resins 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 24h with intermittent shaking. After 24h, metal ion solutions were decanted and unchelated metal ions were estimated by complexometric titration.

K_d values for metal ions in presence of electrolyte (tartaric acid) solution

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

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

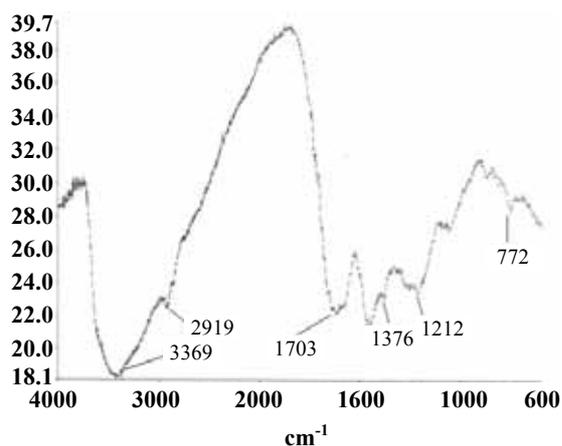


Fig. 1: FTIR of SFM resin

Effect of different concentration and pH of electrolyte (tartaric acid) on metal ion uptake by the synthesized resin was studied. The accurately weighed (0.250 ± 0.001 g) dry resin sample was suspended in the 50 mL electrolyte solution of tartaric acid of different known concentration 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 values using acetate buffer and the resin was equilibrated for 24h. To the suspension, 2.0 mL (5 mg/mL) of solutions of different metal ions under study were equilibrated for 24h with intermittent shaking. After 24h solutions were decanted and unadsorbed metal ions were estimated.

RESULTS AND DISCUSSION

Characterization of SFM resin

The chelating SFM resin possess 9.4 % moisture, 1.22 g/cm^3 true density, 0.7653 g/mL apparent density, 0.3727 void volume fraction, 7.76 mmol/g of dry resin sodium exchange capacity, 7.7605 mmol/cm^3 concentration of fixed ionogenic group and 4.86 mmol/cm^3 volume Capacity. 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) was 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 SFM resin was 70 %.

Infrared spectra show the strong broad band at 3369 cm^{-1} is due to the ν (O-H) stretching of phenolic group and carboxylic acid group. The medium strong band at 2919 cm^{-1} is due to the ν (C-H) stretching of methylene group.

The medium strong band at 1703 cm^{-1} is due to ν (C=O) stretching of ketonic group of aromatic acid. The medium band at 1375 cm^{-1} is due to δ (C-H) bending of Ar-CH₃. The medium broad band at 1212 cm^{-1} is due to ν (C-O) stretching of phenol. The medium band at 772 cm^{-1} is due to tetra-substituted benzene ring. The spectrum of SFM resin is exhibited in Fig. 1.

Elemental analysis

The results of elemental analysis are in good agreement with calculated values of % C, % H and % N as scheme-1. Theoretically (%) 64.68(C), 4.68(H) and nil (N). Found (%) 64.92(C), 5.02(H) and nil (N). The results of the elemental analysis are in good agreement with calculated values. The values of elemental analysis confirm the proposed structure of the resin presented in scheme-I.

Scanning Electron Micrograph (SEM) of Resin

Surface analysis has found to be of great use in understanding the surface features of the material. The morphology of resin exhibits growth of crystals from polymer solutions corresponding to the most prominent organization in polymers on a large scale such as in size of few millimeters of spherulites. Ideally, spherulites are the aggregates of submicroscopic size particles. Spherulites are characterized by secondary structural features, such as faint corrugations. The higher magnification $500\times$ shows coexistence of an appreciable amorphous fraction with a small amount of shallow pits. The surface of SFM (Fig. 2) contributes greater segments of crystalline regions compared to AFR [10].

Optical photographs of resins

The optical photograph of synthesized resin was presented in Fig. 3. It suggests that the resins appear to be reddish brown to black in color

Thermogravimetric Analysis [TGA]

Thermogravimetric analysis involves change in weight of a system under examination as the temperature is increased at predetermined rate and preferably at a linear rate. First step degradation of SFM resin occurs between $415 \text{ }^\circ\text{C}$ to $550 \text{ }^\circ\text{C}$ which shown in Fig.4. Degradation involves 52.4 % weight loss. Here, maximum weight loss takes place at $490 \text{ }^\circ\text{C}$. The second step degradation of SFM resin takes place between $595 \text{ }^\circ\text{C}$ to $655 \text{ }^\circ\text{C}$, which involves 6.0 % of weight loss.

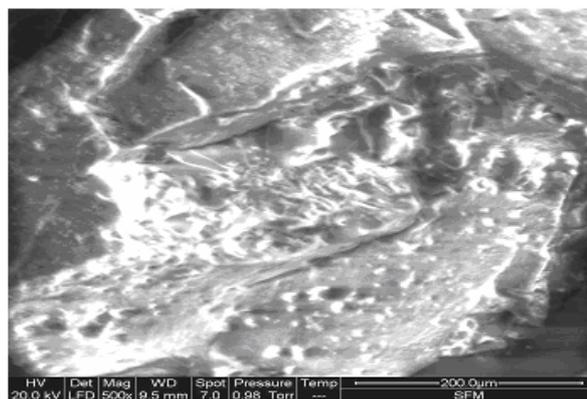
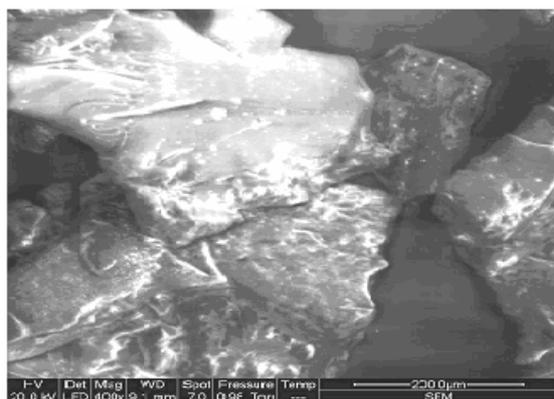
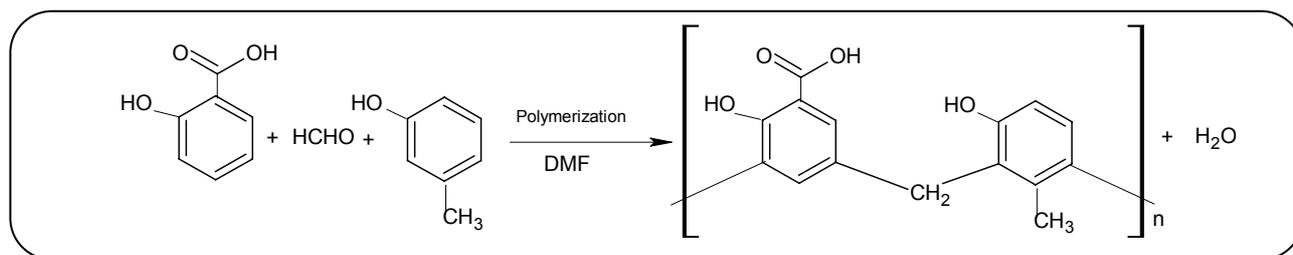


Fig. 2: SEM photographs of SFM resin at (a) 400 × (b) 500 × magnification.



Fig. 3: Optical photograph of SFM resin at 180 × magnification.

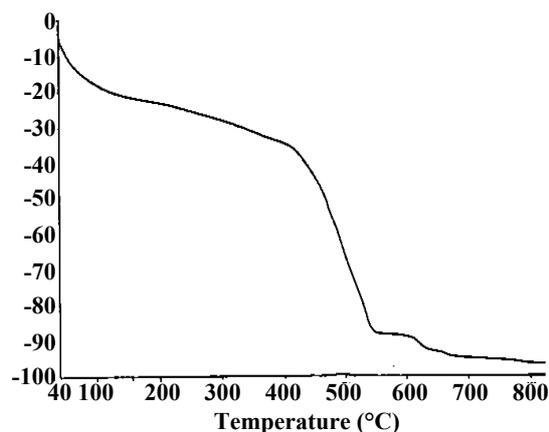


Fig. 4: TGA of SFM resin.

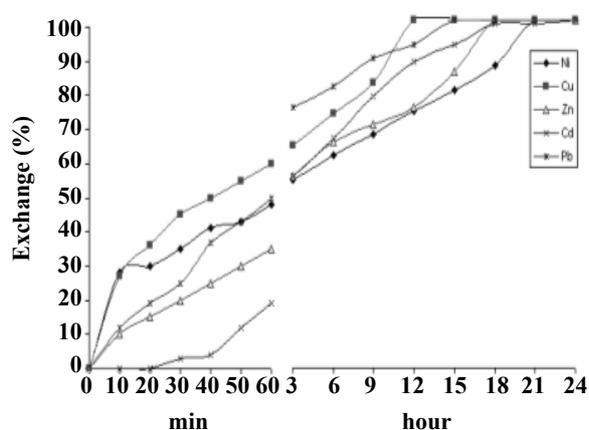
Integral procedural decomposition temperature (IPDT) was calculated by Doyle's method [11]. IPDT expresses the overall thermal stability of the resin, which is 250 °C.

Thermogravimetric analysis has proved to be useful analytical technique in evaluating kinetic parameter such as energy of activation (E^*), enthalpy of activation (H^*), entropy of activation (S^*), free energy of activation (G^*) and order of reaction (n), which provides valuable quantitative information regarding the stability of the resin. In the present paper, we have employed Broido [12],

Horowitz-Metzger [13] and Coats-Redfern [14] methods for the estimation of various kinetic parameters of thermal degradation, which is shown in Table 1. The degradation of SFM resin is second order. Negative value of entropy indicates less randomization within the system. Positive value of enthalpy explains that the decomposition process is endothermic. Positive value of free energy suggests that the decomposition process is slow reaction. In case of m-cresol (SFM) containing resin with non polar $-CH_3$ groups at meta position,

Table 1: Kinetic data of the thermal decomposition reaction of SFM resin [E_a (kJ/mol), S^* (J/kmol), H^* (kJ/mol) and G^* (kJ/mol)].

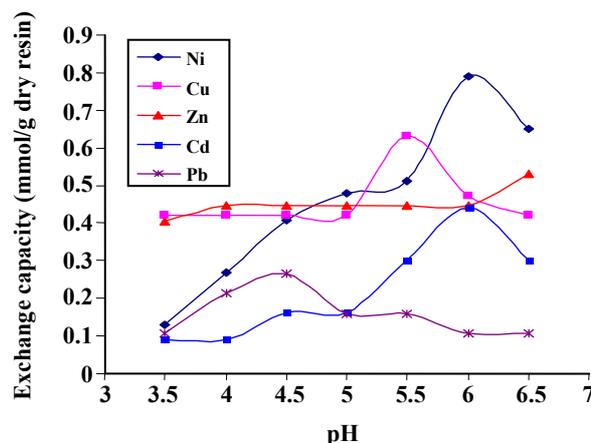
| Step | Properties | Broido method | Horowitz-Metzger method | Order of degradation | Coats-Redfern method |
|------|------------|---------------|-------------------------|----------------------|----------------------|
| 1 | E_a | 38.6 | 39.5 | 2 | 28.67 |
| | S^* | -109.19 | -109.73 | | -109.85 |
| | H^* | 32.75 | 28.65 | | 23.65 |
| | G^* | 109.52 | 105.79 | | 89.90 |
| 2 | E_a | 52.1 | 52.1 | 2 | 58.17 |
| | S^* | -230.27 | -230.27 | | -229.69 |
| | H^* | 44.63 | 44.63 | | 50.70 |
| | G^* | 251.41 | 251.41 | | 256.96 |

**Fig. 5: Rate of exchange for metal ions exchange capacity on SFM resin.**

the macromolecules thus formed are densely packed in absence of non-repulsive forces, thereby producing more compact, crystalline and rigid structure (Fig. 2). Hence, the rigid and more crystalline structure exhibits higher activation energy as compared to resin synthesized from salicylic acid-formaldehyde-resorcinol [15] due to less close packed surface. The crystalline character of SFM could be attributed to its lower capacities and left out residue in TGA.

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 copolymers. From the results, it is observed that the rate of exchange of metal ions is faster in beginning and then slow down. These happen due to elimination or exchange of ions from the solution to the surface of the resin and after the entire available site (group) of resin were occupied. It gives rise to slower rate of exchange. Fig. 5 shows the rate of exchange of metal ion on SFM resin.

**Fig. 6: Effect of pH on metal ion exchange capacity on SFM resin.**

The results reveals that the completion of 50 % of the exchange ($t_{1/2}$) for Cu(II) is after 45 minutes, for Zn(II) and Cd(II) is after 3 hours, for Pb(II) and Ni(II) is after 1 hour. Faster rate of $t_{1/2}$ was exhibited by Cu(II) than that of Zn(II). This is attributed to the fact that the hydrated Cu(II) have smaller radii(0.419 nm) than hydrated Zn(II) (0.430 nm) and thus have greater access to the surface of the resin. The rate of exchange for the post transition metal ions exhibits the reverse trend. For Cd(II) the rate of exchange is slower than that of Pb(II) because of the difference in d orbital.

Effect of pH on exchange capacity

The removal of metal ions from aqueous solution by sorption is highly dependent on pH of the solution that affects the surface charge of the sorbent. The results of the exchange capacity versus pH for different metal ions are presented in Fig. 6. The maximum exchange capacity for Zn(II) is found to be at pH 6.5, while for

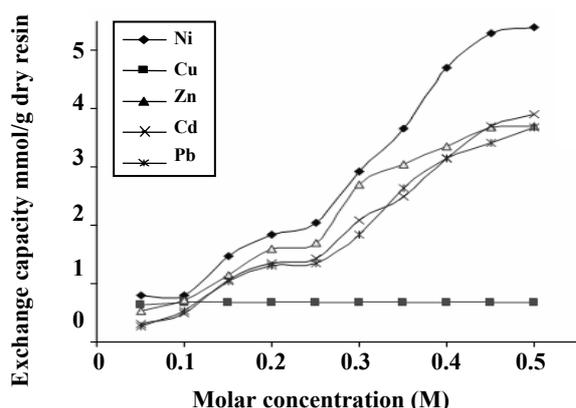


Fig. 7: Effect of concentration on metal ion exchange capacity on SFM resin.

Ni(II) and Cd(II) it is at pH 6.0. For Cu(II) it is at pH 5.5 and for Pb(II) is at pH 4.5. The exchange capacity order is as follows:

$\text{Ni(II)} > \text{Cu(II)} > \text{Zn(II)} > \text{Cd(II)} > \text{Pb(II)}$.

Resin shows very low exchange capacity for Pb(II) and Cd(II) than other metal ions. In the case of Cd(II) and Pb(II) purely electrostatic factors are responsible. Due to the less deep pits, SFM resin exhibits lower ion exchange capacity for Pb(II). Pb(II) has bigger hydrated radii, so it can not easily penetrate to originate in more crystalline region of the polymeric network. Therefore more clean separation could be obtained from binary mixture of either Pb(II) or Cd(II) with transition metal ions such as Ni(II), Cu(II) or Zn(II). The lower capacity of Cd(II) than Zn(II) and Cu(II) may be explained due to greater hydrated-ion radius of Cd(II) than that of Zn(II) and Cu(II). This will result in lower electrostatic interaction between Cd(II) and the coordinating groups and hence, lower complex stability and hence lower capacity [16,17].

Effect of metal ion concentration on exchange capacity

The examination of data presented in Fig. 7 reveals that the amount of adsorbed 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

Batch equilibrium method is more fruitful to determine distribution coefficient (K_d) for the metal ions as a function of tartaric acid concentration. Tartaric acid is strong eluting chelating agent. It contains six oxygen atoms with unshared pair of electron, which form more stable chelating complexes with metal ions than resin-metal complexes. So tartaric acid can easily elute metal ions from resin and give clear separation. The distribution coefficient (K_d) of the different metal ions as the function of pH and concentration of electrolyte solution (tartaric acid) are presented in Table 2. The distribution coefficient of Cd(II) are lower owing to the large size of its hydrated ion. Pb(II) being non-transition metal ion does not follow the *Irving-Williams* order owing to different crystal field stabilization energies. Distribution coefficients were measured for all metal ions as a function of tartaric acid concentration and prediction of whether a separation for a given pair of metal ions is possible by comparing their K_d values. The data of K_d show a random trend in certain case, while for resorcinol containing SFR-C [15] and SFR-M [18] resin, K_d values decrease with increasing electrolyte concentration and increase with increasing in pH. It is expected that the distribution coefficients of metal ions will vary depending on the stability of the metal complexes formed with the chelating groups of the resin. Greater stabilization results in higher distribution coefficients. The present investigation limits the distribution studies up to a certain pH for each metal ion to prevent the hydrolysis of metal ions at higher pH.

Chromatographic column separation of Binary mixture

The superior selectivity towards multivalent cations exhibited by chelating resin has been demonstrated in column experiments by using K_d values. The values of the K_d are shown in Table 2. An ideal situation would be such that one K_d values 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 values. The second metal ion can be eluted by changing the tartaric acid concentration to a level that has a lowest K_d values for second metal ion.

For the separation of binary mixtures, 2 mL of 5 mg / mL of each metal ion solution was taken. The chelating resin in H^+ form was packed into a chromatographic column to form a compact resin bed ~ 15 cm height and 0.4 cm diameter.

Table 2: K_d values of metal ions on SFM resin in tartaric acid media at different pH

| Metal ion | Tartaric acid Conc.(M) | K_d values at different pH | | | | |
|-----------|------------------------|------------------------------|-------|-------|-------|-------|
| | | 3.0 | 3.5 | 4.0 | 5.0 | 6.0 |
| Ni(II) | 0.1 | 240.0 | 310.2 | 165.2 | 182.3 | 182.3 |
| | 0.2 | 262.0 | 310.2 | 340.5 | 135.0 | - |
| | 0.3 | 500.0 | - | - | - | - |
| | 0.5 | 100.0 | 161.2 | 33.5 | 42.3 | 128.0 |
| | 1.0 | - | - | - | - | - |
| Cu(II) | 0.1 | 205.3 | 157.6 | - | - | 20.0 |
| | 0.2 | 300.2 | 100.2 | 69.0 | - | - |
| | 0.3 | - | - | - | - | 290.3 |
| | 0.5 | - | - | - | - | 2.0 |
| | 1.0 | - | - | - | - | - |
| Zn(II) | 0.1 | - | 6.3 | 90.4 | 45.6 | 75.0 |
| | 0.2 | 10.0 | - | - | - | 21.0 |
| | 0.3 | 27.6 | 45.0 | 21.3 | 33.6 | - |
| | 0.5 | 63.5 | 60.0 | 51.6 | - | - |
| | 1.0 | 150.2 | - | 60.0 | - | - |
| Cd(II) | 0.1 | - | 5.3 | 41.3 | - | 41.3 |
| | 0.2 | - | - | 28.5 | 22.6 | 111.0 |
| | 0.3 | 51.5 | 69.5 | 42.5 | 13.6 | 69.3 |
| | 0.5 | 51.5 | 42.5 | 51.3 | 13.6 | 27.3 |
| | 1.0 | - | - | 14.2 | - | 25.6 |
| Pb(II) | 0.1 | 2.0 | 23.6 | 60.0 | 70.0 | 2.0 |
| | 0.2 | 220.0 | 240.5 | 150.2 | - | - |
| | 0.3 | - | 104.3 | 120.6 | 104.3 | 44.0 |
| | 0.5 | 33.0 | 21.5 | 30.2 | 44.3 | 10.0 |
| | 1.0 | - | - | 15.0 | 21.3 | - |

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.

Separation of Cu(II) from Pb(II) was performed, at initial pH 4.0 by selective elution of Cu(II) with 0.3 M tartaric acid solution and Pb(II) with 0.1 M tartaric acid solution at pH 3.0, which is shown in Fig. 8. The elution percentage of Cu(II) and Pb(II) was found to be 73% and 94% respectively. In case of separation of Pb(II) from Zn(II), the resin column was equilibrated at pH 3.0. Pb(II) was eluted with 1.0 M tartaric acid. The first few fractions contained only Pb(II) and the later fractions contain only Zn(II) which was eluted with 0.2 M tartaric acid at pH 3.0. There was no cross contamination in the separation which is shown in Fig. 9. The elution percentage of Pb(II) and Zn(II) was found to be 92% and 89% respectively. In the separation of Ni(II) from Cd(II), Ni(II) was eluted first at 6.0 pH and 0.2 M tartaric acid concentration and then sorbed Cd(II) was eluted with 0.3 M tartaric acid at pH 3.0 which is shown in Fig. 10. The elution percentage of Ni(II) and Cd(II) was found to be 90 % and 70 % respectively.

CONCLUSIONS

The present work has been focused on the preparation, characterization and chelating properties of salicylic acid-formaldehyde-m-cresol resin. The chelating properties of this resin are influenced by the medium, particularly the pH of the solution and the nature and concentration of counter ion used. In the present study, it can be concluded that SFM resin is an effective material for the preconcentration and separation of trace metal ions. The separation is more clear and cleaner with no use of organic solvent as in solvent extraction. The SFR-M [15] resin is more selective for transition metal ions; while reported SFM resin is more selective for post-transition metal ions. The morphology of the SFM resin exhibits a more crystalline structure rather than SFR-C [18] and SFR-M [15] resin. The crystals are smaller in surface area with more closely packed structures with no visible pits. This could be the reason of low ion-exchange capacity of higher hydrated size of metal ions (lead ion). The presence of heavy metal ions viz Pb(II) and Cd(II) in aquatic systems pose heavy risks to human health. Therefore, removal of such metal ions from water bodies may be considered as an interesting and important research activity. A perusal of results indicates that for

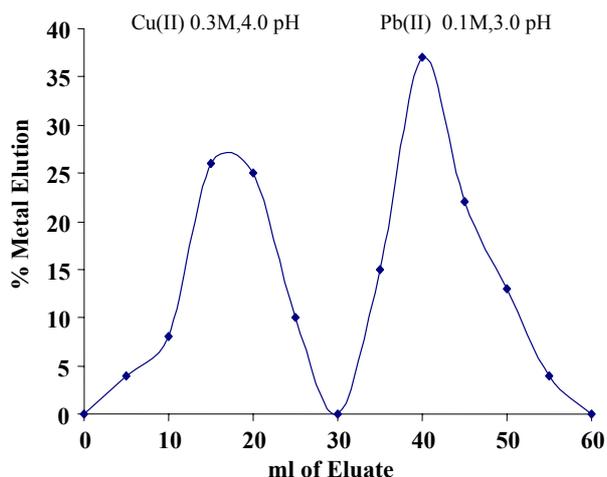


Fig. 8: Separation of Cu(II) and Pb(II) on SFM resin.

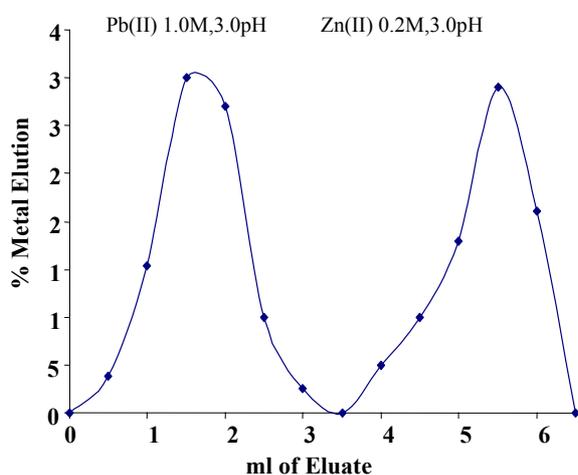


Fig. 9: Separation of Pb(II) and Zn(II) on SFM resin.

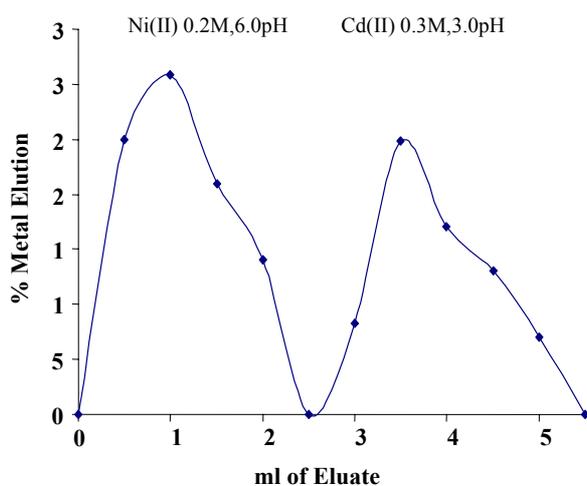


Fig. 10: Separation of Ni(II) and Cd(II) on SFM resin.

attaining equilibrium Cu(II) takes 12 h whereas Ni(II), Zn (II), Pb (II), and Cd (II) require 15-21 h for attaining the same. It is similar to that reported resins derived from salicylic acid-furfural-hexamine [19] and salicylic acid-acetaldehyde-thiourea [20]. Both these reported resins took about 22-24 h to attain equilibrium. Hydroxy group at ortho position in SFM resin gives more thermal stability to the resin as compared to amino group at ortho position in AFM resin [21] and degraded in two steps. SFM resin was successfully used as sorbent to remove transition metal ions from electroplating industrial wastewater which contains Cu(II),Cr(IV),Fe(II) and Ni(II). However this will be the part of our future paper publication.

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