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Studies of Chelation Ion-exchange Properties of Copolymer Resin Derived from Salicylic Acid and its Analytical Applications

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A B S T R A C T

Chelating ion-exchange resin was synthesized from salicylic acid-formaldehyde-resorcinol (SFR) using DMF as solvent at 80 ± 2ºC. The resin was characterized by FTIR and elemental analysis. The thermal analysis (TGA and DTG) was performed at the heating rate of 10ºC/min in N_2 atmosphere. Broido and Horowitz-Metzger methods were used to estimate the activation energy (E_a) of various steps of thermal degradation. The morphology of the resin was studied by optical microscopy and scanning electron micrographs (SEM) at different magnifications. The physico-chemical properties of this ion-exchange resin were studied. The effect of pH, metal ion concentration and rate of exchange of metal ions were also studied by employing batch equilibrium method. The quantitative separation of metal ions from binary [cadmium (II)-lead (II)] and ternary [zinc (II)-copper (II)-nickel (II)] synthetic mixtures were done by column chromatography at 25 ± 2ºC. The constituents of brass were also analyzed by selective sorption on column at optimized distribution coefficient (K_d) values.

Key Words:

chelating resin;
batch equilibration;
column chromatography;
distribution coefficient,
copper;
nickel;
zinc;
cadmium;
lead.

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INTRODUCTION

The main objective of the most studies on chelating resins, is preparation of insoluble functionalized polymers which can provide more flexible working conditions together with good stability and high capacity for certain metal ions [1-3]. Salicylic acid has been used extensively as an analytical reagent in the determination of metal ions due to its chelating property. The polymeric resin from salicylic acid and formaldehyde was derived by DeGeiso et al. [4] in 1962. They have studied the ion-exchange capacity and selectivity of salicylic

acid-formaldehyde copolymer with Fe^{3+} and UO_2^{2+} ions as a function of pH. Patel et al. [5,6] have prepared the terpolymer of salicylic acid/*p*-hydroxy benzoic acid and thiourea with trioxane in the presence of acid catalyst with different molar proportions of monomers. Kapadia et al. [7,8,9] prepared ion-exchange resins from various phenolic derivatives like salicylic acid, gallic acid, β-resorcylic acid, anthranilic acid, 8-hydroxyquinoline, and hydroquinone using DMF as solvent. They have studied their anion as well as cation-exchange properties towards various metal ions.

Attachment of multidentate ligands to insoluble polymeric supports is a technique commonly utilized for the preparation of selective ion-exchange resins, which are capable of separation and purification of metal ions. The polymeric chelates of Ni (II), Co (II), and Cu (II) have been prepared from poly(salicylaldehyde-acrylate) divinylbenzene resin [10]. Bavanker et al. [11] have also prepared terpolymer from salicylaldehyde-biuret with trioxane and studied its phsicochemical properties. A number of terpolymers derived from phenol derivatives have been studied and reported along with their chelating ion-exchange properties. For example, Karunakaran et al. [12] have synthesized terpolymer from *o*-nitrophenol-thiourea-formaldehyde and Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and UO_2^{2+} were used for chelation. Das [13] has derived copolymer from thiosemicarbazone derivatives of phenolic compound. Terpolymers of 8-hydroxy quinoline-formaldehyde-resorcinol/catechol were reported by Shah et al. [14,15] and chromatographic column separation for various metal ions such as Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} have carried out using the quinoline base resins. Mubarak et al. [16] have studied the chelation behaviour of the phenolic-formaldehyde polymers, poly(2,4-dihydroxybenzoic acid-3,5-dimethylene), poly(2-hydroxybenzoic acid-3,5-dimethylene) and poly(3-hydroxybenzoic acid-4,6-dimethylene) towards the trivalent lanthanide metal ions such as La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, and Tb^{3+} by a static batch equilibrium technique at 25ºC as a function of contact time, pH, and concentration. Polymer supported reagents [17] containing various ligands have been studied for their selective complexation towards various metal ions. Dabrowski et al. [18] have efficiently removed trace impurities and toxic metals from industrial waste water by various ion-exchangers.

So far no resin based on salicylic acid-formaldehyde-resorcinol in DMF media has been synthesized for the quantitative separation of transition and post-transition metal ions. As industrial effluents are often rich in transition metal ions, removal of these metals is an important task for industries. Therefore, we have studied the use of ion-exchanger for the removal and separation of heavy trace metal ions. In this paper, synthesis and characterization of the above resin are reported together with the conditions for the effective separation of transition and post-transition metal ions. This resin has also been applied to analysis of constituents of brass alloy. An appreciable higher ion-exchange capacity for heavy metal ions was exhibited by the present resin (SFR) which contains more acidic characters of the monomer.

EXPERIMENTAL

Materials

Salicylic acid (Ranbaxy Fine Chemicals S.A.S. Nagar) purified by rectified spirit. Formaldehyde (37%) (Qualigens Fine Chemicals, Mumbai) was used as received. Resorcinol (SRL Mumbai, extra pure) was used as received.

Metal solutions were prepared by dissolving appropriate amount of the acetates of the metals in double distilled water and standardized by EDTA titration [19].

Resin Synthesis

Salicylic acid (13.8 g, 0.1 mol) was taken in a 250 mL three-necked round bottom flask (fitted with thermometer, stirrer and addition funnel) and dissolved in 20 mL DMF to give clear solution. A solution of resorcinol (11 g, 0.1 mol) in 10 mL DMF was taken in addition funnel and added to above solution with constant stirring. To the above solution formaldehyde (0.3 mol, 37%) was added from additional funnel at the rate of 1 mL/min with constant stirring. Then the reaction mixture was refluxed on water bath at 80 ± 2ºC for 2-3 h with constant stirring during which the mixture turned to a reddish brown soft gel. A gel was separated from the reaction vessel and cured in an oven

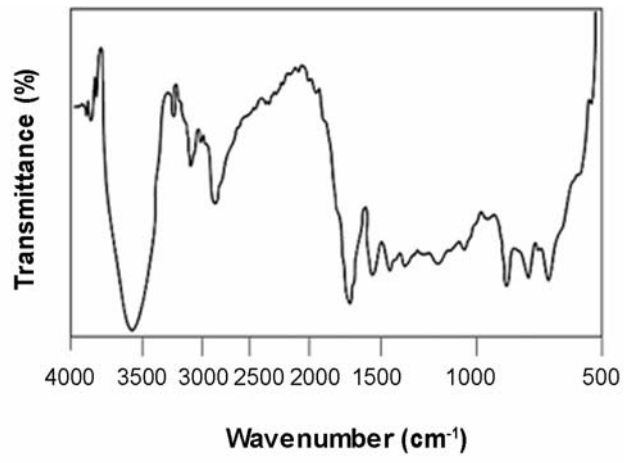


Figure 1. FTIR Spectrum of SFR resin.

at 70-75ºC for 12 h. As carboxylic acid groups are normally decomposed above 100ºC, the resin was cured below 90ºC.

The resulting resin was first washed with DMF to remove unreacted monomer and finally washed with hot deionized water. After complete washing, the yield of the resin was found 61% (15.2 g). This purified and dry resin sample was finely ground and passed through 20 mesh screen and than 50 mesh screen to obtain uniform particle size (20-50 mesh). The resin was found non-melting and insoluble in almost all organic solvents and also in acids and alkalies of higher strength. Resin was stored in polyethylene bottle. This resin was directly used for spectral, elemental, thermal and morphological studies.

IR Spectrum of the synthesized resin sample had been scanned in KBr pallet on a Shimadzu FTIR Spectrophotometer model-8201PC, which is shown in Figure 1. The elemental analysis was carried out on a Carlo Erba Elemental Analyser model 1160. The results of elemental analysis are in good agreement with calculated values of %C, %H and %N, which are given in Table 1. The thermograms (TGA and DTG) of SFR were taken on a Mettler TA 4000 (Switzerland) at constant heating rate of 10ºC/min in

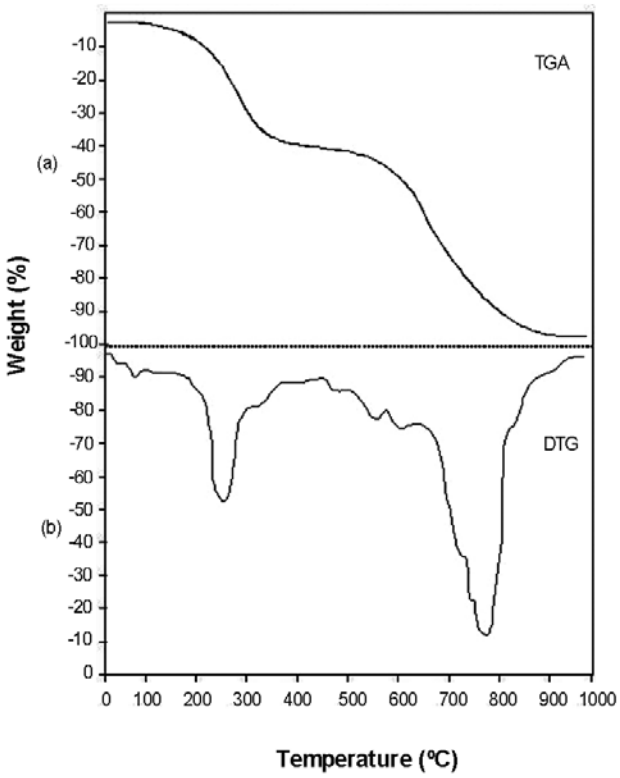


Figure 2. TGA (a), and DTG (b) thermograms of SFR resin at heating rate of 10ºC/min in N_2 atmosphere.

nitrogen atmosphere (Figure 2). Broido [20] and Horowitz-Metzger [21] methods were used to calculate the energy of activation of thermal degradation of SFR. The results are given in Table 2. The surface analysis was performed using an optical microscope (Olympus SZX 12, Japan) and scanning electron microscope (Philips XL30, Japan) at different magnifications, which are shown in Figures 3 and 4, respectively.

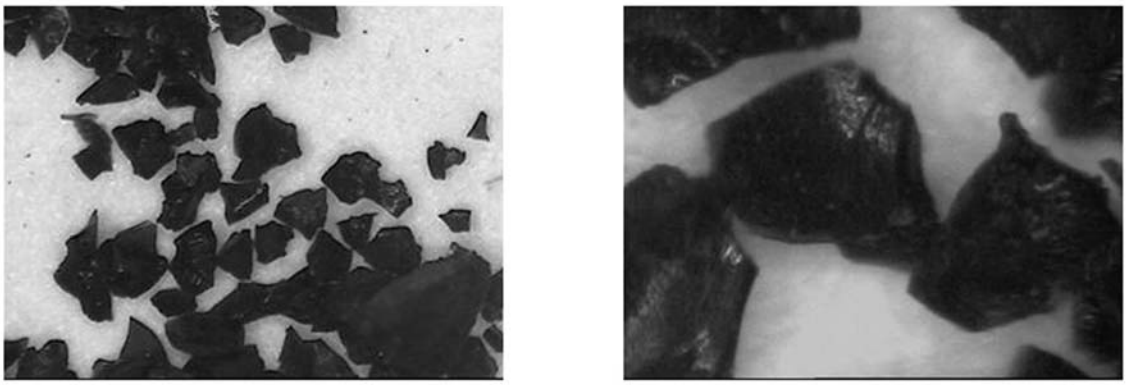
To convert the resin sample in H^+ form, resin sample having uniform particle size (20-50 mesh) was equilibrated with 1 M HCl solution for 24 h and washed with deionized water till it was free from chloride by testing with silver nitrate solution. This H^+ form of resin was used for further studies. The

Table 1. Elemental analysis of resin.

Analysis calculated (found) (%)		
C	H	N
61.34	6.26	-
(61.58)	(6.08)	-

Table 2. Activation energy of degradation of resin.

Activation energy (kJ/mol)			
Broido method		Horowitz-Metzger method	
Step-I	Step-II	Step-I	Step-II
25.71	32.98	26.12	33.17



(a) (b)

Figure 3. Optical photographs of SFR resin at: (a)180×, and (b) 400× magnifications.

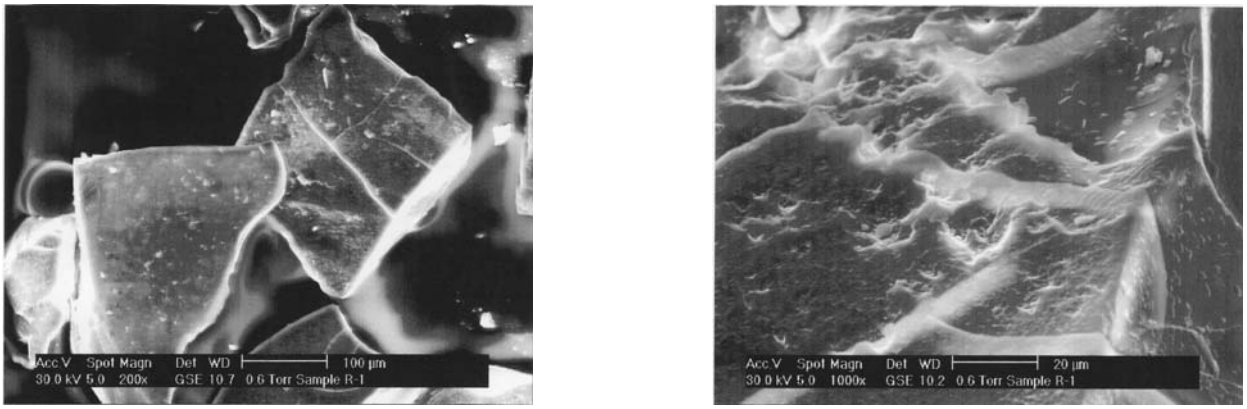
Table 3. Physico-chemical properties of resin.

No	Properties	Values (SD)
1	Moisture content (%)	7.0 (±0.5)
2	Solid (%)	93 (± 0.5)
3	True density	1.12 (± 0.01) g/mL
4	Apparent density	0.85 (± 0.01) g/mL
5	Void volume fraction	0.384 (± 0.001)
6	Sodium exchange capacity	4.13 (± 0.01) mmol/g
7	Concentration of fixed ionogenic group	4.30 (± 0.02) mmol/mL
8	Volume capacity	2.67 (± 0.01) mmol/mL

batch equilibration method was adopted for various ion-exchange properties. The physico-chemical properties like moisture content(%), solid(%), apparent density, true density, void volume fraction, and sodium exchange capacity were studied according to literature methods [22]. The results are presented in Table 3. The adsorption properties such as effect of pH on exchange capacity, effect of concentration on exchange capacity, rate of exchange of metal ions, and effect of electrolyte (tartaric acid) on distribution coefficient (K_d) for different metal ions as a function of pH and concentration were also studied [23].

Percentage Moisture Content

The H^+ form of dry resin (0.5 g) was equilibrated with 30 mL of distilled water for 48 h. The swollen resin was collected by filteration, adhering trace of water was removed by pressing with filter paper and sample was weighed. Then swollen resin was dried in oven at 90-100ºC for 8 h and reweighed after cooling in desiccator. From the weight of swollen and dry resin,



(a) (b)

Figure 4. SEM Micrographs of SFR resin at: (a) 200×, and (b) 1000× magnifications.

moisture content(%) was calculated by eqn (2).

$$\text{Solid}(\%) = \frac{\text{Weight of oven dried resin}}{\text{Weight of the resin before drying}} \times 100 \quad (1)$$

$$\text{Moisture content}(\%) = 100 - \text{Solid}(\%) \quad (2)$$

True density, eqn (3), apparent density, eqn (4) and void volume fraction, eqn (5) were also calculated:

$$\text{True density } (d_{res}) = \frac{W_r - W}{(W_s - W_{rs}) + (W_r - W)} \quad (3)$$

where, W= weight of the specific gravity bottle, W_r= weight of the specific gravity bottle containing resin, W_s= weight of the specific gravity bottle containing water, W_{rs}= weight of the specific gravity bottle containing both water and resin.

$$\text{Apparent density } (d_{col}) = \frac{\text{Weight of resin}}{\text{Volume of resin}} \quad (4)$$

$$\text{Void volume fraction} = 1 - \frac{d_{col}}{d_{res}} \quad (5)$$

Total Exchange Capacity

The total exchange capacity of the resin is the total number of exchanging sites available per unit volume of water swollen resin.

About 1.0 g exactly weighed dry resin (H^+ form) having uniform particle size (20-50 mesh) was taken in 250 mL Erlenmeyer flask. To this 200 mL standardized solution of 0.1 M sodium hydroxide in 1 M sodium chloride was added. The mixture was equilibrated for 24 h with intermittent stirring. After 24 h, 50 mL aliquots of the supernatant liquid were withdrawn and titrated against standard 0.1 M HCl solution. The total cation exchange capacity was calculated according to following formula (eqn (6)).

$$\text{CEC} = \frac{(200 \times \text{Normality of NaOH})}{\text{Weight of sample } (\text{Solid}(\%)/100)} - \frac{(4 \times \text{Volume of HCl} \times \text{Normality of HCl})}{\text{Weight of sample} \times (\text{Solid}(\%)/100)} \quad (6)$$

where, CEC is cation exchange capacity of the resin. Concentration of fixed ionogenic group, C_r (eqn (7)) and volume capacity, Q (eqn (8)) were also calculated.

$$C_r = \frac{d_{res} \times (100 - \text{Moisture content}(\%)) \times \text{CEC}}{100} \quad (7)$$

$$Q = (1 - \text{Void volume fraction}) \times C_r \quad (8)$$

Effect of pH on Exchange Capacity

To study the effect of pH on metal ion adsorption, it is necessary to buffer the resin and the solutions used. For this, buffer solutions of pH range 3-6 were prepared from 0.2 M acetic acid and 0.2 M sodium acetate solution. An Elico pH meter model CL-44 was used for pH measurement. An accurately weighed (0.25 g) resin having uniform particle size (20-50 mesh) was equilibrated with buffer in different stoppered bottles for 24 h, so that resin attained the desired pH value. After 24 h, buffer solutions were decanted and 50 mL of 0.2 M metal ion solutions of varying pH from 3-6 were added. Metal solutions were equilibrated at room temperature for 24 h with intermittent shaking. After 24 h, solutions were decanted and the unadsorbed metal ions were estimated by complexometric titration with 0.1 M EDTA solution using appropriate indicators. A blank experiment was also run simultaneously. The metal uptake was calculated by a different method [23]. The same method was followed throughout the study to calculate the ion-exchange capacity.

Effect of Metal Ion Concentration on Exchange Capacity

To study the effect of metal ion concentration on resin uptake of different metal ions, the resin was equilibrated with acetate buffer at desired pH values (pH value of highest exchange) for 24 h and then buffer solutions were decanted. The accurately weighed (0.25 g) dry resin having uniform particle size (20-50 mesh) 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 (25 ± 2ºC) for 24 h with intermittent shaking. After 24 h, the metal ion solutions were decanted and unchelated metal ions were estimated.

Rate of Exchange of Metal Ions

For this experiment an accurately weighed (0.25 g) dry resin (20-50 mesh) was taken in different glass stoppered bottles and equilibrated with buffer solution of desired pH value for 24 h. After decanting buffer solution, 50 mL (0.2 M) metal ion solution of the same pH was added. The amount of unchelated metal ions was determined at fixed time intervals.

Effect of Electrolyte Concentration and pH on Distribution Coefficients of Metal Ions

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, is defined as follows:

$$K_d = \frac{\text{mmol of metal ion in resin}}{\text{mmol of metal ion in solution}} \times \frac{\text{Volume of solution}}{\text{Weight of dry resin}}$$

Although this distribution coefficient is measured on a batch basis, it can be used to predict elution behaviour for metals eluted from an ion-exchange column. To separate two substances, conditions should be selected such that the distribution coefficient of one is low (preferably 1 or less) so that the elution from the column will be rapid. The distribution coefficient of the other substance under the same conditions

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

Metal ion	Tartaric acid Concentration (M)	K_d Values in tartaric acid at different pHs				
		3.0	3.5	4.0	5.0	6.0
Ni (II)	0.1	98.83	75.22	60.60	37.85	11.95
	0.2	57.00	47.52	30.11	18.90	8.0
	0.3	21.00	17.25	10.89	8.71	2.51
	0.5	3.92	3.21	1.55	-	-
	1.0	1.30	-	-	-	-
Cu (II)	0.1	396.52	322.00	287.95	127.35	90.90
	0.2	192.00	177.96	123.77	99.87	50.22
	0.3	100.02	90.96	67.87	57.11	37.55
	0.5	87.90	67.91	42.47	23.01	8.08
	1.0	18.05	12.92	7.00	2.92	-
Zn (II)	0.1	592.00	407.00	333.40	166.00	120.71
	0.2	445.70	343.09	309.27	171.10	92.00
	0.3	401.00	277.81	241.30	139.37	67.60
	0.5	380.50	312.70	222.85	101.00	28.39
	1.0	280.17	211.57	187.17	99.27	7.37
Pb (II)	0.1	828.23	587.62	440.59	310.51	247.10
	0.2	517.00	473.73	301.77	250.67	189.73
	0.3	390.32	295.00	220.22	181.73	121.85
	0.5	152.71	210.13	178.15	120.91	92.30
	1.0	170.13	145.70	90.27	52.64	11.09
Cd (II)	0.1	565.00	443.00	299.80	143.31	87.50
	0.2	370.81	215.70	153.99	98.98	50.99
	0.3	252.11	170.77	101.22	53.00	19.28
	0.5	98.23	50.09	31.13	-	-
	1.0	31.47	31.47	10.69	-	-

should be as large as possible so that this substance will be tightly held by the resin.

Effect of different concentrations and pH of electrolyte (tartaric acid) on metal ion uptake by the synthesized resin was studied. The accurately weighed (0.25 g) dry resin sample having uniform particle size (20-50 mesh) was suspended in a 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 values using acetate buffer and the resin was equilibrated for 24 h. To the suspension, 2.0 mL (5 mg/mL) solutions of different metal ions under study were equilibrated for 24 h with intermittent shaking. After 24 h, solutions were decanted and unadsorbed metal ions were estimated. The results of K_d values are given in Table 4.

Ion-exchange Chromatography

The glass column (length ca. 25 cm, i.d. ca. 0.5 cm) was used as chromatographic column. The water swollen resin (10 g) having uniform particle size (20-50 mesh) was taken in a beaker and covered with deionized water. This slurry (1:2 resin:water) was poured along the walls of the column, allowing the particles to settle so as to form the compact resin bed free from air pockets. The resin in the column was kept still and covered with water. This column (length 9.2 cm and 10 g) was used for the separation of different heavy metal ions.

Selective elutions on column were carried out for equimolar mixture (2 mL, 5 mg/mL solution of each metal) of two and three metal ions in concentration with ratio of 1:1 and 1:1:1 for binary [Pb (II)-Cd (II)] and ternary [Ni (II)-Cu (II)-Zn (II)] synthetic mixtures, respectively. The solution mixtures were passed through the column at a flow rate of 0.3 mL/min.

Tartaric acid with different concentrations 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 K_d values, which are given in Table 4. After each elution the metal ion concentrations were determine.

Analysis of Brass

The constitutents of brass was also analyzed by the column chromatography. A 100 mg brass sample was dissolved in about 2 mL of concentrated nitric acid and solution was evaporated just to dryness. The residue was dissolved in 1 mL of 0.1 M hydrochloric acid and solution filtered. The filtrate and washing were diluted to volume of 100 mL in a standard measuring flask with deionized water. A 5-mL aliquot of this solution, adjusted to the desired pH was passed through the resin column at a flow rate of 0.3 mL/min to allow sorption of the constituents of brass. After each fraction of elution, leached metal ions were estimated.

RESULTS AND DISCUSSION

Spectral Characterization of Resin

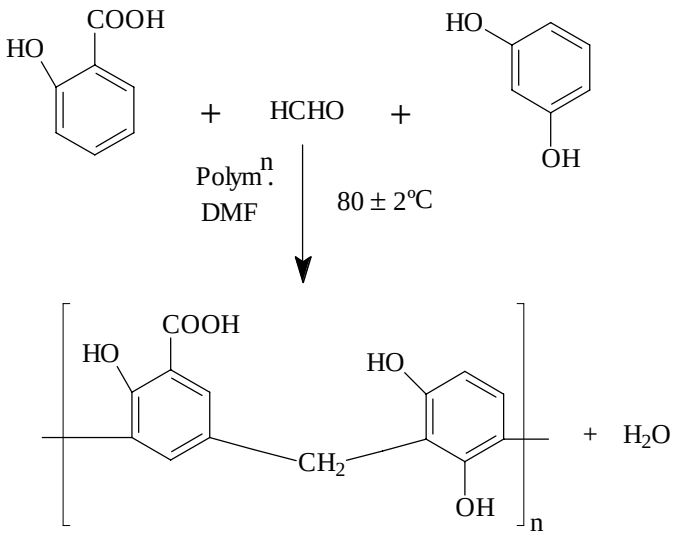
FTIR Spectrum of the resin is shown in Figure 1. The strong band at 3490 cm^{-1} is due to the ν(O-H) stretching of phenolic group. The weak medium band at 3074 cm^{-1} is due to the ν(C-H) stretching of aromatic ring. The presence of medium band at 2910 cm^{-1} is due to the ν(C-H) stretching of methylene group. The presence of broad band at 2612 cm^{-1} is due to ν(C-OH) stretching of carboxylic group. The medium strong band at 1653 cm^{-1} can be assigned to ν(C=O) stretching of aromatic acid group. The weak medium band at 1462 cm^{-1} is due to δ(C-H) deformation of methylene group. The bond at 1221 cm^{-1} can be assigned to the aromatic δ(O-H) bending of phenol. The medium band at 850 cm^{-1} is due to the δ(C-H) bending of 1,2,3,4-tetra substituted benzene ring. FTIR Data match with the probable structure shown in Scheme I, which confirms the polymerization of monomers.

Elemental Analysis

The %C, %H and %N were calculated from the general formula ($C_{14}H_{11}O_7$) of the repeating unit of the assumed structure (Scheme I) of the resin. The results of the elemental analysis are in good agreement with calculated values of %C, %H and %N (Table 1). The values of elemental analysis confirm the proposed structure of the resin presented in Scheme I.

Thermogravimetric Analysis

The examination of thermograms (Figure 2) reveals that resin sample undergoes degradation in two steps



Scheme I

like salicylic acid-formaldehyde polymer [4]. The first step decomposition starts at 190ºC which extends up to 290ºC involving 20% weight loss. The second step decomposition begins at 470ºC and extends up to 820ºC with 78% weight loss. The first step in the thermal degradation of the resin may be due to the decarboxylation [5] and further degradation in the second step may be due to the random degradation reaction affording simpler degradation products. It is very difficult to draw any conclusion from the magnitude of the thermal activation because the decomposition mechanism is expected to be very difficult.

The thermogravimetric analysis has proved to be useful analytical technique in evaluating kinetic parameter such as activation energy (E_a), which provides valuable quantitative information regarding the stability of the material. Various methods have been proposed to estimate the kinetic parameters of thermal degradation. In the present communication, we have employed Broido [20] and Horowitz-Metzger [21] methods for the estimation of activation energy for thermal degradation. The values of E_a of various steps involved are evaluated from the slope of the least square plots of relevant data. The value of activation energy calculated according to Broido and Horowitz-Metzger methods are in good agreement, which is shown in Table 2.

Optical and SEM Photographs

Surface analysis has found great use in understanding the surface features of the material. The morphology of the reported resin sample was investigated by optical photographs and scanning electron micrographs at different magnifications. In the present communication we have presented optical photographs of 180× and 400× magnifications and SEM photographs of 200× and 1000× magnifications, which are shown in Figures 3 and 4, respectively. The white bar at the bottom of the optical and SEM micrographs represents the scale. The resin appeared to be reddish brown in colour. The morphology of resin polymer shows a fringed model of the crystalline-amorphous structure. The fringes represent transition state between the crystalline and amorphous phases. The resin exhibits more amorphous characters with less closed packed surface having deep pits (Figure 4b). Due to the deep pits, resin exhibits higher exchange capacity for Pb (II) ion. This could be the reason of bigger hydrated Pb (II) ion, which can easily penetrate into the deep pits. The degradation in TGA is expected to originate in an amorphous region of the polymeric network. The macromolecules having larger percentage of amorphous character tend to degrade steeply (Figure 2a) during the thermal degradation.

Effect of pH on Metal Ion Uptake

Chelating ligand forms complexes with various metal ions at specific pH conditions. Wide difference in optimum pH conditions of two or more metal ions indicates increased selectivity and specificity of the

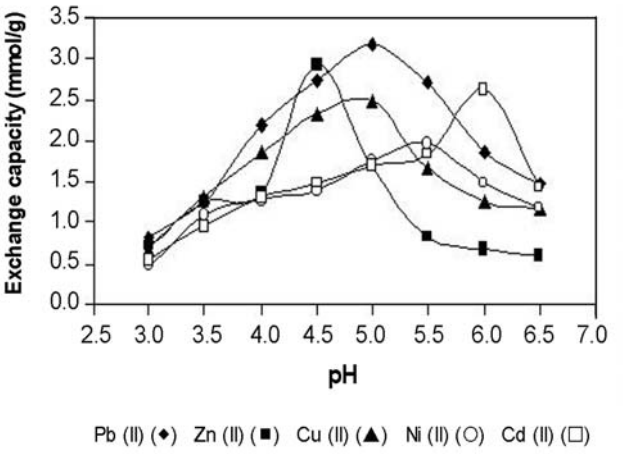


Figure 5. Effect of pH on metal ion-exchange capacity.

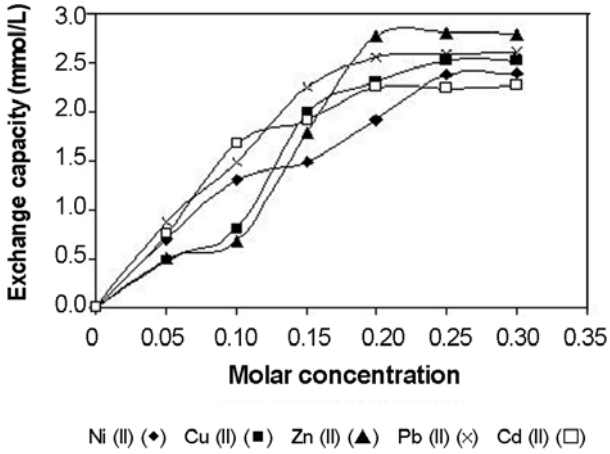


Figure 6. Effect of concentration on metal ion-exchange capacity.

chelating group for different metal ions. Therefore, the synthesized resin used to study the effect of variation in pH on chelating ability of the resin towards various metal ions. The results are presented as exchange capacity versus pH for different metal ions in Figure 5. It is observed that maximum capacity for Ni (II) was at pH 5.5, for Cu (II) at pH 5.0, for Zn (II) at pH 4.0, for Cd (II) at pH 6.5, and for Pb (II) it was found to be at pH 5.5. The selective order for the metal ions is as follows: Pb (II) > Zn (II) > Cd (II) > Cu (II) > Ni (II). No specific trend was observed. This may be due to the difference in their crystal field stabilization energy, which results in the formation of metal complex with different stabilities at different pHs.

An increase in pH increases the negatively charged nature of the sorbent surface. This leads to an increase in the electrostatic attraction between positively charged metal ions and negatively charged sorbent and results in increase in the adsorption of metal ions. The decrease in the removal of metal ions at lower pH is due to the higher concentration of H^+ ions presented in the reaction mixture which compete with the metal ions for the sorption sites on the sorbent surface. Decrease in sorption at higher pH is due to the formation of insoluble hydroxy complexes of the metal ions.

Effect of Metal Ion Concentration on Exchange Capacity

The experimental data presented in Figure 6 show the effect of metal ion concentration on its uptake by the sorbent.

The examination of data reveals that the amount of adsorbed metal ion increases with the increase in concentration of metal ions up to a particular limit and then becomes constant. 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 the same whereas more metal ions are available for sorption and subsequently the sorption becomes almost constant thereafter. For this resin, saturation occurs at about 0.25 M concentration of metal ion solution.

Rate of Exchange for Metal Ions

Perusal of data in Figure 7 reveals the comparison of the rate of metal ion uptake of resin copolymer at different time intervals. The result shows that the time required for 50% exchange ($t_{1/2}$) for different metal ions was about 55-70 min. The fast rate of exchange in the beginning can be explained on the basis of the law of mass action. The rate of metal ion adsorption of the resin was determined to ascertain the shortest time period for which equilibrium could be carried out. A perusal of results indicates that for attaining equilibrium Ni (II) takes 12 h whereas Cu (II), Zn (II), Pb (II), and Cd (II) require 15-18 h for attaining the same. It is similar to that reported resins derived from salicylic acid-furfural-hexamine [7] and salicylic acid-acetaldehyde-thiourea [8]. Both these reported resins took about 22-24 h to attain equilibrium. But

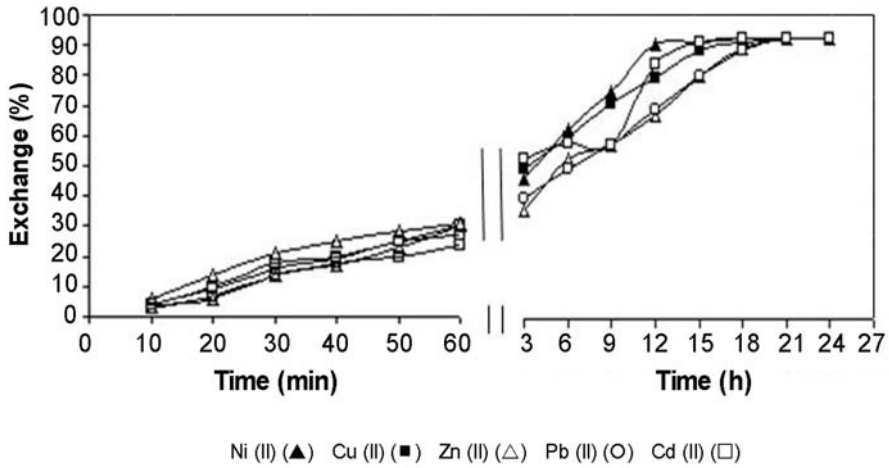


Figure 7. Rate of metal ion-exchange on SFR resin.

salicylic acid-benzidine-furfural [9] resin took less than 2 h to attain the same. No general trend is observed, this may be due to their difference in various physical properties like particle size distribution, pore size and physical core structure, which affect the rate of exchange significantly.

Effect of Electrolyte Concentration and pH on Distribution Coefficients of Metal Ions

The distribution coefficient values of the metal ions as the function of pH and concentration of electrolyte solution were studied. The K_d value decreases with increasing electrolyte concentration and increases with increase in pH, which is presented in Table 4. 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. The K_d values decrease with increase in electrolyte concentration and also decrease with increase in pH of the electrolyte. To achieve more efficient separation of metal ion in shorter time, maximum K_d value difference should be selected for optimized condition of chromatography.

Amongst all the metal ions under investigation, Ni (II) ion shows lower K_d values, whereas Pb (II) exhibits higher K_d values. 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. It was observed that the order of the distribution coefficients for different metal ions do not follow the Irving-Williams order, owing to different crystal field stabilization energies. The distribution coefficients of Zn (II) is higher than that of Ni (II) and Cu (II) owing to more stable complex of zinc may be formed on the resin as compared to copper and nickel. The distribution coefficients of Cd (II) are lower, owing to the larger size of its hydrated ion. Lead being non-transitional metal does not follow the Irving-Williams order.

Ion-exchange Chromatography

Separation of Pb (II) and Cd (II) from equimolar synthetic mixture (2 mL of 5 mg/mL solution of each metal) was achieved by selective sorption of Cd (II) at pH 5.0 with 0.5 M tartaric acid. Pb (II) does not form chelate at pH 5.0 in 0.5 M tartaric acid. Thus Cd (II) was separated from Pb (II). To elute Cd (II),

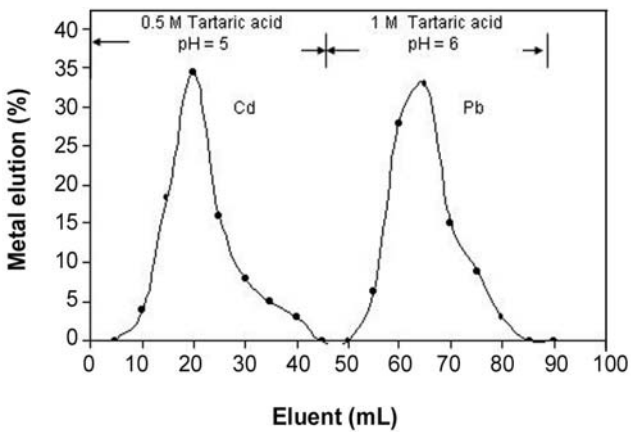


Figure 8. Separation of Pb (II)-Cd(II) from binary synthetic mixture by SFR resin column at 25 ± 2ºC.

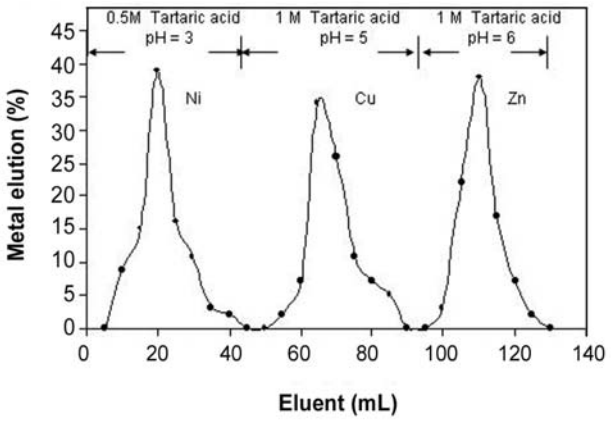


Figure 9. Separation of Ni (II)-Cu (II)-Zn (II) from ternary synthetic mixture by SFR resin column at 25± 2ºC.

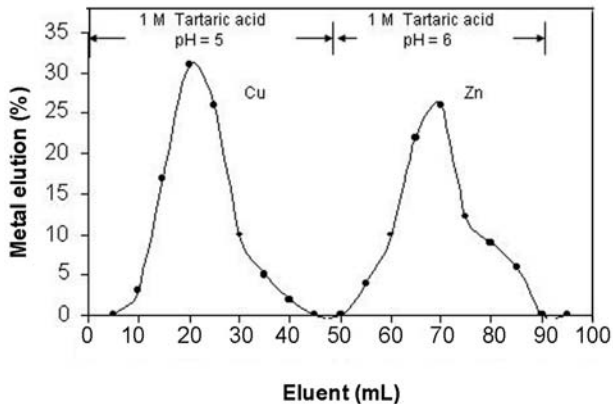


Figure 10. Separation of the brass components by SFR resin column at 25 ± 2ºC.

0.5 M tartaric acid was passed down the column at the flow rate of 0.3 mL.min^{-1} and its amount was estimated titrimetrically. First few fractions contain only Cd (II) and then Pb (II) were eluted by 1.0 M tartaric acid of pH 6.0. These fractions contain only Pb (II). No cross-contamination was observed for this separation. The recovery of Cd (II) was 94.6% and Pb (II) was 90.5%. The elution curve is shown in Figure 8.

Separation of Ni (II), Cu (II), and Zn (II) from equimolar synthetic mixture (2 mL of 5 mg/mL solution of each metal) was done by selective sorption on column. Ni (II) does not form chelate at 3.0 pH by 0.5 M tartaric acid. After complete elution of Ni (II), Cu (II) was eluted at pH 5.0 by 1.0 M tartaric acid and Zn (II) was eluted at pH 6.0 by 1.0 M tartaric acid. No cross-contamination was observed because there is a large difference in their K_d values at particular pH and concentration. For this ternary system, recovery of Cu (II) was 94.0%, Ni (II) was 90.0% and Zn (II) was 86.5%. The elution curve is shown in Figure 9.

Analysis of Brass

Cu (II) does not form the chelate at pH 5.0 by 1.0 M tartaric acid. Therefore, Cu (II) was separated from Zn (II) during first 45 mL elution with 1 M tartaric acid at pH 5.0. Then Zn (II) was eluted with 1.0 M tartaric acid at pH 6.0. No cross-contamination was observed for this separation. The recovery of Cu (II) was 95% and for Zn (II) was 91%. The elution curve is shown in Figure 10.

CONCLUSION

The resin shows lower percentage of moisture content compared to other reported resins [8,9]. The lower moisture(%) content indicates the high degree of cross-linking in this resin. Void volume fraction of resin is relatively lower than other reported resin indicating the lower rate of exchange. From the result of rate of exchange it is observed that Ni (II) takes 12 h for attaining equilibrium, while other metal ions take about 15-18 h. The pH titration study of the resin was carried out and results are examined. General trend of chelating ability of resin is Pb (II) > Zn (II) > Cd (II) > Cu (II) > Ni (II). Thus, resin can be used for removal of heavy toxic metals. From the results of K_d values it is observed that there is a considerable difference between the distribution coefficient of each metal ion at optimum condition, which can be used in the separation of heavy metal ions. We applied two synthetic mixtures for separation such as Pb (II)-Cd (II) and Ni (II)-Cu (II)-Zn (II) and separated them successfully using optimum condition of K_d values. We also successfully analyzed the constituents of brass using reported resin by column chromatography.

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