

Synthesis, Characterization and Chelation Ion-Exchange Studies of a Resin Copolymer Derived from 8-Hydroxyquinoline-Formaldehyde-Catechol

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A chelating ion exchange resin was synthesized from 8-hydroxyquinoline and catechol using formaldehyde as a cross linking agent at 120 ± 2 °C in DMF solution. The resin was characterized by FTIR and elemental analysis. The morphology of the synthesized resin was studied by optical photograph and scanning electron microscopy (SEM). Various kinetic parameters such as energy of activation (E_a), enthalpy of activation (H^\ddagger), entropy of activation (S^\ddagger), free energy of activation (G^\ddagger), order of reaction (n) and pre-exponential factor (A) of various steps of thermal decomposition have been calculated from thermogravimetric results. The physico-chemical properties of the resin have been studied. The total cation exchange capacity was measured and effect of pH and metal ion concentration on ion exchange capacity were studied. The rate of cation exchange reactions and distribution coefficient values in tartaric acid media at different pH were also studied using batch equilibration method.

Keywords: Chelating resin, Batch equilibration, Kinetic parameters, Distribution coefficient

INTRODUCTION

The extraction of metal ions using chelating ion exchange resins is a green analytical method since it does not involve the use of toxic chlorinated organic solvents, which are very frequently used in conventional liquid-liquid extraction technique or other methods [1]. The main objective of the most of the research works 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 [2-4]. The interest in this type of chelating resins are due to the rapid adsorption of metal ions, higher selectivity and less swelling, in comparison with the analogous organic polymers [5,6].

A condensation reaction between 5-amino-8-hydroxy-

quinoline and terephthalaldehyde yielded a bis-functional Schiff base, which was used to produce coordination polymers containing transition metal ions [7]. Chelating ion exchange resins were also prepared by copolycondensation of 8-hydroxyquinoline or phenol derivatives like *o*-aminophenol, resorcylic acid or resorcinol with formaldehyde [8]. Antico *et al.* synthesized a gel type chelating ion exchange resin from glycol methacrylate with 8-hydroxyquinoline and used it to study the separation of Pb(II) and Cu(II) in their chloride solution [9]. The chelating ion exchange resins were also synthesized by Friedel-Craft's condensation of 8-hydroxyquinoline [10] and substituted 8-hydroxyquinoline [11] with 1,2-dichloroethylene. The synthesized resins were proved to be selective for certain metal ions over a wide pH range.

The chelating behavior of poly (8-hydroxyquinoline-5,7-dimethylene) [12] and its crosslinked polymer [13] derived

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from reaction with various amounts of bisphenol-A towards some trivalent lanthanide ions such as La(III) and Gd(III) has been investigated by a static batch equilibration method.

Vernon *et al.* prepared oxine containing resins and studied their chelation properties towards transition metal ions [14,15]. From stability tests, they have suggested that the gel type polymers must never be allowed to dry; otherwise their advantageous properties are destroyed. Shah *et al.* [16,17] and Warshwsky *et al.* [18] reported some resins based on 8-hydroxyquinoline and substituted 8-hydroxyquinoline, respectively, along with their chelation properties towards transition and post transition metal ions.

So far no resin based on 8-hydroxyquinoline-formaldehyde-catechol in DMF medium has been reported for the quantitative removal and separation of transition and post transition metal ions. As industrial effluents are often rich in transition and post transition metal ions, removal of these metals is an important industrial task. The work described in the present communication deals with the synthesis, characterization and thermal studies of the above resin along with the systematic studies of various ion-exchange properties of the resin.

EXPERIMENTAL

Materials

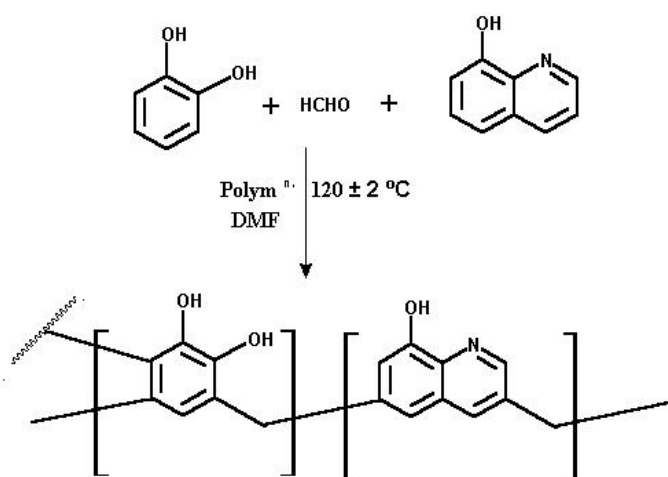
8-Hydroxyquinoline (Ranbaxy fine chemicals, S.A.S. Nagar, India) and formaldehyde (Qualigence fine chemicals, Mumbai, India) were used as received. Catechol (Glaxo extra pure) was purified by rectified spirit. Metal ion solutions were prepared by dissolving appropriate amount of metal acetates in double distilled water and standardized by EDTA titration [19].

Synthesis Method

8-hydroxyquinoline (14.5 g, 0.1 mol) was ground to a fine powder and taken in a 250 ml round bottom flask and dissolved in DMF (25 ml) to give a clear yellow solution. Formaldehyde (7.5 ml, 0.25 mol as 37%) was added and stirred until a red colored solution was obtained. A solution of catechol (11 g, 0.1 mol) in 10 ml of DMF was added to above solution and stirred for 3 h. Then the mixture was refluxed on a water bath at 90 ± 5 °C with constant stirring for 3-5 h and

then on sand bath at 120 ± 5 °C for 7-8 h until a viscous solution with the formation of a hard mass of brown color resin was obtained. The synthesized resin was withdrawn from the reaction vessel and cured in an oven at 70-80 °C for 12 h. The resulting resin was washed with DMF and with deionized water in order to remove unreacted monomers as well as impurities. After the complete washing cycle, the production yield of the resin synthesized reaction was found to be 59% (19.5 g). The purified and dried resin sample was finely ground and sieved to obtain uniform particle of 50-70 mesh size and stored in polyethylene bottle. This sieved resin was then characterized using different instrumental analysis techniques and was used for all of the experiments during the research period. The solubility tests of resin in different solvent were performed at room temperature and pressure with intermittent shaking. The resin was found to be insoluble in all common organic solvents like acetone, ethanol, benzene, DMF, DMSO, chloroform *etc.* and all acids and alkalis of higher strengths.

Infra-Red spectra of the synthesized resin sample had been obtained using KBr pellets on a FTIR spectrophotometer (Shimadzu, model-8201PC). The FTIR spectra with assignment of peaks are shown in Fig. 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 is presented in Table 1. The thermal curves (TGA and DTG)



Scheme 1

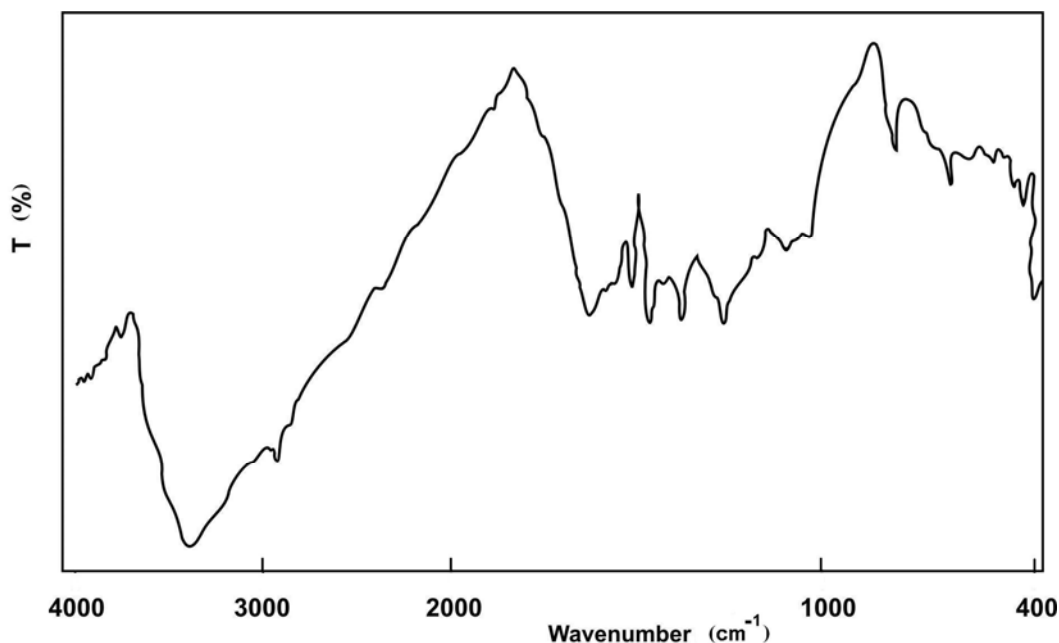


Fig. 1. FTIR spectrum of resin.

of the resin sample, which were taken on a Mettler analyzer (model, TA 4000) at constant heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in N_2 atmosphere, are shown in Fig. 2. Kinetic parameters of the thermal decomposition reaction have been calculated using various methods *viz.* Horowitz-Metzger [20], Freeman-Carroll [21] and Coats-Readfern [22]. The results are presented in Table 2. The surface analysis was done using an optical microscope (Olympus SZX 12, Japan) and scanning electron microscope (Philips XL30, Japan) at different magnifications, and the resulting patterns are shown in Fig. 3 and Fig. 4, respectively.

To convert the resin sample into its H^+ form, it 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 batch equilibrium method was adopted to study the ion-exchange properties.

The physico chemical properties like moisture and solid contents, apparent density, true density, void volume fraction and sodium exchange capacity were studied according to the literature methods [14] and the results are presented in Table

Table 1. Elemental Analysis of the Resin

| | %Calculated (%Found) | | |
|--|----------------------|--------|--------|
| | C | H | N |
| | 73.81 | 4.65 | 5.01 |
| | (72.81) | (4.54) | (4.81) |

3. The sorption properties such as rate of exchange, effect of pH on exchange capacity, effect of the cation concentration on exchange capacity and distribution coefficient (K_d) values for different metal ions as a function of pH and concentration of electrolyte were studied according to the literature methods [23,24]. The value of void volume fraction was found to be 0.36, while other reported resins. 8-hydroxyquinoline-formaldehyde [15] and 8-hydroxyquinoline-formaldehyde-resorcinol [16] exhibited void volume fraction values of 0.54 and 0.59, respectively.

Rate of Exchange of Metal Ions

For this experiment, an accurately weighed (0.250 ± 0.001

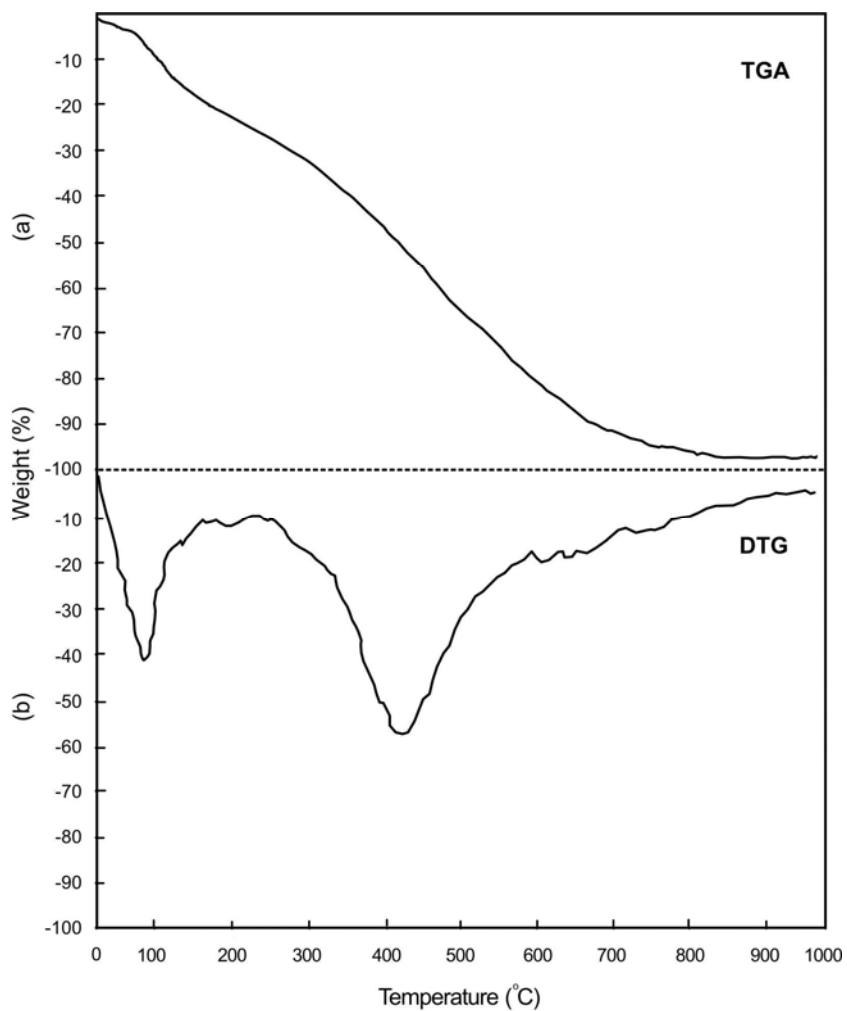


Fig. 2. TGA and DTG curves of resin in N_2 atmosphere at the heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

Table 2. Kinetic Data of the Thermal Decomposition Reaction of Resin

| Step | T range ($^\circ\text{C}$) | T peak ($^\circ\text{C}$) | Parameters | Horowitz- Metzger method | Freeman- Carroll method | Coats- Redfern method |
|------|---------------------------------|--------------------------------|---|-----------------------------|----------------------------|--------------------------|
| I | 80-150 | 102 | E_a (kJ mol^{-1}) | 19.4 | 18.8 | 18.0 |
| | | | A (s^{-1}) | 2.5×10^7 | - | 3.0×10^7 |
| | | | S^\ddagger ($\text{J mol}^{-1}\text{K}^{-1}$) | -421 | -417 | -418 |
| | | | G^\ddagger (kJ mol^{-1}) | 117 | 116 | 115 |
| | | | H^\ddagger (kJ mol^{-1}) | 323 | 315 | 320 |
| II | 230-600 | 442 | E_a (kJ mol^{-1}) | 9.6 | 8.9 | 8.8 |
| | | | A (s^{-1}) | 1.0×10^5 | - | 1.3×10^5 |
| | | | S^\ddagger ($\text{J mol}^{-1}\text{K}^{-1}$) | -172 | -169 | -169 |
| | | | G^\ddagger (kJ mol^{-1}) | 105 | 102 | 108 |
| | | | H^\ddagger (kJ mol^{-1}) | 48.8 | 46.8 | 48.2 |

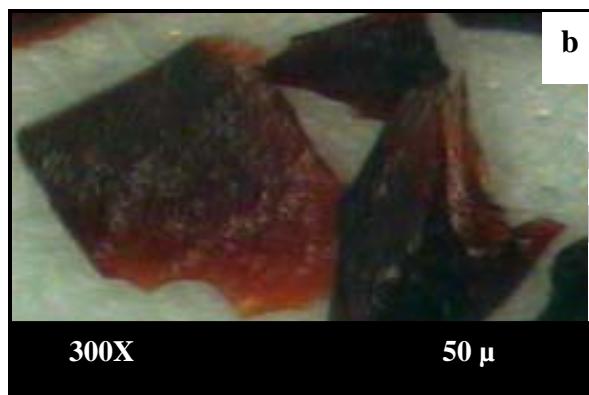
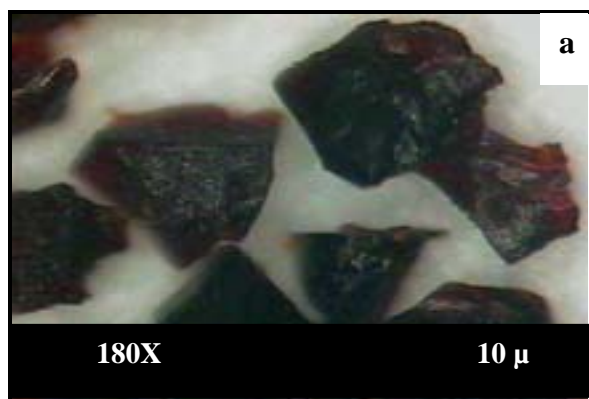


Fig. 3. Optical photograph of resin at (a) 180X and (b) 300X magnifications.

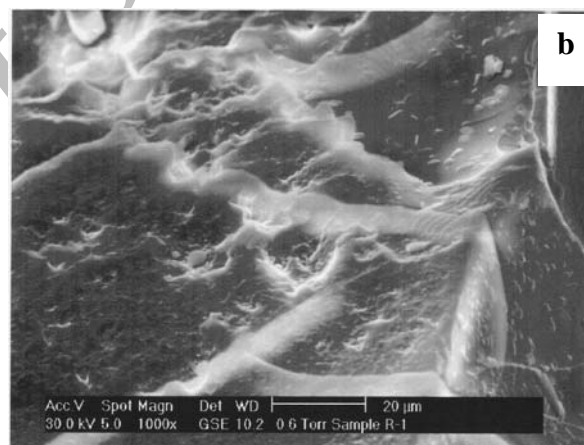
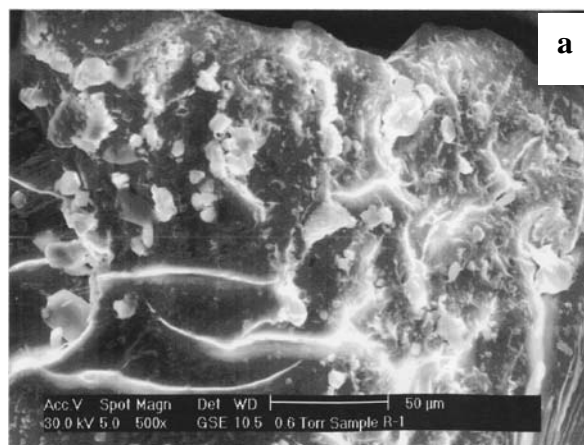


Fig. 4. SEM photograph of resin at (a) 500X and (b) 1000X Magnifications.

Table 3. Physicochemical Properties of Resin

| Property | Value (S.D.) |
|--|---|
| %Moisture content | 5.64 (± 0.05) |
| %Solid | 94 (± 0.05) |
| True density | 0.75 (± 0.01) g cm ⁻³ |
| Apparent density | 0.48 (± 0.01) g cm ⁻³ |
| Void volume fraction | 0.36 (± 0.025) |
| Sodium exchange capacity | 5.68 (± 0.01) mmol g ⁻¹ |
| Concentration of fixed ionogenic group | 4.06 (± 0.02) mmol cm ⁻³ |
| Volume capacity | 2.5 (± 0.01) mmol cm ⁻³ |

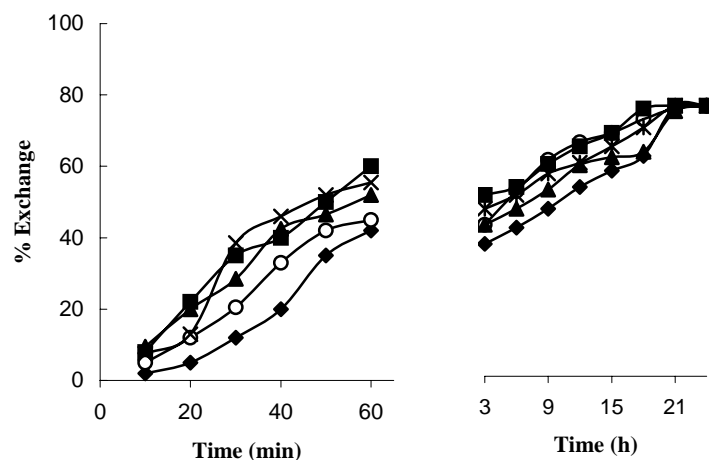


Fig. 5. Rate of exchange of cations on resin: (♦) Ni(II), (■) Cu(II), (▲) Zn(II), (○) Cd(II), (×) Pb(II).

g) dry resin in the H^+ form was taken in different glass stoppered bottles and equilibrated with buffer solutions of desired pH values for 24 h. After decanting the buffer solution, 50 ml (0.2 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. The results are shown in Fig. 5.

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 3-6 were prepared from 0.2 M acetic acid and 0.2 M sodium acetate solutions [19]. A pH meter (Elico, model CL-44) was used to measure the pH. Different sets of weighed (0.250 ± 0.001 g) dry resin were equilibrated with buffer in different stoppered bottles for 24 h, so that resin attained desired pH value. After 24 h, the buffer solutions were decanted and 50 ml of 0.2 M metal ion solutions of varying pH from 3-6 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 was measured by complexometric titration with 0.1 M EDTA solution using an appropriate indicator. A blank experiment was also run simultaneously. The metal uptake was calculated by difference method. The same method was followed throughout the study to calculate the ion exchange capacity of the resin as:

Exchange capacity =

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

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 resin was equilibrated with acetate buffer at desired pH values (pH value of highest exchange) for 24 h and then buffer solutions were decanted. An accurately weighed (0.250 ± 0.001 g) dry resin was equilibrated with metal ion solutions (50 ml) of varying molar concentration (i.e., 0.05 M, 0.10 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, the 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 is defined as:

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

Although this distribution coefficient is measured on a batch basis, it can be used to predict elution behavior of metal ions eluted from an ion exchange column. To separate two substances, conditions should be selected such that the distribution coefficient of one of them is low (preferably 1 or less) so that it elution from the column will be rapid, while the distribution coefficient of the other substance under the same conditions should be as large as possible (more than 10 times) so that this substance will be tightly held by the resin [25].

Effect of different concentrations and pH of electrolyte (tartaric acid) on metal ion uptake by the synthesized resin was studied. An accurately weighed (0.250 ± 0.001 g) dry resin sample was suspended in the 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 of solutions of different metal ions under study (5 mg ml^{-1}) was added and equilibrated for 24 h with intermittent shaking. After 24 h, the solutions were decanted and unadsorbed metal ions were estimated. The results of K_d values are given in Table 4.

RESULTS AND DISCUSSION

Spectral Characterization of Resin

The FTIR spectrum of the resin is shown in Fig. 1. A strong band at 3380 cm^{-1} is due to the $\nu(\text{O-H})$ stretching of phenolic group, a medium band at 3074 cm^{-1} is due to the $\nu(\text{C-}$

Table 4. K_d Values of Metal Ions at Various Tartaric Acid Concentrations and pH Values

| Metal ion | [Tartaric acid] (M) | K_d values at different pH | | | | |
|-----------|------------------------|------------------------------|--------|-------|-------|-------|
| | | 3.0 | 3.5 | 4.0 | 5.0 | 6.0 |
| Ni(II) | 0.1 | 105.2 | 100.7 | 85.0 | 72.0 | 60.0 |
| | 0.2 | 85.0 | 73.0 | 65.0 | 36.3 | 20.0 |
| | 0.3 | 35.0 | 32.0 | 10.0 | 0.9 | - |
| | 0.5 | - | - | - | - | - |
| | 1.0 | - | - | - | - | - |
| Cu(II) | 0.1 | 1096.0 | 661.4 | 537.2 | 209.0 | 166.2 |
| | 0.2 | 616.7 | 313.6 | 139.7 | 118.0 | 81.8 |
| | 0.3 | 266.2 | 118.0 | 81.8 | 52.8 | - |
| | 0.5 | 66.6 | 66.6 | 40.4 | 52.8 | - |
| | 1.0 | 13.8 | 18.1 | 10.7 | 9.4 | - |
| Zn(II) | 0.1 | 1835.2 | 1324.4 | 437.0 | 404.9 | 200.6 |
| | 0.2 | 666.7 | 620.4 | 238.0 | 114.2 | 133.1 |
| | 0.3 | 592.2 | 302.8 | 98.5 | 70.6 | 58.5 |
| | 0.5 | 132.5 | 114.6 | 70.7 | 27.8 | 37.2 |
| | 1.0 | 83.9 | 37.2 | 27.8 | 10.9 | - |
| Pb(II) | 0.1 | 2111.7 | 951.8 | 620.4 | 436.3 | 275.3 |
| | 0.2 | 644.8 | 620.4 | 238.1 | 114.2 | 133.1 |
| | 0.3 | 436.8 | 319.2 | 97.3 | 82.0 | 33.6 |
| | 0.5 | 133.1 | 87.2 | 81.9 | 44.1 | 5.3 |
| | 1.0 | 11.9 | 44.1 | 33.6 | 16.8 | 2.3 |
| Cd(II) | 0.1 | 236.9 | 300.4 | 187.4 | 147.9 | 46.2 |
| | 0.2 | 187.4 | 300.4 | 147.8 | 66.8 | 46.2 |
| | 0.3 | 65.8 | 147.9 | 65.7 | 14.3 | 1.3 |
| | 0.5 | 46.2 | 88.6 | 29.3 | - | 1.3 |
| | 1.0 | 16.2 | 14.4 | 1.4 | - | - |

H) stretching of aromatic ring and the presence of a medium-strong band at 2930 cm^{-1} is due to the $\nu(\text{C-H})$ stretching of methylene group. The bands at 1630 , 1500 and 1460 cm^{-1} can be assigned to $\nu(\text{C=N})$ heterocyclic ring and $\nu(\text{C=C})$ aromatic ring stretching, respectively. A band at 1460 cm^{-1} is also due to $\delta(\text{C-H})$ deformation of methylene group [16]. The presence of a medium-strong band at 1380 cm^{-1} can be assigned to in plane $\delta(\text{O-H})$ bending of aromatic and a band at 1260 cm^{-1} is due to aromatic $\nu(\text{C-O})$ stretching. A sharp single band at 790 cm^{-1} , which can be assigned to the presence of 1,2,3,4-tetra substituted benzene ring [17], confirms the polymerization of monomers.

Elemental Analysis

Theoretical percentage of carbon, nitrogen and hydrogen content of the resin were calculated from the general formula ($\text{C}_{15}\text{H}_{10}\text{NO}_3$) of the repeating unit of the probable structure (Scheme 1). Table 1 shows that the results of the elemental analysis are in good agreement with calculated values. The elemental analysis results are in support of the proposed structure of the resin presented in Scheme 1.

Thermogravimetric Analysis

The obtained result of TGA and DTG (Figs. 2a and 2b) reveals that the resin sample undergoes degradation in two steps, as reported for the 8-hydroxyquinoline-formaldehyde-resorcinol resin [16]. In the first step, decomposition starts at $80\text{ }^\circ\text{C}$ and extends up to $150\text{ }^\circ\text{C}$ involving 23% weight loss. The observed weight loss should be due to dehydration. The second step decomposition, which begins at $230\text{ }^\circ\text{C}$ and extends up to $600\text{ }^\circ\text{C}$, with 57% weight loss is most probably be due to the random cleavage of polymeric resin affording simpler degradation products [26]. It is very difficult to draw any conclusion from the magnitude of the thermal activation because the decomposition mechanism is expected to be quite complex [27].

The thermogravimetric analysis has proved to be a useful analytical technique in evaluating kinetic parameter such as energy of activation (E_a), enthalpy of activation (H^\ddagger), entropy of activation (S^\ddagger), free energy of activation (G^\ddagger), order of reaction (n) and pre-exponential factor (A), which provides valuable quantitative information regarding the stability of the material. Various methods have been proposed by different

investigators to estimate the kinetic parameters of thermal degradation reaction. In the present paper, we have employed Horowitz-Metzger [20], Freeman-Carroll [21] and Coats-Redfern [22] methods for the estimation of various kinetic parameters of thermal degradation. From the Horowitz-Metzger equation the value of C_s is found to be 0.360, which indicates that the decomposition follows the first order kinetics. This is further confirmed by the Freeman-Carroll's method in which the linear plot of $[\Delta\log(dw/dt)/\Delta\log W_r]$ vs. $[(\Delta T)^{-1}/\Delta\log W_r] \times 10^3$ intersects the y axis at unity. Pre-exponential term (A) was calculated using two different methods viz. Horowitz-Metzger and Coats-Redfern. The values are given in Table 2. To calculate the entropy of activation, enthalpy of activation and free energy of activation following equations are employed [28], respectively:

$$S^\ddagger = 2.303 R \log(Ah/kT) \quad (1)$$

$$H^\ddagger = E_a - RT \quad (2)$$

$$G^\ddagger = H^\ddagger - TS^\ddagger \quad (3)$$

where, h and k are Plank's and Boltzmann's constants, respectively.

The values of kinetic parameters, calculated according to all the three methods employed in present communication, are in good agreement with each other (Table 2).

Optical and SEM Photographs

The morphology of the reported resin sample was investigated by optical photographs and scanning electron micrographs, which are shown in Fig. 3 and Fig. 4, respectively. The resin appeared to be dark brown in color. 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 [29]. The resin exhibits more amorphous character with closed packed surface having deep pits (Figs. 4a and 4b) as it compared with anthranilic acid-formaldehyde-resorcinol resin reported earlier [29].

Rate of Exchange for Metal Ions

The exchange of metal ions on resin exhibits a time dependent phenomenon. The rate of exchange for different

metal ions was to ascertain the shortest time period for which equilibrium could be carried out [3]. The graph shown in Fig. 5 indicates that the time required for 50% exchange ($t_{1/2}$) for nickel(II) and cadmium(II) is 3 h and for copper(II), zinc(II) and lead(II) are 50, 56 and 48 min, respectively. The fast rate of exchange in the beginning can be explained on the basis of law mass action. The faster rate of exchange facilitates column chromatographic separation. Kinetics of metal ion exchange mainly depends on various physical properties including particle size distribution, pore size, physical core structure and diffusion of counter ion [14,15].

Effect of pH on Exchange Capacity

The removal of metal ions from aqueous solution by sorption is highly dependent on pH of the solution which affects the surface charge of the sorbent [3]. Chelating ligands form complexes with various metal ions at specific pH conditions [4]. Therefore, the synthesized resin was used to study the effect of variation in pH on its chelating ability towards various metal ions. The results of the exchange capacity vs. pH for different metal ions are presented in Fig. 6. The results show that sorption of metal ions are increased with increasing in pH up to a maximum value and thereafter decreased. The maximum sorption of Cd(II) took place at pH 5, Cu(II) at pH 6 and Ni(II), Cu(II) and Pb(II) at pH 4. The selectivity order for metal ions is Pb(II) > Zn(II) > Cu(II) > Cd(II) > Ni(II).

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 increased sorption of metal ions. At lower pH, the removal of metal ions is decreased due to the higher concentration of H^+ ions present in the reaction mixture which compete with the metal ions for the sorption sites at the surface. Meanwhile, the observed decrease in sorption capacity is due to the formation of insoluble metal ion hydroxides [30].

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 increasing concentration of metal ions in solution until a maximum value,

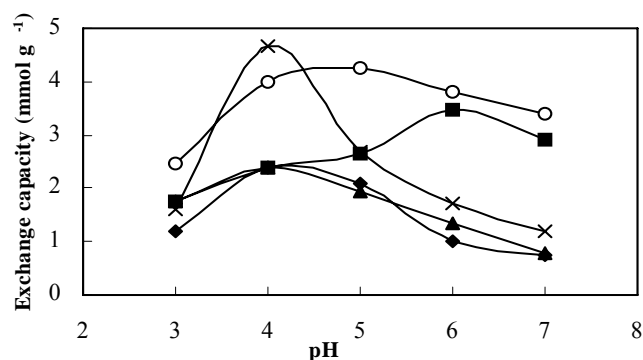


Fig. 6. Effect of pH on cation exchange capacity: (◆) Ni(II), (■) Cu(II), (○) Cd(II), (▲) Zn(II), (×) Pb(II).

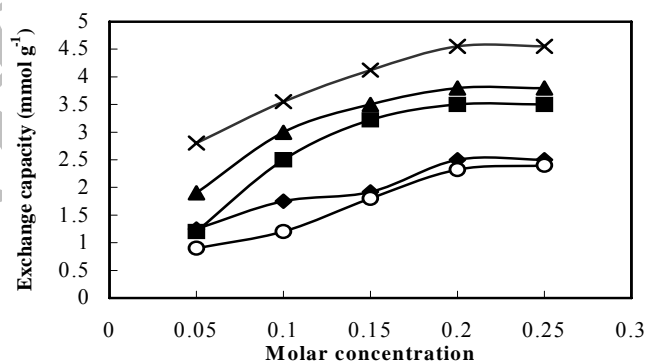


Fig. 7. Effect of cation concentration on exchange capacity: (◆) Ni(II), (■) Cu(II), (▲) Zn(II), (○) Cd(II), (×) Pb(II).

and will remain constant upon further increase in metal concentration. At lower concentration of metal ions, the number of metal ions available in solution is low as compared to the available sites on the sorbent [30]. However, at higher concentrations the available sites of sorption remain same whereas more metal ions are available for sorption and subsequently the sorption becomes almost constant then after [16,17].

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

The distribution coefficient values (K_d) for different metal ions were determined by the batch equilibration method. The K_d values of the metal ions were studied as a function of pH and concentration of electrolyte solution and the results are

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 [16]. As is obvious from Table 4, at all electrolyte concentrations and entire pH range, the K_d values decrease in the order $Pb(II) > Zn(II) > Cu(II) > Cd(II) > Ni(II)$. Meanwhile, in all cases, the K_d values decrease with increasing electrolyte concentration. Obviously, to achieve more clear separation of metal ions, large ΔK_d values should be selected on the same experimental conditions [25].

CONCLUSIONS

The synthesized resin shows lower moisture content compared to other reported resins [16,17], indicating the high degree of cross-linking in this resin. Void volume fraction of resin is relatively lower than other reported resins [15,16] causing a lower exchange rate. From the results of exchange rate studies, it was found that copper(II) takes 18 h to attain equilibrium, while it takes 21 h for other metal ions. General trend of chelating ability of resin is $Pb(II) > Zn(II) > Cd(II) > Cu(II) > Ni(II)$. The K_d determinations revealed that there is a considerable difference between the distribution coefficients of metal ions at optimum condition, which can be used in the successful separation of heavy metal ions.

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