



CHELATION ION EXCHANGE PROPERTIES OF COPOLYMER RESIN DERIVED FROM 2, 4-DIHYDROXYBENZOIC ACID, MELAMINE AND FORMALDEHYDE

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ABSTRACT

The chelating ion-exchange resin 2,4-DHBAMF was synthesized by the condensation of 2,4-dihydroxybenzoic acid and melamine with formaldehyde in the presence of acid catalyst using varied molar ratios of reacting monomers. Terpolymer resin composition has been determined on the basis of elemental analysis. The number average molecular weight of this resin was determined by conductometric titration in non-aqueous medium. The identification of resin structure was performed by UV-Visible, FTIR and NMR analysis. The morphological behavior of the resin has been studied by Scanning Electron Microscopy (SEM). The chelating ion-exchange resin proved to be a selective ion exchange resin for certain metals. Chelating ion exchange properties of this terpolymer resin was studied for, Cu^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} and Fe^{3+} ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurement of the distribution of a given metal ion between the terpolymer resin sample and a solution containing the metal ion. The study was carried out over a wide pH range and in media of various ionic strengths.

Key words: Synthesis, Polycondensation, Resins, Ion-exchangers, Distribution ratio.

INTRODUCTION

Ion-exchange may be defined as the reversible exchange of ions between the substrate and surrounding medium. Ion-exchange technique can remove traces of ionic impurities from water / process liquors and gives out a product of ultra pure quality in a simple, efficient and technoeconomically viable manner. Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotic purification and separation of radio isotopes and find large scale applications in water treatment and pollution control^{1,2}.

Xu and coworkers³ synthesized an Imidazole type magnetic chelating resin. The adsorption capacity of this resin was studied for Hg^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Mg^{2+} and Co^{2+} . They reported a effective adsorption of Cu^{2+} and higher selectivity for Cd^{2+} and Hg^{2+} .

Masaram and coworkers⁴ reported chelating ion-exchange resin derived from salicylic acid, hexamethylene diamine and formaldehyde and separation of metal ion by selective adsorption in the resin

column. The terpolymer resin showed a higher selectivity for Fe^{3+} , Cu^{2+} and Ni^{2+} ions than for Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions.

Bastia et al.⁵ synthesized terpolymer resins derived from semicarbazone of 2-hydroxy acetophenone, substituted benzoic acid and formaldehyde using acid catalyst. They studied the ion exchange properties and influence of electrolyte on the metal uptake of Cu^{2+} , Ni^{2+} , Zn^{2+} , Mg^{2+} and Mn^{2+} ions. They have also reported the distribution of metal ions at different pH. J. D. Joshi and co-workers⁶ have synthesized, characterized and studied the ion exchange properties of poly [(2,4-dihydroxybenzophenone) butylenes] resin for various heavy metal ions.

In an earlier communication⁷⁻⁹ from this department a number of such terpolymers have been reported. So far no resin based on 2,4-dihydroxybenzoic acid, melamine and formaldehyde in acid media has been synthesized for the quantitative separation of 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 metal ions. In this paper synthesis and characterization of the above resin are reported together with the conditions for the effective separation of metal ions.

EXPERIMENTAL

Materials

2,4-Dihydroxybenzoic acid, melamine and formaldehyde (37%) were purchased from the market and are from Merck, India. Solvent like N, N-dimethyl formamide and dimethyl sulphoxide were used after distillation. All other chemicals used were of chemically pure grade.

Preparation of 2,4-dhbamf terpolymer resin

The 2,4-DHBAMF terpolymer resin was prepared by condensing 2,4-dihydroxybenzoic acid (1.54 g, 0.1 mol) and melamine (1.26 g, 0.1 mol) with formaldehyde (11.1 mL, 0.3 mol) with the molar ratios of 1 : 1 : 3 in the presence of 2 M HCl as a catalyst (scheme 1). The mixture was heated at $126 \pm 2^\circ\text{C}$ in an oil bath for 5 h. The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was repeatedly washed with hot water to remove unreacted monomers. The air dried terpolymer resin was extracted with ether to remove excess of 2,4-dihydroxybenzoic acid - formaldehyde copolymer, which might be present along with 2,4-DHBAMF terpolymer resin. It was further purified by dissolving in 8% NaOH solution and filtered. It was then precipitated by drop wise addition of 1 : 1 (v/v) conc. HCl / water with constant stirring and filtered. The process was repeated twice. The resulting polymer sample was washed with boiling water and dried in vacuum at room temperature. The purified terpolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yield of this terpolymer resin found to be 82.37% (Table 1).

Characterization of the terpolymer

The terpolymer resin was subjected to elemental analysis for C, H, N on a Coleman C, H, N analyzer. The number average molecular weight \overline{Mn} was determined by non aqueous conductometric titration in DMF using ethanolic KOH as the titrant.

Electronic absorption spectrum of the copolymer in DMF was recorded on Shimadzu double beam spectrophotometer in the range of 190-700 nm. Infrared spectra of 2, 4-DHBAMF terpolymer resin was recorded in nujol mull on Perkin- Elmer-spectrum RX-I spectrophotometer in the range of $4000 - 500 \text{ cm}^{-1}$.

Proton NMR spectra of newly prepared terpolymer resin has been scanned on a Bruker Advance –II 400 MHz NMR spectrophotometer and DMSO-d₆ was used as a solvent.

Ion-exchange properties

The ion-exchange properties of the 2,4-DHBAMF terpolymer resin were determined by the batch equilibrium method and the data for the 2, 4-DHBAMF terpolymer resin has been presented in this report.

Determination of metal uptake in the presence of various electrolytes and different concentrations

The terpolymer sample (25 mg) was suspended in an electrolyte solution (25 mL) of known concentration. The pH of suspension was adjusted to the required value by using either 0.1 M HNO₃ or 0.1 M NaOH. The suspension was stirred for 24 h. at 25⁰C. To this suspension 2 mL of 0.1 M solution of metal ion has been added and the pH was adjusted to the required value. The mixture was again stirred at 25⁰C for 24 h and filtered. The solid was washed and the filtrate and washings were combined and the metal ion content was determined by titration against standard EDTA. The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments. The experiment was repeated in the presence of several electrolytes.

Evaluation of the rate of metal uptake

In order to estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments were carried out, in which the metal ion uptake by the chelating resin was determined at time intervals of 1h at 25⁰C (in the presence of 25 mL of 1M NaNO₃ solution). It was assumed that under the given conditions, the state of equilibrium was established within 24 h. The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after certain time related to that at the state of equilibrium.

Evaluation of the distribution of the metal ions at different pH

The distribution of each one of the eight metal ions i.e. Fe³⁺, Cu²⁺, Hg²⁺, Cd²⁺, Co²⁺, Zn²⁺, Ni²⁺ and Pb²⁺ between the polymer phase and the aqueous phase was determined at 25⁰C in the presence of a 1M NaNO₃ solution. The experiments were carried out as described above at different pH values. The distribution ratio 'D' is defined by the following relationship:

$$D = \frac{\text{Weight (in mg) of metal ions taken up by 1g of terpolymer}}{\text{Weight (in mg) of metal ions present in 1 mL of solution}}$$

RESULTS AND DISCUSSION

The newly synthesized and purified 2,4-DHBAMF terpolymer resin was found to be yellow in colour. The terpolymer was soluble in DMF, DMSO, aqueous KOH and NaOH solution and insoluble in almost all other organic solvents. The resin was analyzed for carbon, hydrogen and nitrogen content. The synthesized 2,4-DHBAMF resin do not show sharp melting point but undergo decomposition above 225⁰C.

The molecular weight \overline{Mn} of the terpolymer resin was determined by non-aqueous conductometric titration in DMF against KOH in a 50% (v/v) DMF / alcohol mixture using 100 mg of resin sample. A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of terpolymer was made. Inspection of such a plot revealed that there are many breaks in the plot. From this plot the first and the last break were noted. The calculation of \overline{Dp} by this method is based on the following consideration. (1) The first break correspond to neutralization of the more acidic phenolic

hydroxyl group of all the repeating units; and (2) the break in the plot beyond which a continuous increase in conductance is observed represents the stage at which the phenolic hydroxyl group of all repeating units is neutralized. The average degree of polymerization \overline{Dp} is given by the relation¹⁰.

$$\overline{Dp} = \frac{\text{Total meq. of base required for complete neutralization i.e. last break}}{\text{Meq. of base required for smallest interval i.e. first break}}$$

The number average molecular weight \overline{Mn} could be obtained by multiplying the \overline{Dp} by the formula weight of the repeating unit. The results are shown in Table 2.

Uv-visible spectra

The UV-visible spectra (Fig. 1) of the 2,4-DHBAMF terpolymer resin in pure DMSO was recorded in the region 200 - 850 nm at a scanning rate of 100 nm min⁻¹ and at a chart speed of 5 cm min⁻¹. The terpolymer sample displayed two characteristic broad bands at 250 – 280 and 290 – 340 nm. These observed positions for the absorption bands indicate the presence of a carbonyl group (ketonic) having a carbon – oxygen double bond which is in conjugation with the aromatic nucleus. The latter band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition while the former band (less intense) may be due to $n \rightarrow \pi^*$ electronic transition¹¹.

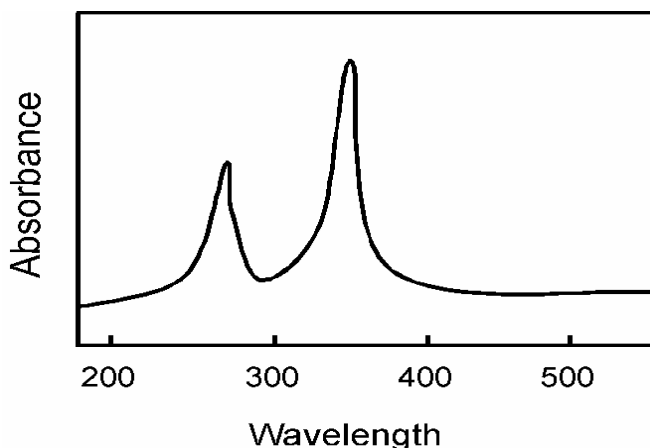


Fig. 1: UV-Visible spectra of 8-HQ 5-ACF copolymer

Infrared spectra

The IR-spectra of 2,4-DHBAMF terpolymer resin was shown in Fig. 2 and IR spectral data are shown in Table III. A broad band appeared in the region 3320 cm⁻¹ - 3324 cm⁻¹ may be assigned to the stretching vibration of the phenolic hydroxy groups exhibiting intermolecular hydrogen bonding¹². The presence of weak peak at 2362 cm⁻¹ - 2379 cm⁻¹ describes the –NH- in the melamine moiety may be ascribed in the polymeric chain^{12,13}. The sharp band displayed at 1573 cm⁻¹ - 1620 cm⁻¹ may be due to the stretching vibration of carbonyl group. A weak band at 1447 cm⁻¹ - 1449 cm⁻¹ is ascribed to aromatic ring. The sharp and weak band at 1279 cm⁻¹ to 1344 cm⁻¹ suggests the presence of -CH₂- methylene bridges¹³. In the polymer chain 1, 2, 3, 4, 5- pentasubstitution of aromatic ring is recognized from the bands appearing at 812.3-813.7¹⁴.

¹H NMR spectra of 2,4-DHBAMF terpolymer resin was shown in Fig. 3 and show a weak signal appearing at 9.8 ppm may be due to carboxylic proton. Single peak appearing at 7.2 ppm may be due to aromatic proton (Table IV). The intense singlet signal appeared in the 5.2 ppm can be assigned to phenolic

proton of Ar-OH¹². The medium triplet signal appeared at 0.9 – 3.1 ppm may be due to amido protons –CH₂-NH- polymer chain¹³. Also the medium doublet signal in the range of 1.9 to 3.1 ppm is attributed to the protons of methylenic bridge Ar-CH₂-NH- of polymeric chain¹⁴.

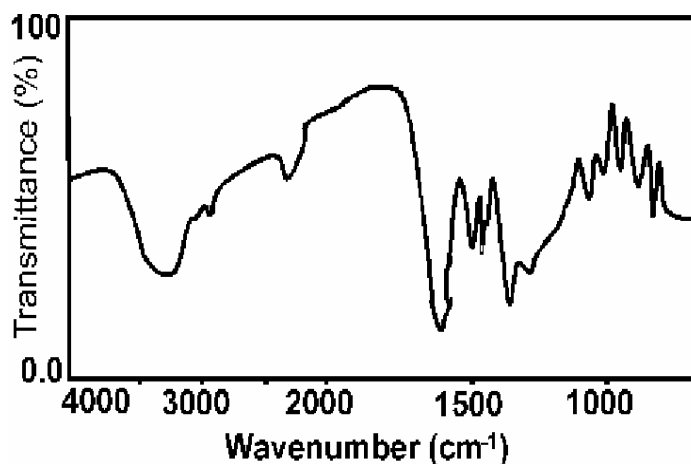


Fig. 2: IR spectra of of 8-HQ 5-ACF copolymer Nuclear magnetic resonance spectra

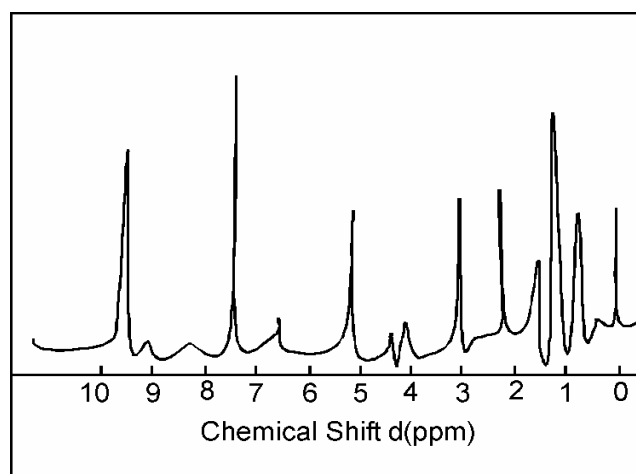


Fig. 3: NMR Spectra of 8-HQ 5-ACF copolymer

Scanning electron microscopy (sem)

Scanning electron micrograph (SEM) of 2,4-DHBAMF resin with x4000 magnification was shown in Fig. 4. The terpolymer exhibits spherulites. The spherulites are typical crystalline form and grow in high viscous and concentrated solution. But, in present case the spherulites composed of simplest structural form having smoother surface with deep pits. It is observed that the resin shows more amorphous character with less closed packed surface having deep pits. The resin thus possesses higher ion exchange capacity for Fe³⁺ ions.

Ion-exchange properties

The results of the batch equilibrium study carried out with the terpolymer resin 2,4-DHBAMF are presented in Tables V, VI and VII. From the study with six metal ions under limited variation of experimental conditions, certain generalization may be made about the behavior of the terpolymer resin.

Effect of electrolytes on the metal uptake

We examined the influence of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} at various concentrations on the position of the equilibrium of metal resin interactions. Examination of the data given in Table V reveals that the amount of Fe^{3+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} and Ni^{2+} ions taken up by the 2,4-DHBAMF sample increases with increasing concentration of ClO_4^- , NO_3^- and Cl^- and decreases with increasing concentration of SO_4^{2-} . This may be explained in terms of the stability constants of the complexes viz. Fe^{3+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} and Ni^{2+} ions form with these anions¹³. SO_4^{2-} might form rather strong complexes with Fe^{3+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} and Ni^{2+} ions, while ClO_4^- , NO_3^- and Cl^- might form weak complexes and therefore, might not be expected to influence the position of the Fe^{3+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} and Ni^{2+} chelates equilibrium as much as SO_4^{2-} . This may be explained on the basis of the stability constant of the complexes with those metal ions¹⁴⁻¹⁶. This type of trend has also been observed by other investigator in this field.

Rate of metal ion uptake

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried out while operating as close to equilibrium conditions as possible. Table VI shows the dependence of rate of metal ion uptake on the nature of the metal. Fe^{3+} ion required about 3 h for the establishment of equilibrium while Cu^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Ni^{2+} ions required almost 6 h for equilibrium. The rate of metal uptake follows the order $\text{Fe}^{3+} < \text{Cu}^{2+}, \text{Cd}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}$ for the terpolymer resin^{3,17}.

Distribution ratios of metal ions at different pH

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results given in Table VII. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the 2,4-DHBAMF terpolymer increases with increasing pH of the medium^{14,15}. The study was carried out up to a definite pH value for the particular metal ion to prevent hydrolysis of the metal ions at higher pH. The magnitude increases, however, is different for different metal cations. The 2,4-DHBAMF terpolymer resin take up Fe^{3+} ion is more selectively than any other metal ions under study. Co^{2+} and Zn^{2+} ions have a low distribution ratio in the range of pH 4-6. This could be attributed to the low stability constant, i.e. weak ligand stabilization energy, of the metal complexes. The order of distribution ratio of metal ions measured in the pH range 1.5 to 6.5 is found to be $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+}$. Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions¹⁶⁻¹⁸. For example, the result suggest the optimum pH 6.0 for the separation of Ni^{2+} and Cu^{2+} with distribution ratio 'D' as 272.76 and 549.81 respectively using the 2,4-DHBAMF terpolymer resin as ion exchanger. Similarly for the separation of Cd^{2+} and Fe^{3+} the optimum pH is 2.5, at which the distribution ratio 'D' for Cd^{2+} is 8.0 and for Fe^{3+} is 608. The lowering in the distribution ratio of Fe^{3+} was found to be small and hence, efficient separation could be achieved.

Since a acidic group plays a key role in the ion exchange phenomena, the amount of metal adsorbed by each sample depends upon its 2,4-DHBA content. As the pH of the medium increase, the amount of metal adsorbed by the polymer also increase and follow the trend of $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+}$. The Fe^{3+} adsorption were studied in the pH range 1.5 to 3.0 and it is also increase with increasing pH. From the result of distribution ratio it can be observed that the polymer shows highest affinity for Fe^{3+} whereas least affinity for Cd^{2+} . Due to the considerable difference between the adsorption capacity at different pH, rate of metal uptake and distribution ratio at equilibrium it may be possible to use the polymer for separation of particular metal ions from there admixture.

CONCLUSION

Condensation polymerization is a novel and easy method for preparation of 2,4-DHBAMF terpolymer resin. The resin was fully characterized with regard to morphology and composition by SEM, UV-Visible, FTIR and NMR studies. The result showed that the particles had micron size of 5 μm . The 2,4-DHBAMF resin can absorb Fe^{3+} and Cu^{2+} ion more firmly than the other ions. The order of adsorption for different metal ions on 2,4-DHBAMF resin was $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+}$. The metal absorption is totally depends on the 2,4-dihydroxybenzoic acid content and thus it play an important role in ion-exchange phenomenon.

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