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Research Article

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Synthesis and batch equilibrium adsorption chromatographic study of p-Cresol – Melamine - Formaldehyde terpolymer resin

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ABSTRACT

The terpolymer resin p-CMF was synthesized by the condensation of p-Cresol (p-C) and Melamine (M) with Formaldehyde (F) in the presence of acid catalyst at 150°C proved to be a selective chelating ion exchange terpolymer for certain matter. The chelating ion-exchange properties of this synthesized terpolymer were studied for different metal ions such at Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. A batch equilibrium method adsorption chromatography was employed in the study of the selectivity of metal ion uptake involving the measurements of the distribution of a given metal ion between the terpolymer sample and a solution containing the metal ion. The study was carried out over a wide pH range, shaking time and in media of various ionic strengths. The terpolymer 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.

Keywords: Synthesis, polycondensation, resins, adsorption, ion-exchange.

INTRODUCTION

Ion-exchange has attained the status of unit operation in chemical industries and has mostly replaced operations like distillation and other traditional methods of separations. Chelation ion-exchange chromatography become a very powerful technique in the extraction of trace and ultra trace materials[1], separation of rare earths, removal of contamination and in many other industrial separation and process of purification and concentration. For analytical work synthetic organic ion-exchangers are chiefly of interest. Extensive literature is available to interpret the experimental results in the light of practical applicability of various terpolymer resins. Lutfor et al[2] prepared a chelating ion-exchange resin contain amidoxime functional group, was characterized by FTIR spectra TG & DSC analysis and the chelating behavior of the prepared resin was studied with Cu(II), Zn(II), Ni(II), Cd(II) and Pb(II) metal ions. The chelating ion-exchange properties of 2,4-dinitrophenylhydrazone of 2-hydroxyacetophenone-formaldehyde resin[3] and oxime of 2-hydroxyacetophenone-substituted benzoic acid-formaldehyde resins[4] for different metal ions have been studied. Three phenol-formaldehyde chelating resins, poly (8-hydroxy quinoline-5, 7-diylmethylene), poly (8-hydroxy quinoldine-5, 7-diylmethylene) and poly (2-amino phenol 5, 7 diylmethylene) were synthesized and characterized by Ebraheem [5]. The ion-exchange capacity, effect of electrolyte as metal ion up take, rate of metal uptake of distribution of metal ion at different pH with resin copolymer derived from thiosami-carbazone derivatives of phenolic compound shows higher order than the resin copolymer derived from semicarbazone derivative [6]. The purpose of the present work is to explore the synthesis of new terpolymer resin p-cresol-melamine-formaldehyde and to study its application as an ion-exchanger for different metal ions, using batch equilibrium method according to earlier study [7, 8].

EXPERIMENTAL SECTION

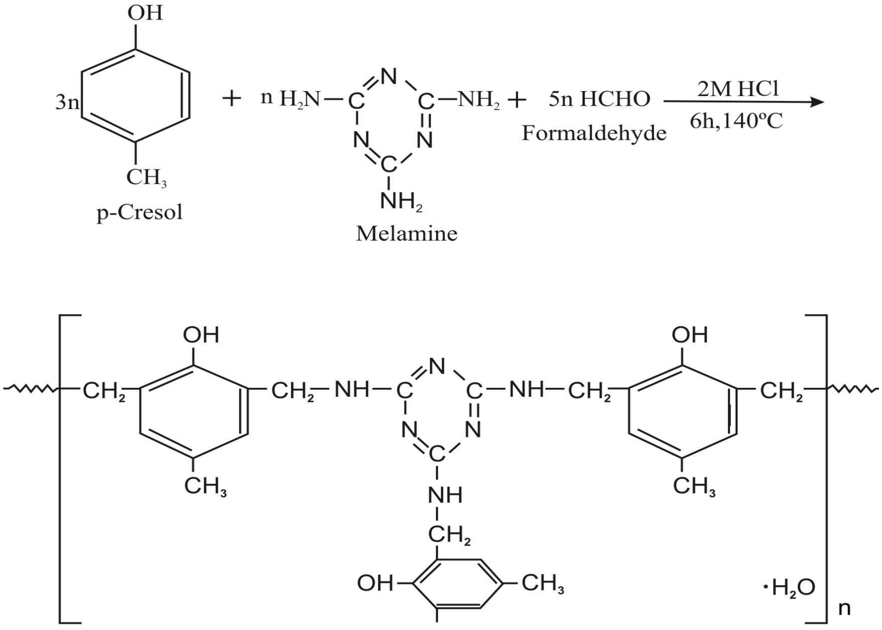
Starting Materials:

The important chemicals (starting materials) like p-cresol, melamine and formaldehyde etc. used in the preparation of new p-CMF-III terpolymer resin were procured from the market and were of Analar or Chemically pure grade, and wherever necessary the purity was tested and confirmed by TLC.

Synthesis of p-CMF-III terpolymer resin

A mixture of p-cresol (0.3mol) and melamine (0.1 mol) with formaldehyde (0.5 mol) was carried out in the presence of 2M (200ml) HCl as catalyst by molar ratio of 3:1:5 of reacting monomers, was taken in a round bottom flask fitted with water condenser and heated in an oil bath at 150ºC ± 2ºC for 6 hrs with occasional shaking to ensure thorough mixing. The temperature of electrically heated oil bath was controlled with the help of dimmerstat. The cream coloured resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction is shown as follows in Fig. 1.

The solid product was repeatedly washed with cold distilled water, dried in air and powdered with the help of agate mortar and pestle. The powder was washed many times with hot water followed by methanol to remove the unreacted starting materials, if any. The properly washed powder was dried in vacuum desicator over anhydrous calcium chloride. The resin was further purified by reprecipitation technique. The terpolymer was dissolved in 8% NaOH, filtered and reprecipitated by dropwise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with rapid stirring to avoid the lump formation. The process of reprecipitation was repeated twice. The terpolymer resin p-CMF-III so obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desicator over anhydrous calcium chloride.



p-CMF-III terpolymer resin

Fig.1 Reaction and expected structure of p-CMF-III terpolymer resin

Ion-exchange property

The ion-exchange property of the p-CMF-III terpolymer resin was determined by the batch equilibrium method.

Determination of metal uptake in the presence of electrolyte of different concentrations

The terpolymer sample (25mg) was suspended in an electrolyte solution (25ml) of known concentration. The pH of the suspension was adjusted to the required value by using either 0.1m HNO_3 or 0.1M NaOH. The suspension was stirred for 24H at 30ºC. To this suspension 2 ml of 0.1m solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 30ºC for 24 hrs and filtered. The solid was washed and the filtrate and washing were combined and the metal ion content was determined by titration against standard EDTA (ethylene diamine tetra-acetic acid). 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. The results are presented in Fig. 2.

Evaluation of rate of metal uptake

In order to estimate the time require to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type described above were carried out, in which the metal ion taken up by the chelating resins was determined from time to time at 30ºC. (in the presence of 25ml of 1M $NaNO_3$ solution). It was assumed that, under the given conditions, the state of equilibrium was established within 24 hrs. The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to that at the state of equilibrium. The results are presented in Fig. 3.

Distribution of metal ion at different pH

The distribution of each one of the seven metal ions i.e., Cu (II), Ni(II), Co(II), Zn(II), Cd(II), Pb(II), and Fe(III) between the polymer phase and the aqueous phase was determined at 30ºC and in the presence of 1M $NaNO_3$ solution. The experiments were carried out as described above at different pH values. The distribution ratio, D, is defined by the following relationship.

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

The results are presented in Fig 4.

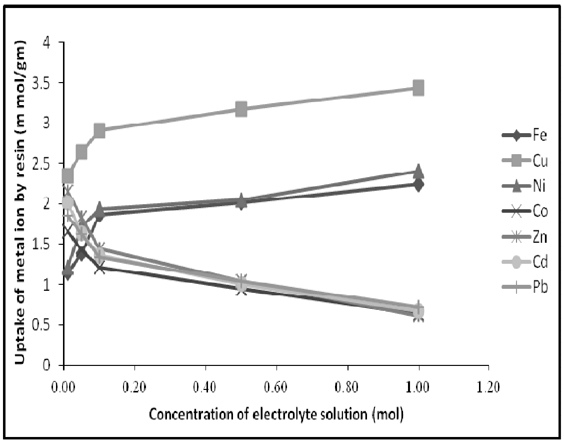
RESULTS AND DISCUSSION

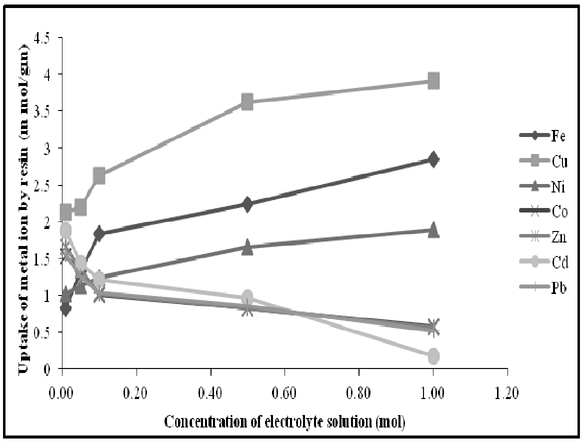
With a view to ascertain the selectivity of the p-CMF-III terpolymer for the selected metal ion, we have studied the influence of various electrolyte on the selectivity of metal ions, the rate of metal uptake and the distribution ratio of metal ions between the terpolymer and solution containing the metal ions.

Batch equilibrium technique developed by Gregor et al and De Geiso et al was used to study ion exchange properties of p-CMF-III terpolymer resins. The results of the batch equilibrium study carried out with the terpolymer p-CMF-III are presented in Fig. 2, 3 and 4. Seven metal ions Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} in the form of aqueous metal nitrate solution were used. The ion exchange study was carried out using three experimental variables: a) Electrolyte and its ionic strength b) Shaking time and c) pH of the aqueous medium, Among these three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymers[9-11].

Effect of Electrolytes and their concentrations on metal ion uptake capacity

We examined the influence of ClO_4^-, NO_3^-, Cl^- and So_4^{2-} at various concentrations on the equilibrium of metal-resin interaction. Fig. 2 shows that the amount of metal ions taken up by a given amount of terpolymer depends on the nature and concentration of the electrolyte present in the solution. In the presence of perchlorate, chloride and nitrate ions, the uptake of Fe(III), Cu(II) and Ni(II) ions increase with increasing concentration of the electrolytes, whereas in the presence of sulphate ions the amount of the above mentioned ions taken up by the terpolymer decreases with increasing concentration of the electrolyte. Moreover, the uptake of Co(II), Zn(II), Cd(II) and Pb(II) ions increase with decreasing concentration of the chloride, nitrate, perchlorate and sulphate ions[12]. This may be explained on the basis of the stability constants of the complexes with those metal ions. SO_4^{-2} might form rather strong complexes with Fe^{3+}, Ni^{2+}, Cu^{2+} ions while NO_3^-, Cl^- and ClO_4^- might form weak complexes and therefore might not be expected to influence the position of the Fe^{3+}, Ni^{2+} and Cu^{2+} chelates equilibrium as much as SO_4^{-2} , NO_3^-, Cl^- and ClO_4^- might form rather strong chelates with CO^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} chelates equilibrium. This type of trend has also been observed by other investigators in this field [10-12].





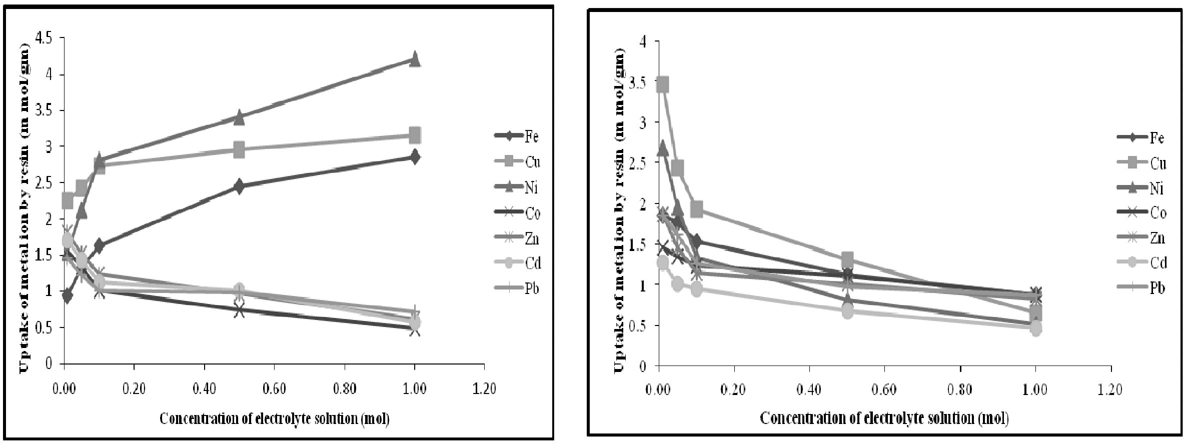


Fig. 2 Uptake of several metal ions by p-CMF-III terpolymer resin at five different concentrations of electrolyte solution

Rate of uptake for metal ions as a function of time

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried to while operating as close to equilibrium conditions as possible. Fig. 3 shows the results of rate of uptake of metal ion on p-CMF-III terpolymer resin. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given polymer. The result shows that the time taken for the uptake of the different mental ions at a given stage depends on the nature of the metal ion under given conditions. It is found that Fe (III) ions require about 3hrs for the establishment of the equilibrium, whereas Cu (II), Ni(II), Co(II) and Zn (II) ions required about 5hrs. Thus the rate of metal ions uptake follows the order Cu (II) > Ni (II) > Co (II) ≈ Zn (II) > Cd(II) > Pb (II) for all of the terpolymer[13].

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 Fig. 4. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ion taken up by the p-CMF-III terpolymer increases with increasing pH of the medium. The magnitude of increase, however, is different for different metal cations. The p-CMF-III terpolymer resin take up Fe (III) ion more selectively than any other metal ions under study. The order of distribution ratio of metal ions measured in pH range 1.5 to 6.5 is found to be Fe (III) > Cu (II) > Ni (II) > Co (II) > Zn (II) > Cd (II) > Pb (II). 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 ions [13].

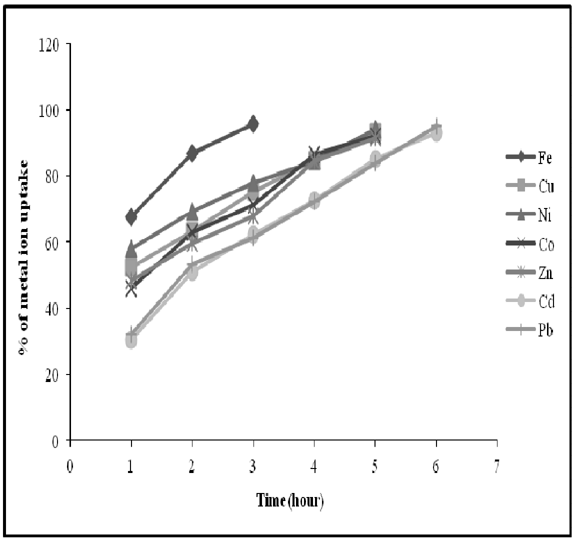


Fig. 3. Comparison of the rate of metal ion (m) uptake by p-CMF-III terpolymer resin

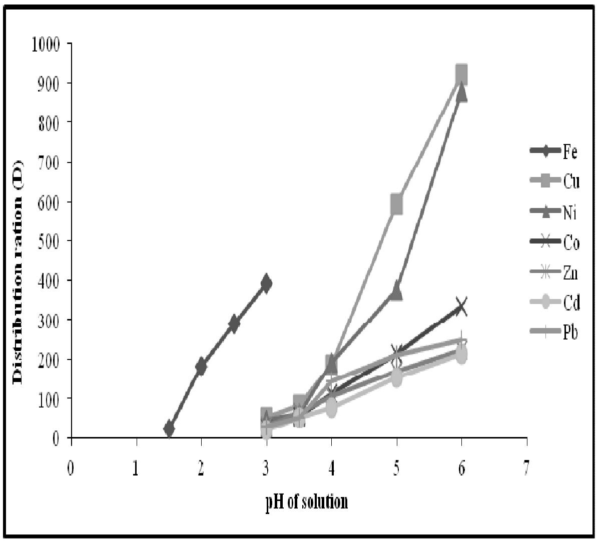


Fig. 4. Distribution ratio D of various metal ions as function of the pH by p-CMF-III terpolymer resin

For example, the result suggest the optimum pH 6.0, for the separation of Co(II) and Ni (II) with distribution ratio 'D' at 415.4 and 854.4 respectively using the p-CMF terpolymer resin as ion-exchanger. Similarly, for the separation of Cu (II) and Fe (III) the optimum pH is 3, at which the distribution ratio 'D' for Cu (II) is 66.1 and that for Fe (III) are 341.5. The lowering in the distribution of Fe (III) was found to be small and, hence, efficient separation could be achieved.

In order to assess the potential for separation of metal ions Fe^{3+} from other metal ions, the following combinations of metal solutions were prepared : (1) Fe^{3+} and Cu^{2+} (2) Fe^{3+} and Ni^{2+} (3) Fe^{3+} and CO^{2+} (4) Fe^{3+} and Zn^{2+} (5) Fe^{3+} and Cd^{2+} (6) Fe^{3+} and Pb^{2+}. The solution for separations were prepared by mixing 1ml of 0.1m solutions of Fe^{3+} with 1ml of 0.1m solution of Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. Selective uptake of the metal ions was studied by adjusting the optimum pH of 3. Distribution ratios of Fe^{3+} at pH 3 in the mixture with metal ions Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} were found to be 321, 316, 312, 318, 315 and 325 respectively, i.e. slight lower then 341 found when Fe^{3+} alone was studied. The lowering in the distribution ratios of Fe3+ was found to be small and hence efficient separation could be achieved.

CONCLUSION

1. A terpolymer p-CMF-III, based on the condensation reaction of p-Cresol and melamine with formaldehyde in the presence of acid catalyst was prepared.
2. The p-CMF-III terpolymer resin is a selective chelating ion-exchange terpolymer resin for certain metals.
3. 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.

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