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Ion-exchange chromatography of 8-hydroxyquinoline 5-sulphonic acid-melamine-formaldehyde polymer resin-II

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ABSTRACT

The polymer resin 8-HQ5-SAMF-II was synthesized by the condensation of 8-Hydroxyquinoline5-sulphonic acid (8-HQ5-SA) and melamine (M) with Formaldehyde (F) in the presence of acid catalyst at 130°C proved to be a selective chelating ion exchange polymer for certain metals. The eco-friendly applications of this polymer resin was studied with respect to its chelating ion-exchange properties The chelating ion-exchange properties of this synthesized polymer was 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 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 polymer 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 polymer 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.

Key words: Adsorption, distribution ratio, ion- exchange, chromatography, resin.

INTRODUCTION

The presence of heavy metals in the environment is a cause of concern due to their acute and long term toxicity. Cadmium, Mercury, Iron, Nickel, Lead are the hazardous metals present in environmental area. The removal of these metals needs certain technique; Ion-exchange is one of the powerful techniques for this purpose. Ion-exchange has attained the status of a 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 polymer resins. The purpose of the present work is to explore the synthesis of new polymer resin II 8-Hydroxyquinoline5-sulphonicacid - melamine-formaldehyde and to study its application as an ion-exchanger for different metal ions, using batch equilibrium method according to earlier study [2 – 4].

MATERIALS AND METHODS

Chemicals

8-hydroxyquinoline 5-sulphonic acid and melamine (Loba Chem., Mumbai) and formaldehyde (37% w/v) (S.D. Fine Chem. Ltd. Mumbai)

Synthesis of 8-HQ5-SAMF-II polymer

The 8-HQ5-SAMF-II polymer was prepared (Fig.1) by condensing 8-hydroxy quinoline 5-sulphonic acid (8-HQ5-SA; 4.86g, 0.2 mol) and melamine (M; 1.26g, 0.1 mol) with 37% formaldehyde (F;11.1 ml, 0.4 mol) in a mol ratio of 2:1:3 in the presence of 2M 200 ml HCl as a catalyst at $130^0C \pm 2^0C$ for 6h in an oil bath. The reaction and suggested structure of 8-HQ5-SAMF-II polymer has been given in Fig.1.

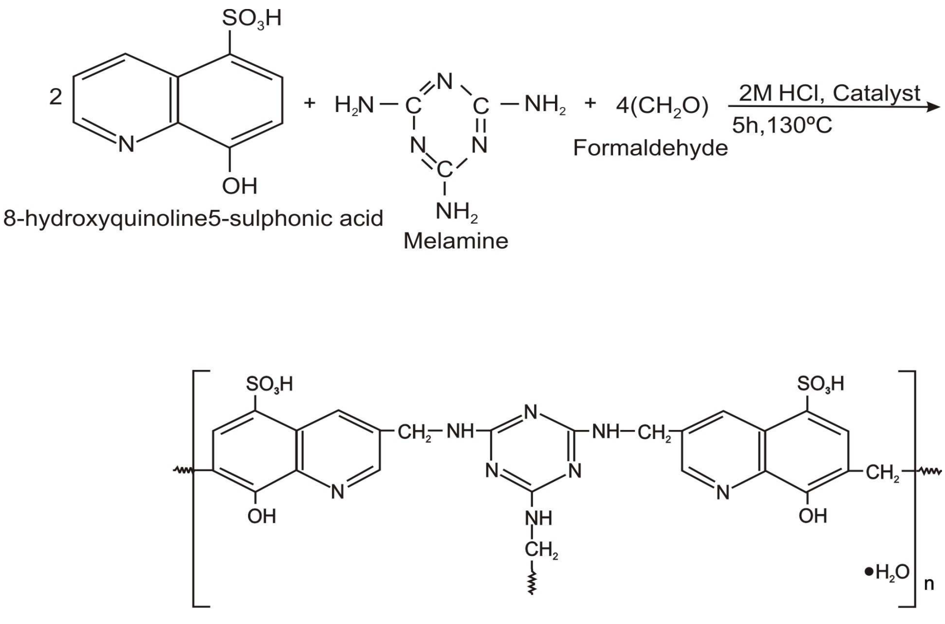


Fig. 1 Reaction and suggested structure of representative 8-HQ5-SAMF-II polymer resin

Ion-Exchange property

The ion-exchange property of the 8-HQ5-SAMF-II polymer resin was determined by the batch equilibrium method developed by Gregor and De. Geiso et al. with seven metal ions viz. Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} in the form of metal nitrate solution.

The ion exchange study was carried out to investigate the following three aspects.

Influence of different electrolytes and their different concentrations on the amount of metal ion uptake –

The following experimental procedure was applied in order to study the effect of the nature of various electrolytes and concentrations on the amount of metal ion taken up by polymer resin sample.

25 mg polymer resin was suspended in 25 ml electrolyte solution of known concentration. The pH of this suspension was adjusted before and after stirred for 24 hrs at 30ºC, to this adds 2 ml of 0.1M metal ion solution, adjusted pH again to the required value and stirred again 24 hrs. The suspension then filtered and filtrate was titrated against standard EDTA solution. Similarly the blank experiment was also carried out in the same manner without adding polymer sample. The amount of metal ion uptake was calculated from the difference between at blank experiment and the reading in actual experiment.

$$\text{Metal ion adsorbed (uptake) by resin} = (X-Y)\, Z \text{ millimols / gm.}$$

Where,

'Z' ml is the difference between actual experimental reading and blank reading.
'X' mg is metal ion in the 2ml 0.1M metal nitrate solution before uptake.
'Y' mg is metal ion in the 2ml 0.1M metal nitrate solution after uptake.

Evaluation of rate of metal ion uptake –

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 rate of metal uptake can be determined.

$$\begin{array}{c}\text{\% of amount of metal} \\ \text{ions} \\ \text{taken up at different time}\end{array} = \frac{\text{Amount of metal ion absorbed x 100}}{\text{Amount of metal in absorbed at equillibrium}}$$

Percentage of metal ion adsorbed after 1 hr = (100X) / Y

Where,

'X' mg of metal ion adsorbed after 1 hr and 'Y' mg of metal ion is adsorbed after 25 hrs, then by Using this expression, the amount of metal adsorbed by polymer after specific time intervals was calculated and expressed in terms of percentage metal ion adsorbed. This experiment was performed using 0.1M metal nitrate solution of Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} *and* Pb^{2+}.

Evaluation of the distribution of metal ion at different pH –

The distribution of each of seven metal ions was determined between polymer-phase and aqueous phase in pH range 2.5 to 6.5 using similar experiments described above. The distribution of metal can be determined as follows.

$$D = \frac{\text{Amount of metal ion on resin}}{\text{Amount of metal ion in solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of resin (g)}}$$

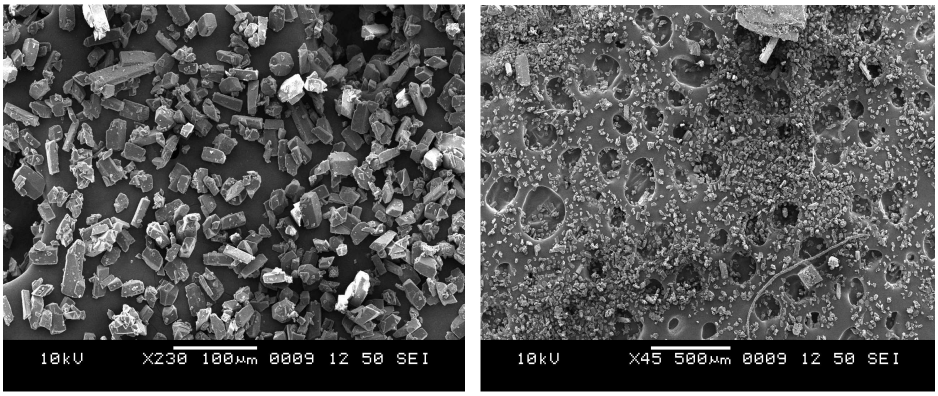
Metal ion adsorbed (uptake) by the resin $= \left(\frac{ZX}{Y}\right)\frac{2}{0.025}$

Where, 'Z'= is the difference between actual experiment reading and blank reading,
'C' = gm is the amount of metal ion in 2ml 0.1M metal nitrate solution,
'Y' = gm of metal ion in 2ml of metal nitrate solution after uptake.

RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM)

Fig. 2 shows the scanning electron microscopy (SEM) micrographs of the pure 8-HQ5-SAMF-II polymer sample at 1500X and 3000X magnification [5]. The morphology of resin exhibits growth of crystals from polymers solution corresponding to the most prominent organization in polymers on a large scale such as in size of few millimeters spherulites. The morphology of resin shows a fringed micelle model of the crystalline-amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. The micrograph of pure sample shows the presence of crystalline-amorphous layered morphology which is the characteristic of polymer. The monomers have crystalline structure but during condensation polymerization of some crystalline structure lost into amorphous nature. The amorphous nature shows chelating nature of the polymer.



(A) **(B)**

Fig. 2: SEM micrographs of 8-HQ5-SAMF-II polymer resin.

Ion-Exchange property

With a view to ascertain the selectivity of the 8-HQ5-SAMF-II polymer resin for the selected metal ion, it was studied the influence of various electrolytes on selectivity, the rate of metal uptake and the distribution ratios of the metal ions between the polymers and solution containing metal ions. This study made certain generalization about the behaviour of the polymer resin sample [5- 8].

Influence of different electrolyte on the metal ion uptake –

The data presented in Fig.3and 4 indicate that the amount of metal ions taken up by a given amount of polymer depends on the nature and concentrations of electrolyte present in the solution. In the presence nitrate (NO_3^-) ions the uptake of Fe^{3+},Cu^{2+} and Ni^{2+} ions increase with increasing concentration of the electrolyte, whereas' in the presence sulphate ion (SO_4^{2-}), it is decreased with increasing concentration of electrolyte. Moreover the uptake of Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions decreases with increasing concentrations of the NO_3^- and SO_4^{2-}, which can be explained on the basis of the stability constant of the complexes of metal ions with ions of electrolytes[9-11]. If has been noticed that lower pH was not suitable when concentrated electrolytes were used.

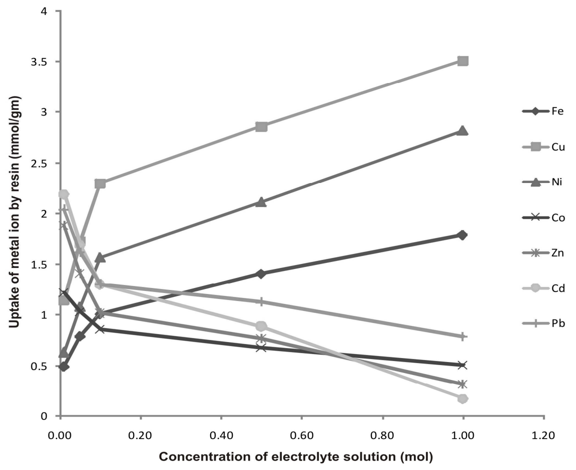


Fig. 3 Uptake of several metal ions by resin at five different concentrations of electrolyte solution $NaNO_3$

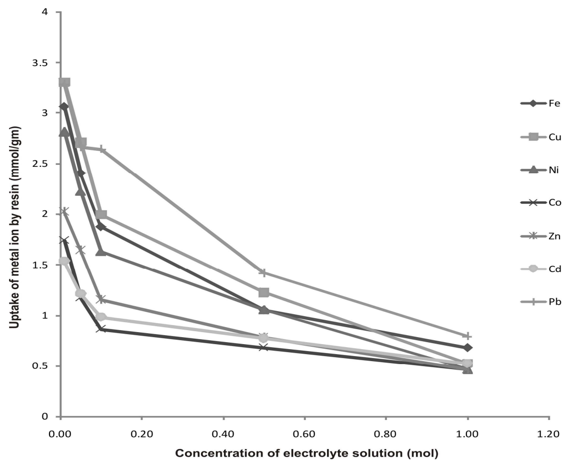


Fig. 4 Uptake of several metal ions resin at five different concentrations of electrolyte solution Na_2SO_4

Evaluation of rate of metal ion uptake –

The data presented in Fig.5 indicates that the rate metal ion uptake depends upon nature of metal ion [12-14]. The rate of metal ions means the change in concentration of metal ions in aqueous solution containing polymer sample. Fe^{3+} requires 3 hrs and rest of metal ion require 5 and 6 hrs for establishing the equilibrium. The order of rate of metal ion uptake is found to be $Fe^{3+} > Cu^{2+} \approx Ni^{2+} > Co^{2+} \approx Zn^{2+} > Cd^{2+} \approx Pb^{2+}$

Evaluation of the distribution rate of metal ions at different pH –

The data presented in Fig.6 indicates that the relative amount of metal ion taken up by HQ5-SAMF-II polymer resin at equilibrium increases with increasing pH of the medium, however the magnitude of increase is different for different metal cations[15,16]. The result indicates that polymer resin sample takes up Fe^{3+} ion more selectively than any other ions under study. The order of distribution ratio of metal ions measured in pH range 2.5 to 6.5 is found to be $Fe^{3+} > Cu^{2+} \approx Ni^{2+} > Co^{2+} \approx Zn^{2+} > Cd^{2+} \approx Pb^{2+}$

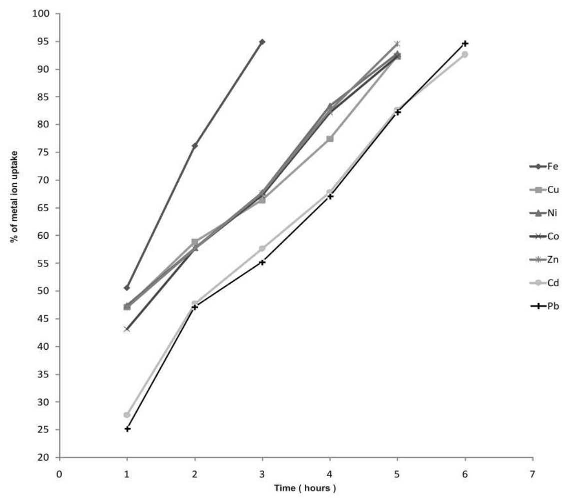


Fig.5 Comparison of the rate by resin

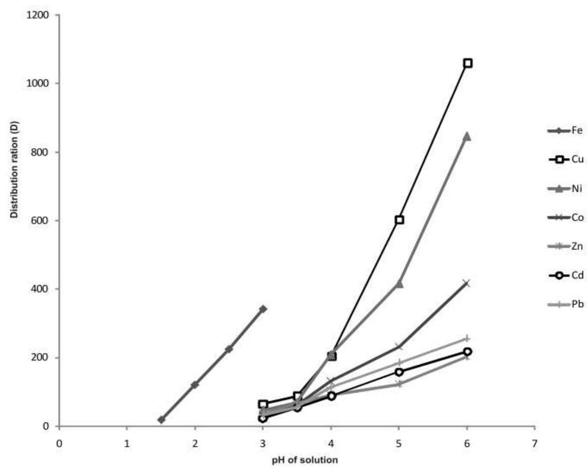


Fig.6 Distributio ratio at different pH

CONCLUSION

A polymer 8-HQ5-SAMF-II, based on the condensation reaction of 8-hydroxyquinoline 5-sulphonic acid and melamine with formaldehyde in the presence of acid catalyst was prepared. 8-HQ5-SAMF-II is a selective chelating ion-exchange polymer resin for certain metals. The polymer 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. This study of ion-exchange reveals that 8-HQ5-SAMF-II polymer resin is proved to be an eco-friendly cation exchange resin and can be used for the removal of hazardous metal ions from the environmental area, for the purification of industrial waste solution and for the purpose of purification and desalination of water.

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