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Metal – Ion Binding Properties of a Terpolymer Resin: Synthesis, and its Application as an Ion- Exchanger

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ABSRACT: *Copolymer (4-HBMF) was synthesized by the condensation of 4-hydroxybenzophenone [HB] and melamine [M] with formaldehyde [F] in presence of acid catalyst using varied molar ratios of reacting monomers. A copolymer composition has been determined on the basis of their elemental analysis and the number average molecular weight of this copolymer was determined by conductometric titration in non-aqueous medium. The viscosity measurement in DMSO has been carried out with a view to ascertain the characteristic functions and constants. The newly synthesized copolymer resin was characterized by IR spectra and* ^1H *NMR spectra. Ion- exchange properties of this resin was studied by batch equilibrium method for* Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} *and* Pb^{2+} *ions over the pH range, 1.5 to 6.5 and in media of various ionic strengths. In presence of nitrates, perchlorate and chloride ions the uptake of Fe(III), Cu(II), Zn(II) and Pb(II) ions increases with the increasing concentration of electrolytes, whereas in presence of sulphate ions, the amount of above mentioned ions taken up by the copolymer resin decreases with the increasing concentration of electrolyte. Study of distribution ratio as a function of pH indicates that the amount of metal ion taken by resin is increases with the increasing pH of medium. The surface morphology of the copolymer resin was examined by scanning electron microscopy.*

***Keywords*: *Adsorption, Distribution ratio, Ion- exchanger, Resins, Synthesis*.**

I. INTRODUCTION

Terpolymer is found very useful application as adhesives high temperature flame resistant, fibres, coating materials, semiconductors, catalysts and ion exchange resins[1-4]. Ion exchange resins have attracted much interest in the recent years due to their application in waste water treatment, metal recovery and for identification of specific metal ions [5-6]. A new chelating sorbent for metal ion extraction under saline conditions has also been studied [7]. Chelating ion exchange properties of resin involving poly [(2, -hydroxy-4 acryoxybenzophenone)] are reported[8]. Copolymers involving 4-hydroxyacetophenone-biuret-formaldehyde [9] are reported for their ion –exchange characteristics. The purpose of present study is to explore the adsorption behavior of eight metal ions Fe^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} on the newly synthesized terpolymer resins 4-HBMF at different pH values, different concentrations of different electrolytes and at different shaking time intervals. The terpolymer resins under investigation are found to be cation exchanger having both ion exchange group and chelating group in the same polymer matrix and the resin can be used selectively for the purpose of purification of waste water. One of the important applications of chelating and functional polymers is their capability to recover metal ions from waste solution. Hence the chelating ion exchange property of the 4-HBMF terpolymer resin was also reported for specific metal ions.

The present study deals with the synthesis and of 4-hydroxybenzophenone-melamine-formaldehyde [4-HBMF] terpolymer resin by spectral methods for the first time. The synthesized terpolymer was characterized by elemental analysis, UV-VIS, FT-IR, ^1H-NMR, intrinsic viscosity and number average molecular weight.

II. EXPERIMENTAL

Chemicals

The important chemicals like 4-hydroxybenzophenone, melamine and formaldehyde used in the preparation of various new 4-HBMF terpolymer resins were procured from the market and were of chemically pure grade.

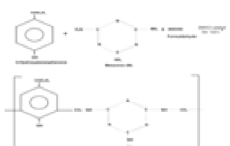

Fig.1 Preparation of 4-HBMF-1 Copolymer Resin

2.1 Synthesis of 4-HBMF Terpolymer resin: The 4-HBMF-I terpolymer resin was prepared by condensing 4-hydroxybenzophenone (1.982gm, 0.1mol), melamine (1.2612gm, 0.1mol), formaldehyde (11.25ml, 0.3mol) in the mole ratio of 1:1:3 in the presence of 2MHCl as a catalyst at 122+2^{o}C for 6h in an oil bath with occasional shaking to ensure through mixing. The reaction and suggested structure of 4-HBMF-I is given in Fig. 1.

In the same way the other terpolymer resin viz. 4-HBMF-II, 4-HBMF-III, 4-HBMF-IV were prepared with the molar ratios 2:1:4, 3:1:5, 4:2:7.

III. CHARACTERIZATION OF 4-HBMF TERPOLYMER RESIN

3.1 Physicochemical and Elemental Analysis

The terpolymer resin was subjected to micro analysis for C, H and N on an Elementar Vario EL III Carlo Erba- 1108 elemental analyzer. The number average molecular weight was determined by conductometric titration in DMSO medium using ethanolic KOH as the titrant by using 25 mg of sample. A plot of the specific conductance against the miliequivalents of KOH required for neutralization of 100 gm of terpolymer resin was made. Inspection of such plot revealed that there were many breaks in the plot. From this plot first break and last break were noted.

3.2 Spectral and surface analysis

Electronic (UV-Visible) spectra of terpolymer resin in DMSO was recorded with a double beam spectrophotometer in ... R spectra of 4-HBMF ... n RX-I,FT-IR spectro... n KBr pallets in the range of 4000-500 cm^{-1} at SAIF , Punjab University, Chandigarh. ^{1}H NMR spectra was recored with Bruker Advance-II 400 NMR spectrophotometer using DMSO as solvent at SAIF , Punjab University, Chandigarh.The surface analysis was performed using scanning electon microscope at different magnification at VNIT Nagpur.

$\overline{DP}$ = Total millequivalents of base required for complete neutralization

3.3 Ion-exchange property

The ion-exchange property of the 4-HBMF terpolymer resin was determined by the batch equilibrium method.

3.3.1 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 24hrs 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. 6 to 10.

3.3.2 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. 10

3.3.3 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.

IV. RESULTS AND DISCUSSION

4.1. Spectral and surface studies

The UV-Visible spectrum of all four 4-HBMF terpolymer resin has been shown in Fig. 2. All the four 4-HBMF terpolymer resin displayed two broad bands at 270-280 nm and 320-380 nm. The observed position of the absorption bands indicates the presence of a phenone COC_6H_5 group and hydroxyl group which is in conjugation with the aromatic nucleus. The band at 320-380 nm is more intense which is accounted for a π-π* transition while the less intense band at 180-300 may be due to n-π*transition [10,11].

4.2. Infrared Spectra

The IR spectra of all four 4- HBMF terpolymer resins are presented in fig 3. IR spectra reaveled that all four 4-HBMF terpolymer resin give rise to nearly same pattern of spectra. A broad band appeared at the region 3742-3746 cm^{-1} may be assigned to stretching vibration of phenolic –OH group exhibiting intramolecular hydrogen bonding[12]. The band at 2924-2931 cm^{-1} is due to stretching of –NH. The band at 1606-1607cm^{-1} may be due to aromatic ring substituted. The band at 1606-1607 cm^{-1} may be due to aromatic ring (substituted). The band at 1347, 1283, 1248 and 784 cm^{-1} may be due to CH_2 bending(wagging and twisting), -CH_2 plane bending.

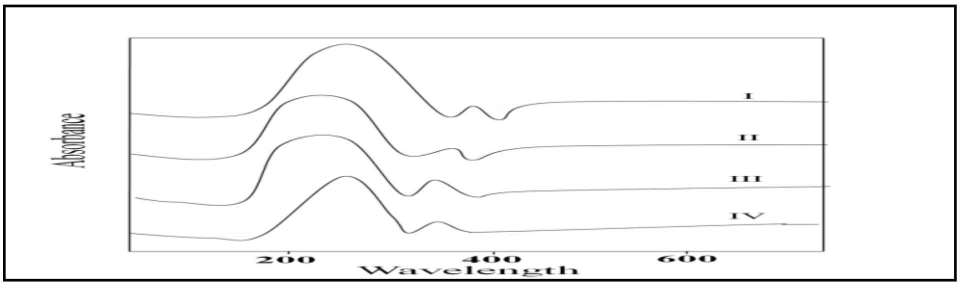

Fig. 2 UV-visible Spectra of 4-HBMF Terpolymer Resins

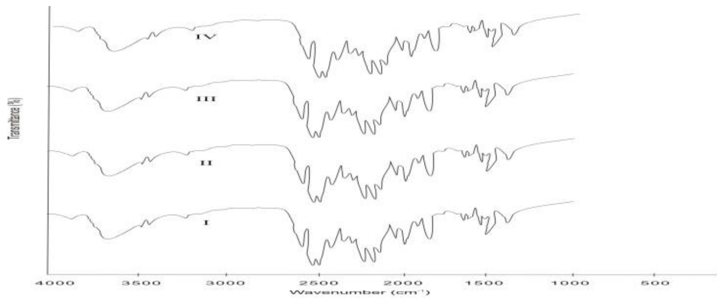

Fig. 3 Infra Red Spectra of 4- HBMF Terpolymer Resins

4.3. Nuclear Magnetic Resonance spectroscopy

^{1}H NMR spectra of all 4-HBMF terpolymer resin are shown in fig 4. The medium signal at 2.52-2.54 ppm may be due to methylene proton of Ar-CH_2 bridge. The signal in the region of 3.42-3.46 ppm may be due to methylene proton of Ar-CH_2-N. The signal in the range of 7.61-7.65 ppm may be due to phenolic hydroxyl group[13]. The singlet in the region 5.33-5.34 ppm may be due to proton of –NH bridge. The weak multiplate signal in the region at 6.85-6.91 ppm may be due to aromatic proton of A r-H.

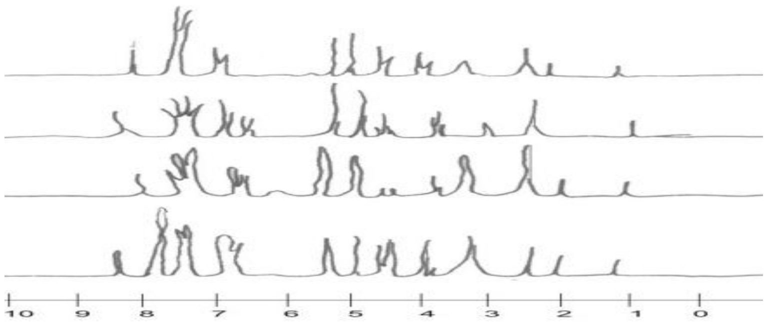

Fig. 4 ^{1}H NMR Spectra of 4- HBMF Terpolymer Resin

4.4 Scanning electron microscopy (SEM)

Surface analysis has found great use in understanding the surface features of the materials. The morphology of the reported sample was investigated by scanning electron micrograph at different magnification which is shown in fig 5.for 4-HBMF. It gives the informatin of surface topography and defect in the structure. The morphology of polymer resin shows spherulites and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of 4-HBMF terpolymer resin sample. The morphology of resin polymer shows also a fringes model of the crystalline amorphous structure. Thus by SEM micrograph morphology of the resin shows the transition between crystalline and amorphous nature, when compared to other resin, the 4-HBMF terpolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.

4.5 Ion- exchange properties

Batch equilibrium technique developed by Gregor et. al and De. Geiso et. al. was used to study ion exchange properties of 4-HBMF terpolymer resins. The results of the batch equilibrium study carried out with the terpolymer 4-HBMF are presented in Fig. 6 to 11. 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[14-16].

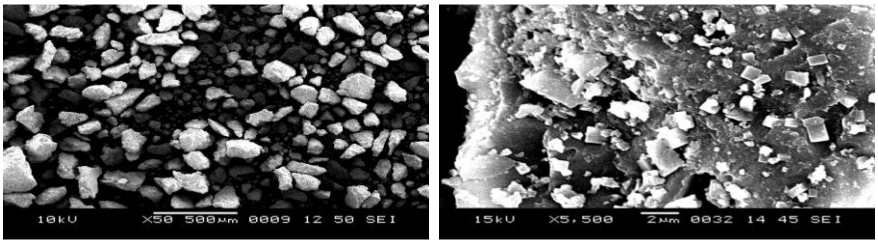

Fig. 5 SEM Micrograph of 4-HBMF-I Terpolymer resin

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. 6,7,8.9 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. This may be explained on the basis of the stability constants of the complexes with those metal ions.

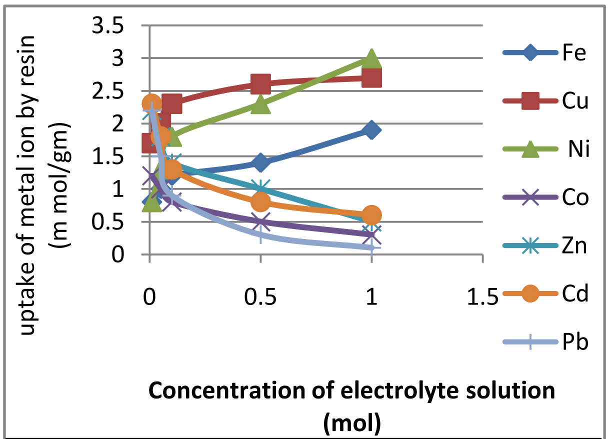

Fig. 6 Uptake of Several Metal Ions by 4-HBMF - I Terpolymer Resin at five different concentration of Electrolyte Solution $NaNO_3$.

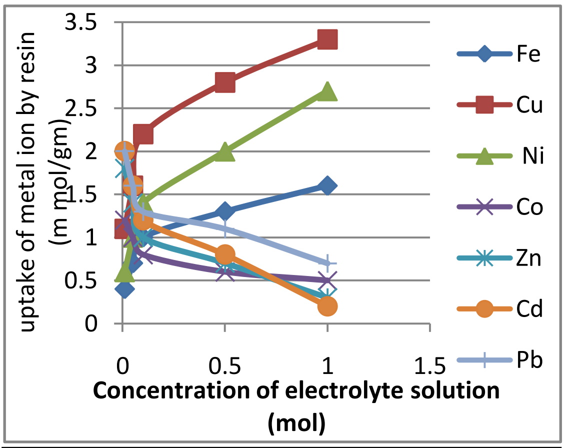

Fig. 7 Uptake of Several Metal Ions by 4-HBMF -I Terpolymer Resin at five different concentration of Electrolyte Solution NaCl.

Evaluation of rate of metal ion uptake

The data presented in Fig 10 indicates that the rate of metal ion uptake depends on the nature of metal ion.[17]. The rate of metal ion means the change in concentration of metal ion in aqueous solution containing polymer sample. Fe^{3+} requires 3hrs and rest of metal requires 5 hrs for establishing equilibrium.

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. 11. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ion taken up by the 4-HBMF terpolymer increases with increasing pH of the medium. The magnitude of increase, however, is different for different metal cations. The 4-HBMF 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 2.5 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.

V. CONCLUSIONS

1. A terpolymer 4-HBMF, based on the condensation reaction of 4-Hydroxybenzophenone and melamine with formaldehyde in the presence of acid catalyst was prepared.
2. 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.
3. This study of ion–exchange reveals that 4-HBMF polymer resin is proved to be eco-friendly cation exchange resin and can be used for the removal of hazardous metal ions from environmental area.

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