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Chelation ion-exchange properties of copolymer resin derived from 2, 2´-dihydroxybiphenyl, biuret, and formaldehyde

S.S. Rahangdale[a], W.B. Gurnule[b,*]

[a]*Department of Chemistry, Jagat Arts, Commerce and Indiraben Hariharbhai Patel Science College, Goregaon 441 018, India*
[b]*Department of Chemistry, Kamla Nehru College, Nagpur 440 009, India, Tel. +0712 2747853, +09096672499;*
Fax: +091 072 2747853; emails: wbgurnule@yahoo.co.in, wbgurnule@gmail.com

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ABSTRACT

Copolymers (2, 2´-dihydroxybiphenyl, biuret and formaldehyde, [2, 2´-HBBF]) were (2, 2´-dihydroxybiphenyl-biuret-formaldehyde) prepared by the condensation of 2, 2´-dihydroxybiphenyl and biuret with formaldehyde in the presence of acid as a catalyst and using different molar proportions of monomers. The resulting copolymers were characterized by infrared, UV-visible and proton NMR spectroscopy. Average molecular weight was determined by conductometric titration in non-aqueous medium. The viscosity measurements carried out in DMF N,N' Dimethylformamide indicate normal behavior. A copolymer proved to be a selective chelating ion-exchange copolymer for certain ions. Chelating ion-exchange properties of this copolymer were studied for Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, and Zn^{2+} ions. 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 and in media of various ionic strengths. The copolymer showed a higher selectivity for Fe^{3+} and Cu^{2+} ions than for Ni^{2+}, Zn^{2+}, and Co^{2+} ions.

Keywords: Synthesis; Ion-exchange; Distribution ratio; Resin; Polycondensation; Chelating resin

1. Introduction

Many copolymers with reactive groups are now being synthesized, tested, and used not only for the macromolecular properties but also for the properties of functional groups. These functional groups provide an approach to a subsequent modification of the copolymers for specific end application [1]. In recent years, some comprehensive work has been published on functional monomers and their copolymers [2,3]. Liu et al. [4] studied the interaction of heavy metal ions and chelating ion-exchange resin containing 8-hydroxyquinoline (8-HQ). The resin has good selectivity to the exchangeable adsorption of heavy metal ions indicating Cu(II), Hg(II), Pb(II), and Mg(II) at pH 5.0 and also suggested that the chelating ion-exchange resin containing 8-HQ could be used to enrich heavy metals in water. Bekir [5] has prepared a modified 1,4,8,11-tetraazocyclotridecane (cyclam) and with an AIBN initiator polymerized the modified cyclam. Cyclam-containing polymer in bulk structure was removed from the suspension by filtration after washing and drying.

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*Corresponding author.

The polymeric materials were used for transition metal ion adsorption and desorption of selected ions Cu(II), Ni(II), Co(II), Cd(II), and Pb(II) from aqueous media containing different amounts of these metal ions at different pH values. The adsorption rates were high and the adsorption equilibrium was reached in about 30 min. The affinity order of the transition metal ions was Cu(II) > Ni(II) > Co(II) > Cd(II) > Pb(II) for competitive adsorption. Gurnule et al. [6] have prepared 8-hydroxyquinoline—melamine—formaldehyde (8-HQMF) resin. The chelating ion-exchange properties of this were studied for Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, and Pb^{2+} ions. A batch equilibrium method was used to study the selectivity of metal ion uptake by measuring the distribution of a metal ion between the resin sample and solution containing the metal ion. The study was carried out at different pH ranges and in a medium of different ionic strengths. The copolymer showed higher selectivity for Fe(III), Cu(II), and Ni(II) ions than Co(II), Zn(II), Cd(II), and Pb(II) ions.

The purpose of the selection of these monomers for the present study is to explore the adsorption behavior of seven metal ions, such as Fe^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}on the newly synthesized copolymer resins 2, 2´-HBBF at different pH values, different concentrations of different electrolytes, and at different shaking time intervals. Some commercially available ion-exchange resins are given in Table 1 [7].

The present study deals with the synthesis and characterization of 2, 2´-HBBF copolymer resin by polycondensation using HCl as catalyst for the first time. The synthesized copolymer was characterized by IR, ^{1}H NMR, and average molecular weight determination. One of the important applications of chelating and functional polymers is their capability to recover metal ions from waste solutions. Hence, the chelation ion-exchange property of the 2, 2´-HBBF copolymer resin was also reported for specific metal ion.

2. Experimental setup

2.1. Materials

2, 2´-dihydroxybiphenyl and biuret were used as received from SRL, Mumbai, India. Stock solutions, such as Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, and Zn^{2+} were prepared by dissolving their nitrate salt in distilled water. Formaldehyde (37%) (Qualigens Fine Chemicals, Mumbai, India) was used as received. Solvents, such as N, N´-dimethyl formamide and dimethyl sulfoxide were used after distillation.

2.2. Synthesis of 2, 2´-HBBF copolymers

The 2, 2´-HBBF copolymer was prepared by condensing 2, 2´-dihydroxybiphenyl (1.862 gm, 0.01 mol) and biuret (1.3 gm, 0.01 mol) with formaldehyde (7.5 ml, 0.02 mol) in the presence of 2 M HCl as a catalyst at 118 ± 2˚C in an oil bath for 5 h [8,9]. The cream-colored polymer obtained was washed with hot water and finally with ether to remove excess of acid monomer. The properly washed resin was dried, powdered, and extracted with diethyl ether and then with petroleum ether to remove 2, 2´-dihydroxybiphenyl-formaldehyde copolymer which might be present along with the 2, 2´-HBBF copolymer. It was further purified by dissolving in 10% NaOH and then filtered. The copolymer was then reprecipitated by dropwise addition of 1:1 (v/v) conc. HCl/water with constant stirring and filtered. The method was repeated thrice. The resulting polymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified terpolymer was finely ground to pass through 300 mesh sieves and kept in a vacuum over silica gel. The yield of the terpolymer was found to be about 82% and reaction is shown in Fig. 1.

Table 1
Commercially available ion-exchange resins

Trade name	Functional group	Polymer matrix	Ion-exchange capacity (mmol g^{-1})
Amberlite IR-120	$-C_6H_4SO_3H$	Polystyrene	5.0–5.2
Duolite C-3	$-CH_2SO_3H$	Phenolic	2.8–3.0
Amberlite IRC-50	–COOH	Methacrylic	9.5
Duolite ES-63	$-OP(O)(OH)_2$	Polystyrene	6.6
Zeocarb-226	–COOH	Acrylic	10.00
Dowex-1	$-N(CH_3)_3$ Cl	Polystyrene	3.5
Amberlite IRA-45	$-NR_2$, –NHR, $-NH_2$	Polystyrene	5.6
Dowex-3	$-NR_3$, –NHR, $-NH_2$	Polystyrene	5.8
Allassion A WB-3	$-NR_2$, $-N^+R_3$	Epoxy-amine	8.2

2.3. Characterization of copolymers

The copolymer resins were subject to elemental analysis for carbon, hydrogen, and nitrogen on Elemental Vario EL III Carlo Erba 1108 Elemental Analyzers at Sophisticated Analytical Instrumentation Facility, Panjab University, Chandigarh. The viscosities were determined using a Tuan–Fuoss [10] viscometer fabricated in our research laboratory at six different concentrations ranging from 0.3 to 0.05 wt % of resin in dimethylformamide (DMF) at 30°C. Intrinsic viscosity $[\eta]$ was calculated by the Huggins's Eq. (1) and the Kraemmer's Eq. (2), similar to earlier coworkers [11,12].

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2 C \quad (1)$$

$$\ln \eta_r/C = [\eta] - K_2[\eta]^2 C \quad (2)$$

The number-average molecular weights ($\bar{M}n$) were determined by non-aqueous conductometric titration in DMF, using ethanolic KOH as the titrant. A plot of the specific conductance against the milliequivalents of potassium hydroxide required for the neutralization of 100 gm of copolymer was made.

Electronic absorption spectra of the copolymers in DMSO were recorded on Perkin-Elmer Lambda 15 spectrophotometer. Infrared spectra of 2, 2′-HBBF copolymers were recorded on Perkin- Elmer 983 spectrophotometer in KBr pallets in the wave number region of 4,000–400 cm^{-1}. ^{1}H NMR spectra were recorded on Bruker Avance-II 400 MHz proton NMR spectrometer DMSO-d$_6$ was used as a solvents at Sophisticated Analytical Instrumentation Facility, Panjab University, Chandigarh.

The ion-exchange properties of the 2, 2′-HBBF copolymer resins were determined by the batch equilibrium method [13]. The ion-exchange properties of all the four resins have been studied. However, only the data for the 2, 2′-HBBF-I copolymer resin have been presented in this report.

The copolymer sample (25 mg) was suspended in an electrolyte solution (25 ml) of known concentration. The pH of the suspension was adjusted to the required value by using either 0.1 M HNO_3 or 0.1 M NaOH. The suspension was stirred for a period of 24 h at 25°C. To this suspension, 2 ml of a 0.1 M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24 h and filtered [14,15]. The copolymer was washed, and the filtrate and washings were combined and estimated for the metal ion content by titration against standard ethylene diamine tetraacetic acid. A blank experiment was also carried out in the same manner without adding the polymer sample. The blank was again estimated for the metal ion content. The amount of metal ion taken up by the polymer in the presence of the given electrolyte of known concentrations results from the difference between the blank reading and the reading in the actual experiment. The experiment was repeated in the presence of several electrolytes.

In order to estimate the time required 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 estimated from time to time at 25°C (in presence of 25 ml of 1 M $NaNO_3$ solution). It was observed that under the given conditions, the state of equilibrium was established within 24 h. The rate of metal uptake is expressed as the percentage of the amount of metal ions taken up after certain time in the state of equilibrium.

The distribution of each one of the five metal ions i.e. Fe^{3+}, Cu^{2+}, Co^{2+}, Zn^{2+}, and Ni^{2+} between the polymer phase and the aqueous phase was estimated at 25°C and in the presence of a 1 M $NaNO_3$ solution. The experiments were carried out as described above at different pH values.

The distribution ratio "*D*" is defined by the following relationship:

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

3. Results and discussion

The probable structures of the copolymers have been determined on the basis of elemental analysis and spectral data. Copolymer samples were in powder form having cream color and were soluble in pyridine, DMF, and DMSO. Exact melting points of these samples could not be found out as they started softening at 175°C. These resins were analyzed for carbon, hydrogen, and nitrogen content. Elemental analysis of copolymer resin was found to be in agreement with the calculated values [C-59.30% (Found), 61.34% (Calc), H-4.15% (Found), 4.79% (Calc), N-9.39% (Found), 10.41% (Calc)].

3.1. Molecular weight determination

The number-average molecular weights $\bar{M}n$ were determined by non-aqueous conductometric titrations. Copolymers synthesized from equimolar proportions of 2, 2′-HB and biuret have comparatively higher molecular weights in the series. The use of formaldehyde is larger than stoichiometric proportions which gave low molecular weight copolymers (Fig. 1).

Note: Intrinsic viscosity = 0.065 dl g^{-1}, $K_1 = 2.62$, and $K_2 = -2.10$, $K_1 + K_2 = 0.52$, Mn = 1937.

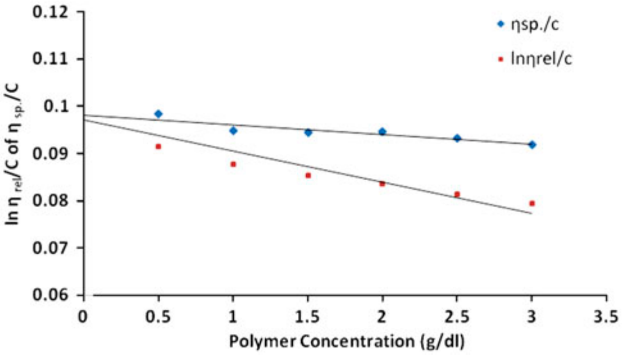

Fig. 2. Viscometric plots of 2, 2´-HBBF copolymer resin.

3.2. Viscometric study

The viscometric measurements were carried out in DMF and reduced viscosity vs. concentration (3.0–0.5 g dl^{-1}) was plotted (Fig. 2) for each set of data. The intrinsic viscosity [η] was determined from the corresponding linear plots. The following equations were used to determine the Huggin and Kraemmer constant, respectively.

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2C \tag{1}$$

$$\ln \eta_r/C = [\eta] - K_2[\eta]^2C \tag{2}$$

In accordance with the above relations, the plots of η_{sp}/C and $\ln \eta_r/C$ against C were linear giving the slopes K_1 and K_2, respectively. Intercepts on the viscosity function axis gave [η] values in both the plots. The calculated values of constants K_1 and K_2 in most of the cases satisfy the relation $K_1 + K_2 = 0.5$ (Huggin). It has been observed that the copolymer having higher $\bar{M}n$ shows higher values of [η].

3.3. Electronic spectra

The UV-visible spectra of all the 2, 2´-HBBF copolymer samples in pure DMF were recorded (Fig. 3). The perusal of the UV-visible spectra of copolymers showed almost similar nature. The spectra of these copolymers exhibit two absorption maxima in the region 210–240 and 310 nm. These observed positions of the absorption bands indicate the presence of the carbonyl group (ketonic) having a carbon–oxygen double bond, which is in conjugation with the aromatic nucleus. The appearance of former band (more intense) can be accounted for the π→π* transition while the later bond (less intense) may be due to the n→π* electronic transition. The shift from the basic value (viz. 240 and 320 nm, respectively) may be due to the conjugation effect, and presence of the phenolic hydroxy group (auxochromes) is responsible for hyperchromic effect i.e. ε_{max} higher values [16,17].

3.4. IR spectra

The IR spectrum of 2, 2´-HBBF copolymer resin is presented in Fig. 4. A broad band containing several

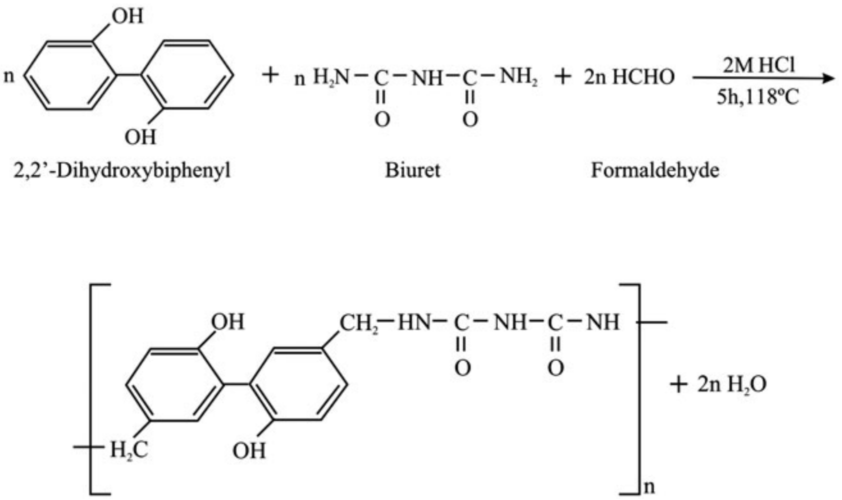

Fig. 1. Proposed reaction for 2, 2´-HBBF terpolymer resin.

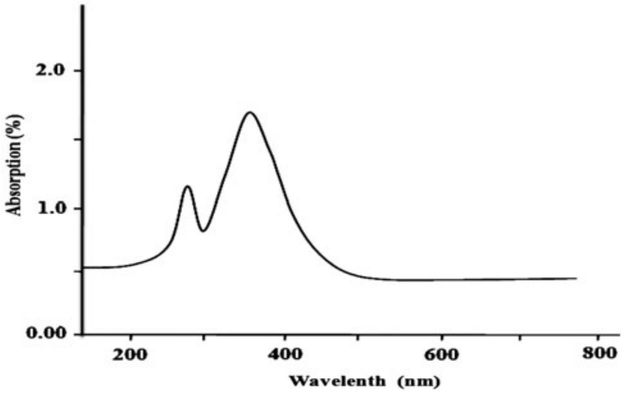

Fig. 3. Absorption spectrum of 2, 2´-HBBF copolymer resin.

inflections appearing in the region 3,296–3,398 cm $^{-1}$ may be assigned to the stretching vibration of –OH of the polymeric-associated phenolic group and the intermolecular bonding between the hydroxyl groups in a polymeric chain [18–20]. The bands at 780–818, 1,223–1,231, and 1,349–1,350 cm^{-1} suggest the presence of methylene bridges. A sharp peak at about 1,529–1,596 cm^{-1} may be ascribed to aromatic skeletal ring breathing modes. The band displayed at 1,640–1,683 cm^{-1} may be due to the stretching vibration of C=O of biuret molecules [17,21]. 1, 2, 3, 5-tetra substitution of the aromatic acid ring is recognized from bands appearing at 910–919, 1,020–1,027, 1,115–1,120, and 1,193–1,200 cm^{-1}, respectively [16,22]. The presence of –NH in biuret is difficult to assign as the region for the stretching vibration of –NH is rendered complex due to the chelated –OH. However, the medium broad band at nearly 2,921–2,936 cm^{-1} may be due to –NH of the biuret unit [21].

3.5. NMR spectra

H^1 NMR spectrum of 2, 2´-HBBF copolymer is shown in Fig. 5 and the NMR spectra of 2, 2´-HBBF copolymer resin was scanned in DMSO-d$_6$ solvent. The weak multiplet signals (unsymmetrical pattern) in the region δ 7.0–8.1 ppm are due to aromatic protons. The methylenic protons of the Ar–CH$_2$–N moiety may be recognized as signals, appearing in the region δ 2.6–3.8 ppm [17,18,23]. The signals in the region δ 6.4–7.4 ppm are attributed to the protons of –NH–bridges [17,18,23]. The signals in the range of δ 3.2–3.6 ppm are attributed to phenolic hydroxyl protons. This significant downfield chemical shift of the protons of the phenolic –OH group clearly indicates intramolecular hydrogen bonding of OH with the carbonyl group present in the biuret moiety [18,23].

3.6. Scanning electron microscopy

Surface analysis has found great use in understanding the surface features of the materials. The morphology of the reported resin sample was investigated by scanning the electron micrographs at different magnifications, which are shown in Fig. 6. It gives the information of surface topology and defect in the structure. The resin appeared to be dark brown in color. The morphology of copolymer resin shows spherulites and fringed model. The spherulites are complex polycrystalline formation having a good

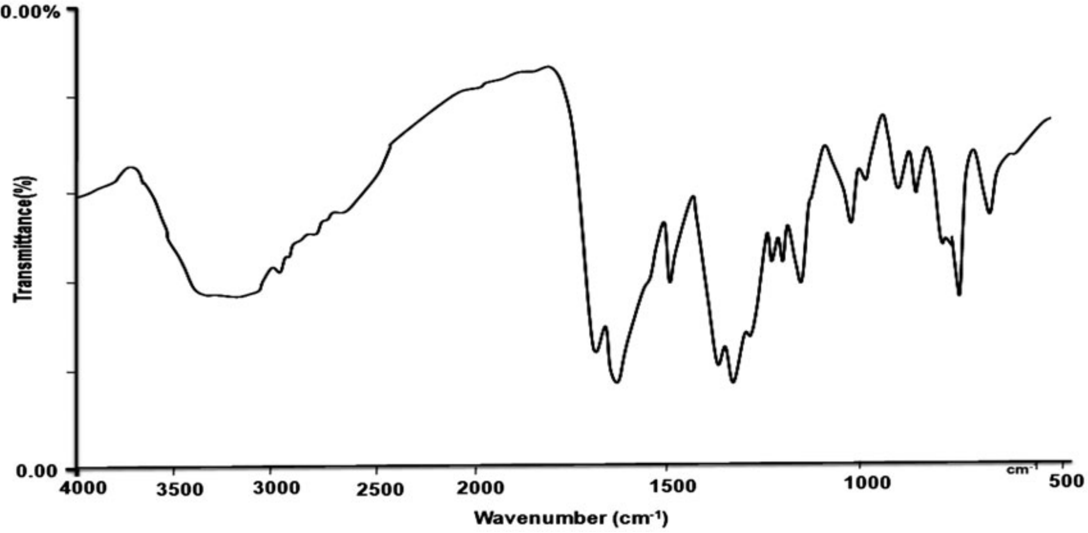

Fig. 4. Infrared spectrum of 2, 2´-HBBF copolymer resin.

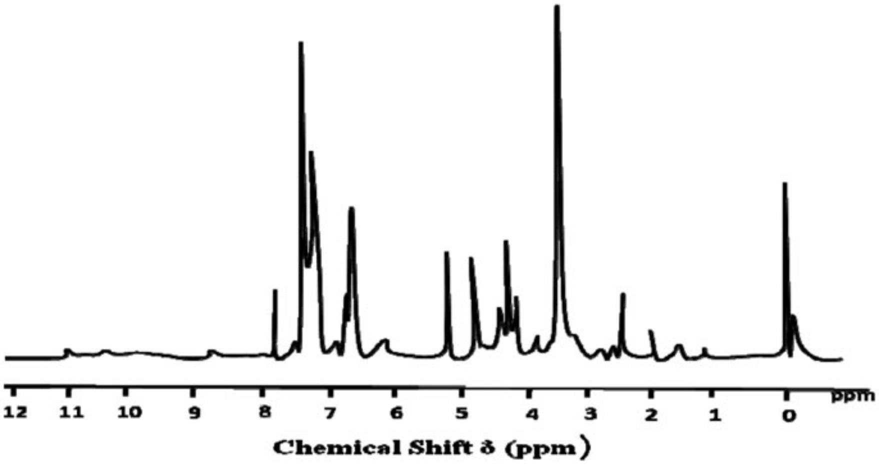

Fig. 5. Proton NMR spectrum of 2, 2´-HBBF copolymer resin.

smooth surface. This indicates the crystalline nature of 2, 2´-HBBF copolymer resin sample. The morphology of resin polymer shows also a fringes model of the crystalline amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer, but the photograph shows the fringed and scatted nature having shallow pits that represent the transition between crystalline and amorphous. When compare to the other resin [24], the 2, 2,-HBBF copolymer resin is more amorphous in nature, hence shows higher metal ion-exchange capacity. The structure of polychelate is shown in Fig. 7.

3.7. Ion-exchange properties

The results of the batch equilibrium study carried out with the copolymer resin sample 2, 2´-HBBF are presented in Figs. 8–13. From this study with five metal ions under limited variation of experimental conditions, certain generalization may be made about the behavior of the copolymer sample.

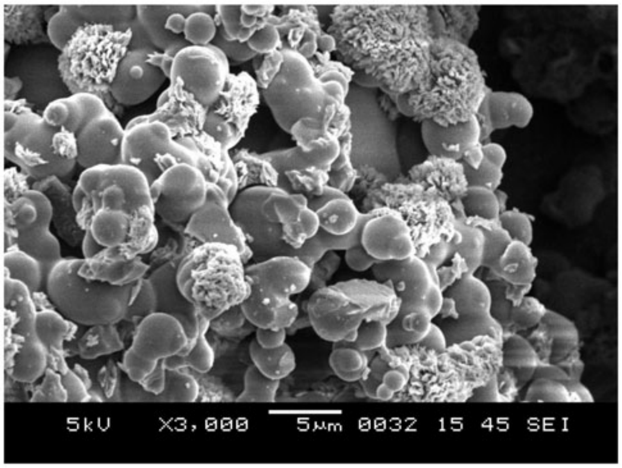

Fig. 6. SEM micrograph of 2, 2´-HBBF copolymer resin.

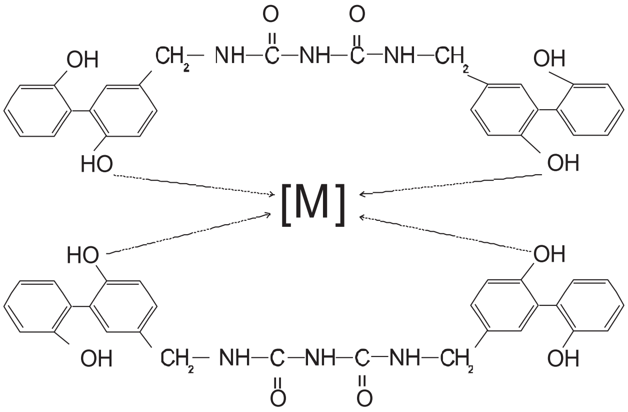

Fig. 7. Structure of polychelate.

With a view to ascertain the influence of various electrolytes on the selectivity of metal ions, the rate of metal uptake and the distribution ratio of metal ions between the copolymer and the solution containing the metal ions, by using batch equilibrium method [24] was investigated. Data of experimental procedure for direct EDTA titration is presented in Table 2.

3.7.1. Effect of electrolytes on metal uptake

We examined the effect of NO_3^-, Cl^-, SO_4^{2-}, and ClO_4^- at various concentrations on the equilibrium of metal–resin interaction of constant pH. Figs. 8–11 show that the amount of metal ions taken up by a given

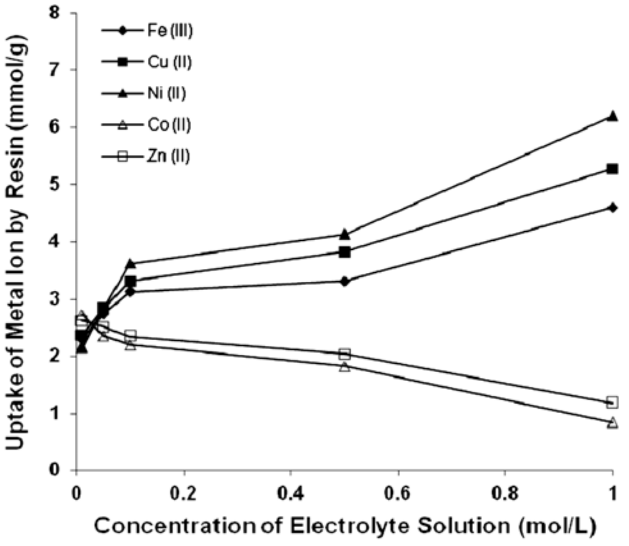

Fig. 8. Uptake of several metal ions by 2, 2′-HBBF copolymer resin at five different concentrations of $NaNO_3$ electrolyte solution.

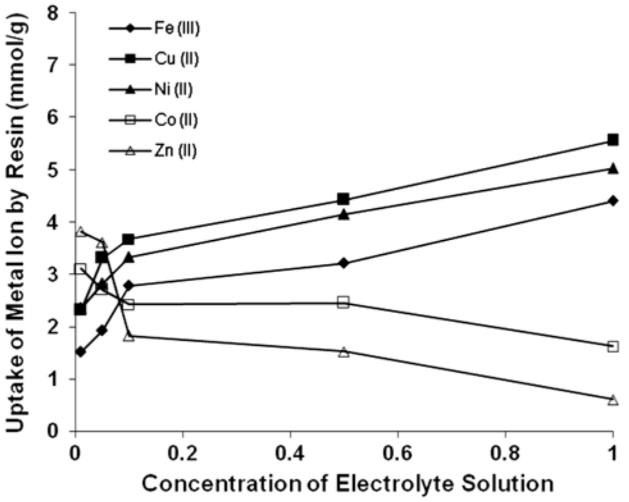

Fig. 9. Uptake of several metal ions by 2, 2′-HBBF copolymer resin at five different concentrations of NaCl electrolyte solution.

amount of copolymer resins depends on the nature and concentration of the electrolyte present in the solution. Generally, as the concentration of the electrolyte increases, ionization decreases and the number of ligands decreases in the solution, which forms the complex with less metal ions, and more ions are available for adsorption. The variable metal ions uptake capacity of 2, 2′-HBBF copolymer resins may be due to the strong and weak complex formation between electrolyte ligands and metal ions [25,26].

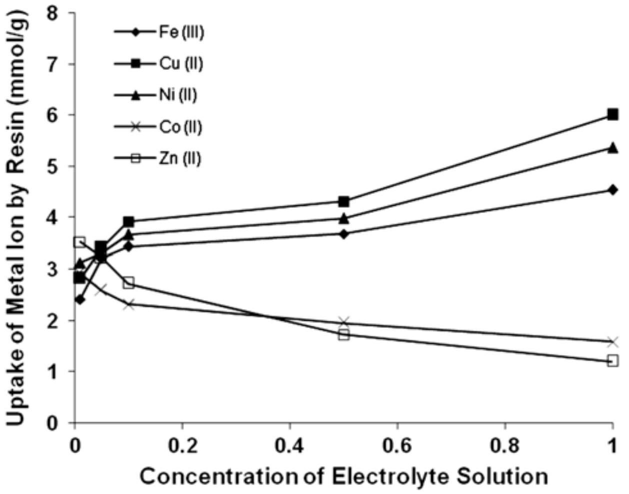

Fig. 10. Uptake of several metal ions by 2, 2′-HBBF copolymer resin at five different concentrations of $NaClO_4$ electrolyte solution.

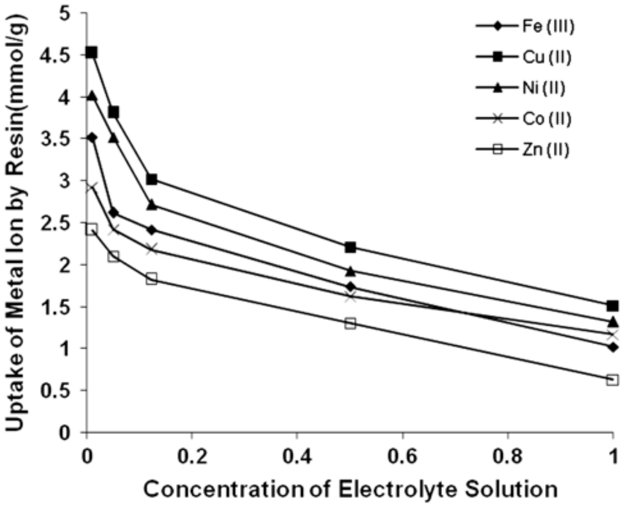

Fig. 11. Uptake of several metal ions by 2, 2′-HBBF copolymer resin at five different concentrations of Na_2SO_4 electrolyte solution.

$$\begin{array}{l}\text{Electrolyte solution} + \text{metal} \\ \quad\text{ion solution} + \text{polymer}\end{array} \rightarrow \begin{array}{l}\text{electrolyte ligand} - \text{metal} \\ \text{ion chelates} + \text{Polymer} - \\ \text{metal ion chelates}\end{array}$$

If the electrolyte ligand–metal ion complex is weaker than the polymer–metal ion chelates, the polymer can easily break the electrolyte ligand–metal complex which makes the more number of metal ions free. As more metal ions can form complex with polymer, the uptake of metal ion is more. However, if this comp polymer–metal ion chelates, more metal ions

Table 2
Data of the experimental procedure for direct EDTA titration

Metal ion	Buffer used	Indicator used	Color change
Fe(III)	Dil.HNO_3/dil.NaOH	Variamine blue	Blue–Yellow
Cu(II)	Dil.HNO_3/dil.NaOH	Fast sulfon black	Purple–Green
Ni(II)	Aq.NH_3/NH_4Cl	Murexite	Yellow–Violet
Zn(II)	Aq.NH_3/NH_4Cl	Salochrom	Wine Red–Blue
Co(II)	Hexamine	Xylenol orange	Red–Yellow

form strong complex with electrolyte ligand which make metal uptake capacity lower by polymer.

In the presence of perchlorate, chloride, and nitrate ions, the uptake of Fe(III), Cu(II), and Ni(II) ions increases with increasing concentration of the electrolytes, whereas in the presence of sulfate ions the amount of the above-mentioned ions taken up by the copolymer decreases with increasing concentration of the electrolyte. Moreover, the uptake of Co(II) and Zn(II) ions increases with decreasing concentration of the chloride, nitrate, perchlorate, and sulfate ions. This may be explained based on the stability constants of the complexes with those of metal ions. The stability of the complexes depends on the charge of metal ions and nature of ligands. Among all the above four ligands, SO_4^{2-} is a strong ligand, due to the presence of more number of electrons for donation to the metal ion during complex formation, which forms strong and stable complexes with all the five metal ions under study. Therefore, overall metal uptake is less in sodium sulfate electrolyte and on increasing the concentration of SO_4^{2-} ions in solution more and more number of metal ions can form complex with SO_4^{2-} ligands, remaining less number of ions are left available for the uptake of polymer, decreasing the metal uptake capacity in SO_4^{2-}- electrolyte. The ligands NO_3^-, Cl^-, and ClO_4^- may form weak complexes with Fe^{3+}, Cu^{2+}, and Ni^{2+} metal ions as pH may be lower, therefore may increase the metal uptake capacity of the polymer. While the ligands NO_3^-, Cl^-, and ClO_4^- may form strong complexes with Co^{2+} and Zn^{2+} at somewhat higher pH, therefore if the concentration of these ligands increases more complex formation might be possible, which decreases the metal uptake capacity of the copolymer.

When the concentration of electrolyte is zero, there is no negative ion (ligand) in metal ion solutions and there is no complex formation. All metal ions may be available for the adsorption on the polymer. Hence, show maximum uptake of ions by 2, 2´-HBBF copolymer resins. As there is no complex formation, there is no problem of strong and weak nature. Hence, all metal ions show comparably high uptake on the polymer at zero concentration. Zero concentration of the electrolyte may not affect the metal uptake capacity of the polymer.

After adsorption when the solution is filtered and the polymer is shaking with dilute HCl, there is an exchange of metal ion and H^+ ions; metal ions enter in the acid solution at H^+ ions adsorbed on the polymer, this phenomena is known desorption, or regeneration of polymer. The regenerated polymer can again be used for re-adsorption by shaking it with metal ion solution. Adsorption and re-adsorption depend on the concentration of metal ions but desorption does not.

3.7.2. 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. Fig. 12 shows the dependence of the rate of metal ion uptake on the nature of the metal. 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 metal ions at a given stage depends on the nature of the metal ion under given conditions. It is found that Fe^{3+} ions require about 3 h for the establishment of the equilibrium, whereas Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} ions required about 5 h. Thus, the rate of metal ion uptake follows the order $Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} = Zn^{2+}$ for 2, 2´-HBBF copolymer [25–28].

3.7.3. Distribution ratios of metal ion at different pH

The effect of pH on the amount of metal ions distributed between two phases can be explained by the result given in Fig. 13. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the 2, 2´-HBBF copolymer increases with increasing pH of the medium [13,25–28]. The magnitude of increase, however, is different for different metal cations. The 2, 2´-HBBF copolymer resin takes up Fe^{3+} ion more selectively

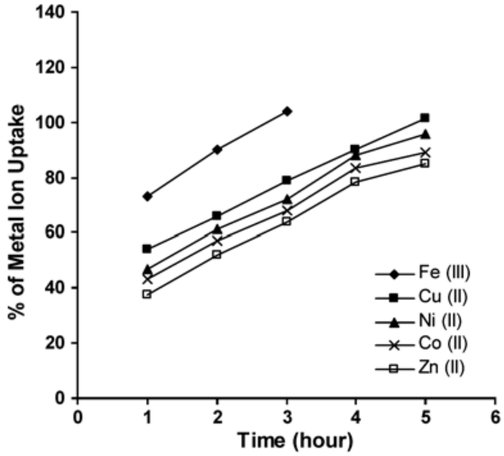

Fig. 12. Comparison of the metal ion (M) uptake by 2, 2´-HBBF copolymer resin.

than any other metal ions under study. The order of distribution ratio of the metal ions measured in the pH range 2.5–6.5 is found to be $Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$. 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 ions [13,29–34]. For example, the result suggests an optimum pH of 6.0 for the separation of Co^{2+} and Ni^{2+} with the distribution ratio "*D*" as 470.1 and 1,324.1 for Co^{2+} and Ni^{2+}, respectively, using the 2, 2´-HBBF copolymer resin for ion exchang. Similarly, for the separation of Cu^{2+} and Fe^{3+} the optimum pH is 2.5, at which the distribution ratio "*D*" for Cu^{2+} is 66.1 and that for Fe^{3+} is 522.1. The lowering in the distribution ratio of Fe^{3+} was found to be small and, hence, efficient separation could be achieved.

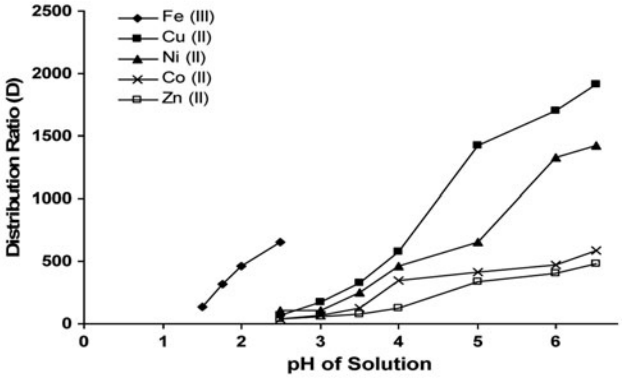

Fig. 13. Distribution ratio *D* of various metal ions as function of the pH by 2, 2´-HBBF copolymer resin.

3.8. Reusability of the resin

The major benefit of the prepared resin is their reusability after the exchange process. The resin, once used, can be recovered back to its original form by desorption of the chelated metal ions using concentrated nitric acid. The metal-free resin can be reused after repeated washing with water. The recycling of the purified resin with the addition of chosen metal ion solution results in the uptake of almost the same amount as it was initially adsorbed. The retention of metal ion uptake capacity even after few cycles of repeated exchanges, suggests that the resin can be reused as a cation exchanger.

4. Conclusions

A copolymer 2, 2´-HBBF based on the condensation reaction of 2, 2´-dihydroxybiphenyl and biuret with formaldehyde in the presence of acid catalyst has been prepared. The spectral characterizations on the basis of spectral analysis of the copolymer confirm the linear structure. The semi crystalline-amorphous nature of the 2, 2´-HBBF copolymer resin was confirmed by scanning electron microscopy (SEM) studies and reveals that the copolymer can act as an effective ion exchanger for various trivalent and divalent metal ions such as Fe^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+} ions. This study of ion-exchange reveals that 2, 2´-HBBF copolymer resin is an eco-friendly cation exchange resin and can be used for the removal of hazardous metal ions from the environment for the purification of industrial waste solution, and for purification and desalination of water. Thus, 2, 2´-HBBF copolymer has significant applications as an ion-exchange resin in waste water treatment, metal recovery, and for the identification of specific metal ions.

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