Arabian Journal of Chemistry (2016) 9, S648–S658

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

An eco-friendly synthesis, characterization, morphology and ion exchange properties of terpolymer resin derived from *p*-hydroxybenzaldehyde

Deepti B. Patle [a], **Wasudeo B. Gurnule** [b,*]

[a] *Department of Chemistry, Laxminarayan Institute of Technology, Rashtrasant Tukdoji Maharaj, Nagpur University, Nagpur 440010, India*
[b] *Department of Chemistry, Kamla Nehru College, Sakkardara, Nagpur 440 009, India*

Received 3 April 2011; accepted 11 July 2011
Available online 6 August 2011

KEYWORDS

Synthesis;
Characterization;
Metal ion uptake;
Distribution coefficient;
Resin;
Batch equilibrium

Abstract A novel chelating terpolymer resin has been synthesized through the terpolymerization of *p*-hydroxybenzaldehyde and biuret with formaldehyde (*p*-HBBF) in 1:1:2 mol ratio using hydrochloric acid as a reaction medium by condensation technique. The synthesized terpolymer resin was characterized by elemental analysis, FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy. On basis of the spectral studies, the structure of the terpolymer resin was proposed. The physico-chemical parameters have been evaluated for the terpolymer resin. Non-aqueous conductometric titration was used to determine the average molecular weight and polydispersity of the *p*-HBBF terpolymer resin and the intrinsic viscosity was also determined. The semicrystalline nature of the synthesized terpolymer was established by scanning electron microscopy (SEM). Terpolymer (*p*-HBBF) synthesized is proved to be selective chelating ion exchange terpolymer resin for certain metals. Chelating ion exchange properties of this polymer was studied for Fe^{3+}, Cu^{2+}, Cd^{2+}, Zn^{2+}· Ni^{2+} and Pb^{2+} ions. A batch equilibrium method was employed in the study of the selectivity of the distribution of a given metal ions between the polymer sample and a solution containing the metal ion. The morphology of the terpolymers was studied by scanning electron microscopy, showing amorphous nature of the resins therefore can be used as a selective ion-exchanger for certain metal ions.

1. Introduction

Ion exchangers have been used commercially on a worldwide basis for almost a century due to diverse applications in many fields such as water softening and deionization (Singh and Saraf, 2009), extraction of uranium (Michael Pratik et al., 2007), isolation and purification of antibiotics (Katkamwar et al., 2009), in hydrometallurgy for separation and purifica-

---

[*] Corresponding author. Tel.: +91 9096672499, 0712 2747853; fax: +91 0712 2747853.
E-mail address: wbgurnule@yahoo.co.in (W.B. Gurnule).

Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2011.07.013
1878-5352

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

tion of waste water treatment (Rong Li et al., 2001) and pollution control (Burkanudeen and Karunakaran, 2002). The presence of heavy metals in environment is a cause of concern due to their acute and long-term toxicity. Lead and mercury are the major hazardous metals present in the environmental wastewater. Thus, removal of trace heavy metals from the environmental area have become of increasing interest and there is a strong need for a reliable analytical procedure that can be applied for the removal and determination of these metals at very low concentrations (Patel et al., 2007).

Since long, considerable interest has been developed in the synthesis of ion-exchange resin having selective properties and containing selective functional groups. A cross linked styrene/maleic acid chelating matrix has been reported for its higher ability to remove the metal ions such as Cr, Fe, Ni, Cu, and Pb (Patel et al., 2008). Acidic polymers such as poly (methacrylic acid) and poly (acrylic acid) have the tendency to remove the metal ions like Ag^+, Cu^{2+}, Co^{2+}, Ni^{2+} and Cr^{3+} at different pH and polymermetal ion ratios (Patel et al., 2004). Salicylic acid and melamine with formaldehyde terpolymer was found to have higher selectivity for Fe^{3+}, $Cu^{2+}$and Ni^{2+} ions than for Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions (Shah Bhavna et al., 2008). Resin synthesized by the condensation of a mixture of phenol or hydroxybenzoic acid with formaldehyde and various amines have also been reported (Michael et al., 2007). The metal ion uptake increases with increasing molar proportions of the terpolymer synthesized from substituted benzoic acid (Shah Bhavna et al., 2006). *o*-Nitrophenol and thiourea with paraformaldehyde terpolymer were identified as excellent cation exchangers for Zn^{2+} and Co^{2+} ions (Silverstein and Webster, 1998). Salicylic acid–formaldehyde–resorcinol resin has been synthesized and explored its use for the removal and separation of heavy metal ions from their binary mixtures (Singru et al., 2008). 8-hydroxyquinoline-formaldehyde-catechol terpolymer was found to have lower moisture content indicating the high degree of crosslinking in the resin (Aswar and Munshi, 1995). Phenolic schiff bases derived from hydroxybenzaldehydes and 4,4′diaminodiphenyl ether have been reported as better chelating resin for Cu(II) leading to its separation from a mixture of Cu(II) and Ni(II) ions (Gurnule et al., 2003).

Recently, our research group synthesized a chelating terpolymer resin using an eco-friendly technique and reported for its good binding capacity for Fe^{2+} and Cu^{2+} ions (Hiwase et al., 2010). In this article, we describe the synthesis of terpolymer derived from *p*-hydroxybenzaldehyde and biuret with formaldehyde (*p*-HBBF). The synthesized terpolymer resin has been characterized by elemental analysis, spectral studies (UV–Visible, FTIR ^{13}C NMR and ^{1}H NMR) and viscometric measurement. The surface feature of the terpolymer resin was established by SEM. The metal ion uptake capacity of the terpolymer resin by batch equilibrium method for Pb^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+} and Fe^{3+} ions in different electrolytes, pH ranges and time intervals were also studied and reported for the first time. Some commercially available ion-exchange resins are given in Table 1.

Structural studies of terpolymer with the aid of different physico-chemical methods have received wide attention because of their utility as high temperature materials, ion exchangers, semiconductors etc. *p*-Hydroxybenzaldehyde is good for medicine, spices and the LCD intermediates. It is also used in the production of antibacterial synergist TMP (trimethoprim), Amoxycillin, hydroxyl ammonia benzyl cephaloridine, artificial Tianma, Rhododend, Bezafibrate, esmolol (Fennel is used in the production of spices, vanillin, and ethyl vanillin and raspberry ketone). Like that urea is a versatile material for making whiteboard, floors, tiles, fire retardant fabrics and for more industrial uses of biuret.

The adsorption behavior of these metal ions are based on the affinity differences toward the chelating resins as functions of pH, electrolyte concentrations and shaking time. The terpolymer resins under investigations 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 o-APUF terpolymer resin was also reported for specific metal ions. Pollution by toxic heavy metals due to their toxicities in relatively low concentration and tendency to bioaccumulate in the ecosystem, agriculture and human body have received wide spread attention in recent years. Various approaches such as ion-exchange, reverse osmosis, electro dialysis, precipitation and adsorption techniques have been developed for the removal and recovery of the metal ions from sewage and industrial wastewater. Among these techniques, many research works have focused on metal ions removal by adsorption on chelating polymers, because they are reusable, easily separable, and with higher adsorption capacity and selectivity having physical and chemical stabilities.

2. Materials and method

2.1. Chemicals and reagents

The important chemicals (starting materials) like *p*-hydroxybenzaldehyde (Across Organic, Fisher Scientific, India), biuret (Across Organic, Fisher Scientific, India) and formaldehyde

(S.D. Fine Chemicals) used in the preparation of new *p*-HBBF terpolymer resin were procured from the market and were of chemically pure grade, and wherever necessary the purity was tested and confirmed by thin layer chromatography.

2.2. Synthesis of p-HBBF terpolymer resin

The *p*-HBBF terpolymer resin was synthesized by the condensation polymerization of *p*-hydroxybenzaldehyde (0.1 mol) and biuret (0.1 mol) with formaldehyde (0.2 mol) in hydrochloric acid medium at 126 ± 2 °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 washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove excess of *p*-hydroxybenzaldehyde – formaldehyde terpolymer, which might be present along with the *p*-HBBF terpolymer. The dried resin was further purified by dissolving in 8% NaOH and regenerated in 1:1 (v/v) HCl/water. The purified terpolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in a vacuum over silica gel. The yields of these terpolymer resins were found to be 86% and the melting point was found to be in the range of 430–450 K. The sieved resin was used for further characterization. The reaction sequence of the synthesis of *p*-HBBF terpolymer resin is shown in Scheme 1 and the composition determination of terpolymer was examined by elemental analysis. Since *p*-HBBF terpolymer contains phenolic (–OH) group and aldehydic (–CHO), it plays a key role in the ion exchange phenomenon, because of its higher tendency of capturing metal ions. Thus *p*-HBBF terpolymer is a synthetic terpolymer resin and has immense applications as an ion exchange resin in waste water treatment, metal recovery and for the identification of specific metal ions.

2.3. Characterization of terpolymer resin

2.3.1. Physicochemical and Elemental Analysis

The terpolymer resin was subject to micro analysis for C, H and N on an Elementar Vario EL III Carlo Erba 1108 elemental analyzer. The number average molecular weight $\overline{M}n$ 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 milliequivalants of potassium hydroxide required for neutralization of 100 g of terpolymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot the first break and the last break were noted. The calculation of $\overline{M}n$ by this method is based on the following consideration (Rahangdale et al., 2009): (1) the first break corresponds to the stage at which the first acidic phenolic hydroxyl group is neutralized, and (2) the last break observed beyond the first break represents the stage at which phenolic hydroxyl group of all the repeating units are neutralized. On the basis of the average degree of polymerization, ($\overline{DP}$) the average molecular weight has to be determined by the following Eq. (1)...

$$\overline{\mathrm{DP}} = \frac{\text{(Total milliquivalents of base required for complete neutralization)}}{\text{(Milliquivalents of base required for smallest interval)}} \tag{1}$$

$$\overline{M}n = \mathrm{DP} \times \text{molecular weight of the repeating unit}$$

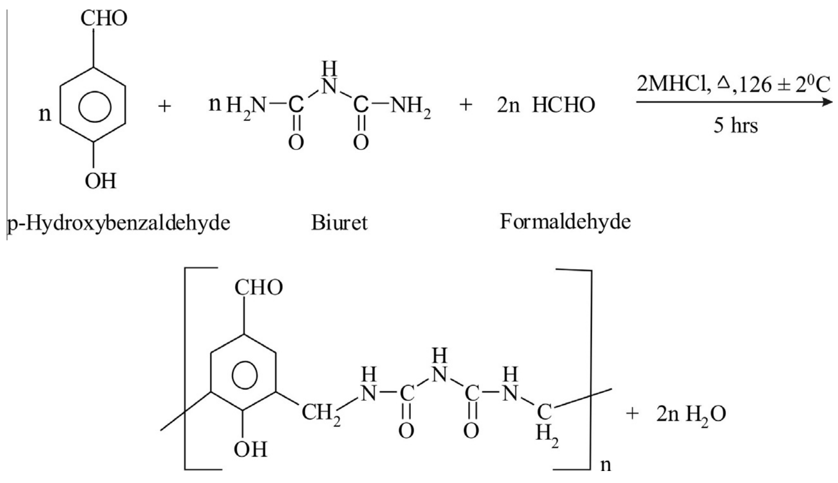
The intrinsic viscosity was determined using a Tuan-Fuoss viscometer (Atia et al., 2005) at six different concentrations ranging from 0.3 to 0.05 wt.% of resin in DMSO at 30 °C. Intrinsic viscosity (η) was calculated by the Huggin's Eq. (2) (Joshi et al., 2006) and the Kraemer's Eq. (3) (Prabhakaran and Subramanian, 2003).

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

$$\mathrm{In}\ \eta_{rel}/C = [\eta] - K_2[\eta]^2.\ C \tag{3}$$

2.3.2. Spectral and surface analysis

Electronic (UV–visible) absorption spectra of the terpolymer in DMSO was recorded with a double beam spectrophotometer fitted with an automatic pen chart recorder on themosensitive paper in the range of 200–850 nm at L.I.T. RTM, Nagpur University Nagpur. Infrared spectra of *p*-HBBF terpolymer resin were recorded in najol mull with a Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pallets in the range of 4000–500 cm^{-1} at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Proton NMR and



Scheme 1 Synthesis and suggested structure of *p*-HBBF terpolymer resin.

^{13}C NMR spectra were recorded with Bruker Adanve-II 400 NMR spectrophotometer using DMSO-d_6 as a solvent, at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. The surface analysis was performed using scanning electron microscope at different magnifications. SEM has been scanned by a JEOL JSM-6380A Analytical Scanning Electron Microscope at VNIT, Nagpur.

The results of elemental analysis and spectral analysis determine that the *p*-HBBF terpolymer is composed by *p*-hydroxybenzaldehyde, biuret and formaldehyde.

2.4. Ion-exchange properties

The ion-exchange properties of the *p*-HBBF terpolymer resin were determined by the batch equilibrium method. We studied the influence of various electrolytes, the rate of metal uptake and distribution of metal ions between the terpolymer and solutions.

2.4.1. Determination of metal uptake in the presence of electrolytes of different concentrations

The terpolymer 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 N HCl or 0.1 N NaOH. The suspension was stirred for a period of 24 h at 25 °C. To this suspension was added 2 ml of a 0.1 M solution of metal ion and the pH was adjusted to the required value. The mixture was again stirred at 25 °C for 24 h and filtered (Zalloum and Mubarak, 2008; Patle Deepti et al., 2011). 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 (Patle Deepti et al., 2010). The experiment was repeated in the presence of other three electrolytes such as NaCl, $NaClO_4$ and Na_2SO_4.

2.4.2. Evaluation of the rate of metal ion uptake

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 resin was determined from time to time at 25 °C (in the presence of 25 ml of 1 M $NaNO_3$ 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 amount of metal ions taken up after certain time related to that at the state of equilibrium.

2.4.3. Evaluation of the distribution of metal ions at different pH

The distribution of each one of the six metal ions i.e. Fe(III), Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II) between the polymer phase and the aqueous phase was determined at 25 °C and in the presence of a 1 M $NaNO_3$ solution. The experiment was carried out as described earlier at different pH values. The distribution ratio "D" is defined by the following relationship

$$\mathbf{D} = \frac{\{\text{Wt. (in mg) of metal ions taken up by1 gm of terpolymer}\}}{\{\text{Wt. (in mg) of metal ions present in 1 ml of terpolymer}\}}$$

3. Results and discussion

3.1. Physicochemical and elemental analysis

The resin sample was light pink in color, insoluble in commonly used organic solvents, partially soluble in dimethyl formamide, tetrahydrofuran, pyridine and concentrated H_2SO_4 but it was completely soluble in dimethyl sulfoxide (DMSO). The melting point of this terpolymer was determined by using electrically heated melting point apparatus and is found to be in the range of 430–450 K. The resin was analyzed for carbon, hydrogen and nitrogen content. Based on the analytical data, the empirical formula of the terpolymer resin is found to be $C_{11}H_{14}N_3O_5$, which is in good agreement with the calculated values of C, H, N and O. The resin was analyzed for carbon, hydrogen, and nitrogen content C = 49.25% (Cal) and 49.11% (F); H = 5.26% (Cal) and 5.02% (F); N = 15.66% (Cal) and 15.26% (F); O = 29.82% (Cal) and 29.11% (F).

The number average molecular weight ($\overline{Mn}$) could be obtained by multiplying the $\overline{DP}$ by the formula weight of the repeating unit (Patel and Manavalan, 1984; Vyas and Kapadia, 1980). The calculated molecular weight for *p*-HBBF resin is 600320.

Viscometric measurement was carried out in DMSO at 30 °C. *p*-HBBF resin showed normal behavior. The intrinsic viscosity was determined by the Huggin's Eq. (2) and Kraemer's, Eq. (3) which is 0.26 and 0.28, respectively. In accordance with the above relations, the plot of ηsp/c and ηrel/c against C was linear giving as slopes K_1 and K_2 (0.54), respectively. The intercept on the axis of viscosity function gave the (η) value in both the plots (Vyas and Kapadia, 1981; Amin and Kapadia, 1997). The values of (η) obtained from both relations were in good agreement with each other.

3.2. Spectral and surface studies

The UV–visible spectrum (Fig. 1) of *p*-HBBF terpolymer sample in pure DMSO was recorded in the region 190–800 nm.

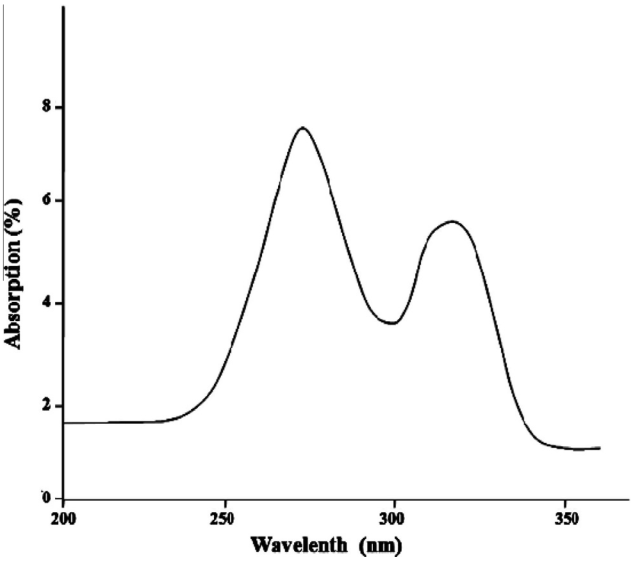


Figure 1 Electronic spectra of *p*-HBBF terpolymer resin.

The *p*-HBBF terpolymer sample displayed two characteristic broad bands at 260 and 315 nm (Bavanker et al., 1999; RM, 1969). These observed position for absorption bands indicate the presence of a carbonyl (>C═O) group having a carbon oxygen double bond which is in conjugation with the aromatic nucleus. The later band can be accounted for $n \rightarrow \pi^*$ transition while the former band may be due to $\pi \rightarrow \pi^*$ transition. The bathochromic shift (shift toward longer wavelength) from the basic value of the C═O group *viz*. 310 and 240 nm, respectively, may be due to the combined effect of conjugation and phenolic hydroxyl group (auxochrome).

The IR-spectra of *p*-HBBF terpolymer is presented in Fig. 2. The IR spectra revealed that the terpolymer gives rise to nearly similar pattern of spectra (Table 2). A band which appeared in the region 3337–3316 cm^{-1} may be assigned to the stretching vibration of the phenolic hydroxyl groups exhibiting intermolecular hydrogen bonding. The presence of weak peak at 2878–2878 cm^{-1} describes the –NH– in biuret moiety may be ascribed in the co polymeric chain (Azarudeen Raja et al., 2009; Kalsi, 1995). The presence of methyl and methylene vibrations at 2950–2846 cm^{-1} gives sharp and weak peaks. The sharp band displayed at 1631–1628 cm^{-1} may be due to the stretching vibration of carbonyl group of both, ketonic as well as biuret moiety. The sharp and weak bonds obtained at 1381–1380 cm^{-1} suggest the presence of $–CH_2–$ methylene bridges in the terpolymer chain. The presence of 1, 3, 4, and 5-pentasubstitution of aromatic ring is recognized from the weak bond appearing at 898–897 cm^{-1}, respectively.

^1H NMR spectrum of *p*-HBBF terpolymer is shown in Fig. 3 and proton NMR data are specified in Table 3 (Roy et al., 2004; Mondal and Das, 2003; Mane et al., 2009). ^1H NMR spectra of *p*-HBBF terpolymer show weak multiplicity signals (unsymmetrical pattern) in the region 7.61–7.74 (δ) ppm which may be due to the aromatic protons. The weak multiply signals appearing at 5.21–5.32 (δ) ppm may due to the amido $–CH_2$ –NH–CO linkage. A signal appeared in the region 4.89–4.92 (δ) ppm may be due to proton of methelenic bridges ($Ar–CH_2–N$) of polymer chain. A weak signal which appeared in the region of 2.12–2.57 (δ) ppm may be due to the Ar–CHO group. The signal in the range of 3.40–3.60 (δ) ppm is attributed to phenolic –OH proton.

A ^{13}C NMR spectrum of *p*-HBBF terpolymer resin is shown in Fig. 4. The peaks which appeared at 122.14, 128.71, 129.49, 132.88 and 154.94 ppm may be corresponded to carbons present in aromatic benzophenone ring. The peak which appeared at 163.11 ppm may be corresponding to the carbonyl group of the biuret moiety. The medium peak which appeared at 116.33 ppm may confirm the presence of the –C–NH group of terpolymer resin. The peak which appeared at 66.56 ppm may be due to the presence of the –C–OH group in the aromatic benzophenone group. The peaks which appeared at 39.91 to 40.27 ppm may be due to the $–CH_2$ – bridge

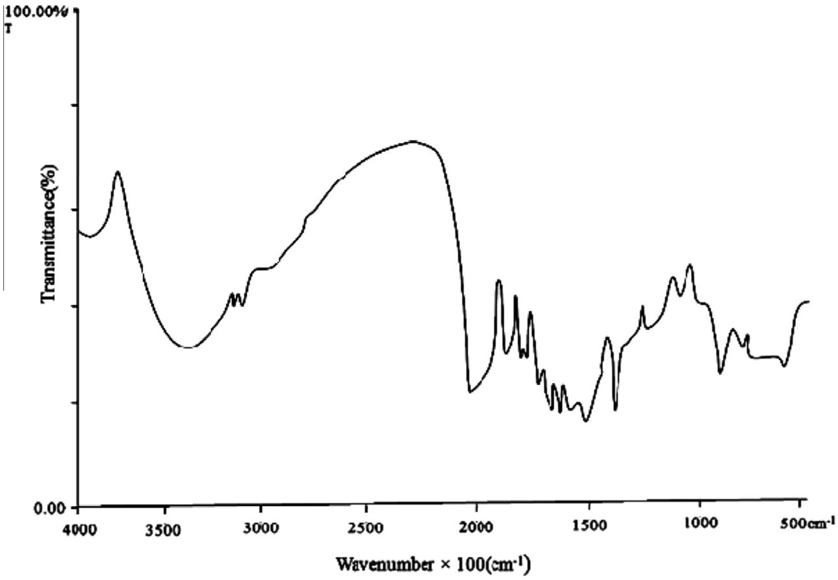


Figure 2 Infrared spectrum of *p*-HBBF terpolymer resin.

Table 2 FT-IR frequencies of *p*-HBBF terpolymer resin.

Assignment	Expected wave number (cm^{-1})	Observed wave number (cm^{-1}) *p*-HBBF
–OH (phenolic)	3100–3500	3335.5 b, st
>C═O(ketonic and biuret)	1630–1680	1631.4 sh, st
>NH (amido)	1533–3000	2878.9 sh, w
Aromatic ring	1445–1485	1475.7 sh, w
$>CH_2$ (methylene bridges)	1250–1340	1380.3 sh, m
1,2,3,4,5 substitution in benzene skeleton	857.9	897.7 sh, w

Sh = sharp; b = broad; st = strong; m = medium; w = weak.

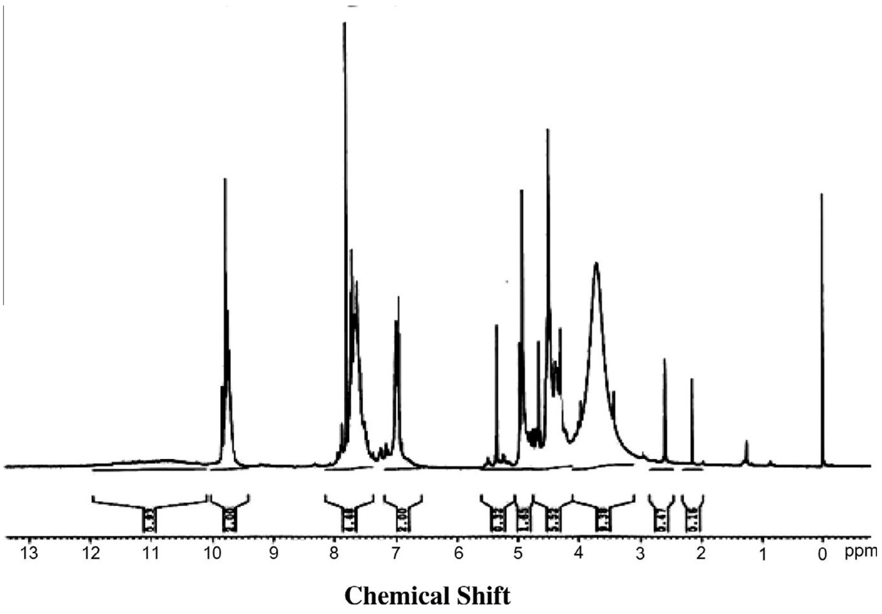


Figure 3 Proton NMR spectra of *p*-HBBF terpolymer resin.

Table 3 ^{1}H NMR spectral data of *p*-HBBF terpolymer resin in DMSO-d$_6$.

Chemical shift (δ) ppm of copolymer *p*-HBBF	Nature of proton assigned
7.61–7.74	Aromatic proton of Ar–H
3.40–3.60	Proton of Ar–OH
5.21–5.32	Amido proton of –CH$_2$–NH–CO– linkage
4.89–4.92	Methylene proton of Ar–CH$_2$–NH moiety
2.12–2.57	Proton of Ar–CHO

in terpolymer resin. All these peaks confirmed that the 4-HBPBF terpolymer resin must have linear structure.

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 electron micrographs at different magnification, which is shown in Fig. 5. It gives the information of surface topology and defect in the structure. The resin appeared to be dark drawn in color. The morphology of the polymer resin is shown by the spherule and fringed model. The spherules are complex polycrystalline formations having a good and smooth surface. This indicates the crystalline nature of *p*-HBBF terpolymer resin sample. The morphology of resin polymer shows also a fringe 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 scattered nature having shallow pits represent the transition between crystalline and amorphous. The resin exhibits more amorphous characters with closed packed surface having deep pits, which is shown Fig. 5. Due to the deep pits, resin exhibits higher exchange capacity for Pb(II) ions (as well as other many metal ions). This could be the reason of bigger nitrated Pd(II) ions, which can easily penetrate into the deep pits. Thus by SEM micrographs, morphology of the resin shows the transition between crystalline and amorphous nature. When compared to the other resin (Gupta et al., 2008; Kaur, 2009), the *p*-HBBF terpolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.

3.3. Ion-exchange properties

With a view to ascertain the selectivity of the terpolymer resin for the selected metal ions, we have studied, 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 terpolymer and solution containing the metal ions, are analyzed by using the batch equilibrium method (Rahangdale et al., 2008; Tarase et al., 2008). Data of experimental procedure for direct EDTA titration is presented in Table 4.

The *p*-HBBF terpolymer (Scheme 1) shows that the group –OH and –NH contain lone pair of electrons, which can be donated to the metal ion during complex formation. Hence it shows chelating behavior. When the polymer is suspended in metal ion solution, the chelating tendency of terpolymer forms the cyclic complex with the metal ion, which absorbs the metal ion from the solution to the surface of the polymer. This mechanism of adsorption of metal ion by polymer ligands is known as metal uptake of polymer. As the metal uptake concentration of metal ion in solution decreases, this can be determined by titration with standard EDTA solution. The metal uptake capacity of polymer is different for different metal ion, is also known as selectivity of polymer toward the uptake of metal ion. The metal uptake of terpolymer depends on three variables, concentration of electrolyte solution, shaking time and pH of the solution. The chelating behavior of *p*-HBBF terpolymer was studied with these three variables by keeping two variable constant at each time.

$$\text{Polymer} + \text{ metal ion solution} + \text{ shaking} \rightarrow \text{polymer} - \text{metal ion chelate}$$

(Metal uptake capacity of polymer depends on stability of polymer – metal ion chelate).

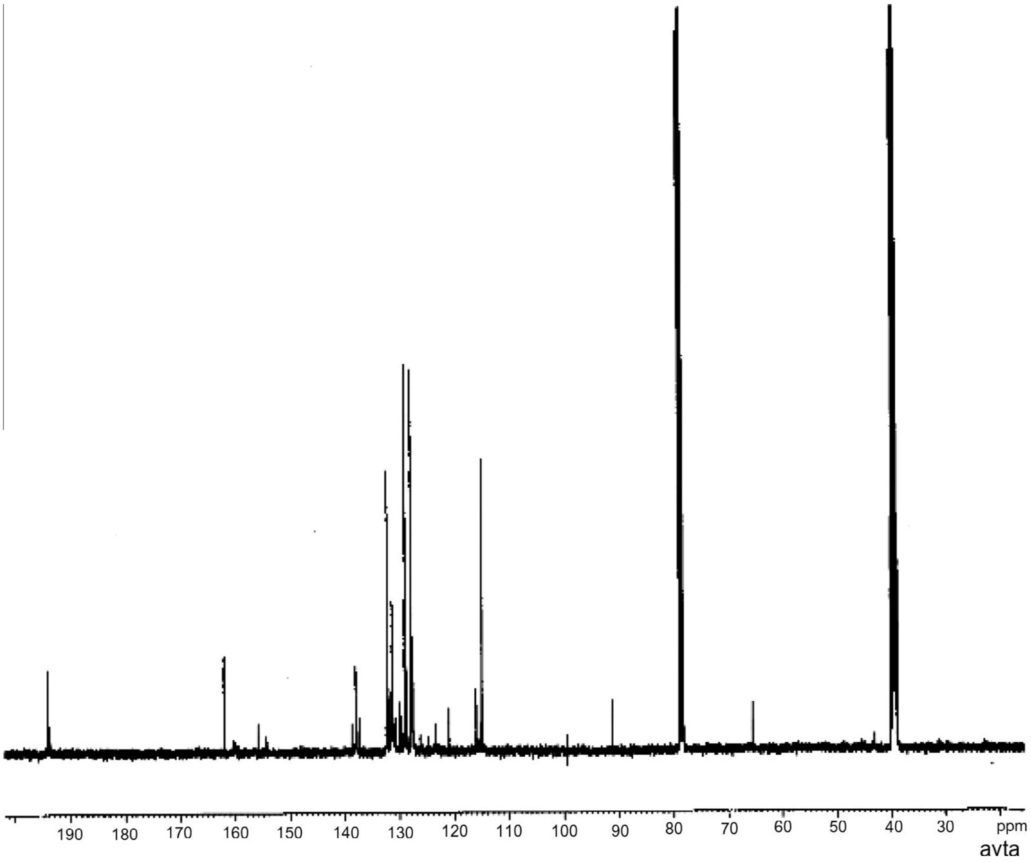


Figure 4 ^{13}C NMR spectra of *p*-HBBF terpolymer resin.

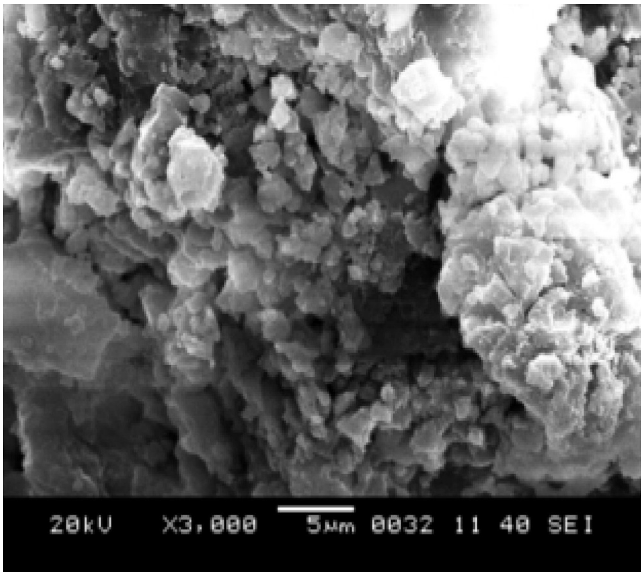


Figure 5 SEM micrographs of *p*-HBBF terpolymer resin at 3000× magnification.

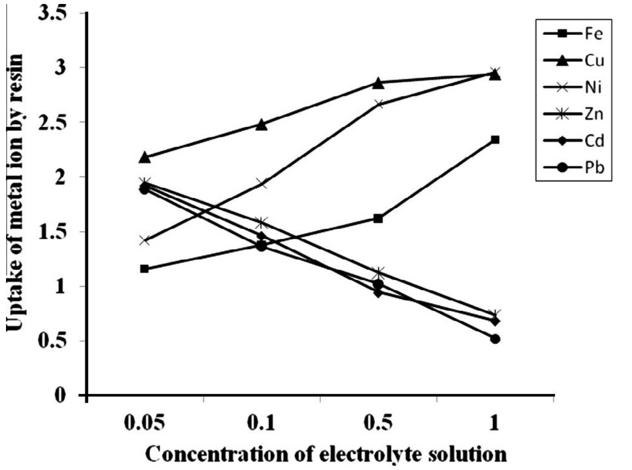
Table 4 Data of experimental procedure for direct EDTA titration.

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 sulfone black	Purple–green
Ni(II)	Aq.NH_3/NH_4Cl	Murexite	Yellow–violet
Zn(II)	Aq.NH_3/NH_4Cl	Salochrom	Wine red–blue
Cd(II)	Hexamine	Xylenol orange	Red–yellow
Pb(II)	Hexamine	Xylenol orange	Red–yellow

Batch equilibrium technique developed by Gregor et al. and DeGeiso et al. was used to study of ion exchange property of *p*-HBBF terpolymer resin. The result of the batch equilibrium study carried out with the terpolymer resin *p*-HBBF is presented in Figs. 6–11. Eight metal ions Fe^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{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 three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymer (Patle Deepti et al., 2011; Patel and Manavalan, 1984; Vyas and Kapadia, 1980).

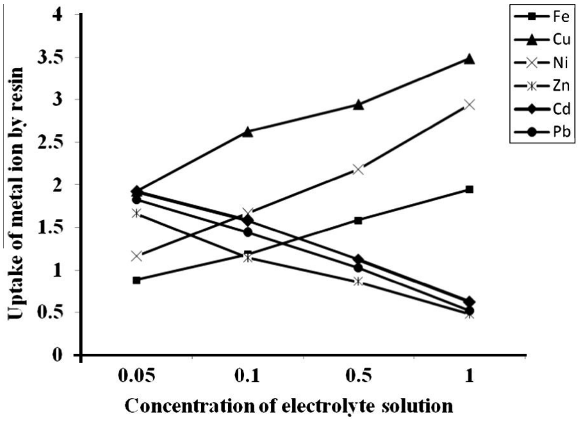
3.3.1. Effect of electrolytes and their concentration on the metal ion uptake capacity

We examined the influence of NO_3^-, Cl^-, SO_4^{2-} and ClO_4^- at various concentrations on the equilibrium of metal-resin interaction of constant pH. Different metal ions have different pH in solution, which have been mentioned in Figs. 6–9, which show that the amount of metal ions taken up by a given



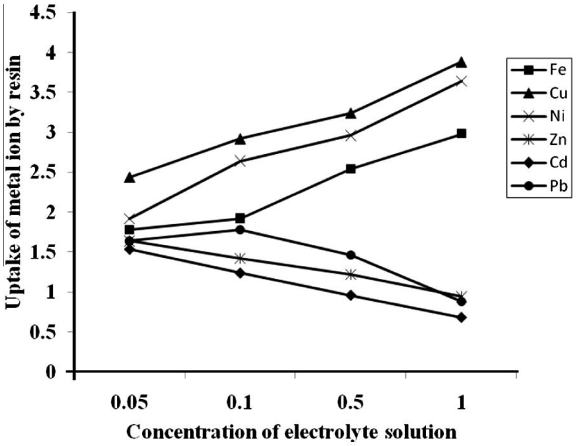
[M(NO$_3$)$_2$]=0.1 Mol/l; Volume of metal ion solution = 2ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.
pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0

Figure 6 Uptake of several metal ions by *p*-HBBF terpolymer resin at five different concentrations of electrolyte solution of NaNO$_3$.



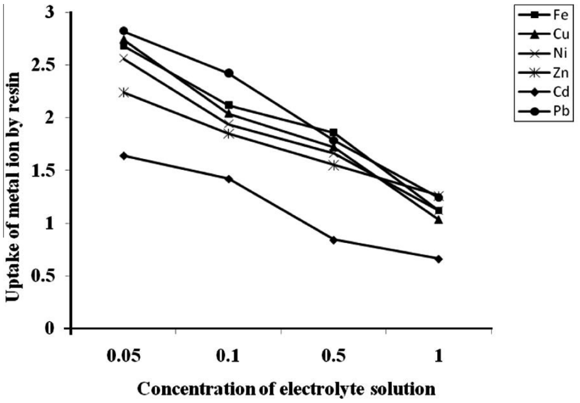
[M(NO$_3$)$_2$]=0.1 Mol/l; Volume of metal ion solution = 2ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.
pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0

Figure 7 Uptake of several metal ions by *p*-HBBF terpolymer resin at five different concentrations of electrolyte solution of NaCl.



[M(NO$_3$)$_2$]=0.1 Mol/l; Volume of metal ion solution = 2ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.
pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0

Figure 8 Uptake of several metal ions by *p*-HBBF terpolymer resin at five different concentrations of electrolyte solution of NaClO$_4$.



[M(NO$_3$)$_2$]=0.1 Mol/l; Volume of metal ion solution = 2ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.
pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0

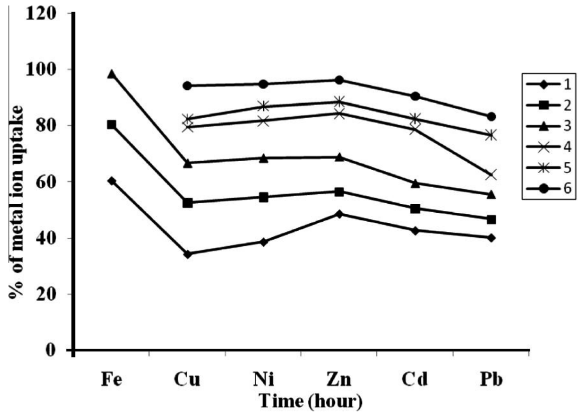
Figure 9 Uptake of several metal ions by *p*-HBBF terpolymer resin at five different concentrations of electrolyte solution of Na$_2$SO$_4$.

amount of terpolymer depends on the nature of concentration of the electrolyte present in the solution.

Generally as concentration increases of the electrolyte, the ionization decreases, the number of ligands decreases in the solution which form the complex with less metal ions and more ions are available for adsorption. The variable metal ions uptake capacity of *p*-HBBF terpolymer may be due to the strong and weak complex formation between electrolyte ligand and metal ion. When the concentration of electrolyte is zero then there is no negative ion (ligand) in metal ion solutions, no complex formation. All metal ions may be available to the adsorption on the polymer. Hence show maximum uptake of ion by *p*-HBBF terpolymer. As there is no complex formation, there is no problem of strong and weak nature, hence all metal ions show comparable uptake on the polymer at zero concentration. Zero concentration of electrolyte may not affect the metal uptake capacity of polymer. Hence on increasing concentration there should be an increase in uptake of metal ion. But trend disturbed due to formation of more stable complex with more number of ligands which decrease the number of metal ions available for adsorption, hence uptake decreases.

If electrolyte ligand–metal ion complex is weaker than polymer metal ion chelates, the more metal ion can form complex with polymer hence uptake of metal ion is more. But if this complex is strong than polymer – metal ion chelates, more metal ions form strong complex with electrolyte ligand which make metal uptake capacity lower by 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, this phenomena is known as desorption, or regeneration of polymer. The regenerated polymer can again be used for

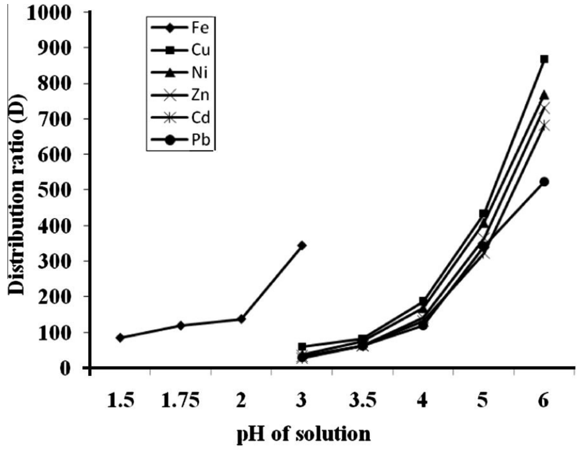


$[M(NO_3)_2]$=0.1 mol/l; volume of metal nitrate=2ml; $NaNO_3$= 1.0 mol/l; volume of electrolyte=25ml, Room temperature

Metal ion uptake = (Amount of metal ion absorbed x 100) / (amount of metal ion absorbed at equilibrium)

pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0;

Figure 10 Comparison of the rate of metal ion uptake by *p*-HBBF terpolymer resin.



D= weight (mg) of metal ions taken up by 1 g of copolymer / weight (mg) of metal ions present in 1ml of solution.

$[M(NO_3)_2]$=0.1 mol/l; volume of metal nitrate=2ml; $NaNO_3$= 1.0 mol/l; volume of electrolyte= 25ml, time=24hrs (equilibrium state) at Room temperature.

pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0

Figure 11 Distribution ratio (*D*) of various metal ions as function of different pH by *p*-HBBF terpolymer resin.

re-adsorption by shaking it with metal ion solution. Adsorption and re-adsorption depend on concentration of metal ions but desorption does not.

In the presence of nitrates, perchlorate and chloride ions, the uptake of Fe(III), Cu(II) and Ni(II) ions increases with increasing concentration of electrolytes, whereas in the presence of sulfate ions, the amount of above mentioned ions taken up by the terpolymer resin decreases with increasing concentration of the electrolyte (Vogel, 1978; Agrawal et al., 2011). Moreover, the uptake of Zn(II), Cd(II) and Pb(II) ions increases with decreasing concentration of the nitrates, perchlorate, chloride and sulfate ions. Above $NO_3{}^-$, Cl^- and $ClO_4{}^-$ ions form weak complex with the above metal ions, while SO_4^{-2} form stronger complex thus the equilibrium is affected. This may be explained on the basis of the stability constants of the complexes with those metal ions and nature of ligands. The stability of the complexes depends on the charge of metal ions and nature of ligands. Among all above four ligands SO_4^{2-} is a strong ligand, due to having more number of electrons for donation to the meal ion during complex formation, forms strong and stable complex with all the six metal ions under study, therefore overall metal uptake is less in sodium sulfate electrolyte and on increasing concentration of SO_4^{2-} ions in solution, more and more metal ions can form complex with SO_4^{2-} ligands, less number of ions remain left available for uptake of polymer, decreasing metal uptake capacity in SO_4^{2-} electrolyte, while the ligands $NO_3{}^-$, Cl^- and $ClO_4{}^-$ may form weak complex 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 $C1O_4^-$ may form strong complex with Cd^{2+}, Zn^{2+} and Pb^{2+} at some higher pH, therefore if the concentration of these ligands increases the more complex formation might be possible, which decreases the metal uptake capacity of the terpolymer. This type of trend has also been observed by other investigators in this field (Rahangdale et al., 2010; Singru et al., 2010). The ratio of physical core structure of the resin is significant in the uptake of different metal ions by the resin polymer. The amount of metal ion uptake by the *p*-HBBF terpolymer resin is found to be higher when comparing to the other polymeric resins.

3.3.2. Rate of metal ion uptake 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 out while operating as close to equilibrium condition as possible. During rate of metal ion determination, the concentration of metal ion and electrolyte solution and pH of the solution remain constant and pH of each metal ion is different which is given in Fig. 10. As shaking time increases the polymer gets more time for adsorption, hence uptake of metal ions increases. Fig. 10 shows the results of rate of uptake of metal ion on *p*-HBBF 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 terpolymer. The Fig. 10 shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of metal ions under given conditions. It is found that Fe(III) ions required about 3 h for the establishment of the equilibrium, whereas Cu(II), Ni(II), Zn(II) and Pb(II) ions required about 5 or 6 h. Thus the rate of metal ions uptake follows the order Fe(III) > Cu(II) > Ni(II) > Zn(II) > Cd(II) > Pb(II) for the terpolymer (Samir et al., 2004; Rahangdale et al., 2010).

The rate of metal uptake may depend upon hydrated radii of metal ions. The rate of uptake for the post transition metal ions exhibit other trend for Cd(II), the rate of uptake is comparable with that of Pb(II) because of difference in 'd' orbital. In this evaluation we find out the shortest period of time is close as the equilibrium condition is acquired. At the equilibrium condition metal has the highest percentage rate of uptake, which is acquired due to 24 h staking. The observation obtained indicates that, time required for the rate of metal ion uptake depends on the nature of the metal ions and may be depend on the ionic size. Thus the rate of metal ion uptake follows the order:

$Fe^{3+} > Cu^{2+} \approx Ni^{2+} > Zn^{2+} > Cd^{2+} \approx Pb^{2+}$

Ionic size 0.55 0.57 0.69 0.90 1.10 1.19

The sequences of rate of metal ion uptake indicate that the rate may depend on size of the ion. The rate is directly proportional to the size of the metal ion. For example Fe^{3+} has more charge and small size, therefore equilibrium is attained within three hours, while other first transition ions Cu^{2+}, Ni^{2+}, and Zn^{2+} have nearly equal cationic size, charges are some: therefore required 5 h to attain equilibrium, while Cd^{2+} and Pb^{2+} have large atomic size, therefore requiring 6 h to attain equilibrium. The trend is in good agreement with earlier co-workers (Rahangdale et al., 2008).

3.3.3. Distribution ratios of metal ions at different pH

The distribution of metal ion depends upon pH of the solution. By increasing pH, the H^+ ion concentration in the solution decreases and only metal ion in the solution available for adsorption increases uptake of metal ions.

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 ions taken up by the terpolymer increase with increasing pH of the medium (Patel and Manavalan, 1984; Rahangdale et al., 2010; Singru et al., 2010; Riswan Ahamed et al., 2010; Burkanudeen et al., 2010). The magnitude of increase, however, is different for different metal cations.

The study was carried from 2.5 up to pH 6.5 to prevent hydrolysis of metal ions at higher pH. For Fe^{3+} ion the highest working pH is 2.5/3, has lower distribution ratio since Fe^{3+} forms octahedral complex with ligand of electrolyte, which shows crowding effect. This steric hindrance may be lower the distribution ratio of Fe^{3+} ion. Cu^{2+} and Ni^{2+} have higher distribution ratio over pH range of 2.5–6.5 which may be due to the less steric hindrance. Thus the value of distribution ratio for given pH depends upon the nature and stability of chelates formation for particular metal ion. The data of distribution ratio show a random trend in certain cases. This may be due to the amphoteric nature of the *p*-HBBF. From the result given in Fig 11, it reveals that with decrease in atomic number, the ion uptake capacity is increasing at that particular pH. In case of Cd(II) and Pb(II), purely electrostatic factors are responsible. The ion uptake capacity of Cd(II) is lower owing to the large size of its hydrated ion than that of Cu(II). The steric influence of the methyl group and hydroxyl group in *p*-HBBF resin is probably responsible for their observed low binding capacities for various metal ions. Thus the interaction of this resin material with various metal ions in an aqueous environment may largely limit the binding sites, which are suitably, disposed in a conformational favorable manner on the surface layer. The higher value of distribution ratio for Cu(II) and Ni(II) at pH 2.6–6.0 may be due to the formation of most stable complex with chelating ligands.

Therefore the polymer under study has more selectivity of Cu^{2+} and Ni^{2+} ions at pH 4.0–6.0 then other ions which from rather weak complex. While at pH 3 the terpolymer has more selectivity of Fe^{3+} ions. The *p*-HBBF 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 2.5–6.5 is found to be Fe(III) > Cu(II) > -Ni(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. For example, the result suggests the optimum pH 6.0, for the separation of Cd(II) and Ni(II) with distribution ratio '*D*' are 273.4 and 778.2, respectively using the *p*-HBBF terpolymer resin as ion-exchanger.

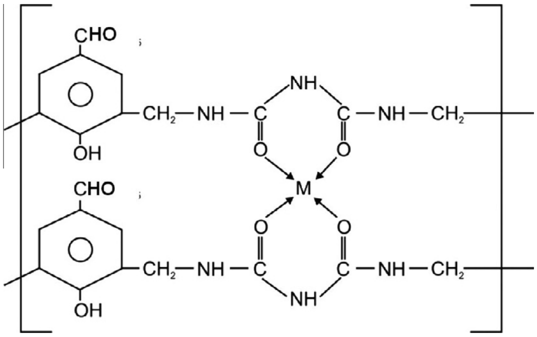


Figure 12 Polychelate formation of *p*-HBBF terpolymer resin.

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 32.6 and that for Fe(III) is 326.2. 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 Zn^{2+} (4) Fe^{3+} and Cd^{2+} (5) Fe^{3+} and Pb^{2+}. The solution for separations were prepared by mixing 1 ml of 0.1 M solutions of Fe^{3+} with 1 ml of 0.1 M solution of Cu^{2+}, Ni^{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+}, Zn^{2+} Cd^{2+} and Pb^{2+} were found to be 293.6, 302.9, 310.9, 309.6, 314.9 and 307.6, respectively, i.e. slight lower than 326.2 found when Fe^{3+} alone was studied. The lowering in the distribution ratios of Fe^{3+} was found to be small and hence efficient separation could be achieved. The structure of polychelate of terpolymer metal ion chelate complex has been given in Fig. 12.

4. Conclusion

p-HBBF terpolymer resin was prepared from *p*-hydroxybenzaldehyde and biuret with formaldehyde in hydrochloric acid medium by condensation technique. Melting point data reveals that the terpolymer has good thermal stability. The semi crystalline nature of the *p*-HBBF terpolymer resins were confirmed by the SEM studies and reveals that the terpolymer can act as an effective ion exchanger for various trivalent and divalent metal ions such as Fe^{+3}, Cd^{+2}, Cu^{+2}, Zn^{+2}, Ni^{+2} and Pb^{+2} ions. Since *p*-HBBF terpolymer contains alcoholic group, it plays a key role in the ion exchange phenomenon. Thus *p*-HBBF terpolymer has immense applications as an ion exchange resin in waste water treatment, metal recovery and for the identification of specific metal ions.

Acknowledgments

Authors are thankful to the Director, Laxminarayan Institute of Technology, Nagpur, India, for providing the necessary laboratory facilities and also thankful to SAIF, Punjab University, Chandigarh for carrying out spectral analysis.

One of the author (W.B. Gurnule) thanks University Grant Commission, New Delhi for financial assistance (F).

References

Agrawal, P.S., Wagh, M.S., Paliwal, L.J., 2011. Arch. Appl. Sci. Res. 3 (2), 29–33.

Amin, S., Kapadia, R.N., 1997. J. Sci. Ind. Res. 56, 540–544.

Aswar, S., Munshi, K.N., 1995. J. Ind. Chem. Soc. 72, 883–886.

Atia, A.A., Donia, A.M., Elwakeel, K.Z., 2005. React. Funct. Polym. 65, 267–275.

Azarudeen Raja, S., Mohamed, A., Riswan, Ahamed, Burkanudeen Abdul, R., 2009. Iran. Polym. J. 18 (10), 821–832.

Bavanker, S.V., Paliwal, L.J., Kharat, R., 1999. Asian J. Chem. 11, 1185–1204.

Burkanudeen, A., Karunakaran, M., 2002. Orient. J. Chem. 18, 65–68.

Burkanudeen, A., Azarudeen, R., Riswan Ahamed, M., Ramesh, P., Vijayan, N., 2010. Iran. Polym. J. 1 (1), 29–34.

Gupta, R.H., Gurnule, W.B., Zade, A.B., 2008. J. Appl. Polym. Sci. 109, 3315–3320.

Gurnule, W.B., Rahangdale, P.K., Paliwal, L.J., 2003. React. Funct. Polym. 55, 255–265.

Hiwase, V.V., Kalambe, A.B., Khedkar, K.M., Deosarkar, S.D., 2010. E. J. Chem. 7 (1), 287–294.

Joshi, J.D., Patel, N.B., Patel, S.D., 2006. Iran. Polym. J. 15, 219–226.

Kalsi, P.S., 1995. Spectroscopy of Organic Compounds, 2nd ed. New Age International, New Delhi.

Katkamwar, S.S., Zade, A.B., Rahangdale, S.S., Gurnule, W.B., 2009. J. Appl. Polym. Sci. 113, 3330–3335.

Kaur, H., 2009. Instrumental Methods of Chemical Analysis. Arihant Electric Press, Meerut.

Mane, V.D., Wahane, N.J., Gurnule, W.B., 2009. J. Appl. Polym. Sci. 111, 3039–3049.

Michael, E.P., Barbe, J.M., Juneja, H.D., Paliwal, L.J., 2007. Eur. Polym. J. 43, 4995–5000.

Michael Pratik, E.P., Barbe, J.M., Juneja, H.D., Paliwal, L.J., 2007. Eur. Polym. J. 43, 4995–5000.

Mondal, B.C., Das, A.K., 2003. React. Funct. Polym. 53, 45–49.

Patel, M.M., Manavalan, R., 1984. J. Indian Chem. Soc. 61, 490–494.

Patel, S.A., Shah, B.S., Patel, R.M., Patel, P.M., 2004. Eur. Polym. J. 13, 445–453.

Patel, M.M., Kapadia, M.A., Patel, G.P., Joshi, J.D., 2007. React. Funct. Polym. 67, 746–757.

Patel, J.M., Patel, M.G., Patel, H.J., Patel, K.H., Patel, R.M., 2008. J. Mac. Mol. Sci. 45, 281–288.

Patle Deepti, B., Gurunule, W.B., Zade, A.B., 2010. Arch. Appl. Sci. Res. 2 (1), 261–276.

Patle Deepti, B., Gurunule, W.B., Zade, A.B., 2011. Der. Pharma. Chem. 3 (3), 341–353.

Prabhakaran, D., Subramanian, M.S., 2003. Talanta 59, 1227–1236.

Rahangdale, S.S., Gurunule, W.B., Zade, A.B., 2008. J. Appl. Polym. Sci. 108, 747–756.

Rahangdale, S.S., Gurunule, W.B., Zade, A.B., 2009. Indian J. Chem. 48A, 531–535.

Rahangdale, S.S., Gurunule, W.B., Zade, A.B., 2010. Arch. Appl. Sci. Res. 2 (6), 53–58.

Riswan Ahamed, M., Azarudeen, R., Karunakaran, M., Karikalan, T., Manikandan, R., Burkanudeen, A., 2010. Int. J. Chem. Environ. Eng. 1 (1), 7–12.

Rong Li, X., Huang, M., Yang, Y., 2001. Polymer 42, 4099–4107.

Roy, P.K., Rawat, A.S., Choudhary, V., Rai, P.K., 2004. J. Appl. Polym. Sci. 94, 1771–1779.

Patel, S.A., Shah, B.S., Patel, R.M., Patel, P.M., 2004. Iran. Polym. J. 13 (6), 445–453.

Shah Bhavna, A., Shah Ajay, V., Shah Pathik, M., 2006. Iran. Polym. J. 15, 809–819.

Shah Bhavna, A., Shah Ajay, A., Patel Nayan, B., 2008. Eur. Polym. J. 17, 3–17.

Silverstein, R.M., Webster, F.X., 1998. Spectrometric Identification of Organic Compounds, 6th ed. John Wiley, New York, 217-248.

Silvestein, R.M., Bassler, G.C., Morril, T.C., 1969. Spectrometric Identification of Organic Compounds, 2nd ed. Wiley, New York.

Singh, A., Saraf, S.K., 2009. Int. J. Polym. Mater. 58 (10), 499–508.

Singru, R.N., Zade, A.B., Gurunule, W.B., 2008. J. Appl. Polym. Sci. 109, 859–868.

Singru, R.N., Zade, A.B., Gurunule, W.B., 2010. Iran. Polym. J. 19 (3), 169–183.

Tarase, M.V., Gurunule, W.B., Zade, A.B., 2008. J. Appl. Polym. Sci. 108, 738–746.

Vogel, A.I., 1978. A Text Book of Quantitative Inorganic Analysis, 4th ed. Longman, London.

Vyas, M.V., Kapadia, R.N., 1980. Indian J. Technol. 18, 411–415.

Vyas, M.V., Kapadia, R.N., 1981. Indian J. Technol. 19, 491–494.

Zalloum, R.M., Mubarak, S.M., 2008. J. Appl. Polym. Sci. 109, 3180–3184.