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Synthesis, characterization and ion-exchange properties of a terpolymer derived from 4-hydroxybenzophenone, biuret and formaldehyde

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ABSTRACT

The terpolymer resins (4-HBPBF) have been synthesized by the condensation of 4-hydroxybenzaldehyde (4-HBP) and biuret (B) with formaldehyde (F) in the presence of acid catalyst and using 2:1:3 molar proportions of the reacting monomers. Terpolymer resins composition has been determined on the basis of elemental analysis and the number average molecular weight of these resins was determined by conductometric titration in non-aqueous medium. Viscometric measurements in Dimethyl sulphoxide (DMSO) have been carried out with view to ascertain the characteristic functions and constants. The structure of 4-HBPBF-II terpolymer has been elucidated on the basis of elemental analysis and various physicochemical techniques, i.e. UV-Visible, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The morphological feature of the 4-HBPBF-II terpolymer was established by scanning electron microscopy (SEM). The chelating ion-exchange study was carried out over a wide pH range, shaking time and in media of various ionic strengths for six metal ions Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} in the form of their metal nitrate solutions. The terpolymer showed a higher selectivity for Fe^{3+}, Cu^{2+} and Ni^{2+} ions then for Zn^{2+}, Cd^{2+} and Pb^{2+}. Study of distribution ratio as a formation of pH indicates that the amount of metal ion taken by resin is increases with the increasing pH of the medium. The results of the ion-exchange studies reveal that the 4-HBPBF-II terpolymer was found to be an excellent cation-exchanger for selective metal ions.

Keywords – Resin, Synthesis, Ion-exchanger, Adsorption, Distribution ratio.

INTRODUCTION

Ion-exchange may be defined as the reversible exchange of ions between the substrate and surrounding medium. Ion exchange technique can remove traces of ion impurities from water process liquors and given out a product of ultra pure quality in a single efficient and techno-economically viable manner. Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotics, purification and separation of radioisotopes and find large application in water treatment and pollution control [1, 2]. Lutfor et. al. [3] prepared a chelating ion exchange resin containing amidoxime functional group. The chelating poly (amidoxime) resin was characterized by FT-IR spectra, TG and DSC analyses. Samir et. al. [4] synthesized ion exchange resin from 8-quinolinyl methacrylate and characterized by conventional methods. The metal ion uptake capacities of synthesized copolymers were estimated by batch equilibration method using different metal ion solutions under different experimental conditions. Three phenol-formaldehyde chelating resins, poly (8-hydroxyquinoline-5, 7 diylmethylene) and poly (2-aminophenol-5,7 diylmethylene) were synthesized and characterized by Ebraheem [5]. The chelating characteristics of these polymers were studied by a batch equilibrium technique. The ion exchange capacity, effect of electrolyte on metal ion up take, rate of metal uptake and distribution of metal ion at different pH with resin copolymer derived from thiosemicarbazone derivatives of phenol compound shows higher order than the resin copolymer derived from semicarbazone derivatives [6]. Recently much work has been carried out to study the ion exchange properties of anchoring functional chelating groups on the polymeric network. But as compared to anchored resins, the synthesized resins are more advantageous because the synthesized insoluble functionalized polymer can provide good stability and good flexibility in working conditions. Rivas B. L. [7] synthesized crosslinked poly [3-(methacryloyl- amino)-propyl] dimethyl (3-sulfopropyl) ammoniumhydroxide-2-acryl-amidoglycolicacid [PCMAAPDSA-co- AGCO] by radical polymerization and tested the synthesized polymer as an absorbent under competitive and non-competitive conditions for Cu(II), Cd(II), Hg(II), Zn(II), Pb(II) and Cr(III) by batch and column equilibrium procedures. They reported that resin metal ion equilibrium was achieved before 1 h. the resin showed a maximum retention capacity value of 1.084 m.eq.g^{-1} for Hg (II) at pH 2. The recovery of the resin was investigated at 20 ^{0}C under different concentration of HNO_3 and $HClO_4$. Jadhao M.M. and coworker [8] synthesized a terpolymer resin by condensation of 2, 2'dihydroxybiphenyl and formaldehyde in the presence of acid catalyst. They studied chelating ion exchange properties of this polymer for Fe(III), Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurement of the distribution of a given metal ion between the polymer sample and a solution containing metal ions. The study was carried out over a pH range and in media of various ionic strengths. They reported that the polymer showed a higher selectivity for Fe(III), Cu(II) and Ni(II) than for Co(II), Zn(II) Cd(II) and Pb(II) ions.

However, the literature studies have revealed that no terpolymer has been synthesized using the monomer 4-hydroxybenzophenone, biuret and formaldehyde. Therefore, in the present communication we report the synthesis, structural characterization, ion-exchange and thermal degradation studies of 4-HBPBF-II terpolymer. The elemental analysis has been carried out to ascertain the molecular formula and the spectral studies have been used to characterize the complete structure of the 4-HBPBF-II terpolymer.

MATERIALS AND METHODS

2.1. Starting Materials

The important chemicals (starting materials) like 4-hydroxybenzophenone, biuret and formaldehyde used in the preparation of new 4-HBPBF-II 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 4-HBPBF-II terpolymer resin

The new terpolymer resin 4-HBPBF-II was synthesized by condensing 4-hydroxybenzophenone (2.442 g, 2 mol) and biuret (1.03 g, 0.1 mol) with 37 % formaldehyde (11.25 ml, 0.3 mol) in a mol ratio of 2:1:3 in the presence of 2M 200 ml HCl as a catalyst at 126°C ± 2°C for 5hrs in an oil bath with occasional shaking to ensure thorough mixing. The separated cream color terpolymer resin was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove 4-hydroxybenzophenone-formaldehyde copolymer which might be present along with 4-HBPBF-II terpolymer. The terpolymer resin was purified further by dissolving in 8% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The terpolymer sample 4-HBPBF-II thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desicator over silica gel. The yield of the terpolymer resin was found to be 80%. The reaction and suggested structure has been given in Fig. 1.

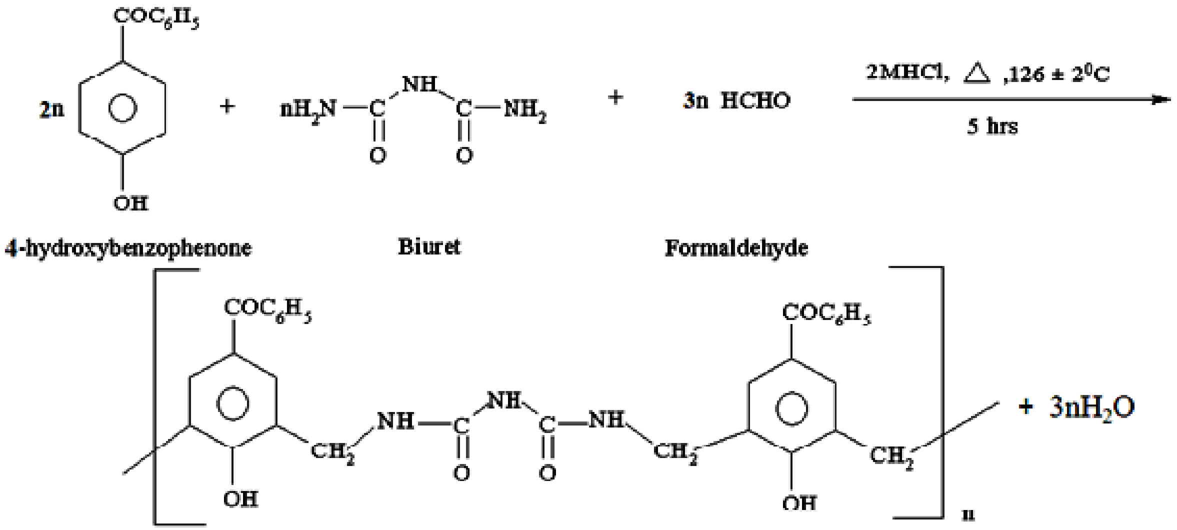


Fig. 1. Reaction and suggested structure of 4-HBPBF-II terpolymer resin

2.3. Characterization of 4-HBPBF-II 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 gm 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 [9-12] : (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 following eq. (1).

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

$\overline{Mn} = \overline{DP}$ × molecular weight of the repeating unit

The intrinsic viscosity was determined using a Tuan-Fuoss viscometer [13] at six different concentrations ranging from 0.3 wt % to 0.05 wt % of resin in DMSO at 30ºC. Intrinsic viscosity (η) was calculated by the Huggin's eq.(2) [14] and Kraemer's eq.(3) [15].

$$\text{In } \eta_{sp}/C = [\eta] + K_1 [\eta]^2.C\text{------------}(2)$$
$$\text{In } \eta_r/C = [\eta] - K_2 [\eta]^2.C \text{ ------------- } (3)$$

2.3.2 Spectral and surface Analysis

Electronic (UV-visible) absorption spectra of the terpolymer resin 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 4-HBPBF terpolymer resin was recorded in najol mull with 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 ^{13}C NMR spectra was 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 scnanned by JEOL JSM-6380A Analytical Scanning Electron Microscope at VNIT, Nagpur.

2.4. Ion-Exchange Properties

The ion-exchange properties of the 4-HBPBF-II terpolymer resin was 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. Some commercially available ion-exchange resins are tabulated in Table 2.

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 hrs at 25ºC. 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 25ºC for 24 hrs and filtered [16, 17]. 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 [18-20]. The experiment was repeated in the presence of other three electrolyte 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 describe above were carried out, in which the metal ion taken up by the chelating resin was determined from time to time at 25ºC (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 hrs. the rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain 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 25ºC and in the presence of a 1M $NaNO_3$ solution. The experiment were carried out as described earlier at different pH values. The distribution ratio "D" is defined by the following relationship……..

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

RESULTS AND DISCUSSION

3.1 Physicochemical and Elemental Analysis

The resin sample was light pink in color, insoluble in commonly used organic solvents, but was soluble in dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, pyridine and concentrated H_2SO_4. The resin synthesized do not show sharp melting point but undergo decomposition above 420-425ºK**.** Based on the analytical data, the empirical formula of the 4-HBPBF-II terpolymer resin is found to be $C_{31}H_{28}N_3O_7$, 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 = 67.11% (Cal) and 67.14% (F); H = 4.94% (Cal) and 5.05% (F); N = 7.23% (Cal) and 7.58% (F).

The number average molecular weight ($\overline{M}n$) could be obtained by multiplying the $\overline{DP}$ by the weight of the repeating unit [21, 22]. The calculated molecular weight for 4-HBPBF-II resin is 7075.64. Viscometric measurement was carried out in DMSO at 30ºC. 4-HBPBF-II resin showed normal behavior. The intrinsic viscosity was determined by the Huggin's eq. (2) and Kraemer's, eq. (3) which is 0.27 and 0.29 respectively. In accordance with the above relations, the plot of $\eta_{sp/c}$ and $\eta_{rel/c}$ against C was linear giving as slopes K_1 and K_2 (0.56) respectively. The intercept on the axis of viscosity function gave the (η) value in both the plots [23]. 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 of 4-HBPBF-II terpolymer resin has been shown in Fig.2. UV-visible spectra of 4-HBPBF-II resin has been recorded in pure DMSO in the region of 200 – 800 nm at a scanning rate of 100 nm min^{-1} and at a chart speed of 5 cm min^{-1}. The spectra of these terpolymers exhibit two absorption maxima in the region 280 nm and 320 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) processing double bond, which is in conjugation with the aromatic nucleus [24, 25]. The appearance of former band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition while the later band (less intense) may be due to $n \rightarrow \pi^*$ electronic transition. The shift from the basic value (viz. 240 nm and 310 nm respectively) may be due to conjugation effect, and presence of phenolic hydroxyl group (auxochromes) is responsible for hyperchromic effect i.e. **Σ**max higher values.

Infrared spectrum of the 4-HBPBF-II terpolymer resin has been shown in Fig.3. A very broad band appeared in the region 3500–3250 cm^{-1} may be assigned to the stretching vibration of the phenolic hydroxyl groups exhibiting intermolecular hydrogen bonding [26]. The sharp band displayed at 1615–1640 cm^{-1} may be due to the stretching vibration of carbonyl group of both, ketonic as well as biuret moiety. The presence of -NH- in biuret moiety may be ascribed to aromatic skeletal ring. The bond obtained at 1374, 1273, and 815 cm-^{1} suggest the presence of methylene bridges in the polymer chain.1, 2, 3, 4, 5 penta-substitution of aromatic ring is recognized from the bonds appearing at 1273, 1163, 1085, 992, and 813 cm^{-1}, respectively.

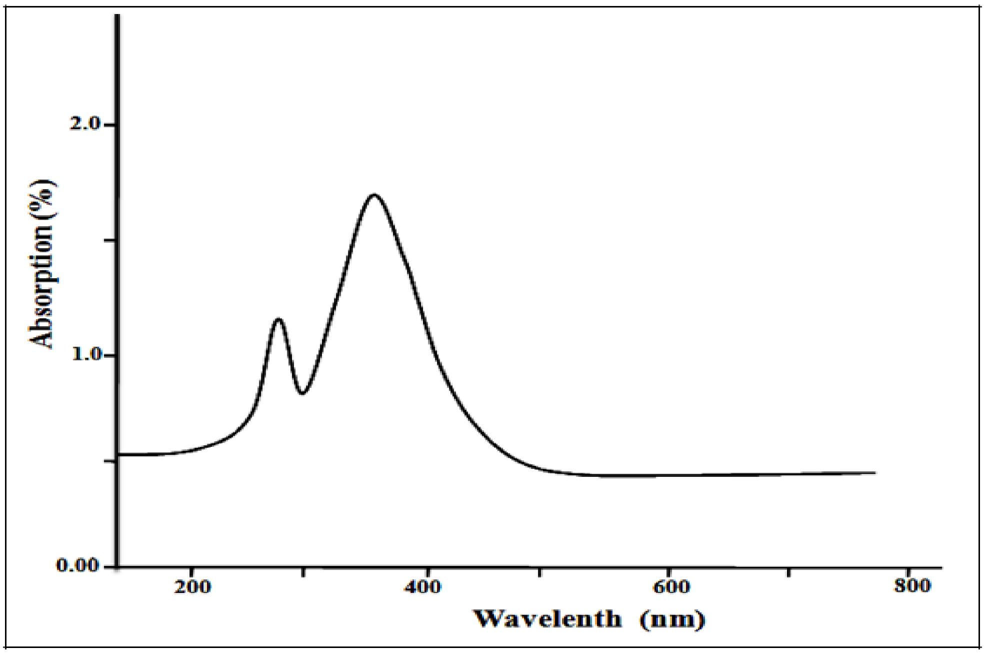


Fig. 2. Electronic spectra of 4-HBPBF-II terpolymer resin

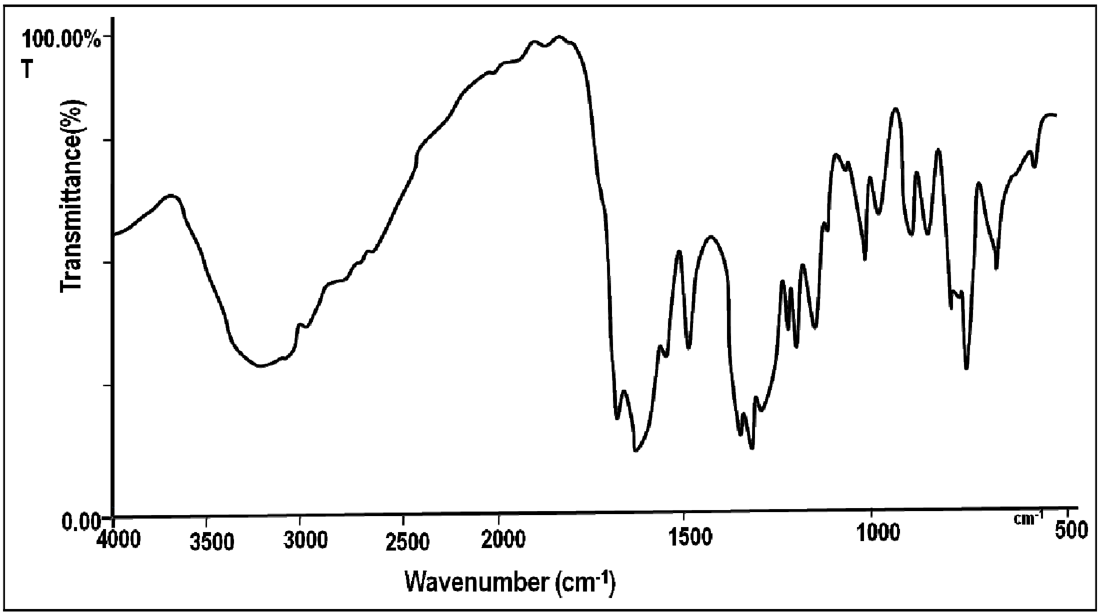


Fig. 3. Infrared Spectra of 4-HBPBF-II terpolymer resin

The ^{1}H NMR spectrum of 4-HBPBF-II terpolymer was scanned in DMSO-d$_6$ and has been shown in Fig. 4. Proton NMR spectra of 4-HBPBF-II terpolymer shows a weak multiplicity signals (unsymmetrical pattern) in the region 7.52 to7.88 (δ) ppm may be due to the aromatic protons [27]. A weak signal appeared in the region of 6.86 – 7.14 shows the presence of imido proton of – CO-NH-CO- linkage. The weak multiply signals appearing at 5.15 – 5.45 (δ) ppm may due to the amido –CH$_2$ -NH-CO linkage. A signal appeared in the region 4.07 – 4.98 (δ) ppm may be due to proton of methelenic bridges (Ar – CH$_2$ – N) of polymer chain. The signal in the range of 3.62 – 3.90 (δ) pp is attributed to phenolic -OH proton.

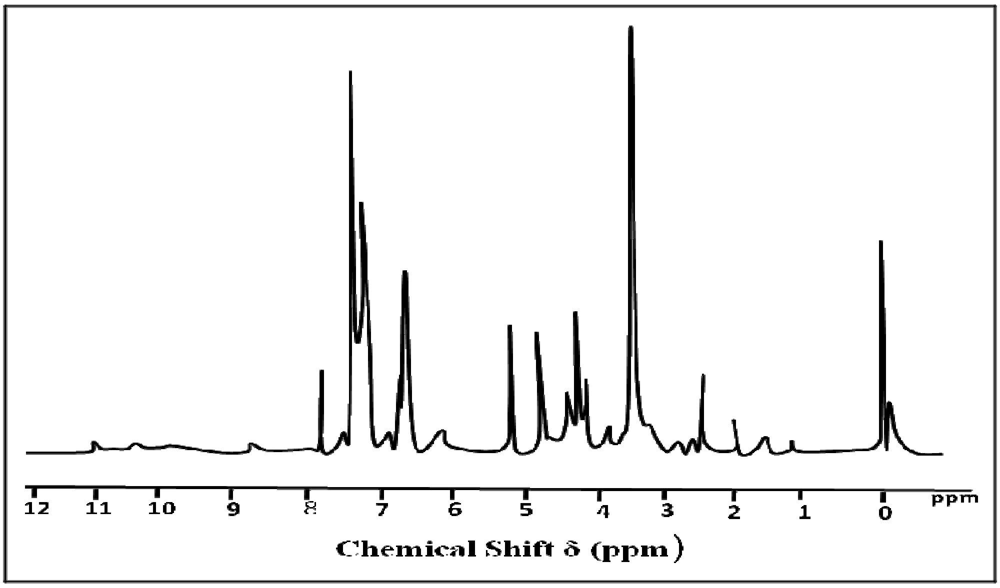


Fig. 4. H^1 NMR Spectra of 4-HBPBF-II terpolymer resin

13C NMR spectrum of 4-HBPBF-II terpolymer resin has been recorded as shown in Fig. 5. The peaks appeared at 121.14, 127.71, 129.09, 131.88 and 155.94 ppm may be corresponded to carbons present in aromatic benzophenone ring [28]. The peak appeared at 162.11 ppm of may be corresponding to carbonyl group of biuret moity. The medium peak appeared at 115.33 ppm may be confirmed the presence of –C-NH group of terpolymer resin. The peak appeared at 65.56 ppm may be due to the presence of –C-OH group in aromatic benzophenone group. The peaks appeared at 38.91 to 40.17 ppm may be due to the $–CH_2$ – bridge in terpolymer resin. All these peaks confirmed that the 4-HBPBF-II terpolymer resin must have linear structure.

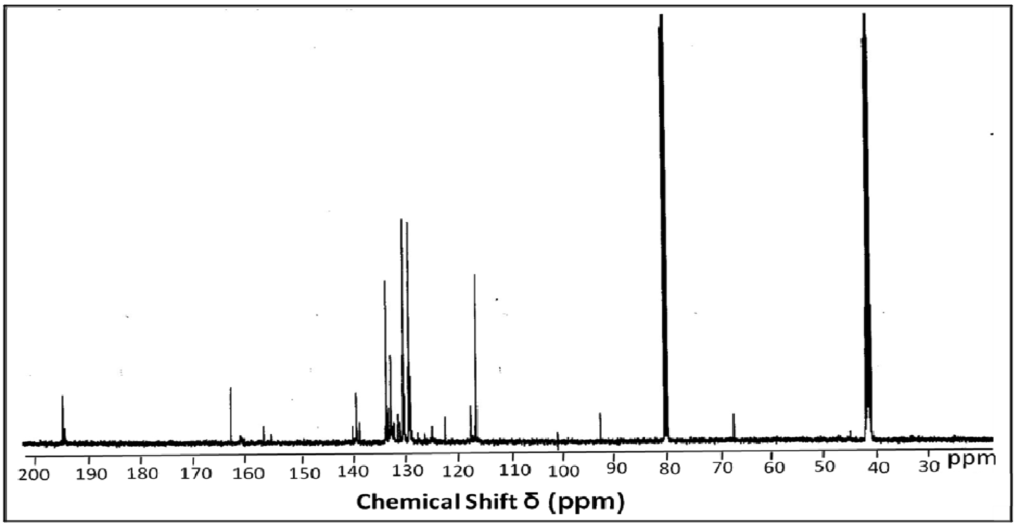
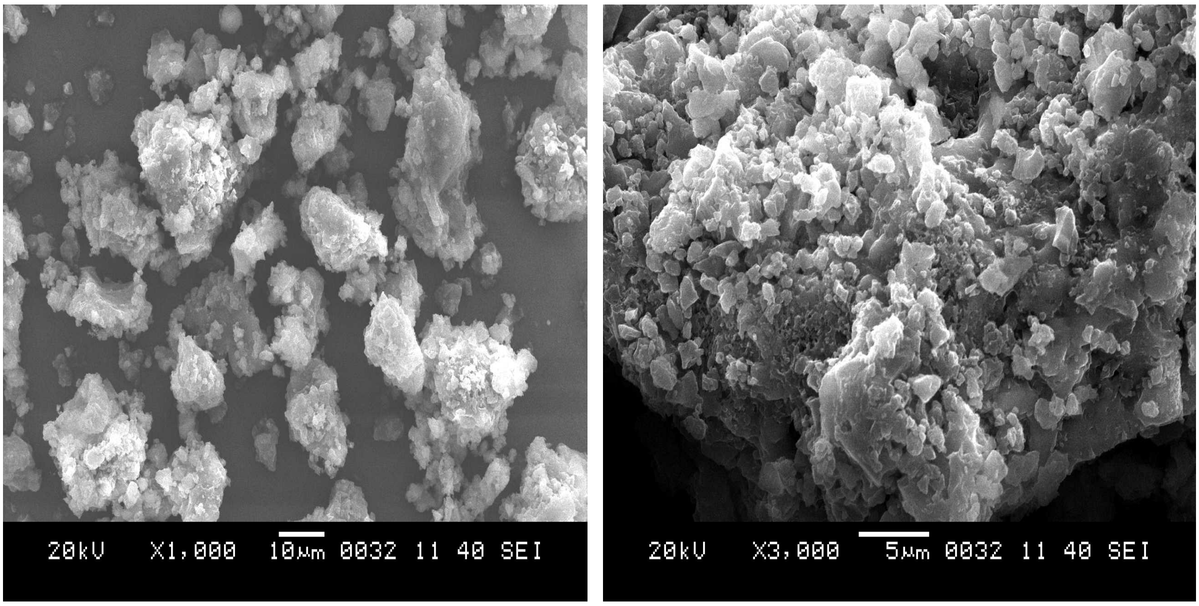


Fig. 5. C^{13} NMR Spectra of 4-HBPBF-II terpolymer resin

Scanning electron micrographs

Surface analysis has found great use in understanding the surface features of the materials. Scanning electron micrographs of the 4-HBPBF-II terpolymer resin has been recorded as shown in Fig.6. at 1500X and 3000X magnification. The SEM micrographs of 4-HBPBF-II terpolymer resin sample exhibits spherulites with deep corrugation. The spherulites are typical crystalline formation and they grow in high viscous and concentrated solution. In the present case, the spherulites are complex polycrystalline. The crystals are smaller in surface area with less closely packed structure. The spherulites morphology of resin exhibit crystalline structure with deep corrugation which is clearly visible in SEM photographs of resin. These evidences indicate that more or less the resin shows amorphous character with less close packed surface having deep pits. The resin thus possesses amorphous nature and showing higher exchange capacity for metal ions [29, 30]. Thus SEM study shows that the 4-HBPBF-II terpolymer resin has crystalline and some amorphous characters. Thus it has the transition structure between crystalline and amorphous. When compare to the other resin, the 4-HBPBF-II terpolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.



6(a) **6(b)**

Fig. 6. Scanning Electron micrographs (SEM) of 4-HBPBF-II terpolymer resin

3.3. Ion-exchange properties

With a view to ascertain the selectivity of the 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, by using batch equilibrium method [31, 32]. Data of experimental procedure for direct EDTA titration is presented in Table 1.

Table 1. Data of experimental procedure for direct EDTA titration

Metal ion	Buffer used	Indicator used	Colour change
Fe(III)	Dil.HNO_3/dil.NaOH	Variamine blue	Blue-Yellow
Cu(II)	Dil.HNO_3/dil.NaOH	Fast sulphon 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

The 4-HBPBF-II terpolymer (Fig. 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 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 solution to surface of polymer. This mechanism of adsorption of metal ion by polymer ligands is known at metal uptake of polymer. Due to 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 towards 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 4-HBPBF-II terpolymer was studied with these three variables by keeping two variable constant at each time.

Polymer + metal ion solution + shaking ⟶ polymer – metal ion chelate
(Metal uptake capacity of polymer depends on stability of polymer – metal ion chelate)

Batch equilibrium technique developed by Gregor et al. and DeGeiso et al. was used to study of ion exchange property of 4-HBPBF-II terpolymer resin. The result of the batch equilibrium study carried out with the terpolymer resin 4-HBPBF-II is tabulated in Table 2-4. Six metal ions Fe^{3+}, Cu^{2+}, Ni^{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 three variables, two were kept constant and only one was varied at a time to evaluable its effect on metal uptake capacity of the polymer [33, 34].

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

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. Different metal ions have different pH in solution, has been mentioned in Table 3, which shows that the amount of metal ions taken up by a given amount of terpolymer depends on the nature of concentration of the electrolyte present in the solution. In the presence of nitrates, perchlorate and chloride ions the uptake of Fe(III), Cu(II), Zn(II) and Pb(II) ions increasing with increasing concentration of electrolytes. Whereas in the present of sulphate ions, the amount of above maintained ions taken up by the terpolymer resin decreases with increasing concentration of the electrolyte [35]. 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.

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 Table 4. As shaking time increases the polymer gets more time for adsorption, hence uptake of metal ions increases. Table 4 shows the results of rate of uptake of metal ion on 4-HBPBF-II 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 result 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 hrs for the establishment of the equilibrium, whereas Cu(II), Zn(II) and Pb(II) ions required about 6 hrs. Thus the rate of metal ions uptake follows the order Fe(III) >>Pb(II), Pb(II) > Zn(II) > Cu(II) for the 4-HBPBF-II terpolymer [36-38].

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 decrease and only metal ion in the solution available for adsorption which increase 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 Table 5. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the terpolymers increase with increasing pH of the medium. The magnitude of increase, however, is different for different metal cations. The study was carried out from 2.5 up to pH 6.5 to prevent hydrolysis of metal ions at higher pH. The selectivity of Fe(III) ion is more for the 4-HBPBF-II terpolymer resin as compare to the any other metal ions under study. The order of distribution ratio of metal ions measured in the range, 1.5 to 6.5 is found to be Fe(III) > Cu(II) > Pb(II) > Zn(II) [38]. 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 [32, 36]. For example, the result suggests the optimum pH 2.5 for the separation of Fe(III) and Zn(II) with distribution ratio 'D' is 387.6 and 76.7 respectively using the 4-HBPBF-II terpolymer resin as ion exchange. Similarly for the separation of Fe(III) at the optimum pH is 2.5 with distribution ratio is 4355.6 for 4-HBPBF-II terpolymer. The lowering in the distribution ratios of Fe(III) was found to be small hence, efficient separation could be achieved. Thus the separation of Fe(III) from other metal having combination (1) Fe^{3+} and Cu^{2+}, (2) Fe^{3+} (3) Fe^{3+} and Zn^{2+} (4) Fe^{2+} and Pb^{2+} are effectively may separate out.

Table 2, 3, 4 and 5 are tabulated here.

Table 2. 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

Table 3. Evaluation of the effect of different electrolytes on the uptake of several metal ions by 4-HBPBF-II terpolymer resin

Metal ion	**Electrolyte (mol./l)**	**pH**	**Weight of metal ion (in mg.$^{-1}$) taken up in the presence of**			
			$NaClO_4$	**NaCl**	**$NaNO_3$**	**Na_2SO_4**
Fe^{+3}	0.01	2.5	0.41	0.29	0.19	0.88
	0.05		0.47	0.36	0.32	0.64
	0.10		0.58	0.48	0.44	0.52
	0.50		0.80	0.76	0.64	0.43
	1.00		0.84	0.82	0.72	0.38
Cu^{+2}	0.01	4.5	0.1	0.08	0.06	0.64
	0.05		0.2	0.13	0.09	0.58
	0.10		0.34	0.25	0.14	0.48
	0.50		0.46	0.32	0.28	0.32
	1.00		0.56	0.46	0.42	0.18
Cd^{+2}	0.01	5.0	0.33	0.11	0.12	1.14
	0.05		0.45	0.23	0.24	1.11

	0.10		0.67	0.34	0.34	0.78
	0.50		0.93	0.78	0.56	0.68
	1.00		0.98	1.22	0.65	0.34
Zn^{+2}	0.01	5.0	0.22	0.09	0.09	0.70
	0.05		0.37	0.14	0.14	0.62
	0.10		0.44	0.24	0.26	0.47
	0.50		0.58	0.56	0.46	0.38
	1.00		0.77	0.72	0.58	0.19
Ni^{+2}	0.01	5.0	0.20	0.08	0.09	0.60
	0.05		0.32	0.10	0.11	0.52
	0.10		0.34	0.20	0.26	0.47
	0.50		0.45	0.40	0.36	0.30
	1.00		0.54	0.62	0.42	0.14
Pb^{+2}	0.01	6.0	0.52	0.23	0.23	1.62
	0.05		0.58	0.46	0.42	1.22
	0.10		1.45	0.76	0.78	0.89
	0.50		2.66	1.67	1.66	0.61
	1.00		2.88	2.17	1.92	0.42

$[M(NO_3)_2]$ = 0.1 mol./lit.; Volume of metal ion = 2 ml. ; Volume of electrolyte solution: 25 ml.; Weight of resin = 25 mg.; Time = 24 hrs, at room temperature

Table 4. Distribution ratio (D) of various metal ion as a function of the pH by 4-HBPBF-II terpolymer resin

Metal ion	Distribution ratio of metal ion at different pH									
	1.5	1.75	2.0	2.5	3.0	3.5	4.0	5.0	6.0	6.5
Fe^{+3}	112.4	128.9	146.9	387.6	-	-	-	-	-	-
Cu^{+2}	-	-	-	42.09	56.79	61.77	72.72	96.29	146.33	192.62
Cd^{+2}	-	-	-	56.92	64.50	167.08	207.41	168.76	254.34	284.36
Zn^{+2}	-	-	-	76.7	124.83	188.55	268.67	466.67	419.05	544.14
Ni^{+2}	-	-	-	38.30	44.009	68.136	92.52	72.72	114.64	326.34
Pb^{+2}	-	-	-	72.36	84.05	144.59	378.95	684.06	1428.3	2466.1

D = Weight (mg.) of metal ion taken up by 1 gm. of copolymer/ Weight (mg.) of metal ions present in 1 ml. of solution.

$[M(NO_3)_2]$ = 0.1 mol. /lit.; Volume of metal solution = 2 ml; Volume of electrolyte solution: 25 ml; Weight of resin = 25 mg; Time = 24 hrs (equilibrium state), at room temperature.

Table 5. Distribution ratio "D" of various metal ion as a function of the pH by 4-HBPBF-II terpolymer resin

Metal ion	Distribution ratio of metal ion at different pH									
	1.5	1.75	2.0	2.5	3.0	3.5	4.0	5.0	6.0	6.5
Fe^{+3}	112.4	128.9	146.9	387.6	-	-	-	-	-	-
Cu^{+2}	-	-	-	42.09	56.79	61.77	72.72	96.29	146.33	192.62-
Cd^{+2}	-	-	-	56.92	64.50	167.08	207.41	168.76	254.34	284.36
Zn^{+2}	-	-	-	76.7	124.83	188.55	268.67	466.67	419.05	544.14
Ni^{+2}	-	-	-	38.30	44.009	68.136	92.52	72.72	114.64	326.34
Pb^{+2}	-	-	-	72.36	84.05	144.59	378.95	684.06	1428.3	2466.1

D = Weight (mg.) of metal ion taken up by 1 gm. of copolymer/ Weight (mg.) of metal ions present in 1 ml. of solution.

$[M(NO_3)_2]$ = 0.1 mol./lit.; Volume of metal solution = 2 ml.; Volume of electrolyte solution: 25 ml.; Weight of resin = 25 mg.; Time = 24 hrs (equilibrium state), at room temperature.

CONCLUSION

The 4-HBPBF-II terpolymer based on the condensation polymerization of 4-hydroxybenzophenone and biuret with formaldehyde in the presence of acid catalyst has been prepared. 4-HBPBF-II is a selective chelating ion-exchange polymer resin for certain metals.

The uptake capacities of metal ions by the terpolymer resin were pH dependent. Due to considerable difference in the uptake capacities at different pH and media of electrolyte, the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to use for separation of particular metal ions from their admixture. This study of ion-exchange reveals that 4-HBPBF-II polymer resin is proved to be an eco-friendly cation exchange resin and can be used for the removal of hazardous metal ions from the environmental area, for the purification of industrial waste solution and for the purpose of purification and desalination of water.

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