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Ion Exchange Properties of a Terpolymer Resin Derived from 2, 4-Dihydroxybenzaldehyde, Oxamide and Formaldehyde

M. V. TARASE, W. B. GURNULE* and A. B. ZADE

Department of Chemistry, Laxminarayan Institute of Technology,
Rashtrasant Tukdoji Maharaj, Nagpur University, Nagpur-440 010, India.

*Department of Chemistry, Kamla Nehru College,
Sakkaradara, Nagpur-440 009. India.

wbgurnule@yahoo.co.in

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Abstract: Terpolymer resins (2,4-DHBOF) were synthesized by the condensation of 2,4-dihydroxybenzaldehyde and oxamide with formaldehyde in the presence of hydrochloric acid as catalyst, proved to be selective chelation ion exchange terpolymer resins for certain metals. Chelation ion exchange properties of these polymers were studied for Fe^{+3} , Cu^{+2} , Hg^{+2} , Cd^{+2} , Co^{+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 study was carried out over a wide pH range and in a media of various ionic strengths. The polymer showed a higher selectivity for Fe^{+3} , Cd^{+2} and Co^{+2} ions than for Cu^{+2} , Hg^{+2} , Zn^{+2} , Ni^{+2} and Pb^{+2} ions.

Keywords: Synthesis, Ion-exchangers, Batch equilibrium, Distribution ratio, Resin

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 FTIR spectra, TG and DSC analyses. The chelating behavior of

the prepared resin was studied with Cu(II), Zn(II), Ni(II), Cd(II) and Pb(II) metal ions. Samir *et al.*⁴ synthesized ion exchange resin from 8-quinolinyl methacrylate and characterized by conventional methods. The thermal analysis was carried out using TGA and DSC. 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), poly (8-hydroxyquinoldine-5,7 diylmethylene) and poly (2-aminophenol-5,7 diylmethylene) were synthesized and characterized by Ebraheem⁵. 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 phenolic compound shows higher order than the resin copolymer derived from semicarbazone derivatives⁶. 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. L⁷ synthesized crosslinked poly [3-(methacryloyl- amino)-propyl]-dimethyl(3-sulfopropyl)ammoniumhydroxide-co-2-acryl-amidoglycolic acid [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.equ. g⁻¹ for Hg(II) at pH 2. The recovery of the resin was investigated at 20 °C under different concentration of HNO₃ and HClO₄.

Jadhao M.M. and coworker⁸ 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.

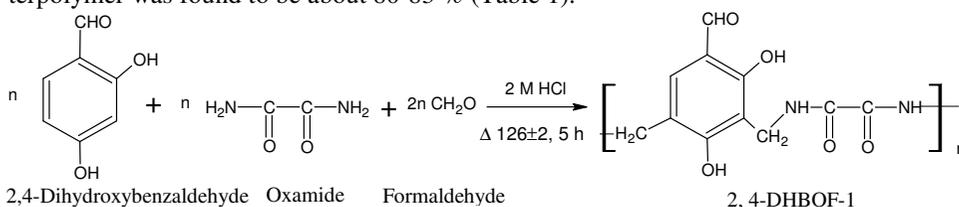
So far no resin based on 2,4-dihydroxybenzaldehyde-oxamide-formaldehyde in acidic media has been synthesized for the quantitative separation of transition metal ions. As industrial influence often rich in transition metal ions, removal of these metals use an important task for industries. Therefore we have studied the use of ion exchanger for removal and separation of heavy metal ions. In this paper synthesis and characterization of the above resin are reported together with the condition for the effective separation of transition metal ions.

Experimental

The chemicals 2,4-dihydroxybenzaldehyde, oxamide and formaldehyde (37%) used are of A. R. grade and chemically pure which is purchased from Merck. Solvents like *N, N*-dimethyl formamide and dimethylsulphoxide were used after distillation.

Preparation of 2, 4-DHBOF terpolymers

The 2,4-DHBOF-I terpolymer resin was prepared by condensing 2, 4-dihydroxybenzaldehyde (1.66 g, 0.1 mol) and oxamide (0.88 g, 0.1 mol) with formaldehyde (7.5 M l, 0.2 mol) in the presence of 2 M HCl as a catalyst at 126 ± 2 °C in an oil bath for 5 h (Scheme 1). The brown colored solid product obtained was immediately removed and extracted with diethyl ether to remove excess of 2, 4-dihydroxybenzaldehyde-formaldehyde copolymer, which might be present along with the 2, 4-DHBOF-I terpolymer. It was further purified by dissolving in 8% NaOH and then filtered. The terpolymer was then reprecipitated by drop wise addition of 1:1 (v/v) conc. HCl / water with constant stirring and filtered. The process was repeated twice. The resulting polymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified terpolymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of the terpolymer was found to be about 80-83 % (Table 1).



Scheme 1. Synthesis of 2, 4-DHBOF-I terpolymer.

Table 1. Synthesis and physical data of 2, 4-DHBOF terpolymers resins.

Terpolymers	Reactants			Catalyst 2 M HCl (aq) mL	Yield, %
	2,4-DHB, m mol.	Oxamide, mol.	Formaldehyde, mol.		
2,4-DHBOF-I	0.1	0.1	0.2	200	82.6
2,4-DHBOF-II	0.2	0.1	0.3	200	83.9
2,4-DHBOF-III	0.3	0.1	0.4	200	81.6
2,4-DHBOF-IV	0.4	0.1	0.5	200	80.3

Similarly, the other terpolymers *viz.* 2, 4-DHBOF-II, 2, 4-DHBOF-III, 2, 4-DHBOF-IV were synthesized by varying the molar ratios of the reacting monomers *i. e.* 2, 4-dihydroxybenzaldehyde, oxamide and formaldehyde in the ratios of 2:1:3, 3:1:4, 4:1:5 respectively.

Analytical and physicochemical studies

The intrinsic viscosities were determined using a Tuan-Fuoss viscometer⁹ at six different concentrations ranging from 0.3 wt % to 0.05 wt % of resin in DMF at 300 °C. Intrinsic viscosity (η) was calculated by the Huggin's⁹ eq. (1) and Kraemer⁹ eq (2).

The elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyser instruments. The UV-Visible studies were out carried using Hitachi 330 UV-VIS-NIR Spectrometer in the range 200-850 nm. The Infrared spectrum was recorded in the region of 500-4000 cm^{-1} on Perkin Elmer Spectrum RX1 FT-IR Spectrometer. ¹H-NMR studied using Bruker Avance-II FT-NMR Spectrometer in DMSO- d_6 solvent. All the analytical and spectral studies for the newly synthesized terpolymer were carried out at Sophisticated Analytical Instrumentation Facility (SAIF) Punjab University, Chandigarh.

Ion exchange properties

To decide the selectivity of 2, 4-DHBOF terpolymers, we studied the influence of various electrolytes, the rate of metal uptake and distribution of metal ions between the terpolymer

and solution. The results of the batch equilibrium study carried out with the terpolymer samples are presented in Tables 5-7.

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

The terpolymer sample (25 mg) was suspended in an electrolyte solution of NaNO₃ (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 2 mL of 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. 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. The experiment was repeated in the presence of other two electrolytes such as NaCl and NaClO₄.

Evaluation of the rate of metal 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 resins was determined from time to time at 25 °C (in the presence of 25 mL of 1 M NaNO₃ solution). It was assumed that under the given conditions, the state of equilibrium was established within 24 h. The rate of metal ions uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to the time, which required for the state of equilibrium.

Evaluation of the distribution of the metal Ions at different pH

The distribution of each one of the five metal ions *i.e.* Fe⁺³, Cu⁺², Hg⁺², Cd⁺², Co⁺², Zn⁺², Ni⁺² and Pb⁺² between the polymer phase and the aqueous phase was determined at 25 °C and in the presence of a 1 M NaNO₃ solution. The experiments were carried out as described above at different pH values. The distribution ratio 'D' is defined by eq. (3).

$$D = \frac{\text{Wt. (mg) of metal ions taken up by 1g of terpolymer}}{\text{Wt. (mg) of metal ion present in 1 mL of terpolymer}}$$

Results and Discussion

The terpolymers which have been use in the present investigation were prepared by the reaction scheme 1. The resin sample was brown in color, insoluble in commonly used solvent, but was soluble in DMF, DMSO, THF, pyridine, concentrated H₂SO₄. No precipitation and degradation occurs of resin in all the solvents. These resins were analyzed for carbon, hydrogen and nitrogen content (Table 2).

Viscometric study

Viscometric measurements were carried out in DMF solution at 30 °C using a Tuan Fouss⁹ viscometer. Reduced viscosity versus concentration (3% - 0.5%) was plotted for each set of data. The intrinsic viscosity [η] was determined by the corresponding linear plots (Figure 1). The following equations were used to determine Huggin's⁹ and Krammer's⁹ constant, respectively:

$$\eta_{sp}/C = [\eta] + k_1.[\eta]^2.C \quad (1)$$

$$\ln \eta_{rel.}/C = [\eta] - k_2.[\eta]^2.C \quad (2)$$

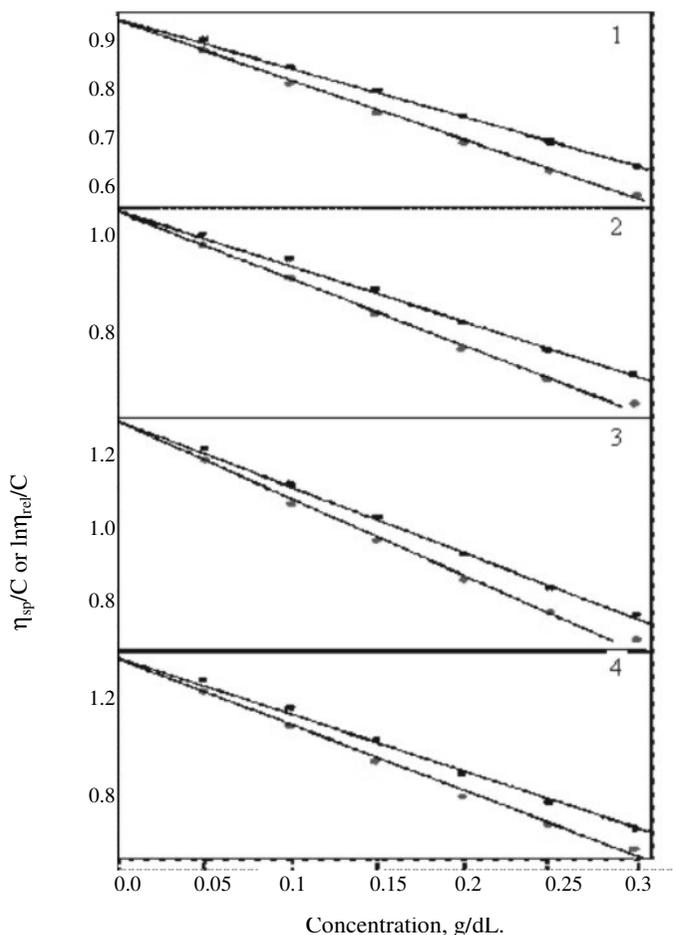


Figure 1. Viscometric plots of terpolymers (1) 2, 4-DHBOF-I, (2) 2, 4-DHBOF-II, (3) 2, 4-DHBOF-III, (4) 2, 4-DHBOF-IV

According to above relations, a plot of η_{sp}/C and η_{rel}/C against C were linear with slopes of k_1 and k_2 respectively. Intercepts on the viscosity function axis gave $[\eta]$ valid in both plots. The calculated values of the constants k_1 and k_2 for the intrinsic viscosities (Table 2) satisfy the relation $k_1 + k_2 = 0.5$ favourably¹⁰. It was observed that terpolymers having higher M_n show a higher value of $[\eta]$.

Table 2. Elemental analysis data of 2, 4-DHBOF terpolymers resins.

Terpolymers	Elemental analysis, %						Intrinsic Viscosity $[\eta]$
	C		H		N		
	Calc.	Found	Calc.	Found	Calc.	Found	
2,4-DHBOF-I	52.8	52.9	4.0	4.09	11.2	11.17	0.91
2,4-DHBOF-II	57.0	56.8	4.0	4.03	7.0	6.94	1.04
2,4-DHBOF-III	58.9	58.7	4.0	4.09	5.09	5.01	1.23
2,4-DHBOF-IV	60.0	59.9	4.0	4.06	4.0	3.94	1.36

Electronic spectra

The UV-visible spectra (Figure 2) of all 2, 4-DHBOF terpolymer samples in pure DMSO were recorded in the region 190 nm – 800 nm. All the four 2,4-DHBOF terpolymers samples displayed two characteristic broad bands at 280 nm and 320 nm. 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 a $\pi \rightarrow \pi^*$ transition while the former band (less intense) may be due to a $n \rightarrow \pi^*$ transitions¹¹.

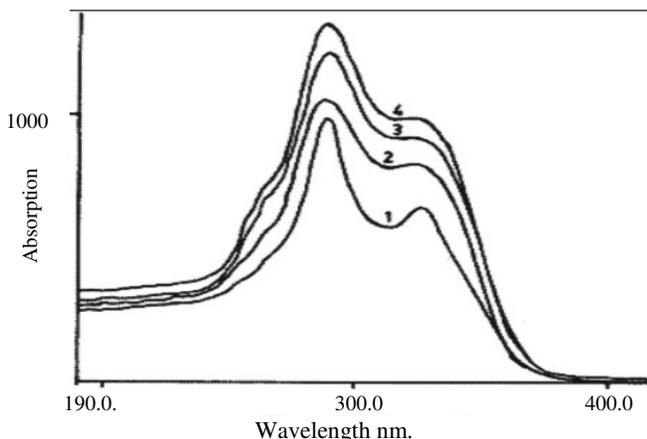


Figure 2. Electronic spectra of terpolymer resins (1) 2, 4-DHBOF-I, (2) 2, 4-DHBOF-II, (3) 2, 4-DHBOF-III, (4) 2, 4-DHBOF-IV.

The bathochromic shift (shift towards longer wavelength) from the basic value of the C=O group *viz.* 310 nm and 240 nm respectively, may be due to the combine effect of conjugation and phenolic hydroxyl group (auxochrome)^{12,13}. It may be observed from the electronic spectra of the 2, 4-DHBOF terpolymers that the absorption intensity gradually increases in the order 2,4-DHBOF -I < 2,4 - DHBOF - II < 2,4 - DHBOF - III < 2,4 - DHBOF - IV. The observed increasing order may be due to introduction of more chromophores (C=O group) and auxochromes (phenolic OH) in the repeat unit structure of the terpolymers.

Infrared spectra

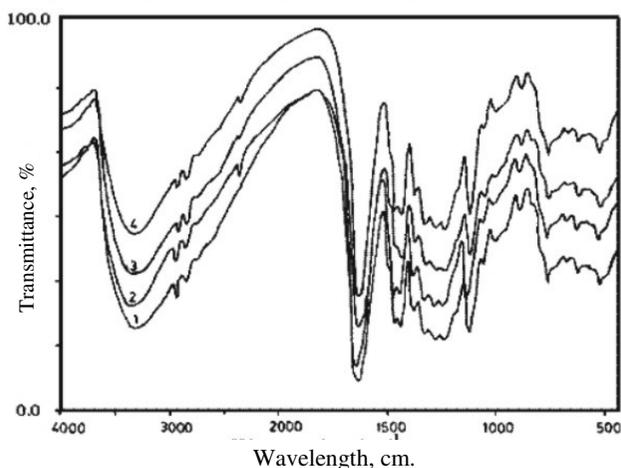
The IR-spectra of all four 2, 4-DHBOF terpolymers are presented in Figure 3. The IR-spectra revealed that all these terpolymers give rise to nearly similar pattern of spectra (Table 3). A band appeared in the region 3337 cm^{-1} - 3316 cm^{-1} may be assigned to the stretching vibration of the phenolic hydroxy groups exhibiting intermolecular hydrogen bonding¹². The presence of weak peak at 2878 cm^{-1} - 2878 cm^{-1} describes the -NH- in biuret moiety may be ascribed in the terpolymeric chain^{12,13}. The presence of methyl and methylene vibrations at 2950 cm^{-1} - 2846 cm^{-1} gives sharp and weak peaks. The sharp band displayed at 1631 cm^{-1} -1628 cm^{-1} may be due to the stretching vibration of carbonyl group of both, ketonic as well as biuret moiety¹⁴. The sharp and weak bond obtained at 1381 cm^{-1} -1380 cm^{-1} suggests the presence of -CH₂- methylene bridges¹⁵ in the terpolymer chain. The presence of 1, 2, 3, 4, 5 - pentasubstitution of aromatic ring is recognized from the weak bond appearing at 898 cm^{-1} - 897 cm^{-1} respectively¹⁵.

Table 3. IR frequencies of 2, 4-DHBOF terpolymers resins.

Assignment	Observed wave number, cm^{-1}			
	2,4-DHBOF-I	2,4-DHBOF-II	2,4-DHBOF-III	2,4-DHBOF-IV
-OH (phenolic)	3335.5 b,st	3337.0 b,st	3323.1 b,st	3316.1 b,st
>NH (amido)	2878.9 sh,w	2878.3 sh,w	2878.6 sh,w	2878.5 sh,w
-CH ₃ , >CH ₂ assymm. symm vib	2850.3 sh,w	2848.6 sh,w	2847.8 sh,w	2846.0 sh,w
>C=O (ketonic and biuret moiety)	1631.4 sh,st	1631.4 sh,st	1630.8 sh,st	1628.9 sh,st
Aromatic ring	1475.7 sh,w	1478.4 sh,w	1479.0 sh,w	1479.4 sh,w
>CH ₂ (methylene bridges)	1380.3 sh,m	1381.5 sh,m	1380.4 sh,m	1381.0 sh,m
1,2,3,4,5substitution in benzene skeleton	897.7 sh,w	898.7 sh,w	898.3 sh,w	898.1 sh,w

¹H-nuclear magnetic resonance spectra

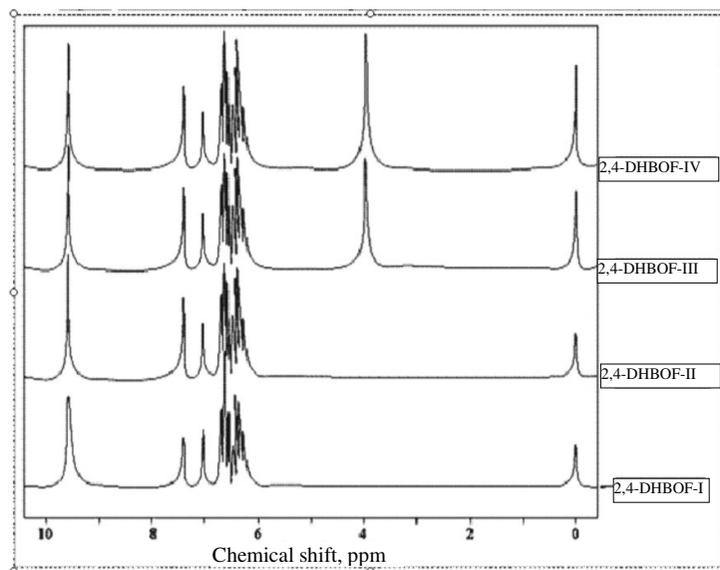
¹H-NMR spectra of all the four 2, 4 DHBOF terpolymers were scanned in DMSO-d₆. The spectral data are given in Table 3 and the spectra are presented in Figure 3. From the spectra it is revealed that all the 2, 4 DHBOF terpolymers gave rise to different pattern of ¹H-NMR spectra, since each of the 2, 4 DHBOF terpolymers possess set of proton having different electronic environments.

**Figure 3.** Infrared spectrum of terpolymer resins (1) 2, 4-DHBOF-I, (2) 2, 4-DHBOF-II, (3) 2, 4-DHBOF-III, 4) 2, 4-DHBOF-IV.

Except 2, 4 DHBOF-I and 2, 4 DHBOF-II the remaining two terpolymers *viz.* 2, 4 DHBOF-III and 2, 4 DHBOF-IV, exhibit singlet signal in the region 3.95 ppm which are due to methylenic protons of Ar-CH₂-Ar bridge^{12,13}. The weak multiplet signals (unsymmetrical pattern) in the region 7.37 ppm are due to aromatic protons. The methylenic protons of the Ar-CH₂-N moiety may be recognized as signal appearing in the region 6.44 ppm^{12,13}. The signal in the region 6.66 ppm are attributed to the protons of -NH- bridges. A medium singlet peaks appeared at 9.51 ppm may be assigned to aldehydic protons of Ar-CHO^{12,13}. The signals in the range of 7.06 ppm are attributed to phenolic hydroxyl protons. This significant downfield chemical shift of the proton of phenolic OH group clearly indicates intramolecular hydrogen bonding of OH with the carbonyl group present at the adjacent *ortho* position^{12,13}.

Table 4. ^1H NMR spectral data of 2, 4-DHBOF terpolymer resins in DMSO-d_6

Chemical shift (δ) ppm of terpolymer				Nature of proton assigned
2,4-DHBOF-I	2,4-DHBOF-II	2,4-DHBOF-III	2,4-DHBOF-IV	
9.51	9.51	9.51	9.53	Aldehydic proton of Ar-CHO
7.37	7.37	7.38	7.38	Aromatic proton (unssymm. Pattern)
7.07	7.08	7.06	7.06	Proton of Ar-OH (phenolic -OH)
6.66	6.66	6.66	6.66	Amido proton of -CH ₂ -NH-CO- linkage
6.56	6.44	6.45	6.44	Methylene proton of Ar-CH ₂ -NH moiety
--	--	3.95 s	3.95 s	Methylene proton of Ar-CH ₂ -Ar linkage

**Figure 4.** Proton NMR Spectra of Terpolymer Resin (1) 2, 4-DHBOF-I, (2) 2, 4-DHBOF-II, (3) 2, 4-DHBOF-III, (4) 2, 4-DHBOF-IV.

On the basis of the nature and reactive position of the monomer elemental analysis, electronic, IR, NMR spectra and molecular weight, the most probable structures have been proposed for these terpolymers as shown in Figure 5.

Ion-exchange properties

The results of the batch equilibrium study carried out with the terpolymer samples 2, 4-DHBOF-I, 2, 4-DHBOF-II, 2, 4-DHBOF-III and 2, 4-DHBOF-IV are presented in Tables 5 - 7. From the study with eight metal ions under limited variation of experimental conditions, certain generalization may be made about the behavior of the terpolymer sample.

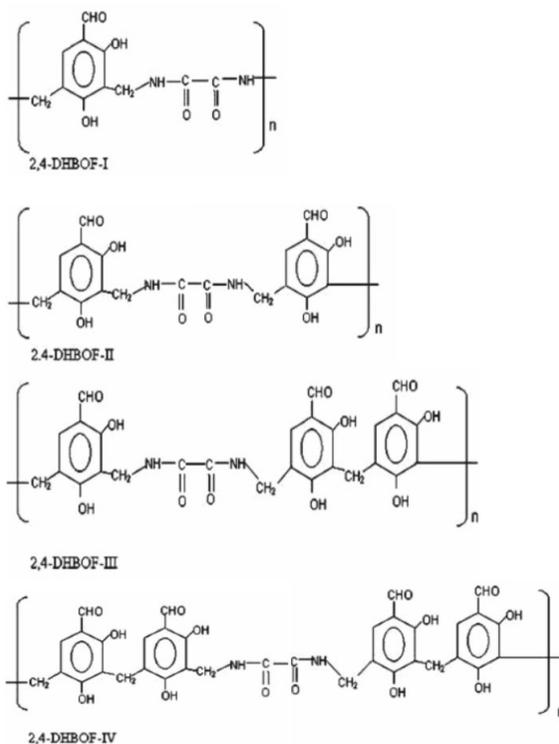


Figure 5. The suggested structures of 2, 4-DHBOF terpolymer resins.

Effect of Electrolytes on Metal Uptake

We examine the effect of NO_3^- , Cl^- , ClO_4^- and SO_4^{2-} at various concentrations on the equilibrium of metal-resin interaction. Table 5 shows that the amount of metal ions taken up by a given amount of terpolymer depends on the nature and concentration of the electrolyte present in the solution. In the presence of nitrate, chloride and perchlorate ions the uptake of Fe^{+3} , Cu^{+2} , Hg^{+2} , Cd^{+2} , Co^{+2} , Zn^{+2} , Ni^{+2} and Pb^{+2} ions increasing with increasing concentration of electrolytes. However in the presence of sulphate ions the uptake capacity decreases with increasing concentration. Moreover the uptake of Fe^{+3} , Cd^{+2} , Co^{+2} ions increases with increasing concentration of nitrate, chloride and perchlorate ions¹⁶⁻¹⁸ as compare to Cu^{+2} , Hg^{+2} , Zn^{+2} , Ni^{+2} and Pb^{+2} ions whereas decreases in presence of sulphate ions. Above nitrate, chloride and perchlorate ions form weak complex with the above metal ions while sulphate ions 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 ions¹⁶⁻¹⁸. This type of trends has been observed by the other investigator in this field.

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 condition as possible. Table 6 show 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 metal ions in the aqueous solution, which is in contact with the given polymer. The results showed 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 required about 3 h for the establishment of the equilibrium, whereas Cu^{+2} , Hg^{+2} , Cd^{+2} , Co^{+2} , Zn^{+2} , Ni^{+2} and Pb^{+2} ions required about 6 h. Thus, the rate of metal ion uptake follows the order $\text{Fe}^{+3} \gg \text{Cd}^{+2} > \text{Co}^{+2} > \text{Hg}^{+2} > \text{Zn}^{+2} > \text{Pb}^{+2} > \text{Cu}^{+2} > \text{Ni}^{+2}$ for the terpolymer¹⁶⁻¹⁸.

Table 5. Evaluation of the effect of different electrolytes on the uptake of several metal ions^a by 2,4-DHBOF-I terpolymers resins.

Metal ion	Electrolyte mol/L	pH	Weight (mg) of metal ion taken up in the presence of			
			NaClO_4	NaCl	NaNO_3	Na_2SO_4
Fe^{+3}	0.01	2.5	0.10	0.13	0.18	0.69
	0.05		0.15	0.21	0.27	0.62
	0.10		0.29	0.34	0.44	0.48
	0.50		0.62	0.64	0.67	0.43
	1.00		0.70	0.71	0.72	0.34
Cu^{+2}	0.01	4.5	0.02	0.04	0.03	0.58
	0.05		0.04	0.07	0.08	0.49
	0.10		0.11	0.21	0.20	0.41
	0.50		0.34	0.57	0.34	0.31
	1.00		0.58	0.66	0.49	0.20
Hg^{+2}	0.01	6.0	0.20	0.25	0.41	2.38
	0.05		0.29	0.37	0.73	2.12
	0.10		0.62	0.89	1.19	1.61
	0.50		1.88	2.01	2.01	1.43
	1.00		2.17	2.35	2.31	1.12
Cd^{+2}	0.01	5.0	0.15	0.23	0.30	1.20
	0.05		0.23	0.32	0.44	1.08
	0.10		0.50	0.58	0.76	0.87
	0.50		1.18	1.24	1.26	0.76
	1.00		1.35	1.40	1.43	0.53
Co^{+2}	0.01	5.0	0.06	0.09	0.19	0.40
	0.05		0.10	0.12	0.27	0.30
	0.10		0.20	0.27	0.42	0.20
	0.50		0.58	0.62	0.63	0.16
	1.00		0.67	0.71	0.70	0.09
Zn^{+2}	0.01	5.0	0.05	0.06	0.16	0.64
	0.05		0.07	0.10	0.25	0.50
	0.10		0.13	0.26	0.39	0.41
	0.50		0.44	0.62	0.53	0.37
	1.00		0.66	0.73	0.62	0.26
Ni^{+2}	0.01	4.5	0.01	0.02	0.01	0.46
	0.05		0.02	0.07	0.001	0.35
	0.10		0.08	0.12	0.003	0.27
	0.50		0.27	0.20	0.005	0.23
	1.00		0.48	0.33	0.007	0.14
Pb^{+2}	0.01	6.0	0.13	0.20	0.37	1.80
	0.05		0.20	0.2	0.56	1.47
	0.10		0.38	0.77	0.93	1.21
	0.50		1.27	1.91	1.50	0.98
	1.00		2.01	2.25	1.83	0.71

^a $[\text{M}(\text{NO}_3)_2] = 0.1 \text{ mol/L}$; Volume = 2 mL; Volume of electrolyte solution = 25 mL; Weight of resin = 25 mg; Time = 24 h at room temperature.

Table 6. Comparison of the rates of metal (M) ion uptake^a by 2, 4-DHBOF-I terpolymers resins.

Metal ion	% of metal ion uptake ^b at different time (h)					
	1	2	3	4	5	6
Fe ⁺³	45.5	69.5	98.0	-	-	-
Cu ⁺²	5.5	15.5	29.5	36.0	49.0	59.0
Hg ⁺²	10.5	16.5	19.5	39.5	61.0	86.5
Cd ⁺²	9.0	11.0	24.5	49.5	69.5	95.5
Co ⁺²	6.5	20.5	39.5	59.5	68.5	90
Zn ⁺²	2.5	10.5	24.5	44.0	57.5	72.0
Ni ⁺²	-	-	0.25	0.50	0.75	1.0
Pb ⁺²	4.0	13.5	26.5	64.5	65.5	66.5

^a[M(NO₃)₂] = 0.1 mol/L.; Volume = 2 mL; Volume of electrolyte solution = 25 mL; Weight of resin = 25 mg; Time = 24 h at room temperature. ^bMetal ion uptake = (amount of metal ion absorbed x 100)/ amount of metal ion absorbed at equilibrium.

Table 7. Distribution ratio D^a of various metal ion as a function of the pH^b by 2, 4-DHBOF-I terpolymers resins.

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	87.12	136.14	212.42	4355.55	-	-	-	-	-	-
Cu ⁺²	-	-	-	59.25	65.70	69.84	120.26	133.33	1688.88	-
Hg ⁺²	-	-	-	33.71	110.86	127.91	378.94	524.13	569.54	757.67
Cd ⁺²	-	-	-	207.40	334.39	484.58	1022.22	1886.42	3861.72	5837.03
Co ⁺²	-	-	-	20.85	85.40	207.40	449.83	1096.29	2133.33	5837.03
Zn ⁺²	-	-	-	37.19	82.05	106.47	172.54	266.66	1392.59	3466.66
Ni ⁺²	-	-	-	-	-	-	0.49	0.89	3.22	5.03
Pb ⁺²	-	-	-	38.09	55.64	72.72	92.51	130.58	176.45	259.69

^aD = Weight (mg) of metal ion taken up by 1 g of terpolymer/ Weight (mg) of metal ions present in 1 mL of solution. ^b[M(NO₃)₂] = 0.1 mol/L.; Volume = 2 mL; Volume of electrolyte solution = 25 mL; Weight of resin = 25 mg; Time = 24 h (equilibrium state), at room temperature.

Distribution ratios of metal Ions at different pH

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results given in Table 7. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the terpolymers increases with increasing pH of the medium¹⁶⁻¹⁸. The magnitude of increase, however, is different for different metal ions. The selectivity of Fe(III) ion is more for the 2, 4-DHBOF terpolymer resins as compare to the any other metal ions under study. The order of distribution ratio of metal ions measured in the pH range 1.5 to 6.5 is found to be Fe⁺³ >> Cd⁺² ≈ Co⁺² > Zn⁺² > Cu⁺² > Hg⁺² > Pb⁺² > Ni⁺². Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different metal ions¹⁶⁻¹⁸. For example, the result suggests the optimum pH 2.5 for the separation of Fe⁺³ and Co⁺² or Cd⁺² the distribution ratios 'D' as 4355.55 and 5837.03 respectively using the 2,4-DHBOF-I terpolymer resin as ion exchanger. Similarly for the separation of Fe⁺³ and Pb⁺²(II) at the optimum pH is 2.5 the distribution ratios are 4355.55 and 259.69 respectively for 2, 4-DHBOF-I terpolymer. The lowering in the distribution ratio of Fe⁺³ was found to be small and hence, efficient separation could be achieved. Thus the separation of Fe⁺³ from other metals having combination (1) Fe⁺³ and Cu⁺² (2) Fe⁺³ and Hg⁺² (3) Fe⁺³ and Zn⁺² (4) Fe⁺³ and Pb⁺² (5) (4) Cu⁺² and Cd⁺² are effectively may separate out.

Conclusion

- 1) The 2,4-DHBOF terpolymer based on the condensation polymerization of 2,4-dihydroxybenzaldehyde and oxamide with formaldehyde in the presence of acid catalyst has been prepared.
- 2) The 2,4-DHBOF terpolymer is a selective chelating ion exchange polymer for certain metals.
- 3) The terpolymer showed a higher selectivity for Fe^{+3} , Cd^{+2} and Co^{+2} than for Cu^{+2} , Hg^{+2} , Zn^{+2} , Ni^{+2} and Pb^{+2} ions.

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