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Chelating ion exchange properties of terpolymer resin 2,4-DHPOF-II derived from 2,4-dihydroxypropiophenone

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ABSTRACT

Terpolymer resin 2,4-DHPOF-II was synthesized by the condensation of 2,4-dihydroxypropiophenone (2,4-DHP) and oxamide (O) with formaldehyde (F) in the presence of 2M HCl as catalyst at 126 ± 1°C. Terpolymer was characterized by UV-visible, IR, ^{1}H NMR spectral and thermal analysis. It is proved to be a selective chelating ion exchange terpolymer for Fe^{+3}, Cu^{+2}, Hg^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2} and Pb^{+2} metal ions. Chelating ion-exchange properties of synthesized terpolymer were studied for above mentioned metal ions. A batch equilibrium method was employed to study the selectivity of metal ion's uptake involving the measurements of distribution of given metal ion between sample and solution. Study was carried out using different parameters like pH range, shaking time and media of various ionic strengths.

Keywords: Terpolymers; Thermal analysis; Ion-exchangers; Distribution ratio; Metal ion uptake

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1. Introduction

Trace organic and inorganic contaminants possessing strong complex forming characteristic are abundantly found in aquatic system. Ion exchange polymers like viz. phenol-formaldehyde, amino-formaldehyde copolymers or phenol-amino-formaldehyde terpolymer can be employed to achieve required degree of removal. Terpolymers possess very useful applications as adhesives, high temperature flame resistant fibres, coating materials, semiconductors, catalysts and ion-exchange resins [1,2]. Ion-exchange resins have attracted much interest in recent years due to their application in waste water treatment, metal recovery and for identification of specific metal ions [4,3]. Ion-exchange has attained the status of a unit operation in chemical industries and has mostly replaced operations like distillation and other traditional methods of separations. Chelation ion-exchange chromatography has become a very powerful technique in extraction of trace and ultra trace materials [5], separation of rare earths, removal of contamination and in many other industrial separation and process of purification and concentration. For analytical work, synthetic organic ion-exchangers are having main interest. Extensive literature is available to interpret the experimental results in the light of practical applicability of various terpolymer resins. Lutfor et al. [6] prepared a chelating ion-exchange resin contain amidoxime functional group was characterized by FT-IR spectra, TG and DSC analysis and chelating behavior of prepared resin was studied with Cu^{+2}, Zn^{+2}, Ni^{+2}, Cd^{+2} and Pb^{+2} metal ions. Chelating ion-exchange properties of 2,4-dinitrophenylhydrazone of 2-hydroxy-acetophenone-formaldehyde resin [7] and oxime of 2-hydroxyacetophenone-substituted benzoic acid-formaldehyde resins [8] for different metal ions have been studied.

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Terpolymer synthesized by using *o*-nitrophenol and thiourea with paraformaldehyde was reported and its chelation ion exchange properties were investigated by a static batch equilibrium method [9]. Poly[(2-hydroxy-4-methoxybenzophenone)ethylene] resin has good binding capacity for the lanthanum (III) at various conditions [10]. The copolymer from 2,4-dichlorophenyl acrylate/8-quinolinyl methacrylate and acrylic copolymer derived from 8-quinolinyl methacrylate was found to be a good cation exchanger as it has pendant ester-bound quinolinyl group [11,12]. Recently, Shah et al. reported the chelating ability of resin synthesized by a microwave irradiation technique involving salicylic acid and formaldehyde with resorcinol [13].

Present study deals with the synthesis and characterization of 2,4-dihydroxypropiophenone-oxamide-formaldehyde-II [2,4-DHPOF-II] terpolymer resin prepared by using previously mentioned monomers by condensation polymerization in presence of acid catalyst for first time. Synthesized terpolymer was characterized by elemental; UV-visible, IR, ^{1}H-NMR spectral and thermal analysis. Further, the chelating ion-exchange property of the 2,4-DHPOF-II terpolymer resin was also reported for specific metal ions.

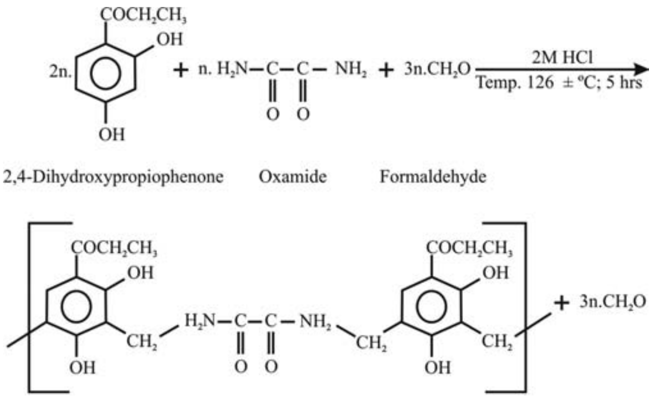
2. Experimental

2.1. Starting materials

All important chemicals (starting materials) like 2,4-dihydroxypropiophenone (2,4-DHP) and oxamide (O) with formaldehyde (F) etc. used in the preparation new 2,4-DHPOF-II terpolymer resin were of A. R. grade and purchased from Merck, India, wherever necessary the purity was tested and confirmed by TLC.

2.2. Synthesis of 2,4-DHPOF-II terpolymer

Terpolymer 2,4-DHPOF-II was synthesized by condensing 2,4-dihydroxypropiophenone (2,4-DHP) (3.32 gm, 0.2 mol) and oxamide (O) (0.88 gm, 0.1 mol) with formaldehyde (F) (15 ml, 0.3 mol) using molar ratio of 2:1:3 in presence of 2M HCl as a catalyst at $126 \pm 1^{\circ}$C for 5 h as described in literature [14]. Brown colored solid terpolymer product obtained was immediately removed and extracted with diethyl ether to remove excess 2,4-dihydroxypropiophenone-formaldehyde copolymer, which might be present along with 2,4-DHPOF-II terpolymer. It was further purified by dissolving in 8% NaOH and then filtered. Terpolymer was then reprecipited by dropwise addition of (v/v) conc HCl/water with constant stirring and filtered and this process was repeated twice. Resulting terpolymer sample was washed with boiling water and dried in a vacuum at room temperature. Purified terpolymer was finally ground to pass through a 300 mesh size sieve and used in all experiments carried out in the ion exchange study (Scheme 1).



Scheme 1. Formation of 2,4-DHPOF-II terpolymers.

2.3. Characterization of terpolymers

Terpolymer was subjected to microanalysis for carbon, hydrogen and nitrogen on a Colemann C, H, and N analyzer at RSIC, Punjab University, Chandigarh. Number average molecular weight ($\overline{Mn}$) of terpolymer resin was determined by using non-aqueous conductometric titration using 25 mg of sample in DMF against alco KOH. Graph was plotted between specific conductance against the milliequivalents KOH required for neutralization of 100 gm of terpolymer. Electronic absorption spectrum of terpolymer in DMSO was recorded on Shimadzu UV-Visible double beam spectrophotometer fitted with automatic pen chart recorder on thermosensitive paper in the range of 200–850 nm. Infrared spectrum of 2,4-DHPOF-II terpolymer was recorded in nujol mull on Perkin- Elmer-spectrum RX-I spectrophotometer in the range of 4000–500 cm^{-1}. ^{1}H-NMR spectrum was recorded on Bruker Advance-II 400 MHz ^{1}H-NMR spectrometer using DMSO-d_6 as a solvent.

2.4. Thermogravimetric analysis

Non-isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of 10°C/min using 5–6 mg of samples in platinum crucible from temperature of 40–800°C and thermogram was recorded. On the basis of obtained results, the decomposition pattern was proposed for the terpolymers (Figure 4).

Table 1
Elemental analysis molecular weight determination and intrinsic viscosity of 2, 4-DHPOF-II terpolymer

Terpolymer	Empirical formula of repeat unit	Empirical weight of repeat unit (gm)	Average degree of polymerization ($\overline{DP}$)	Average molecular weight ($\overline{Mn}$)	Elemental analysis					
					% of C		% of H		% of N	
					Cal.	Found	Cal.	Found	Cal.	found
2,4-DHPOF-II	$C_{23}H_{24}N_2O_8$	456	11.3	5152.8	60.31	60.52	5.43	5.26	7.00	6.14

2.5. Ion-exchange property

Ion-exchange property of 2,4-DHPOF-II terpolymer resin was determined by batch equilibrium method.

2.6. Effect of Electrolytes and their concentrations on metal ion uptake capacity

Terpolymer sample (25 mg) was suspended in an electrolyte solution (25 ml) of known concentration. pH of suspension was adjusted to the required value by using either 0.1M HNO_3 or 0.1M NaOH. The suspension was stirred for 24 h at 30°C and to this 2 ml of 0.1M solution of the metal ion was added and pH was adjusted to the required value again. Mixture was again stirred at 30°C for 24 h and filtered. Precipitate obtained in filter paper was washed; filtrate and washing were combined and metal ion content was determined by titrating against standard EDTA. Same experiment was repeated for other electrolytes understudy. Amount of metal ion uptake by terpolymer is calculated from the difference between a blank reading and experimental reading.

2.7. Rate of uptake for metal ions as a function of time

In order to estimate the time require to reach the state of equilibrium under the given experimental conditions, a series of experiments as described above were carried out, in which the metal ion taken up by the chelating resins was determined from time to time at 30°C (in the presence of 25 ml of 1M $NaNO_3$ solution). It was assumed that, under the given conditions, the state of equilibrium was established within 24 h. Rate of metal ion uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to that at the state of equilibrium.

2.8. Effect of pH on metal ion uptake

Distribution of each of the eight metal ions, i.e. Fe^{+3}, Cu^{+2}, Hg^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2} and Pb^{+2} between the polymer phase and aqueous phase was determined at 30°C in the presence of 1M $NaNO_3$ solution. Experiments were carried out as described above at different pH values. The distribution ratio, '*D*' [15, 16] is defined by the following relationship.

$$D = \frac{\text{wt (mg) of metal ion taken up by 1 ml of terpolymer}}{\text{wt (mg) of metal ion in 1 ml of solution}}$$

3. Results and discussion

Terpolymer sample was brown in color, insoluble in commonly used solvent but soluble in DMF, DMSO, THF, pyridine, concentrated H_2SO_4 like organic solvents. There was no precipitation and degradation of terpolymer occurred in all solvents and melting point is in the range of 540–560°C. It was analyzed for carbon, hydrogen and nitrogen content (Table 1).

3.1. Characterization of terpolymer

Number average molecular weight ($\overline{Mn}$) of terpolymer was estimated by non-aqueous conductometric titration. It could be obtained by multiplying the degree of polymerization $(\overline{Dp})$ by the formula weight of the repeating unit [17,18] which is found to be 5152.8.

UV-visible spectrum of purified 2,4-DHPOF-II terpolymer sample has been recorded in pure DMF as shown in Figure 1. Spectrum of the terpolymer has

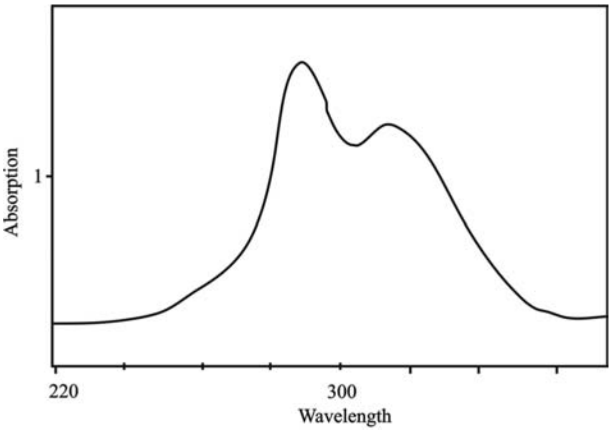


Fig. 1. Electronic spectra of 2,4-DHPOF-II terpolymers.

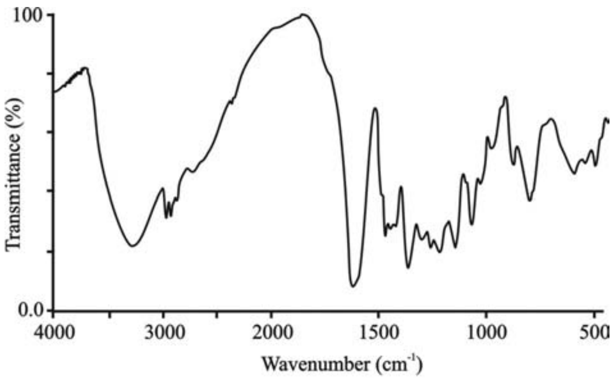


Fig. 2. Infrared spectra of 2,4-DHPOF-II terpolymer.

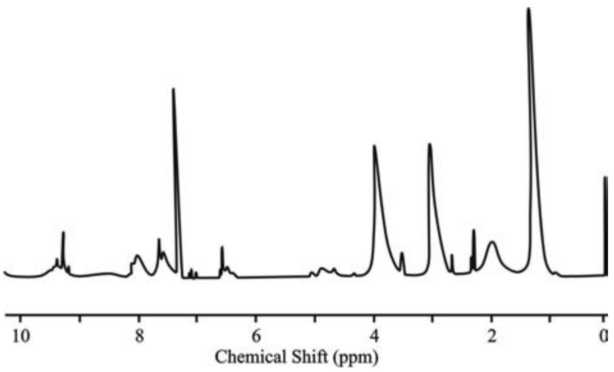


Fig. 3. ^{1}H-NMR spectra of 2,4-DHPOF-II terpolymers.

exhibited two absorption maxima in the region 280 and 320 nm. These observed positions of absorption bands indicate the presence of carbonyl group (ketonic) processing double bond which is in conjugation with the aromatic nucleus. The appearance of former band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition while the later bond (less intense) may be due to $n \rightarrow \pi^*$ electronic transition. The shifting of first absorption maxima of 40 nm from the basic values of 240 to 280 nm and second maxima 20 nm from basic values of 300 to 320 nm may be due to combined effect of conjugation and presence of phenolic –OH group (auxochrome) is responsible for bathochromic shift [19].

FT-IR-spectrum of 2,4-DHPOF-II terpolymer is presented in Figure 2 (Table 2). A broad band appeared in the region 3700–3250 cm^{-1} may be assigned to the stretching vibration of the phenolic –OH groups exhibiting intermolecular hydrogen bonding [20]. Weak peak present at 3000–2975 cm^{-1} describes the –NH– in biuret moity may be ascribed in the terpolymeric chain [20]. Sharp and weak peaks at 2950–2935 cm^{-1} may be given by the presence of methyl and methylene vibrations. A sharp band displayed at 1640–1615 cm^{-1} may be due to the stretching vibration of carbonyl group of both ketonic as well as biuret moity [20,21]. Sharp and weak bond obtained at 1370–1275 cm^{-1} may be due to the presence of –CH$_2$- methylene bridges [21] in the terpolymer chain. The presence of 1, 2, 3, 4, 5-pentasubstitution of aromatic ring may be recognized from the weak bond appearing at 905–860 cm^{-1} respectively [21].

^{1}H-NMR spectrum of 2,4 DHPOF-II terpolymer sample is shown in Figure 3 (Table 3). A weak singlet signals in the region 9.46–9.22 ppm which may be due to the presence of aromatic proton (Ar-H) [21]. A weak singlet signal appearing at 7.98–7.62 ppm may be due to proton of Ar-OH (phenolic –OH). A medium triplet signal appeared at 7.58–7.65 ppm may be due to amido protons –CH$_2$-NH-CO- of polymer chain [21]. A medium doublet signal in the range of 6.52–6.54 ppm is attributed to the protons of methylenic bridge Ar-CH$_2$-NH– of polymeric chain. A medium quartet signal appeared at 6.44–6.55 ppm may be due to the presence of methylenic protons of Ar-CO-CH$_2$-CH$_3$. Also the methyl protons of Ar-CO-CH$_2$-CH$_3$ may be assigned to the peaks at 2.91–2.96 ppm [22].

Table 2
IR frequencies of 2,4-DHPOF-II terpolymer

Functional groups	Observed frequency
–OH (phenolic)	3300.1 b,st
>NH (amido)	2978.3 sh,w
–CH3, >CH2 assymm., symm. vib	2938.6 sh,w
>C=O (ketonic and biuret moity)	1626.8 sh,st
aromatic ring	1478.4 sh,w
>CH2(methylene bridges)	1374.2 sh,m
1,2,3,4,5substitution in benzene skeleton	890.7 sh,w

sh. sharp; b. broad; st. strong; m. medium; and w. weak.

Table 3
^{1}H-NMR Spectral Data of 2, 4-DHPOF-II Terpolymer in DMSO-d6

Nature of proton assigned	Observed chemical shift (ppm)
Aromatic proton (unssymm. Pattern)	9.22s
Proton of Ar-OH (phenolic –OH)	7.87s
Amido proton of –CH2-NH-CO- linkage	7.60 – 7.62t
Methylene proton of Ar-CO-CH2-CH3	7.2q
Methylene proton of Ar-CH2-NH moiety	6.52 - 6.54d
Methyl proton of Ar-CO-CH2-CH3	2.90 – 2.93t

s singlet; d doublet; t triplet; q quartet

Table 4
Thermal behaviour data of 2, 4-DHPOF-II terpolymer resin

Terpolymer resin	Temperature range (°C)	% of weight loss	Degradation of chains
2,4-DHPOF-II	40–168	03.51	H_2O molecule
	168–448	42.03	Two –$COCH_2CH_3$ and four -OH groups
	448–710	81.53	two benzene rings along with three –CH_2- groups
	710–800	98.90	oxamide moiety

3.2. Thermogravimetric analysis

Thermogravimetric analysis is found to be a very useful method to find out thermal stability of polymeric resin. Data of degradation of terpolymer at different temperature have been presented in Table 4 and recorded thermogram has shown in Figure 4. Terpolymer resin exhibited three stages of decomposition after loss of water molecule between 40 and 168°C corresponds to 3.51% loss which may be attributed to calculated 3.79% present per repeat unit of polymer in the temperature range 40–800°C. First step of decomposition was started from 168 to 448°C which represents degradation of two –$COCH_2CH_3$ groups and four -OH groups (42.03% observed and 42.19% calculated). Second step was started from 448 to 710°C corresponding to 81.53% loss of two benzene rings along with three methylenic groups against calculated 81.85%. Third step was started from 710 to 800°C corresponding to loss of remaining oxamide moiety.

On the basis of nature and reactive position of monomer, elemental; UV-visible, FT-IR, ^{1}H-NMR spectral analysis and molecular weight the most probable structure has been proposed for terpolymer sample understudy as shown in Scheme 1.

3.3. Ion exchange properties

With a view to ascertain the selectivity of 2,4-DHPOF-II for the selected metal ion, we have studied the influence of various electrolyte on the selectivity of metal ion, rate of metal ion uptake at different time and distribution ratio of metal ion between terpolymer and solution.

Batch equilibrium technique developed by Gregor et al. [23] and De Geiso et al. [24] was used to study ion exchange properties of 2,4-DHPOF-II terpolymer resins. Results of batch equilibrium study carried out with terpolymer sample are presented in Figures 6 to 11. Eight metal ions Fe^{+3}, Cu^{+2}, Hg^{+2}, Co^{+2}, Cd^{+2}, Zn^{+2}, $Ni^{+2}$and Pb^{+2} in the form of aqueous metal nitrate solution were used. Ion exchange study was carried out using three experimental variables:

(a) Electrolyte and its ionic strength
(b) Shaking time
(c) pH of medium.

Among these three variables a) and c) were kept constant with shaking time of 24 h considering as equilibrium time and only b) was varied with time at constant pH and strength of an electrolyte to evaluate effect of terpolymer on metal uptake capacity [25,26]. Terpolymer-metal ion interaction should be an ion exchange mechanism and the possible model has been designed as in Figure 5.

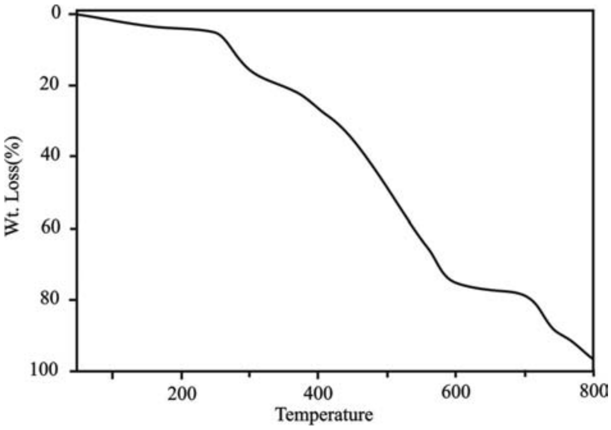


Fig. 4. Thermogram of the 2, 4-DHPOF-II terpolymers.

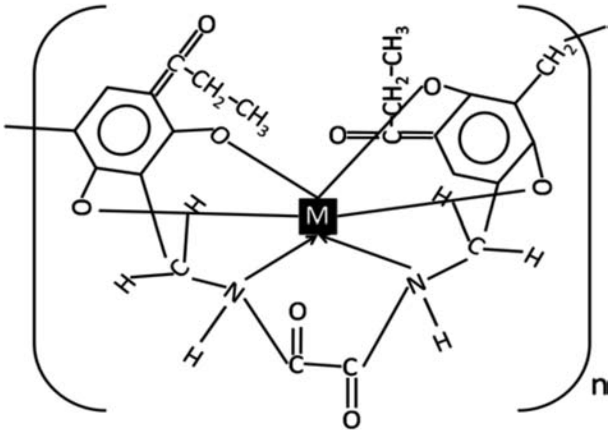


Fig. 5. 2, 4-DHPOF-II terpolymer-metal ion interaction.

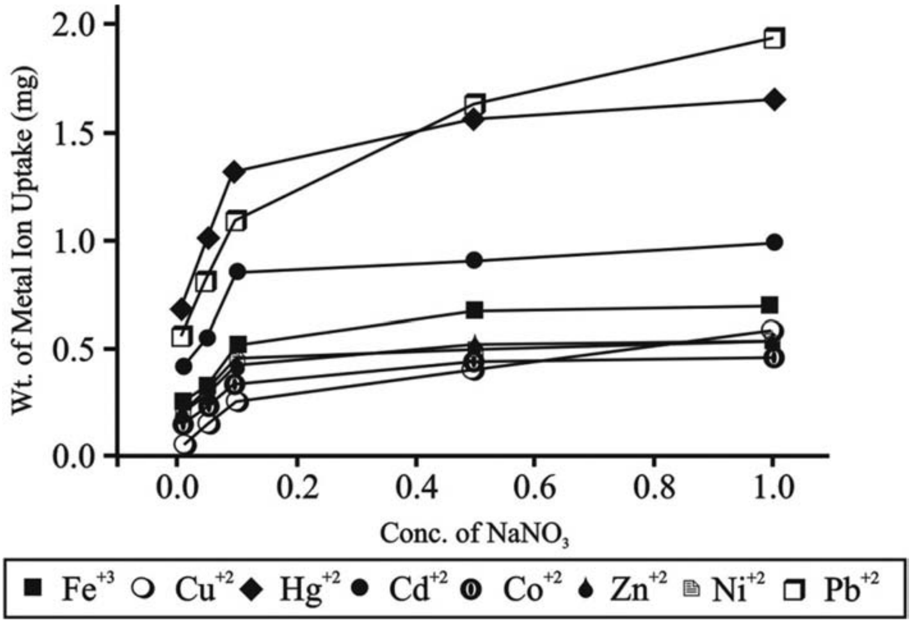


Fig. 6. Uptake of several metal ion[a] by 2, 4-DHPOF-II terpolymer resin at eight different concentrations of electrolyte $NaNO_3$ solution.

3.4. *Effect of electrolytes and their concentrations on metal ion uptake capacity*

In present paper we examined the influence at various concentrations of ClO_4^{-}, NO_3^{-}, Cl^{-} and SO_4^{-2} ions on the equilibrium of metal-resin interaction. Figures 6 to 9 show that the amount of metal ions taken up by a given amount of terpolymer depends on nature and concentration of electrolyte present in solution (Table 5). In presence of ClO_4^{-}, NO_3^{-} and Cl^{-} ions, the uptake of metal ions understudy increases with increasing concentration, whereas in presence of SO_4^{-2} ions decreases with increasing concentration of the

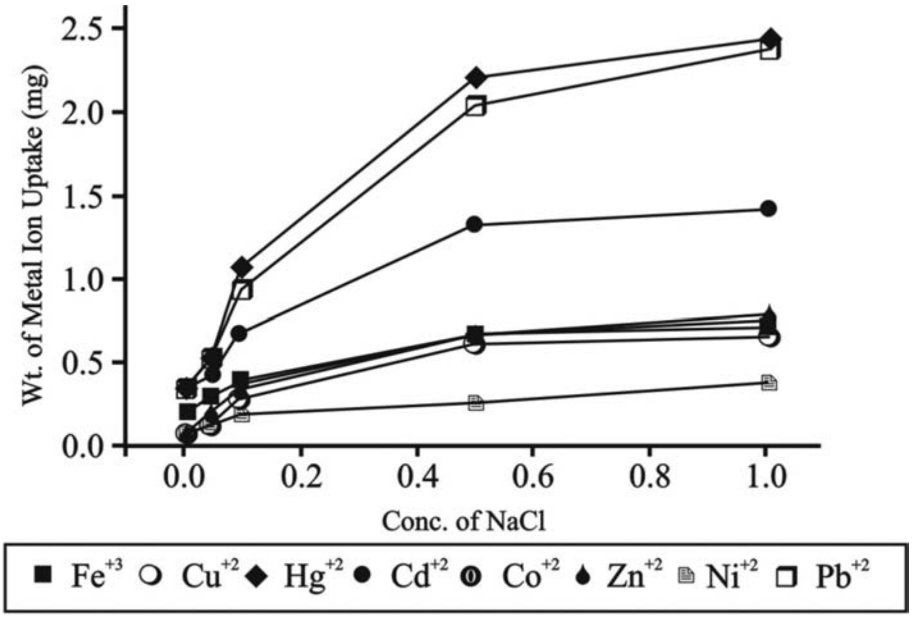


Fig. 7. Uptake of several metal ion[a] by 2, 4-DHPOF-II terpolymer resin at eight different concentrations of electrolyte NaCl solution.

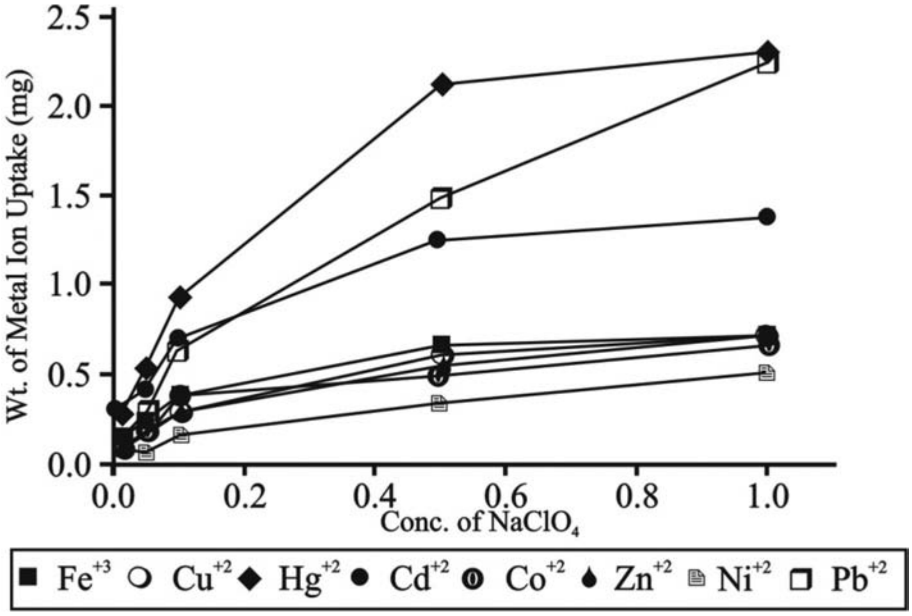


Fig. 8. Uptake of several metal ion[a] by 2, 4-DHPOF-II terpolymer resin at eight different concentrations of electrolyte $NaClO_4$ solution.

electrolyte [27]. This may be happened due to the hindrance of increasing concentration of Na^+ ions in solution which may interact more as compare to the metal ions understudy and also may be explained on the basis of stability constants of complexes with those metal ions. This type of trend has also been observed by other investigators in this field [14,27].

3.5. Rate of uptake for metal ions as a function of time

Rate of metal adsorption was determined to find out the shortest time required for equilibrium. Figure 10 shows the results of rate of metal ion uptake by terpolymer sample (Table 6). Rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with terpolymer understudy.

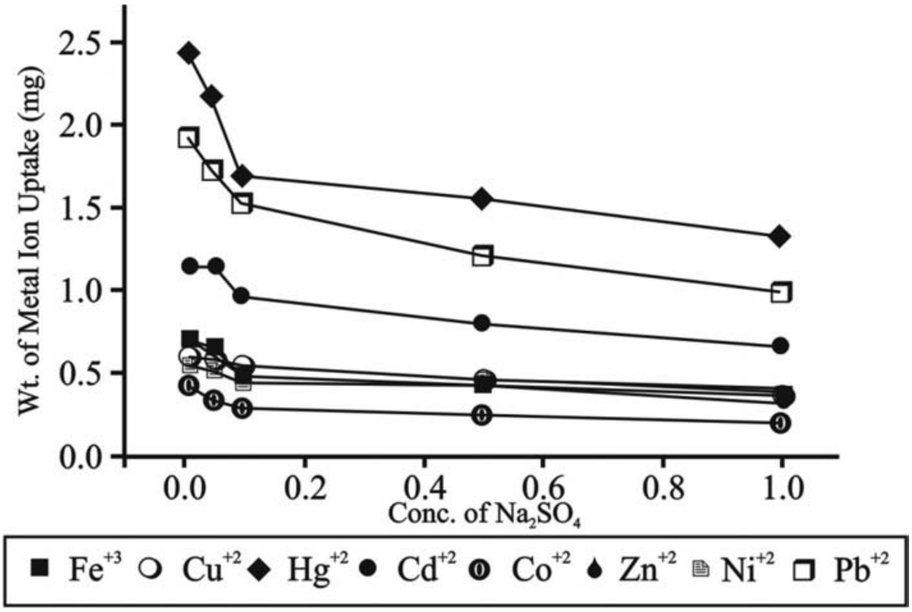


Fig. 9. Uptake of several metal ion[a] by 2, 4-DHPOF-II terpolymer resin at eight different concentrations of electrolyte Na_2SO_4 solution.

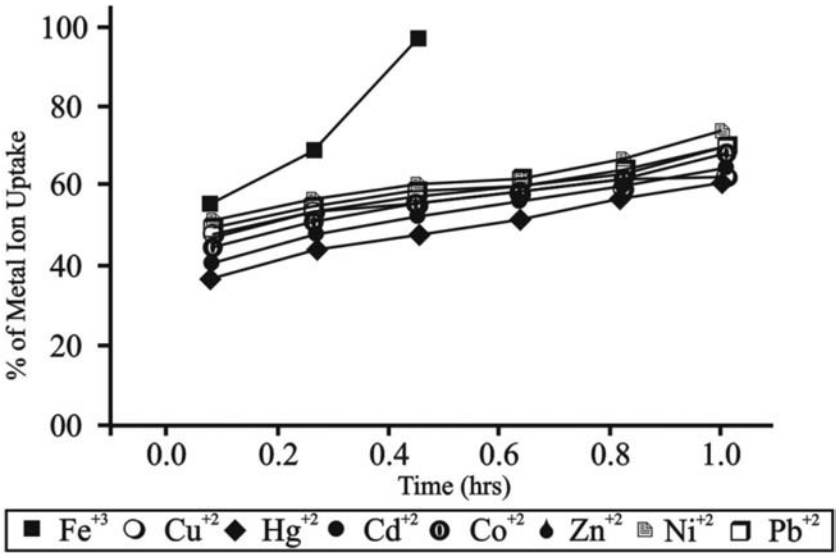


Fig. 10. Comparison of the rate of metal ion[a] uptake[b] by 2, 4-DHPOF-II terpolymer resin.

Results have shown that the time required for the uptake of different metal ions at a given conditions depends on the nature of metal ion. It is found that Fe^{+3} ions require about 3 hrs for the establishment of equilibrium, whereas Cu^{+2}, Hg^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2} and Pb^{+2} ions required about 6 h. Thus, rate of metal ions uptake follows the order of Fe^{+3} > Ni^{+2} > Pb^{+2} > Cu^{+2} > Co^{+2} > Cd^{+2} > Zn^{+2} > Hg^{+2} [14,27].

3.6. *Effect of pH on metal ion uptake*

Effect of pH on amount of metal ions distributed between two phases can be explained by the results given in Figure 11 (Table 7). Data of distribution ratio '*D*' as a function of pH indicate that the relative amount of metal ion taken up by the terpolymer increases with increasing pH of medium. Increase in magnitude, however, it is different for different cations. 2,4-DHPOF-II terpolymer taken up Fe^{+3} ion more selectively than any other metal ions understudy. Order of distribution ratio of metal ions in pH range of 2.5 to 6.5 is found to be Fe^{+3} > Cu^{+2} > Ni^{+2} > Co^{+2} > Zn^{+2} > Cd^{+2} > Pb^{+2} > Hg^{+2}. There is no specific trend was observed which may be due to difference in their crystal field stabilization energy which results in the formation of metal complex with different stability at different pH [16].

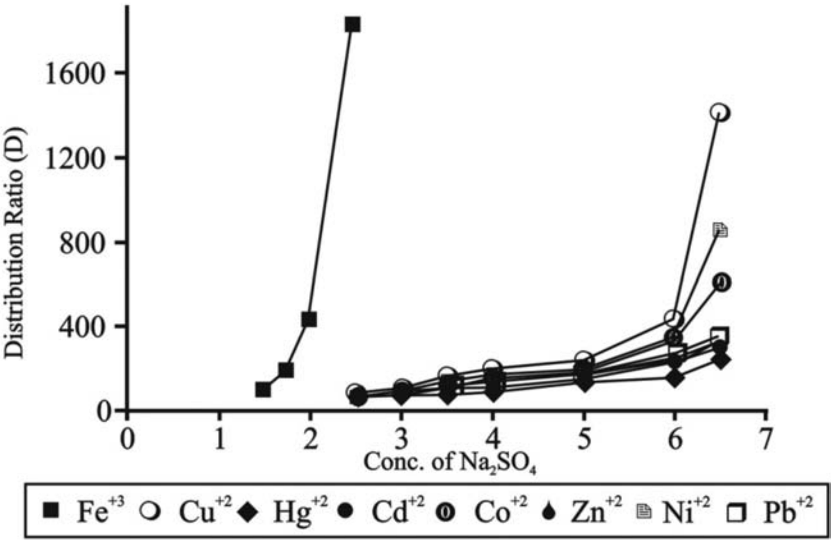


Fig. 11. Distribution ratio D[a] of various metal ion[b] as function of the pH by 2, 4-DHPOF-II terpolymer resin.

Table 5
Evaluation of the effect of different electrolytes on the uptake of several metal ions[a] by 2, 4-DHPOF-II terpolymer resin

Metal ion	Electrolyte (mol/l)	pH	Weight of metal ion (in mg.) taken up in the presence of			
			$NaNO_3$	NaCl	Na_2SO_4	$NaClO_4$
Fe^{+3}	0.01	2.5	0.249	0.179	0.707	0.13
	0.05		0.328	0.294	0.652	0.242
	0.10		0.503	0.387	0.544	0.372
	0.50		0.681	0.67	0.465	0.666
	1.00		0.71	0.72	0.391	0.719
Cu^{+2}	0.01	4.5	0.064	0.085	0.597	0.059
	0.05		0.161	0.119	0.58	0.169
	0.10		0.254	0.288	0.546	0.347
	0.50		0.411	0.627	0.47	0.487
	1.00		0.585	0.69	0.381	0.678
Hg^{+2}	0.01	6.0	0.682	0.361	2.42	0.254
	0.05		1.003	0.535	2.153	0.522
	0.10		1.311	1.07	1.685	0.923
	0.50		1.565	2.206	1.538	2.126
	1.00		1.658	2.447	1.297	2.327
Cd^{+2}	0.01	5.0	0.42	0.337	1.161	0.307
	0.05		0.555	0.45	1.139	0.412
	0.10		0.862	0.689	0.974	0.689
	0.50		0.914	1.334	0.802	1.259
	1.00		0.989	1.439	0.659	1.401
Co^{+2}	0.01	5.0	0.259	0.157	0.436	0.11
	0.05		0.322	0.193	0.35	0.149
	0.10		0.471	0.346	0.295	0.287
	0.50		0.507	0.676	0.236	0.625
	1.00		0.534	0.743	0.196	0.715
Zn^{+2}	0.01	5.0	0.209	0.109	0.689	0.078
	0.05		0.283	0.174	0.588	0.109
	0.10		0.418	0.344	0.484	0.253
	0.50		0.484	0.702	0.423	0.536
	1.00		0.536	0.771	0.327	0.737
Ni^{+2}	0.01	4.5	0.145	0.067	0.54	0.027
	0.05		0.243	0.114	0.509	0.055
	0.10		0.356	0.2	0.45	0.16
	0.50		0.423	0.266	0.431	0.344
	1.00		0.489	0.384	0.368	0.524
Pb^{+2}	0.01	6.0	0.553	0.332	1.906	0.166
	0.05		0.815	0.525	1.727	0.276
	0.10		1.077	0.939	1.519	0.635
	0.50		1.616	2.058	1.188	1.492
	1.00		1.934	2.376	0.981	2.238

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

Thus, results of such type of study are helpful in selecting optimum pH for a selective uptake of a particular cation from a admixture [28]. For example, result suggested at optimum pH 6.0, for the separation of Co^{+2} and Ni^{+2} with distribution ratio '*D*' having 3.344 and 3.151 respectively using 2,4-DHPOF-II terpolymer as an ion-exchanger. Similarly, separation of Cu^{+2} and Fe^{+3} carried out at optimum pH 2.5 having distribution ratio '*D*' 1.823 and 0.08 respectively. Higher distribution of Fe^{+3} shows the efficient separation from other metals.

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 Co^{+2} (4) Fe^{+3} and Zn^{+2} (5) Fe^{+3} and Cd^{+2} (6) Fe^{+3} and Pb^{+2}. Solution for separations were prepared by mixing 1 ml

Table 6
Comparison of the rates of metal (M) ion uptake[a] by 2, 4-DHPOF-II terpolymer resin

Metal ion	% of metal ion uptake[b] at different time (hrs.)					
	1	2	3	4	5	6
Fe^{+3}	55	68	97.5	–	–	–
Cu^{+2}	47.5	53	56.5	59.5	63	69.5
Hg^{+2}	37.5	44.5	48	51.5	56	60
Cd^{+2}	41	48	51.5	55.5	58.5	64.5
Co^{+2}	45	51	55	58	61.5	68
Zn^{+2}	49	52.5	54.5	57.5	59.5	61.5
Ni^{+2}	50.5	56	60	61	66.5	73.5
Pb^{+2}	48.5	54.5	58	61	64.5	70

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

[b] $$\%\text{ of metal ions uptake } = \frac{\text{amount of metal ions absorbed}}{\text{amount of metal ions absorbed at equilibrium}} * 100$$

of 0.1M solutions of Fe^{+3} with 1 ml of 0.1M solution of Cu^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2} Hg^{+2} and Pb^{+2} metal ions each. Selective uptake of metal ions was studied by adjusting the optimum pH of 2.5. Distribution ratios of above mentioned metal ions at pH 2.5 in the mixture were found to be 0.08, 0.067, 0.062, 0.063, 0.079, 0.047 and 0.05 respectively i.e. very much lower than Fe^{+3} and found 1.823. Lowering in distribution ratios of other metal ions with respect to Fe^{+3} has shown that the efficient separation could be achieved at lower pH.

With increase in pH the –vely charged nature of sorbent surface increases which leads to increase in the electrostatic attraction between charged metal ions and –vely charged terpolymer and resulted in increase in exchanging metal ions. Decreasing in removal of metal ions at lower pH is due to the higher concentration of H^+ ions presented in the reaction mixture which compete with metal ions for the sorption sites on the ion exchanger surface [16].

4. Conclusion

1. Terpolymer 2,4-DHPOF-II, based on the condensation reaction of 2,4-dihydroxypropio-phenone and oxamide with formaldehyde in the presence of acid catalyst was prepared.
2. It is a selective chelating ionexchanger for Fe^{+3}, Cu^{+2} Ni^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2}, Pb^{+2} and Hg^{+2} metal ions.
3. The terpolymer resin showed their selectivity as per with respect to pH. With increase in pH the –vely charged nature of sorbent surface increases leading to increase in electrostatic attraction between charged metal ions and –vely charged terpolymer which results in increase in exchanging metal ions.

Table 7
Distribution ratio *D* of various metal ion as a function of the pHb by 2, 4-DHPOF-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}	0.109	0.185	0.419	1.823	-	-	-	-	-	-
Cu^{+2}	–	–	–	0.08	0.093	0.148	0.18	0.223	0.419	1.393
Hg^{+2}	–	–	–	0.047	0.061	0.07	0.084	1.253	1.45	2.343
Cd^{+2}	–	–	–	0.079	0.084	0.104	1.361	1.612	2.18	3.151
Co^{+2}	–	–	–	0.062	0.098	1.28	1.615	1.889	3.344	5.949
Zn^{+2}	–	–	–	0.063	0.066	0.087	1.131	1.42	2.343	3.151
Ni^{+2}	–	–	–	0.067	0.082	0.094	1.306	1.765	3.151	8.468
Pb^{+2}	–	–	–	0.05	0.063	0.08	1.065	1.42	2.074	2.815

[a] $$D = \frac{\text{wt (mg) of metal ion taken up by 1 ml of terpolymer}}{\text{wt (mg) of metal ion in 1 ml of solution}}$$

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

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