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ORIGINAL ARTICLE

Thermal and ion-exchange studies on chelating terpolymer resins derived from *o* cresol urea formaldehyde

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Abstract Terpolymers prepared by condensation of *o* cresol and urea with formaldehyde in presence of acid catalyst (2 M HCl) proved to be selective chelating ion exchange resins for certain metal ions. The molecular weights of the synthesised terpolymers were determined by GPC Technique. TGA analysis was employed to study the thermal stability and the kinetic data like activation energy of the terpolymer resins. Chelation ion exchange properties of these terpolymers were studied for Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurements of distribution of a given metal ion between the polymer samples. The study was carried out over a wide pH range and in media of various ionic strengths.

1. Introduction

Much research work is being carried out on the synthesis and characterization of terpolymers. Literature survey reveals that terpolymer derived from aromatic compounds with substituents like –OH, –COOH, $–NH_2$ with urea and formaldehyde show improved ion exchange properties, thermal resistance properties, coordinating properties, and good storage stability, etc. (Gurnule et al., 2002; Michael et al., 2004; Jadhao et al., 2005; Shah et al., 2006, 2007; Ameta et al., 2007). The aromatic rings offer conjugated rigid structure with high glass transition temperature and strong linkages, allowing good resistance even in harsh environment. Such terpolymers find very useful applications as adhesives, adhesive labels, high temperature flame resistant fibres, fuel hose for automobile applications, microelectronic components like compact discs (Weiser et al., 1994), liquid crystal display device (Miyamoto et al., 1997), ion exchange packs (Lawson and Jay, 2001), etc. Ion exchange resins have attracted much interest in recent years, as in water treatment, metal recovery from dilute solutions, hydrometallurgy (Amin and Kapadia, 1957), antibiotic purification and separation of radio isotopes (Shah et al., 2004), and find large application in water treatment and pollution control (Henry et al., 2004).

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The basic requirements for any polymeric material to be useful as ion exchange resin are: (a) it must be sufficiently hydrophilic to permit diffusion of ions through the structure at a finite and usable rate; (b) it must contain sufficient number of accessible ion exchangeable groups which do not undergo degradation during use; and, (c) the swollen material must be denser than water.

Jadhao and co-worker synthesized a terpolymer resin by condensation 2,2′-dihydroxybiphenyl and urea with formaldehyde (Jadhao et al., 2009) in the presence of 2 M hydrochloric acid (HCl) as a catalyst. They studied chelating ion exchange properties of this polymer for Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the distribution of a given metal ion between polymer sample and solution containing metal ions. The study was carried out over a wide pH range and the polymer was found to show higher selectivity for Fe^{3+}, Cu^{2+}, Ni^{2+} ions than for Zn^{2+}, Cd^{2+}, Pb^{2+} ions. Another Chelating terpolymer synthesised from 2,4 dihydroxyacetophenone biuret formaldehyde by condensation reaction was also reported to have higher selectivity for Fe^{3+} and Cu^{2+} ions (Rahangdale et al., 2009). A chelating ion exchange resin was synthesized from 8-hydroxyquinoline and catechol using formaldehyde as a cross linking agent and the ion exchange capacity was evaluated with various metal ions say, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} (Shah et al., 2008a). Also various kinetic characteristics such as energy of activation (Ea), order of reaction (n) and pre-exponential factor (A) of various steps of thermal decomposition have been calculated from thermogravimetric results. Shah and co-workers (Shah et al., 2008b) reported a chelating ion exchange resin synthesized by condensation of anthranilic acid with formaldehyde and *m*-cresol in DMF media. The ion exchange properties such as rate of metal ion exchange, effect of pH on metal ion exchange capacity, effect of metal ions concentration and distribution coefficient in tartaric acid media were also studied. The thermodynamic parameters also calculated by using various approximations.

The present work reports the synthesis and characterisation of a terpolymer resin (OUF) from *o* cresol, urea and formaldehyde. The work describes the synthesis of the resin in acidic media, characterization, thermal studies of the resin and the systematic studies of various transition metal ion exchange properties of the resin.

2. Materials and methods

2.1. Chemicals

o cresol and urea were of Analytical Grade and used as received from Loba Chemicals, Mumbai. Formaldehyde (37% w/v): (S.D. Fine Chem. Ltd. Mumbai.) was used as received. Metal ion solutions were prepared by dissolving appropriate amount of metal nitrates in double distilled water and standardized by complexometric titration. The other chemicals and solvents procured from Qualigens were used as received without further purification.

2.2. Synthesis of OUF terpolymer

The terpolymer (OUF 1) was synthesized by the condensation of *o* cresol and urea with formaldehyde in the mole ratio of 1:1:2 in the presence of 2 M HCl catalyst. The mixture was heated at 140 ± 2 °C for 5 h. The contents of the flask were shaken periodically to ensure homogeneous mixing. After the refluxing period was over the contents of the flask were poured into crushed ice with constant stirring and left overnight. The separated white coloured resin was filtered off and washed several times with cold water followed by hot water and methanol for removing unreacted monomers. Finally the resin was purified by dissolving in 10% NaOH and reprecipitating with 1:1 (v/v) Conc. HCl/water. The resin thus obtained was washed with cold water followed by hot water and dried in vacuum at 100 °C. The yield of the resin was 72%. The terpolymer (OUF 2) was synthesized by said procedure with *o* cresol and urea with formaldehyde in the mole ratio of 1:1:3 in the presence of 2 M HCl catalyst. The yield of the resin was 69%.

2.3. Characterization

Molecular weights of polymer samples were determined by gel permeation chromatographic technique, using Shimaduzu (Japan) instrument with refractive index detector and polystyrene column is used to determine the molecular weight of all the polymers synthesized. The polymer samples were dissolved in 100% HPLC grade THF and 20 µl of the sample solution was injected and the chromatogram was recorded. The thermal analysis of the both OUF 1 and OUF 2 were carried out in nitrogen atmosphere at a heating rate of 20 °C per minute in Thermal Analyser Instruments model SDT Q600.

2.4. Ion-exchange studies

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

The ion exchange properties of both OUF 1 and OUF 2 terpolymer resins were determined by the batch equilibrium method (Karunakaran and Burkanudeen, 2003). The polymer sample (25 mg) was suspended in an electrolyte solution (25 ml) of known concentration. The different electrolytes used here are $NaClO_4$, NaCl, $NaNO_3$ and Na_2SO_4. The pH of the suspension was adjusted to the required value by using either 0.1 M HNO_3 or 0.1 M NaOH. The suspension was stirred for 24 h at room temperature. 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 once again. The mixture was again stirred 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 the metal ion uptake of the terpolymer was calculated from the difference between a blank experiment without the terpolymer and the reading in the actual experiments. The experiments were performed in the presence of several electrolytes with seven different metal ions: Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}.

2.5. Evaluation of the rate of metal uptake

In order to estimate the time required to reach the state of equilibrium under the given pH, experiments of the type described above were carried out, in which metal ion taken up by the chelating resins was estimated from time to time in the presence of 25 mL of 1 M $NaNO_3$ solutions. It was

Table 1 Molecular weights of OUF terpolymer resins.

Sample name	Mole ratio	$\overline{Mn}$	$\overline{Mw}$	$\overline{MZ}$	Dispersity $\overline{Mw}/\overline{Mn}$	Dispersity $\overline{MZ}/\overline{Mn}$
OUF 1	1:1:2	8860	10,129	11,244	1.14333	1.26908
OUF 2	1:1:3	10,742	12,594	14,409	1.17244	1.34146

assumed that, under the given conditions, the state of equilibrium was established within 24 h. The rate of metal uptake is expressed as the percentage of the amount of metal ions taken up after a certain time related to that in the state of equilibrium. The distribution of each one of the seven metal ions, i.e. Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}, between the polymer phase and the aqueous phase was estimated at room temperature and in the presence of 1.0 M $NaNO_3$ solution.

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

The distribution of each one of the seven metal ions, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}, between the polymer phase and the aqueous phase was estimated in the presence of a 1 M $NaNO_3$ solution. The experiments were carried out as described earlier at pH 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, and 6. The distribution ratio D is defined by the following relationship:

$$D = \frac{\text{Weight(in mg)of metal ion taken up by 1g of polymer}}{\text{Weight(in mg)of metal ion present in 1mL of solution}}$$

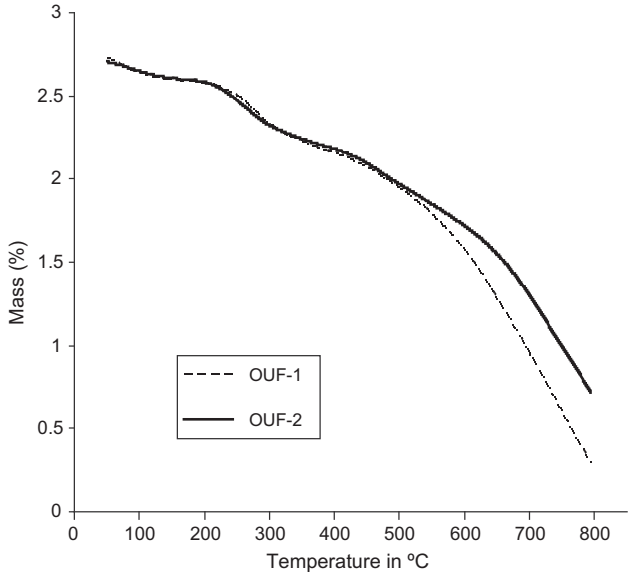

Figure 1 TGA of OUF resins.

3. Results and discussion

3.1. Molecular weight measurement

The molecular weights of polymer samples were determined using gel permeation chromatographic technique and the results are given in the Table 1. The number average molecular weight of OUF 1 was calculated as 8860 while that of OUF 2 was 10,742. All the other average molecular weights show the same trend. From the Table 1, it is clear that the molecular weight of OUF 2 is higher than the molecular weight OUF 1.

The condensation of the formaldehyde with any phenolic derivatives takes place if the ortho and or para positions are free. Usually formaldehyde is used as a cross linking agent in the case of condensation polymers synthesised by employing substituted phenols as one of the monomer (Shah et al., 2008a). Linear or cross-linked three dimensional network structures can be obtained by varying the proportion of phenol(s), formaldehyde and the catalyst. If phenol (P) to formaldehyde (F) ratio (P/F) is less than one; a linear polymer is obtained using an acid catalyst. This material contains methylol groups (–CH_2OH) in the ortho and para positions which undergo condensation in the presence of acid catalyst to yield methylene bridged (–CH_2–) polymeric resin. In the same manner urea reacts with formaldehyde produce mono methylol urea and dimethylol urea. They further undergo condensation to form cross-linked resins. Reaction of *o* cresol with urea and formaldehyde involves the same said condensation reaction which leads, to a cross-linked polymer structure, since the ratio of mono to dimethylol compound formation will depend on the formaldehyde ratio (Brydson, 1999). Hence the extent and nature of cross linked-structure formation depend on the amount of formaldehyde available. The increase in the concentration of formaldehyde results in more methylene bridges between the *o* cresol and urea (Poljansek and Krajnc, 2005). This is observed in our study also. Therefore the increase in the concentration of formaldehyde increases the number of cross links and thereby increases the molecular weight of the polymer sample also.

3.2. Thermogravimetric analysis

The thermograms of the resin samples obtained are shown in Fig. 1. The TGA data of the terpolymers are given in Table 2. The kinetic properties and derivatives of the terpolymer res-

Table 2 TGA data of OUF terpolymer resins.

Terpolymer	T_d (°C)					Char yield at 900 °C
	10	30	50	70	90	
OUF 1	253	502	633	717	796	2.09
OUF 2	253	522	686	731	861	2.40

Table 3 Activation energy of degradation of AFR resin.

Sample name	Energy of activation (Ea) (kJ/mol)		
	Broido method	Horowitz and Metzger method	Murray and White method
OUF 1	29.40	29.63	30.93
OUF 2	31.18	31.40	31.84

ins were calculated by Broido (1969), Horowitz and Metzger (1963) and Murray and White (1955) methods. The calculated energy of activation is presented in Table 3. Thermal stability of the terpolymers was evaluated by the 10% weight loss temperature (T_d, 10), 30% weight loss temperature (T_d, 30), 50% weight loss temperature (T_d, 50), 70% weight loss temperature (T_d, 70) and 90% weight loss temperature (T_d, 90) and char yield at 900 °C. T_d data reveals that the stability of the terpoly-

Table 4 Evaluation of the effect of different electrolytes on the uptake of several metals ions[a] by OUF 1 terpolymer resin.

Metal ion	Electrolyte (mol l^{-1})	pH	Weight (in mg) of metal ion uptake in presence of			
			$NaClO_4$	NaCl	Na_2NO_3	Na_2SO_4
Ni^{2+}	0.01	4.5	3.24	2.48	2.31	3.98
	0.05		3.49	2.89	3.14	3.44
	0.10		3.78	3.78	3.96	2.63
	0.5		4.02	4.11	4.52	1.97
Cu^{2+}	0.01	4.5	2.85	2.47	2.24	4.38
	0.05		3.35	3.32	2.91	3.64
	0.10		3.90	3.89	3.60	2.87
	0.5		4.31	4.47	4.51	2.16
Fe^{3+}	0.01	2.5	2.27	1.43	2.26	3.68
	0.05		3.18	2.58	2.75	2.99
	0.10		3.94	3.13	3.07	2.64
	0.5		4.32	4.04	3.41	1.98
Co^{2+}	0.01	5.0	3.28	3.27	2.89	2.99
	0.05		2.78	2.54	2.55	2.41
	0.10		2.47	2.48	2.34	2.01
	0.5		2.26	2.29	1.57	1.59
Zn^{2+}	0.01	5.0	3.48	3.96	2.68	2.92
	0.05		3.17	3.57	2.54	2.43
	0.10		2.71	2.74	2.29	2.09
	0.5		1.98	1.83	1.96	1.79
Pb^{2+}	0.01	5.5	2.16	2.89	3.06	–
	0.05		2.09	2.34	2.94	–
	0.10		1.67	1.92	2.78	–
	0.5		1.32	1.71	2.22	–
Cd^{2+}	0.01	5.5	2.56	2.75	2.68	2.88
	0.05		2.33	2.51	2.47	2.49
	0.10		2.08	2.35	2.39	2.19
	0.5		1.66	2.02	2.18	1.73

[a] $[M^{n+}\ (NO_3)_n]$ = 0.1 mol/L; volume = 2 mL; volume of electrolyte solution = 25 mL; weight of the resin = 25 mg; time = 24 h at room temperature.

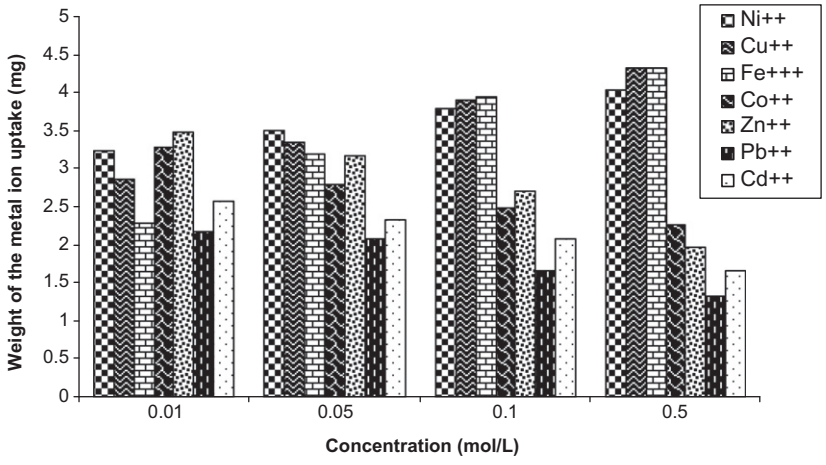

Figure 2 Effect of sodium perchlorate electrolyte on metal ion uptake by OUF 1 resin.

mer OUF 2 is more than OUF 1. The activation energy present here for OUF resins reflects the same. The thermal decomposition of resins can be explained based on its macromolecular structure. The polymer strength depends on the nature of atoms present in the polymer matrix and the distance between them. When compared with the results given in the Table 3,

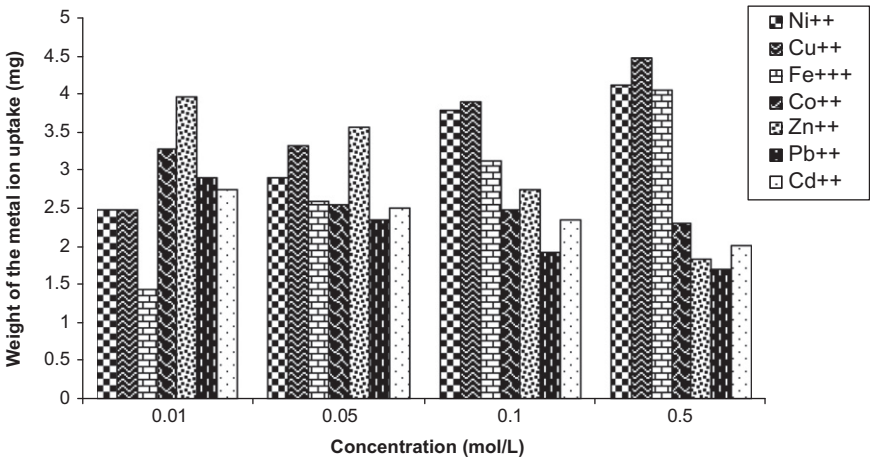

Figure 3 Effect of sodium chloride electrolyte on metal ion uptake by OUF 1 resin.

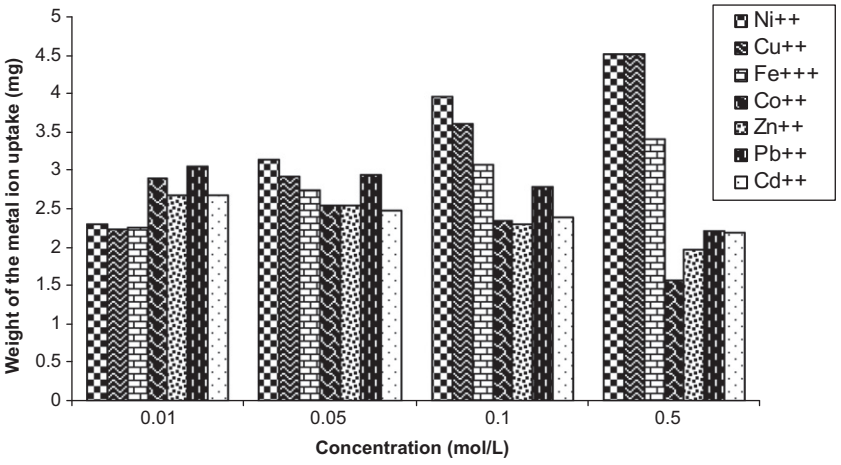

Figure 4 Effect of sodium nitrate electrolyte on metal ion uptake by OUF 1 resin.

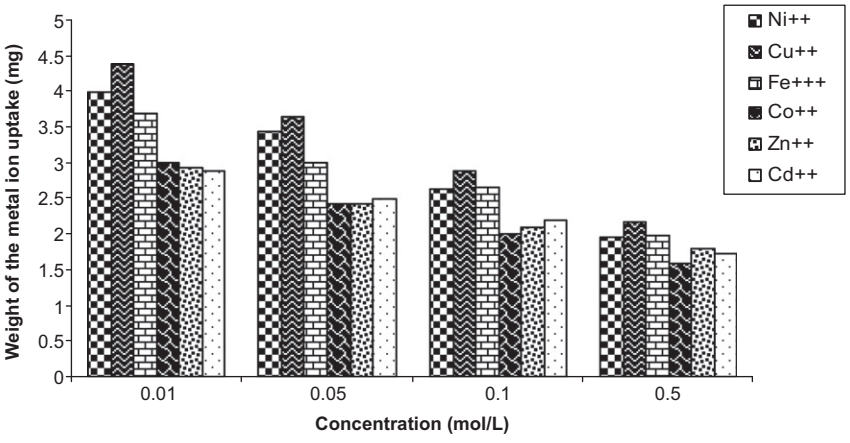

Figure 5 Effect of sodium sulphate electrolyte on metal ion uptake by OUF 1 resin.

OUF 2 possesses high Ea value also an evidence for more cross linked pattern in this resin.

3.3. Effect of electrolytes on the metal uptake

The influence of ClO_4^-, Cl^-, NO_3^- and SO_4^{2-} are examined at varying concentrations at equilibrium of metal-resin interactions. Results given in Table 4 and the bar graphs for the measurements given in Figs. 2–5, reveal that the amount of Ni^{2+}, Cu^{2+} and Fe^{3+}, ions taken up by the OUF 1 terpolymer sample increases with increasing concentrations of ClO_4^-, Cl^-, and NO_3^-, and decreases with increasing concentrations of SO_4^{2-}. On the other hand the uptake of Co^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} ions by the terpolymer increases with decreasing concen-

Table 5 Evaluation of the effect of different electrolytes on the uptake of several metals ions[a] by OUF 2 terpolymer resin.

Metal ion	Electrolyte (mol l^{-1})	pH	Weight (in mg) of metal ion uptake in presence of			
			$NaClO_4$	NaCl	Na_2NO_3	Na_2SO_4
Ni^{2+}	0.01	4.5	3.68	2.83	2.73	4.22
	0.05		3.95	3.26	3.57	3.65
	0.10		4.31	4.09	4.03	2.71
	0.5		4.59	4.51	4.87	1.69
Cu^{2+}	0.01	4.5	3.21	2.90	2.65	4.52
	0.05		3.77	3.66	3.31	3.29
	0.10		4.18	4.09	4.02	2.63
	0.5		4.84	4.64	4.70	1.88
Fe^{3+}	0.01	2.5	2.61	2.37	2.51	4.18
	0.05		3.49	2.89	3.11	3.38
	0.10		3.97	3.70	3.56	2.62
	0.5		4.48	4.81	4.08	1.47
Co^{2+}	0.01	5.0	3.84	3.55	3.31	3.60
	0.05		3.17	2.89	2.96	3.07
	0.10		2.56	2.31	2.64	2.56
	0.5		1.82	1.90	1.62	1.81
Zn^{2+}	0.01	5.0	4.10	4.35	2.99	3.39
	0.05		3.52	3.99	2.73	2.61
	0.10		2.88	3.10	2.07	1.97
	0.5		2.17	2.13	1.76	1.36
Pb^{2+}	0.01	5.5	2.78	3.22	3.41	–
	0.05		2.43	2.66	3.02	–
	0.10		1.81	2.08	2.51	–
	0.5		1.29	1.52	1.89	–
Cd^{2+}	0.01	5.5	3.01	3.06	3.20	3.29
	0.05		2.47	2.60	2.86	2.90
	0.10		1.92	2.11	2.29	2.44
	0.5		1.38	1.63	1.85	1.21

[a] $[M^{n+}\ (NO_3)_n]$ = 0.1 mol/L; volume = 2 mL; volume of electrolyte solution = 25 mL; weight of the resin = 25 mg; time = 24 h at room temperature.

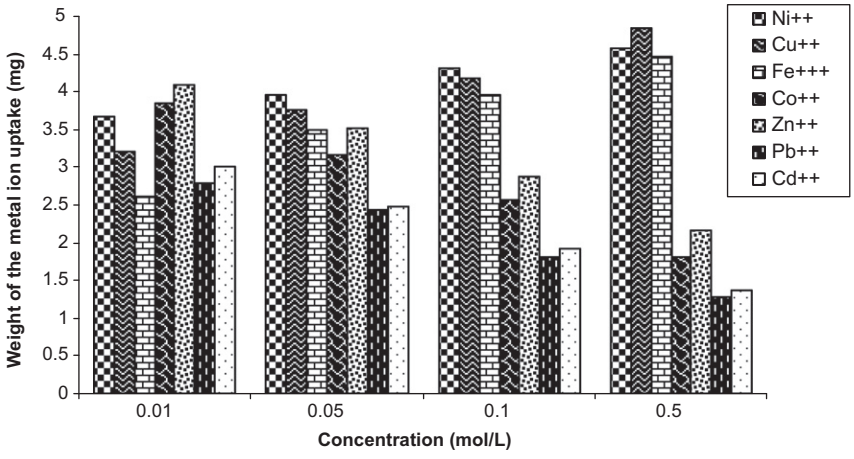

Figure 6 Effect of sodium perchlorate electrolyte on metal ion uptake by OUF 2 resin.

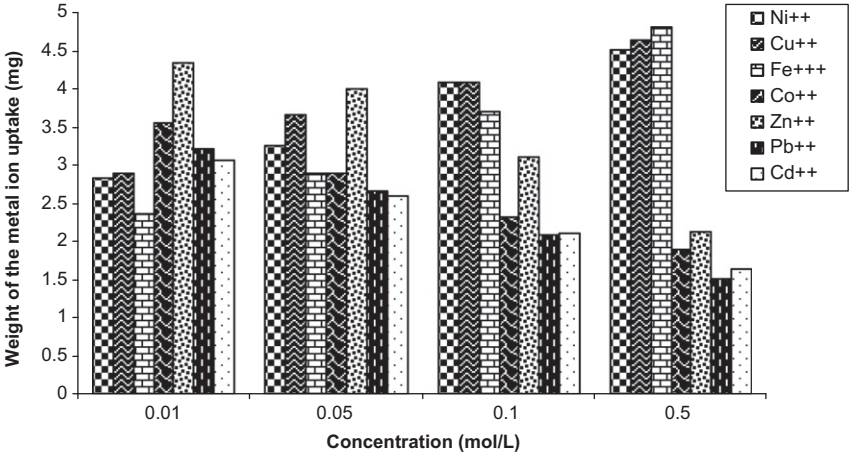

Figure 7 Effect of sodium chloride electrolyte on metal ion uptake by OUF 2 resin.

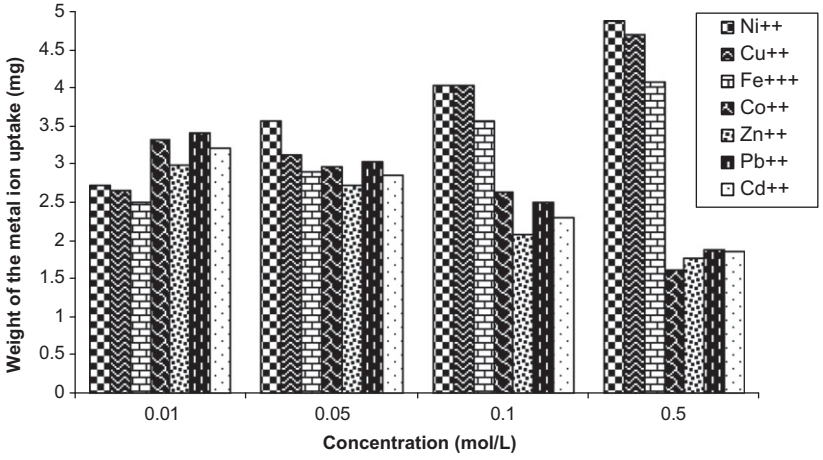

Figure 8 Effect of sodium nitrate electrolyte on metal ion uptake by OUF 2 resin.

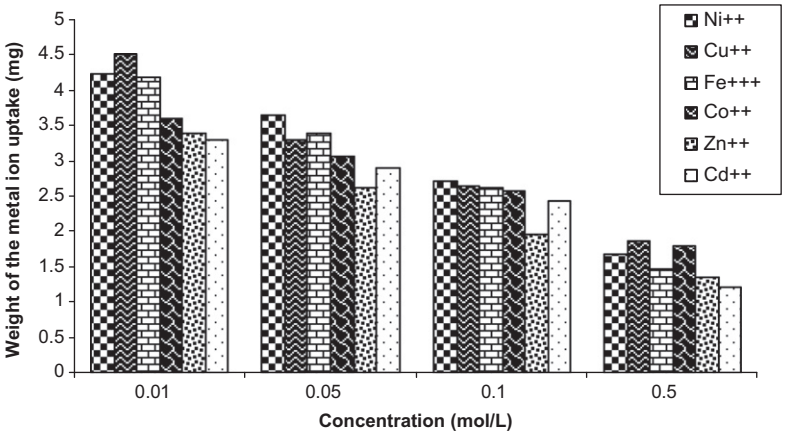

Figure 9 Effect of sodium sulphate electrolyte on metal ion uptake by OUF 2 resin.

trations of ClO_4^-, Cl^-, NO_3^-, and SO_4^{2-}. As reported earlier, this may be explained in terms of the stability constants of the complexes which Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+} and Pb^{2+} ions form with these anions (Joshi et al., 2006; Sillen and Martell, 1964). Sulphate ion form strong chelates with metal ions, while perchlorate, chloride and nitrate ions form weak chelates. Therefore, the influence of ClO_4^-, Cl^- and NO_3^-, is less on the position of metal chelates at equilibrium state.

Table 6 Comparison of the rates of metal (M) ion uptake[a] by OUF 1 terpolymer resin.

Metal ion	pH	% of metal in uptake[b] at different time (h)						
		1	2	3	4	5	6	7
Ni^{2+}	4.5	27	41	52	64	77	92	–
Cu^{2+}	4.5	41	53	60	69	81	93	–
Fe^{3+}	2.5	73	84	91	98	–	–	–
Co^{2+}	5.0	39	51	59	71	81	96	–
Zn^{2+}	5.0	27	39	46	67	78	90	–
Pb^{2+}	5.5	32	43	52	62	80	88	91
Cd^{2+}	5.5	28	41	54	68	83	91	94

[a] $[M^{n+}\ (NO_3)_n]$ = 0.1 mol/L; volume = 2 mL; $NaNO_3$ 1.0 mol/L; volume 25 mL; room temperature.
[b] Metal ion uptake = $\frac{\text{amount of metal ion absorbed} \times 100}{\text{amount of metal ion absorbed at equilibrium}}$.

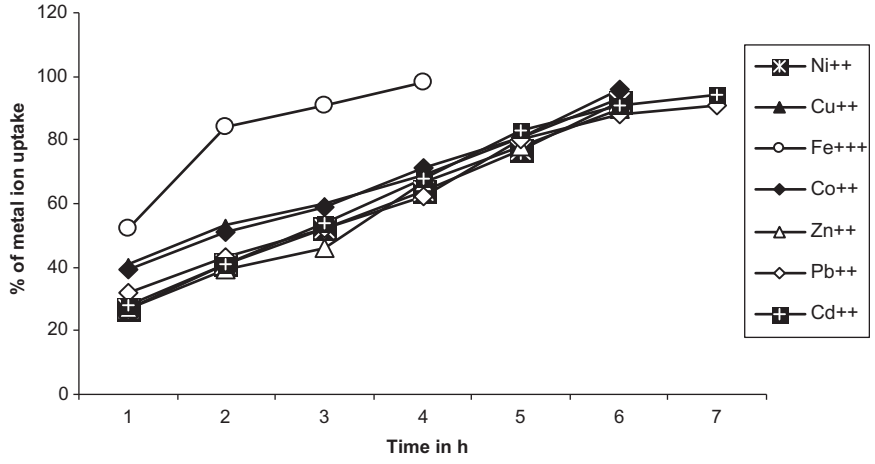

Figure 10 Comparison of the rate of metal ion uptake of OUF 1 terpolymer resins.

Table 7 Comparison of the rates of metal (M) ion uptake[a] by OUF 2 terpolymer resin.

Metal ion	pH	% of metal in uptake[b] at different time (h)						
		1	2	3	4	5	6	7
Ni^{2+}	4.5	29	44	58	69	83	93	–
Cu^{2+}	4.5	43	56	61	71	82	93	–
Fe^{3+}	2.5	76	86	91	98	–	–	–
Co^{2+}	5.0	36	48	60	73	82	94	–
Zn^{2+}	5.0	28	40	46	68	79	92	–
Pb^{2+}	5.5	31	44	50	65	81	89	90
Cd^{2+}	5.5	30	43	53	65	82	88	91

[a] $[M^{n+}\ (NO_3)_n]$ = 0.1 mol/L; volume = 2 mL; $NaNO_3$ 1.0 mol/L; volume 25 mL; room temperature.
[b] Metal ion uptake = $\frac{\text{amount of metal ion absorbed} \times 100}{\text{amount of metal ion absorbed at equilibrium}}$.

But SO_4^{2-} ions have stronger influence on the position of metal chelates. Sulphate ion therefore forms strong complexes with Ni^{2+}, Cu^{2+} and Fe^{3+} ions while ClO_4^-, Cl^-, and NO_3^- form weak complexes with these metal ions. As can be seen sulphate ions forms strong chelates with Co^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}. The same of trend has also been observed by other investigators (Rahangdale et al., 2009; Gurnule et al., 2003; Katkamwar et al., 2009; Butoliya et al., 2009).

The experimental results for OUF 2 are presented in Table 5 and the bar graphs for the measurements given in Figs. 6–9. These results also follow the same trend shown by OUF 1. Comparison of Tables 4 and 5 indicate that OUF 2 absorbs more of metal ions. It can be explained that due to more interlinking of the polymeric network giving rise to increased cavities where the metal ions get embedded easily.

3.4. Rate of metal uptake

The rate of metal absorption is determined to find out the shortest time required for attaining equilibrium. For this the experiment is carried out as close to equilibrium conditions

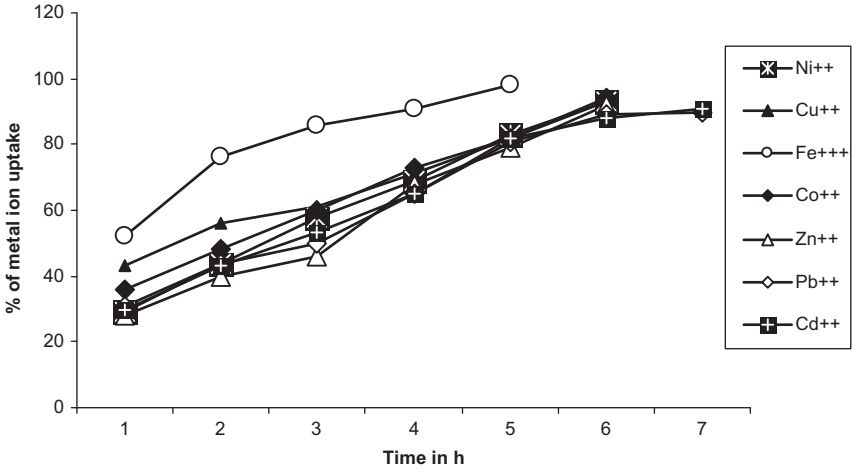

Figure 11 Comparison of the rate of metal ion uptake of OUF 2 terpolymer resins.

Table 8 Distribution ratio D[a] of different metal ions uptake[a] by OUF 1 as a function of pH[b].

Metal ion	Distribution ratio of the metal ion at the pH								
	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0
Ni^{2+}	–	–	97.4	186.2	356.8	548.1	656.1	1246.2	1312.4
Cu^{2+}	–	–	87.6	131.7	321.1	612.4	892.7	1142.6	1324.4
Fe^{3+}	198.6	487.1	534.2	–	–	–	–	–	–
Co^{2+}	–	33.4	57.5	98.1	129.4	161.6	186.0	206.7	243.2
Zn^{2+}	–	–	36.8	84.3	106.6	147.6	237.8	280.8	304.1
Pb^{2+}	–	–	30.4	39.1	76.1	91.5	107.7	223.8	253.3
Cd^{2+}	–	–	28.1	39.3	69.2	81.2	91.9	161.6	191.8

[a] $D = \frac{\text{amount of metal ion absorbed} \times 100}{\text{amount of metal ion in the solution}} \times \frac{\text{volume of solution(ml)}}{\text{weight of resin(g)}}$.
[b] $[M^{n+}(NO_3)_n]$ = 0.1 mol/L; volume = 2 mL; $NaNO_3$ 0.5 mol/L; volume 25 mL; room temperature; time = 24 h (equilibrium state).

Table 9 Distribution ratio D[a] of different metal ions uptake[a] by OUF 2 as a function of pH[b].

Metal ion	Distribution ratio of the metal ion at the pH								
	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0
Ni^{2+}	–	–	124.2	221.5	391.9	612.4	698.3	1314.1	1387.3
Cu^{2+}	–	–	121.6	166.3	378.4	656.9	943.7	1208.2	1376.0
Fe^{3+}	231.5	519.3	686.2	–	–	–	–	–	–
Co^{2+}	–	34.1	60.4	102.9	141.6	174.3	194.1	223.8	257.7
Zn^{2+}	–	–	40.1	82.9	114.3	159.7	254.8	291.2	322.6
Pb^{2+}	–	–	33.2	41.9	79.0	95.6	124.8	254.8	281.3
Cd^{2+}	–	–	31.4	42.8	73.1	92.4	104.9	169.6	207.3

[a] $D = \frac{\text{amount of metal ion absorbed} \times 100}{\text{amount of metal ion in the solution}} \times \frac{\text{volume of solution(ml)}}{\text{weight of resin(g)}}$.
[b] $[M^{n+}(NO_3)_n]$ = 0.1 mol/L; volume = 2 mL; $NaNO_3$ 0.5 mol/L; volume 25 mL; room temperature; time = 24 h (equilibrium state).

as possible. Table 6 and Fig. 10 show the dependence of rate of metal ion uptake by OUF 1 and Table 7 and Fig. 11 that of OUF 2 on the nature of the metal ion. Considering the resin OUF 1, Fe^{3+} ion required almost 4 h for the attaining equilibrium, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions took 6 h and Cd^{2+} and Pb^{2+} ions required almost 7 h. Therefore the rate of metal uptake follows the order: $Fe^{3+} > Co^{2+} \approx Ni^{2+} \approx Cu^{2+} \approx Zn^{2+} > Cd^{2+} \approx Pb^{2+}$. The rate of metal ion uptake by OUF 2 has almost similar that of OUF 1.

3.5. Distribution ratios of metal ions at different pH

The effect of metal ions distribution between two phases is explained by the results shown in the Table 8 and Table 9 for OUF 1 and OUF 2, respectively. The results indicate that the amount of metal ions taken up by the terpolymer increases up to a certain pH. Further increase in pH will hydrolysis the complex (Manavalan and Patel, 1983) and hence the experiment was carried out up to a restrictive pH. The Fe^{3+} ion is taken up more

selectively than any other metal ions under study. The lower distribution ratio of Fe^{3+} is due to steric hindrance (DeGeiso et al., 1962). Amongst the other metal ions, Ni^{2+} and Cu^{2+} ions are taken up by the terpolymers more selectively. The other four metal ions Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} have a low distribution ratio D over the pH range 4–6. This is due to low stability constants, i.e., the weak ligand stabilisation energy of the metal complexes (Davydova and Plate, 1975). In this study, the observed order of distribution ratio of divalent ions is found to be: $Cu^{2+} > Ni2^{+} > Zn2^{+} > Co2^{+} > Pb^{2+} > Cd^{2+}$, which matches well to the results reported. The results of this study are helpful in selecting the optimum pH for the selective uptake of a metal ion from a mixture of different ions. For example, for the separation of Cu^{2+} and Fe^{3+} ions, the optimum pH is 3, at which the distribution ratio D for Cu^{2+} is 87.6 with respect to OUF 1 and that for Fe^{3+} is 534.2. OUF 2 has the distribution ratio D for Cu^{2+} is 121.6 and that for Fe^{3+} is 686.2 at the same pH. Hence, the results of this type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture.

4. Conclusion

The synthesis of terpolymer in the presence of acid medium, *o* cresol-urea–formaldehyde (OUF) with varying proportions of formaldehyde shows that more the formaldehyde concentration greater is the cross linking of the resulting terpolymer giving rise to higher molecular weight resins.

When there is greater molecular weight, as expected, the thermal stability also increased (Fig. 1 and Table 3).

The terpolymer is found to be a good metal ion exchanger and therefore can be used to remove metal ions from effluents and other type of waste water. The trend is more with respect to OUF 2 which has higher molecular weight than OUF 1.

The results show that the terpolymer has the preferential selectivity to Ni^{2+}, Cu^{2+} and Fe^{3+} ions having unfilled 3d level.

It is derived from the Tables 8 and 9 that the metal complexes taken in the present study are pH dependent and each has a definite pH for optimum chelation, a useful property to employ a particular metal to be separated from a solution, using this terpolymer.

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