Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(4):2193-2203

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Studies of Chelation Ion-exchange Properties of Copolymer Resin Derived from p-Cresol, Dithiooxamide and Formaldehyde

Wasudeo B. Gurnule[1]* and Sharayu S. Katkamwar[2]

[1]Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara, Nagpur, Maharashtra, India
[2]Department of Chemistry, Arts, Commerce and Science College, Tukum, Chandrapur, India

---

ABSTRACT

Copolymer resin was prepared by the condensation polymerization of p-cresol and dithiooxamide with formaldehyde in the presence of HCl acid catalyst and using varied molar ratios of reacting monomers. Copolymer resin composition has been determined on the basis of their elemental analysis and number average molecular weights of these resins were determined by conductometric titrations in non-aqueous medium. The viscosity measurement carried out in DMF indicates normal behavior. UV-visible, IR and NMR spectra were studied to elucidate the structure. Ion-exchange properties of this copolymer resin was studied for Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Pb^{2+} ions. A batch equilibrium method was employed in the study of the selectivity of metal-ion uptake involving the measurements of the distribution of a given metal ion between the copolymer sample and a solution containing the metal ion. The study was carried out over a wide pH range and in media of various ionic strengths.

Key words: Polycondensation, distribution ratio, metal ion uptake, chelating resin, batch equilibrium, copolymer.

INTRODUCTION

Ion-exchange resins are not only used in classical aqueous demineralization processes but also as catalysts, semiconductors, catalysts and ion-exchange resins. By tailoring the polymer structure and group functionality to the requirements of the applications, resins are the first choice in chemicals processing and environmental applications. Ion-exchange methods are also employed in numerous operations such as water softening and reduction of metal ions concentration. The early ion exchangers were silicates, fuller's earth and synthetic aluminum silicates e.g., Zeolites. Tree bark substrates [1] were reported to remove efficiently the heavy metals from waste water. Chelating resins were also derived from naturally occurring compounds like guar [2] and guaran [3] by polymer grafting process.

The main objective of the most studies on chelating resins is preparation of insoluble functionalized polymers which can provide more flexible working conditions together with good stability and high capacity for certain metal ions [4]. Chelation ion exchange chromatography become a very powerful technique in the extraction of trace metal ions [5]. The physical properties, moisture content and alloy separation were carried out [6] using quinoline resins. A number of copolymers derived from phenol derivatives have been studied and reported along with their chelating ion-exchange properties. For example, Karunakaran et al. [7] have synthesized copolymer from o-nitrophenol-thiourea-formaldehyde and Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and UO_2^{2+} were used for chelating resin. Das [8] has derived copolymer from thiosemicarbazone derivatives of phenolic compound. Recently, Shah et al reported the chelating ability of the resin synthesized by a microwave irradiation technique involving salicylic acid and formaldehyde with resorcinol [9]. Kapse et al [10] synthesized novel terpolymer having semiconducting nature.

The present study deals with the synthesis and characterization of p-cresol –dithoiooxamide-formaldehyde (p-CDF) copolymer resin by polycondensation method in HCl as catalyst for the first time. The synthesized copolymer was characterized by UV-Visible, IR, ^{1}H NMR and average molecular weight. One of the applications of chelating and functional polymer is their ability to recover metal ion from waste solutions. Hence, the chelation ion-exchange property of the p-CDF copolymer resin was also reported for certain metal ions

EXPERIMENTAL SECTION

The chemicals were all analytical reagent or chemically pure grade. N, N'- Dimethyl formamide (DMF) and dimethylsulfoxide (DMSO) were used after double distillation. p-Cresol (Ranbaxy Fine Chemicals, Mumbai, India), dithiooxamide (S. D. Fine Chemical, Mumbai, India) and 37 % formaldehyde (Qualigens Fine Chemicals, Mumbai, India) were used as received. Metal ion solutions were prepared by dissolving appropriate amount of the nitrates of the metals in double distilled water and standardized by EDTA titration.

Synthesis of copolymer resin

A mixture of p-cresol (1.801gm, 0.1mol), dithiooxamide (1.20gm, 0.1mol) and formaldehyde (7.50ml, 0.2mol) in the presence of 200ml of 2M hydrochloric acid as a catalyst was heated in an oil bath at 122^{0}C for 6h with occasional shaking. The separated brown resinous product was washed with hot water and methanol to remove unreacted monomer. The resinous product so obtained was washed with cold water, dried in air, and powdered. The powdered resin was washed with hot water and dried. Dried resin was then extracted with diethyl ether followed by petroleum ether for the removal of the p-cresol-formaldehyde copolymer that might be present along with the copolymer. The resin was purified by dissolution in 8% NaOH and by reprecipitation through the drop wise addition of 1:1 HCI with constant and rapid stirring to avoid the formation of lumps. The process of reprecipitation was repeated twice. The copolymer resin so obtained was filtered, washed with hot water, dried in air, powdered, and stored in vacuum desicator over anhydrous $CaCl_2$. The reaction and suggested structure of p-CDF copolymer is shown in scheme 1.

Characterization of copolymer resin

The copolymer resin was subjected to microanalysis for carbon, hydrogen, and nitrogen on a Elemental Vario ELIII Carlo Erba 1108 elemental analyzer at Central Drug Research Institute (CDRI, Lucknow, India). Sulphur contents were estimated by Messenger method. The number – average molecular weight ($\overline{Mn}$) was determined by conductometric titration in DMF with KOH in a 50% (v/v) DMF/alcohol mixture as the titrant. The Viscosity was determined with a Tuan-Fuoss viscometer fabricated in our laboratory at six different concentrations ranging from 0.5 to 3.0% of the copolymer in DMF at 30^{o}C.

Electronic absorption spectra of p-CDF copolymer resin were recorded in DMSO (Spectroscopic grade) on Shimadzu Double Beam Spectrophotometer in the range of 200-600 nm at Central Drug Research Institute, Lucknow. Infra-red spectra of p-CDF were recorded on Perkin Elmer-Spectrophotometer in KBr pellets in the wave number region of 4000-400 cm^{-1} at Central Drug Research Institute, Lucknow. Nuclear Magnetic Resonance (NMR) spectra of newly synthesized copolymer resin has been scanned on Bruker Advance. 400 NMR spectrometer using DMSO - d_6 solvent at Central Drug Research Institute, Lucknow.

Ion-Exchange Studies

The results of the batch equilibrium study carried out with the copolymer sample of p-CDF. From this study of seven metal ions with limited variations of the experimental conditions, a certain generalization may be made about the behavior of the copolymer sample.

Determination of Metal Uptake in the Presence of Various Electrolyte

The following experimental procedure was applied in order to study the effect of the nature of various electrolytes and concentrations on the amount of metal ion taken up by copolymer resin sample.

The copolymer sample (25mg) was suspended in an electrolyte solution (25ml) of known concentration. The pH of the suspension was adjusted to the required value by using either 0.1M HNO_3 or 0.1M NaOH. The suspension was stirred for 24 hrs at 30^{0}C. To this suspension 2 ml of 0.1M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 30^{0}C for 24 hrs and filtered. The solid was washed and the filtrate and washing were combined and the metal ion content was determined by titration against standard EDTA (ethylene diamine tetra-acetic acid). 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 several electrolytes.

Evaluation of the Rate of Metal-Ion Uptake

To estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments were carried out, in which the metal ion taken up by the copolymer resin was estimated from the time to room temperature (300 K) in the presence of 25 ml of a solution of $NaNO_3$. It was assumed that under the given conditions, the state of equilibrium was established within 24 h. The rate of metal-ion uptake was expressed as the percentage of the amount of metal ion taken up after a certain time related to that in the state of equilibrium.

Evaluation of the Distribution of Metal Ions at Different pH.

The distribution of each one of the seven metal ions [Fe(III), Ni(II), Cu(II), Co(II), Zn(II), Cd(II) and Pb(II)] between the polymer phase and aqueous phase was estimated at 300 K and in the presence of a solution of $NaNO_3$. The experiments were carried out as described. Coefficient (D) was calculated with the following relationship:

$$D = \frac{\text{Weight (in mg) of metal ion taken up by 1 g of resin sasmple}}{\text{Weight (in mg) of metal ions present in 1 ml of solution}}$$

RESULTS AND DISCUSSION

The newly synthesized p-CDF copolymer resin was found to be brown in color. The copolymer is soluble in solvents such as N,N-dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), tetrahydrofuran (THF) and aqueous sodium and potassium hydroxide solutions while insoluble in almost all other organic solvents. The melting point of this copolymer was determined by using electrically heated melting point apparatus and is found to be 420 K.

The composition of p-CDF copolymer resin (represented in scheme 1) obtained on the basis of elemental analysis data was found to be in good correlation to that of the calculated values.

- Calc . for $C_{11}H_{14}O_2S_2N_2$ **:** C, 48.88 %, H, 5.18%, N, 10.37%, S, 23.70%.
- Found **:** C, 48.26%, H, 5.01%, N, 9.98%, S, 23.26%.

The number average molecular weight ($\overline{Mn}$) of this copolymer has been determined by conductometric titration method in non-aqueous medium and using standard potassium hydroxide (0.05M) in absolute ethanol as a titrant. The specific conductance was plotted against milliequivaletns of ethanolic KOH required for neutralization of 100gm of each copolymer. There are several breaks before the complete neutralization of all phenolic hydroxyl groups. The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average one phenolic hydroxyl group [11] of each chain was neutralized From the plot, the first and final breaks were noted. The average degree of polymerization ($\overline{DP}$) and hence the number average molecular weight ($\overline{Mn}$) of all copolymers have been determined using the

$$\overline{DP} = \frac{\text{Total milliequivalents of base required for complete neutralization}}{\text{Milliequivalents of base required for smallest interval}}$$

$$\overline{Mn} = \overline{DP} \text{ x Repeat unit weight}$$

The value of degree of polymerization for p-CDF copolymer resin having empirical formula of repeat unit $C_{11}H_{14}N_2O_2S_2$ and empirical weight of repeat unit is 270g is found to be 14.28 and number average molecular weight is obtained 3855.60 gm. The conductometric titration curve is depicted in Fig. 1.

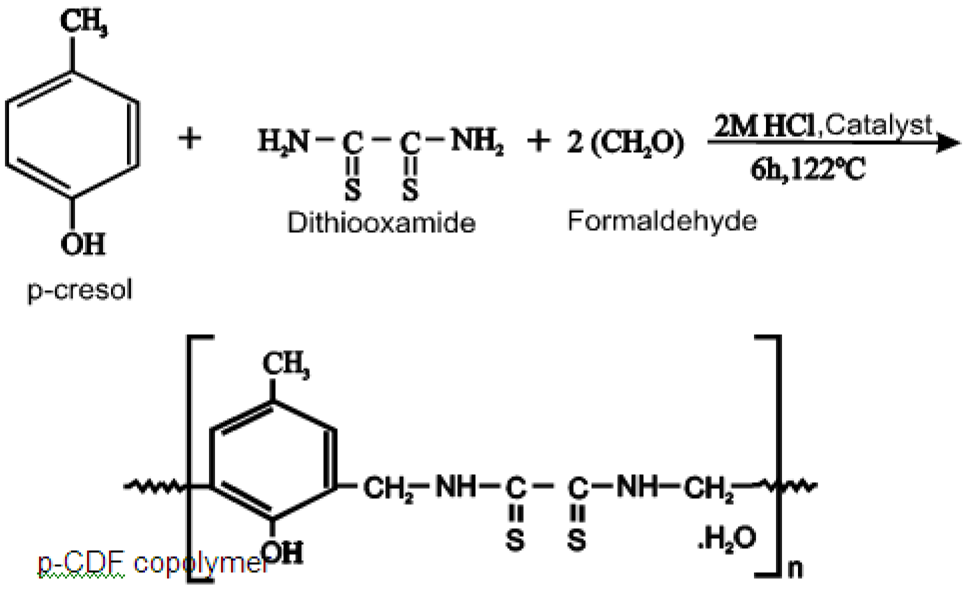
Viscosity measurements were carried out in DMF. The resin showed normal behaviour. The intrinsic viscosity was determined by Huggin's equaltion (1) amd Kraemmer's equation (2).

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2 C \quad \text{..............(1)}$$

$$\ln \eta_{rel}/C = [\eta] - K_2[\eta]^2 C \quad \text{..............(2)}$$

The viscometric plot is shown in Fig. 2. In accordance with the above relations, the plots η_{sp} / C and η_{rel} / C against C were linear giving as slopes K_1 and K_2 respectively. Intercept on the axis of viscosity function gave the [η] value in both the plots. The values of [η] obtained from both relations were in good agreement [12].

The UV-visible spectrum (Fig. 3) of purified copolymer resin exhibits two characteristic bands at 245 nm and 270 nm. These observed positions of the absorption bands indicate $\pi \rightarrow \pi^*$ transition which may be due to C = S double bond. While the latter may be due to $n \rightarrow \pi^*$ transition for the presence of the phenolic hydroxyl group (auxochrome) [13]. This observation is in good agreement with the proposed probable structure for the p-CDF copolymer resin.



Scheme 1 Synthesis of copolymer resin

Table 1 IR Spectral Data of p-CDF copolymer resin

Observed Band Frequency (cm^{-1})	Assignment	Expected band frequency
3596.3 to 3322.1 b	phenolic (OH) intermolecular hydrogen bonding	3700 to 3300
2922.9 m	>NH stretching	2800 to 3500
1659.5 w	>C=S stretching	1600 to 1400
1601.6 Sh	Aromatic ring	1600 to 1500
1483.02 Sh	-CH$_2$- bending	1460
1379.3 b	-CH$_2$- wagging	1280 to 1370
813.2 Sh	-CH$_2$- rocking	710 to 800
861.9, 913.4, 1003.8, 1231.3	1,2,3,5 substitution	900,1000,1100,1200

Sh = sharp, b = broad, St = strong, m = medium and w = weak

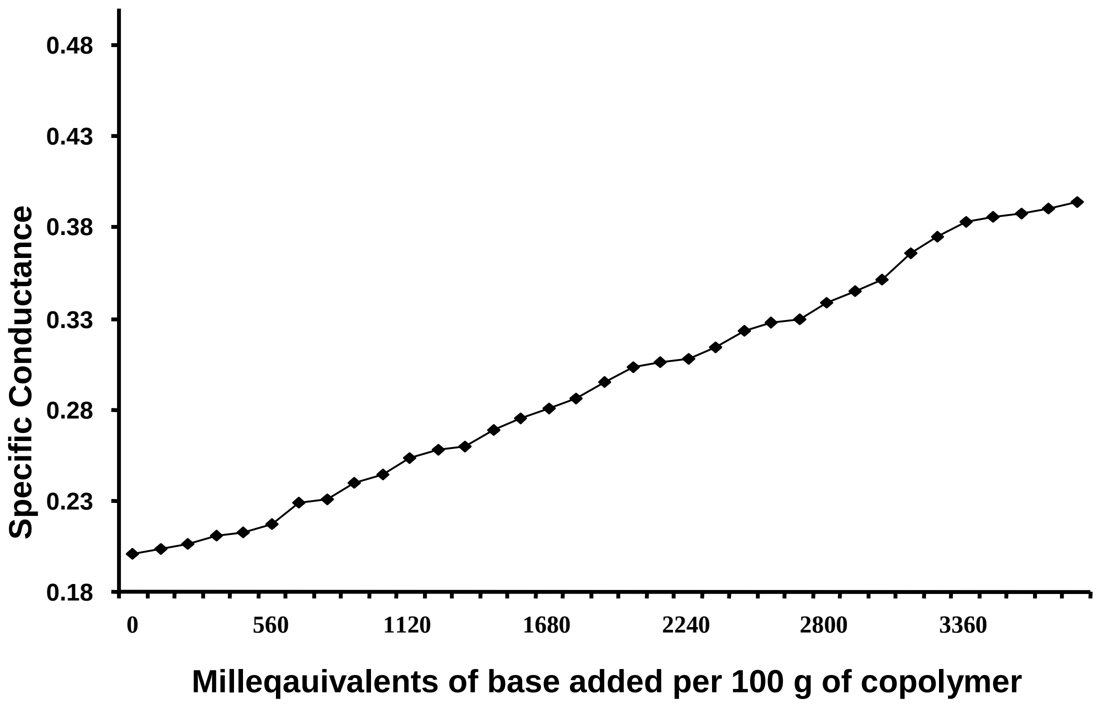


Figure 1. Conductometric titration curve of p-CDF copolymer resin

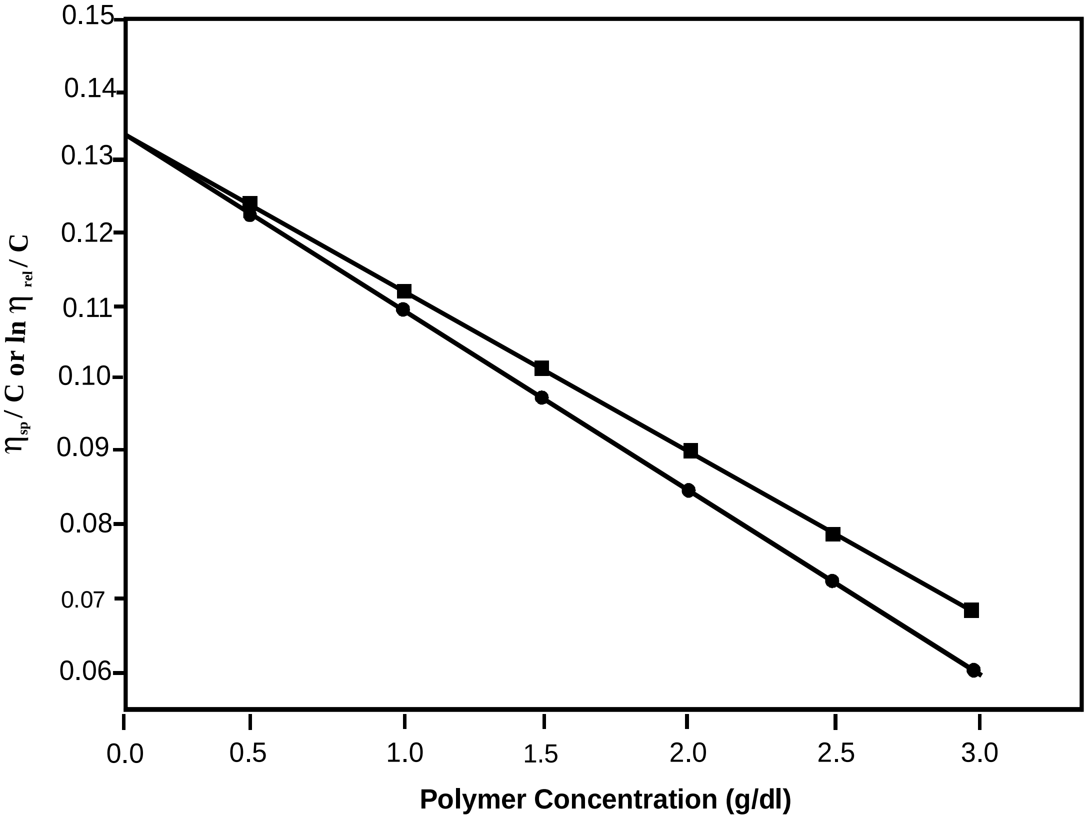


Figure 2 Viscometric Plots of p-CDF copolymer resin

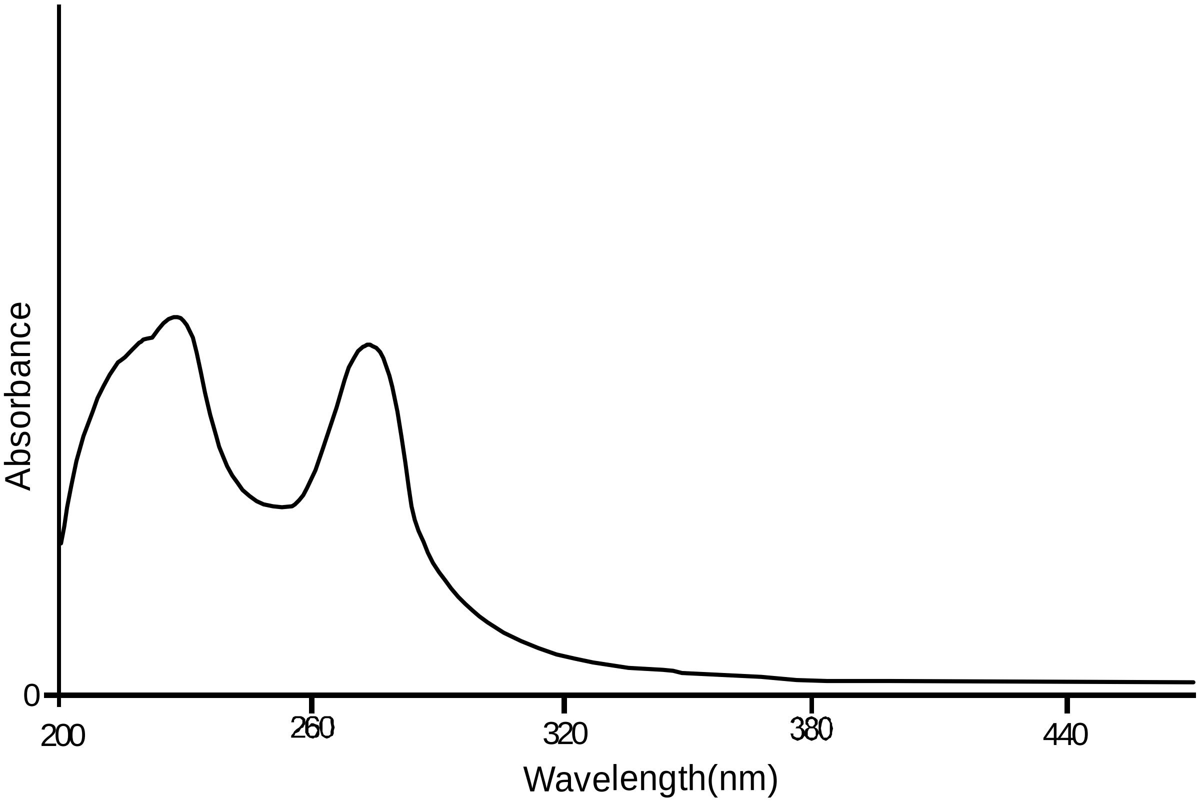


Figure 3 UV-visible spectra of p-CDF copolymer resin

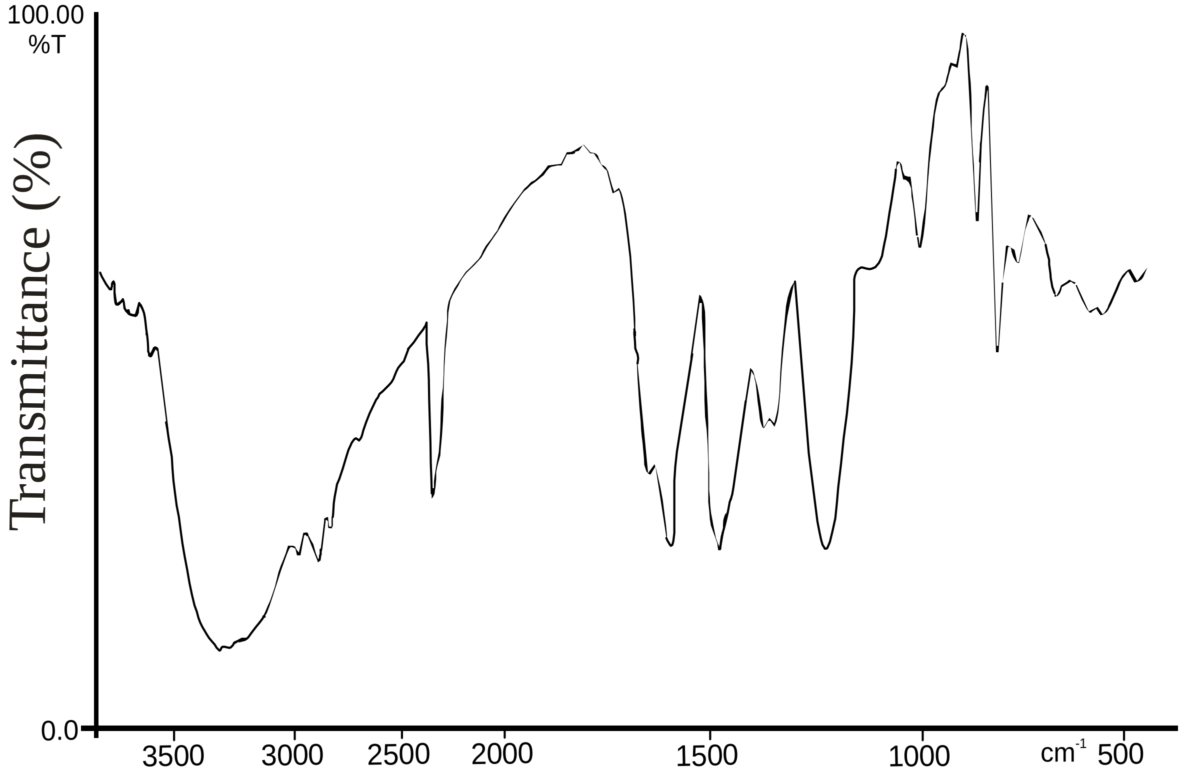


Figure 4 IR spectra of p-CDF copolymer resin

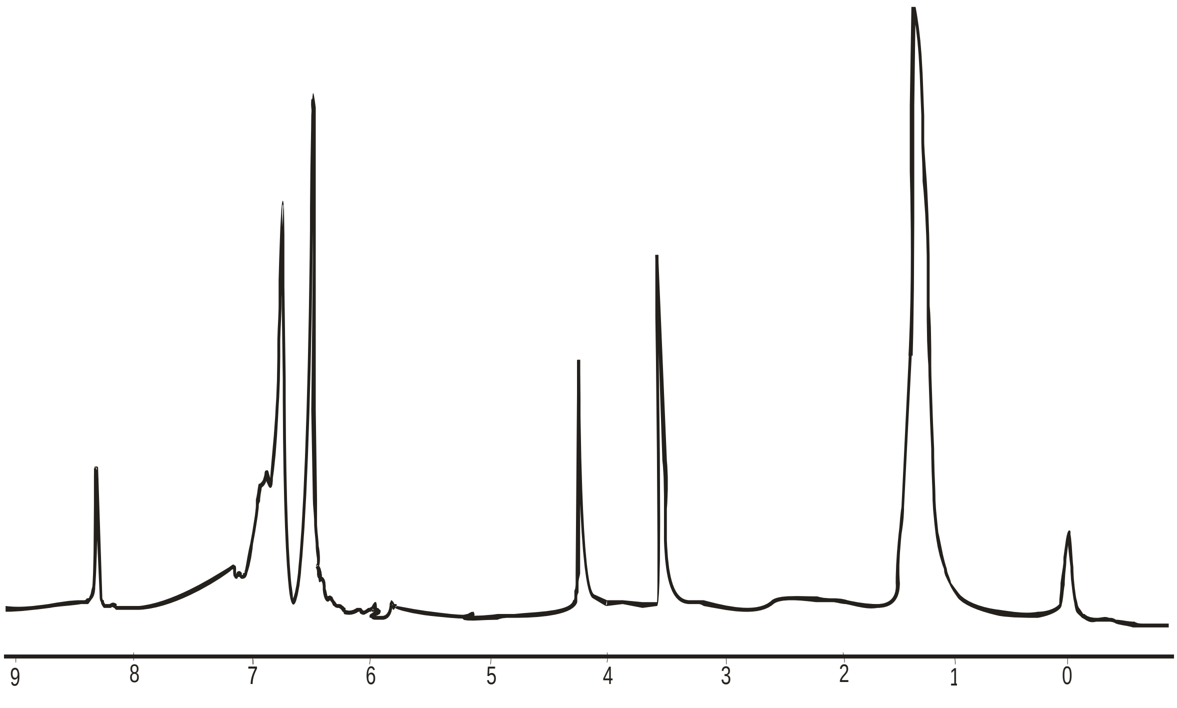


Figure 5 NMR spectra of p-CDF copolymer resin

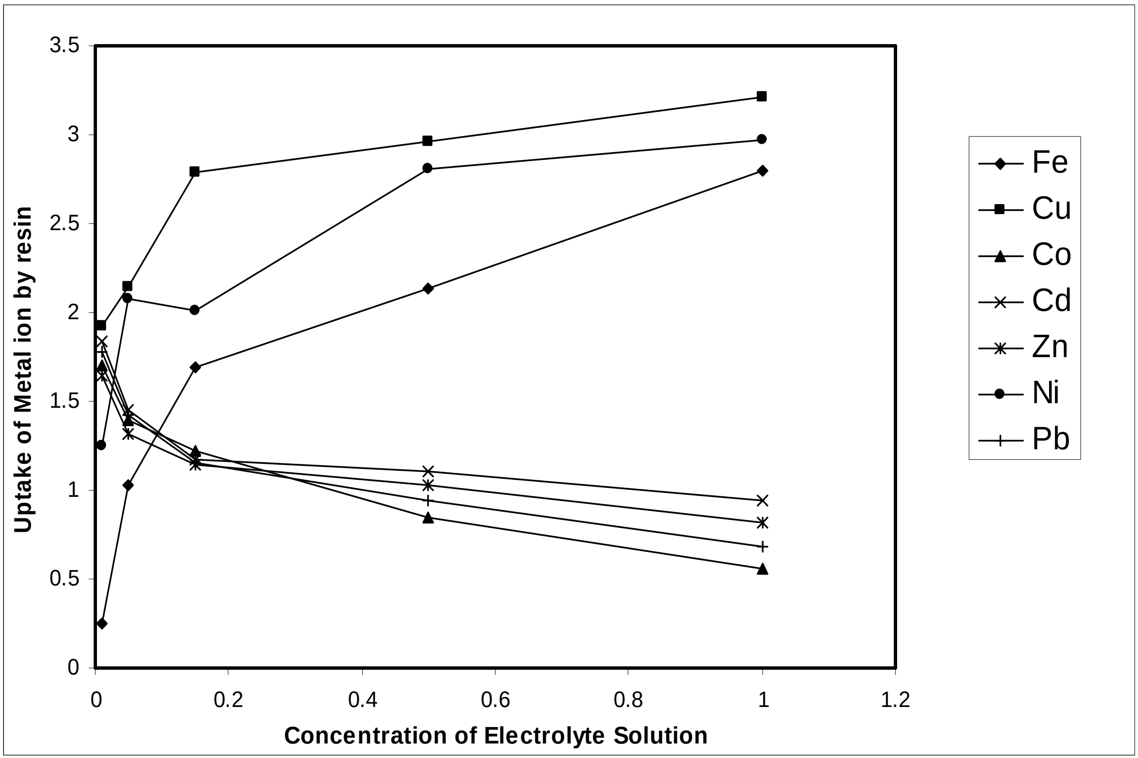


Figure 6 Uptake of several metal ions by p-CDF copolymer resin at five different concentrations of electrolyte solution NaCl

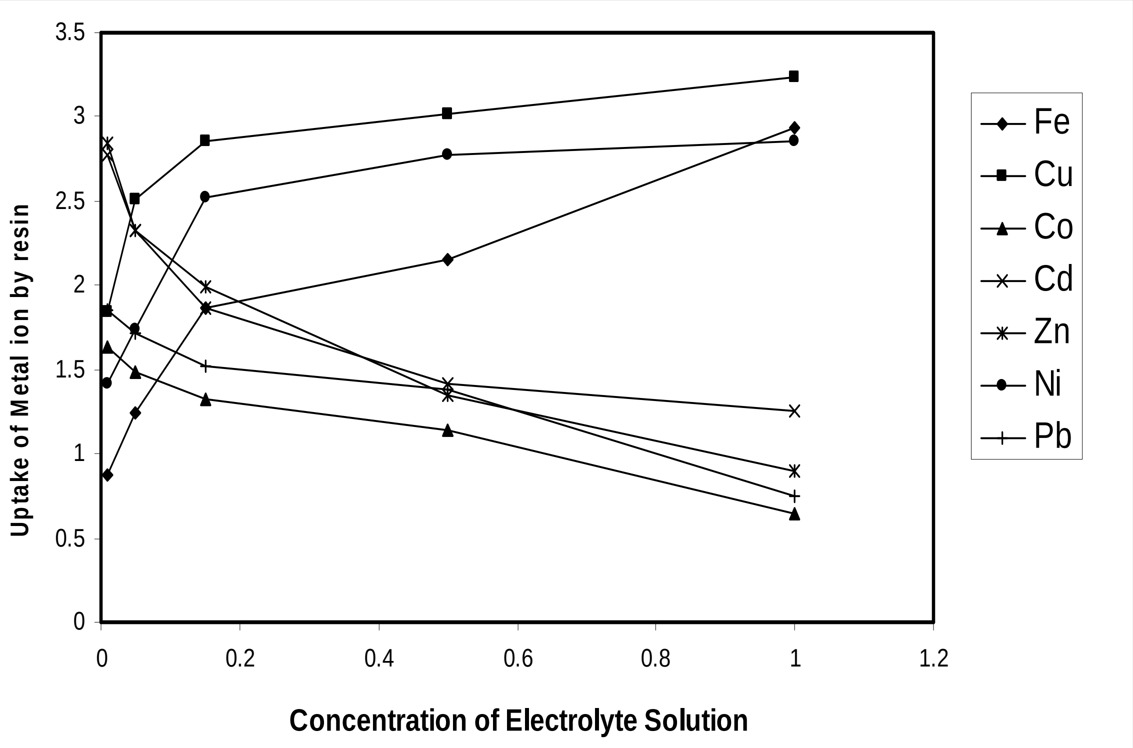


Figure 7 Uptake of several metal ions by p-CDF copolymer resin at five different concentrations of electrolyte solution $NaNo_3$

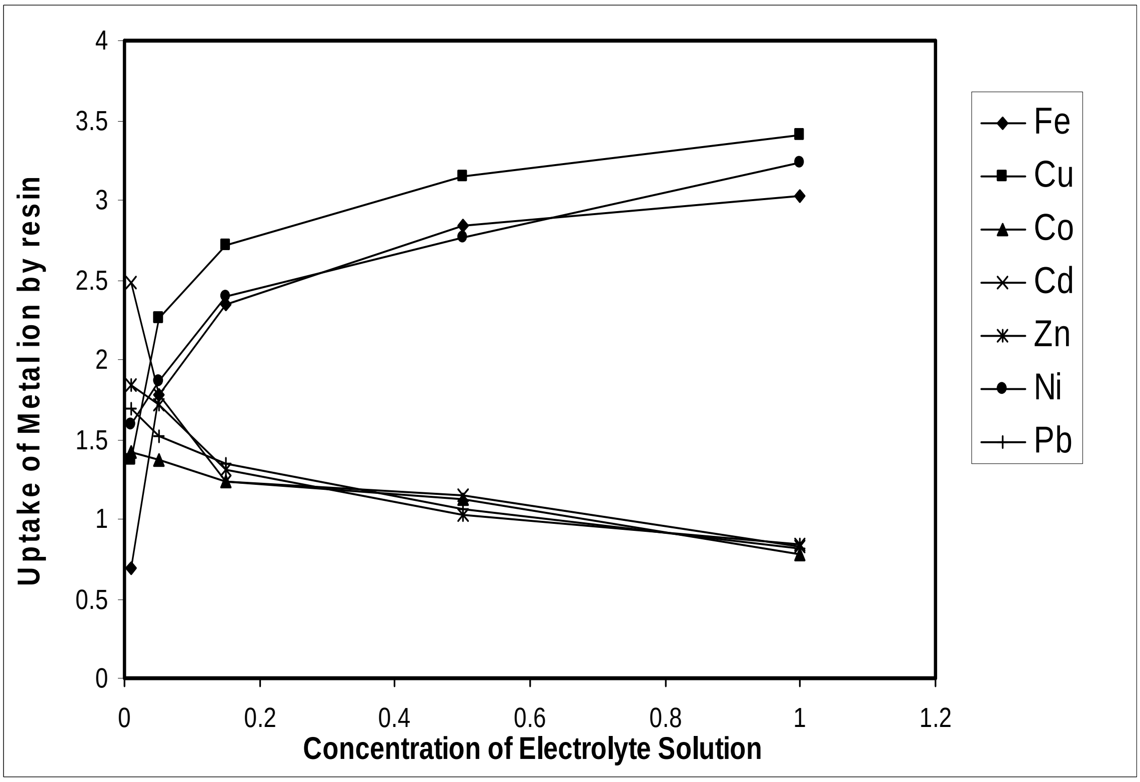


Figure 8 Uptake of several metal ions by p-CDF copolymer resin at five different concentrations of electrolyte solution $NaCIO_4$

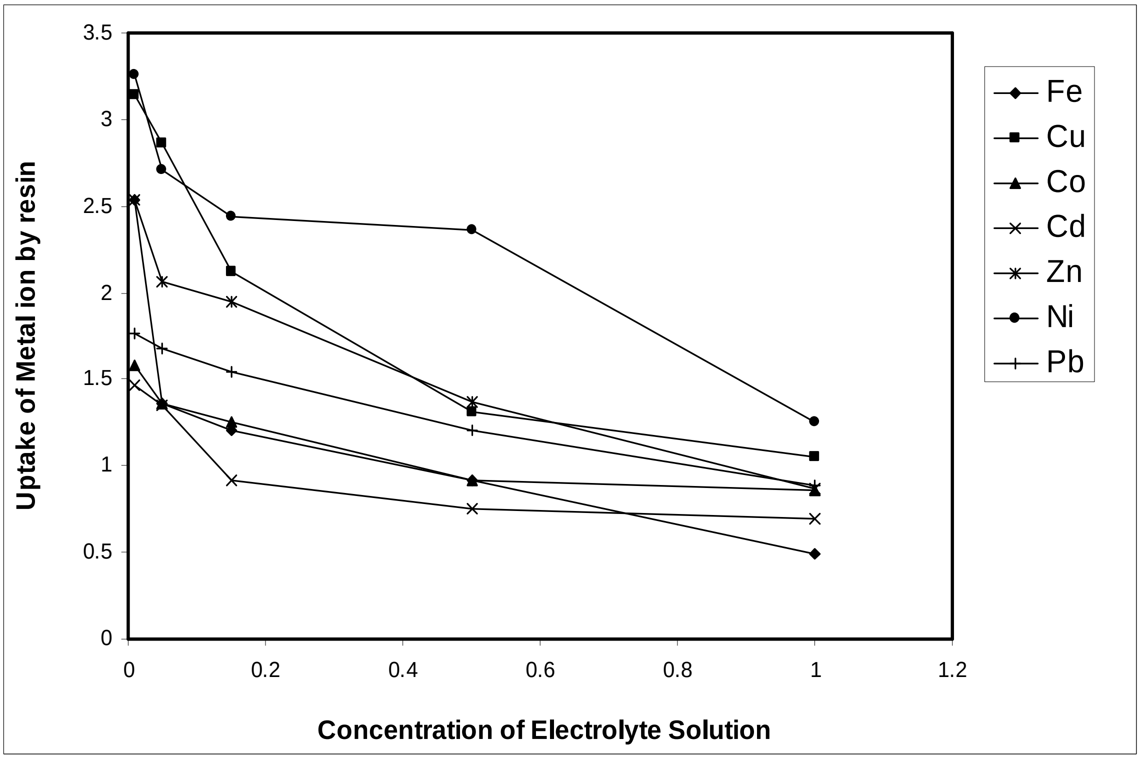


Figure 9 Uptake of several metal ions by p-CDF copolymer resin at five different concentrations of electrolyte solution Na_2SO_4

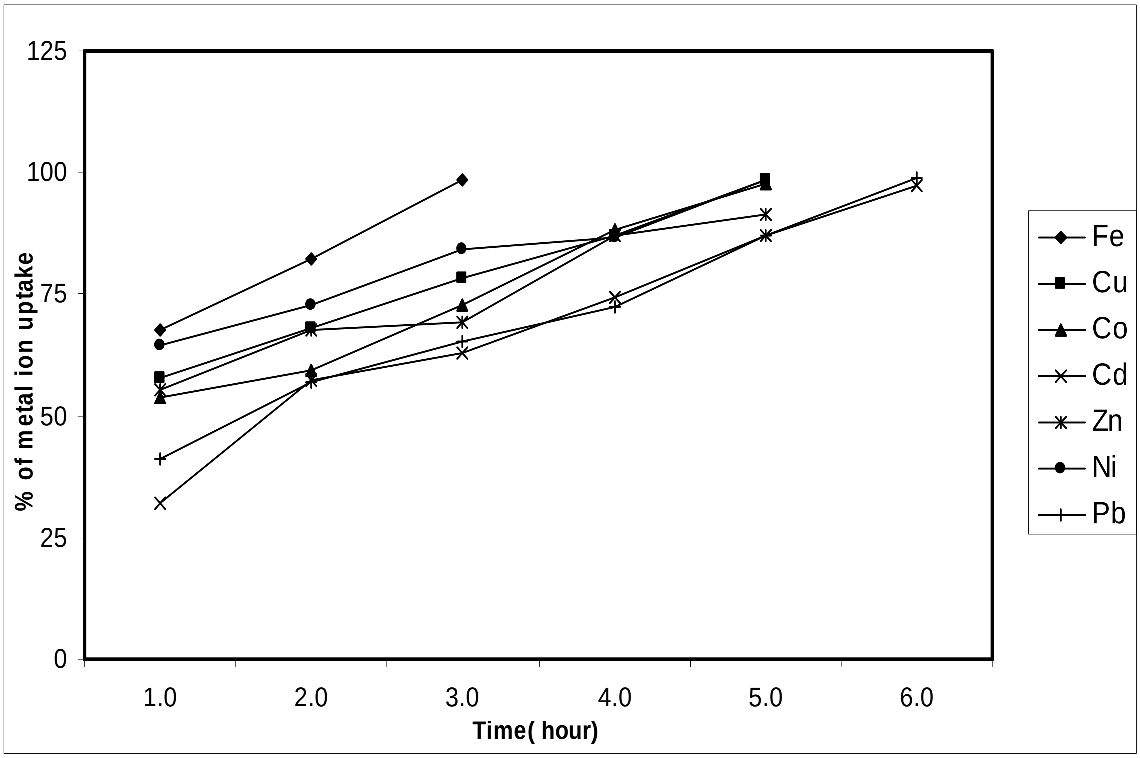


Figure 10 Comparisons of the rate of metal ion uptake by p-CDF copolymer resin

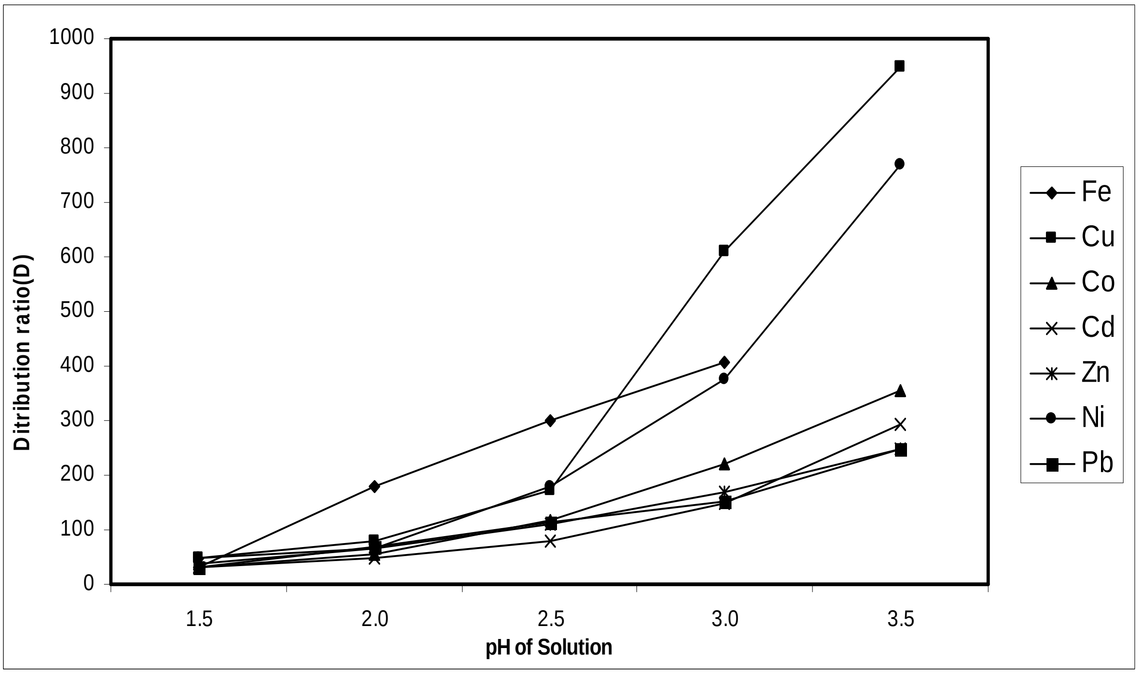


Figure 11 Distribution ratio (D) of various metal ions as function of different pH by p-CDF copolymer resin

Table 2. ^{1}H-NMR Spectral Data of p-CDF copolymer resin

Nature of proton assigned	Observed chemical shift (δ) ppm	Expected chemical shift (δ) ppm
Proton of phenolic -OH	8.48	8.0 to 12.0
Aromatic proton (Ar-H) (unsymmetric pattern)	6.94	6.2 to 8.5
Proton of Ar-NH_2- group	4.36	3.0 to 5.0
Methylene proton of Ar-CH_2- N moiety	3.62	3.0 to 3.5
Thioimide proton of –CS-NH-CS- linkage	6.51	4.0 to 8.5
Methylene proton of Ar-CH_2-Ar moiety	1.42	1.5 to 2.5

The IR spectral data are tabulated in Table 1 and IR spectra p-CDF copolymer is depicted in Fig. 4. A broad absorption band appeared in the region 3596.3 to 3322.1 cm^{-1} can be assigned to the stretching vibrations of the phenolic -OH groups [14]. A medium band at 2922.0 cm^{-1} may be due to stretching vibration of –NH- group. A weak band at 1659.5 cm^{-1} may be due to the stretching vibration of the thio (C=S) group. A sharp peak at 1601.6 cm^{-1} can be assigned to an aromatic skeletal ring. 1,2,3,5 – tetrasubstitutions of the aromatic benzene ring are recognized from bands appearing at 861.9, 913.4, 1003.8 and 1231.3 cm^{-1} respectively. The band at 1483.2 cm^{-1} may be due to -CH_2- bending, 1379.3 cm^{-1} may be due to -CH_2- wagging, 813.2 cm^{-1} may be due to -CH_2- rocking.

Proton NMR spectra of copolymer resin are presented in Fig. 5 and NMR spectra data are incorporated in Table 2 and the chemical shift (δ) ppm observed are assigned on the basis of data available in literature [15]. A signal at 1.42 (δ) ppm is due to methylene protons of Ar-CH_2-Ar- moiety. A signal at 3.62 (δ) ppm is due to methylene proton of Ar-CH_2-N moiety. A signal at 4.36 (δ) ppm is due to proton of Ar-NH_2- moiety. A weak signal at 6.51 (δ) ppm may be due to protons of –NH- bridge. Proton NMR spectra of copolymer resin show a multiplet signal (unsymmetrical pattern) 6.94 (δ) ppm is due to aromatic protons. A signal appeared in the region at 8.48 (δ) ppm can be assigned to proton of phenolic –OH group involved in hydrogen bonding.

Ion-exchange properties

The results of the batch equilibrium study carried out with p-CDF copolymer resin sample are shown in Fig. 6 to 11. From this study, which was carried out with seven metal ions with limited variations of the experimental conditions, certain generalizations can be made about the behaviour of the p-CDF copolymer sample.

Influence of electrolytes on the metal-ion uptake

The influence of chloride, nitrate, chlorate and sulphate at various concentrations on the equilibrium of metal – resin interaction had been examined. Fig. 6 to 9 shows that the amount of metal ions taken up by a given amount of copolymer depends on the nature and concentrations of the electrolyte present in the solution. Fig. 6 shows that in the presence of chloride ions, the uptake of Fe(III), Cu(II) and Ni(II) ions increases with increasing concentrations of the electrolyte. Where as the uptake of Co(II), Zn(II) and Pb(II) ions decreases with increasing concentration of the electrolyte. Fig. 7 shows that in the presence of Nitrate ions, the uptake of Fe(III), Cu(II) and Ni(II) ions increases with increasing concentration of $NaNO_3$ electrolyte. Fig. 8 shows that in the presence of chlorate ions, the uptake of Fe(III), Cu(II) and Ni(II) ions increases with increasing concentration of the electrolyte. Where as the uptake of Co(II), Zn(II) and Pb(II) ions decreases with increasing concentration of electrolyte. Fig. 9 shows that in the presence of sulphate ions, the uptake of Fe(III), Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Pb(II) ions decreases with increasing concentration of $NaSO_4$ electrolyte [16]. This may be explained on the basis of the stability constants of the complexes with those metal ions.

Evaluation of the rates of metal uptake

The rates of ion absorption by p-CDF copolymer resin samples were measured for Fe(III), Ni(II), Co(II), Cu(II), Zn(II) and Pb(II) ions to determine the time required to reach the equilibrium. The term refers to the change with time when they were in contact with the copolymer sample the experiment results, which are shown in Figure 10 show the dependence of the rate of metal-ion uptake on the nature of the metal ions. These results indicate that the time taken for the uptake of the different metal ion at a given stage depended on the nature of the metal ions under the given conditions. A careful examination of the experimental data, which are shown in Fig. 10 shows that Fe(III) ions required almost 3 h for equilibrium. Cu(II), Ni(II), Zn(II) and Co(II) ions required about 5 h, were as Pb(II), Cd(II) ions required almost 6 h for equilibrium. The experimental results revealed that the rate of metal-ion uptake followed the order of Fe(III) > Cu(II) > Ni(II) > Co(II) > Pb(II) > Zn(II) [17].

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 Fig. 11. The distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the p-CDF copolymer increases with increasing pH of the medium [18]. The magnitude of increase, however, is different for different metal cations. The p-CDF copolymer resin take up Fe(III) ion more selectively than any other metal ions under study. The order of distribution ratio of metal ions measured in the pH range 1.5 to 6.0 is found to be Fe(III) > Cu(II) > Ni(II) > Co(II) > Pb(II) > Zn(II). Thus, the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions. For example, the result suggest the optimum pH 3.0 for the separation of Cu(II) and Fe(III) with distribution ratio 'D' as 42.9 and 412.6 for Cu(II) and Fe(III) respectively using p-CDF copolymer resin as ion-exchanger. Similarly, for the separation of Co(II) and Ni(II) the optimum pH is 6.0 at which the distribution ratio 'D' for Co(II) is 360.5 and that for Ni(II) is 720.8. The lowering in the distribution ratio of Fe(III) was found to be small and hence, efficient separation could be achieved.

CONCLUSION

1. A copolymer, p-CDF based on the condensation reaction of p-cresol and dithiooxamide with formaldehyde in the presence of acid catalyst was prepared.
2. p-CDF is a selective chelating ion-exchange copolymer for certain metals.
3. The copolymer showed a higher selectivity for Fe^{3+}, Cu^{2+}, Ni^{2+} than for Co^{2+}, Zn^{2+}, Pb^{2+}.

Acknowledgement

The authors are thankful to the Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow, India. for spectral analysis. One of the author (W. B. Gurnule) thanks to University Grant Commission, New Delhi for financial assistance.

REFERENCES

[1] AMG Pacheco; LIC Barros; MA Reis, Environ*. Pollut.*, **2002**, 120, 79-86.
[2] JH Trivedi; K Kalia, *Carbohyd. Polym.,* **2005**, 60, 117-125.
[3] M Ahuja; AK Rai, *Carbohy. Polym.,* **1997**, 33**,** 57-62.
[4] W Lee; MY Kim, *Bull. Korean Chem. Soc.,* **2002**, 23**,** 1067-1072.
[5] AR Ismaeel; KM Edbey, *J. Chem. Pharma. Res*. **2010**, 2(2), 459-466.
[6] BA Shah; AV Shah; BN Bhandari, *Asian J. Chem.,* **2003**, 15, 117-125.
[7] M Karunakaran; A Burkanudeen, *Orient. J. Chem.,* **2002**, 18**,** 65-68.
[8] SC Das; *J. Indian Chem. Soc.,* **2000**, **77,** 66-69.
[9] BA Shah; AV Shah; BN Bhandari, *Asian J. Chem.,* **2004**, 16**,** 1801-1810.
[10] SK Kapse; VV Hiwase; AB Kalambe; *J. Chem. Pharma. Res;* **2012,** 4(3), 1734-1739.
[11] BA Shah; AV Shah; BN Bhandari., *Iran Polym J.,* **2006,** 15(10), 809-819.
[12] RH Gupta; AB Zade; WB Gurnule, *J. Appl Polym.,* **2008**, 109**,** 3315-3320.
[13] RN Singru; *J. Chem. Pharma. Res;* **2012**, 4(1), 46-53.
[14] MM Patel; MA Kapadia; DP Patel; JD Joshi, *React Funct Polym.,*2007, 67**,** 746-757.
[15] RN Singru; AB Zade; WB Gurnule, *J. Appl Polym.Sci.***8,** 109(2), 859-868.
[16] MM Jadhao; LJ Paliwal and NS Bhave, *Ind J. Chem.,***2005**, 44**,** 542-547.
[17] RS Bhandari; AK Chauhan; Goswami, *J. Chem. Pharma. Res*, **2011**, 3(2), 34-38.
[18] WB Gurnule; PK Rahangdale; LJ Paliwal; RB Kharat, *React Func Polym.,* **2003**, 55**,** 255-265.