RJC

RASĀYAN *J. Chem.*
Vol. 5 | No.3 | 365-375 | July-September | 2012
ISSN: 0974-1496 | CODEN: RJCABP
http://www.rasayanjournal.com

SELECTIVE REMOVAL OF TOXIC METAL IONS FROM WASTE WATER USING PHENOL-FORMALDEHYDE TYPE CHELATING RESINS

Wasudeo B. Gurnule[1]* and Sharyu S. Katkamwar[2]
[1]Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara, Nagpur-440010, Maharashtra, India
[2]Department of Chemistry, Arts, Commerce and Science College, Tukum, Chandrapur-442 401, Maharashtra, India
*E-mail: wbgurnule@yahoo.co.in

ABSTRACT

The concentration of different toxic metals has increased beyond environmentally and ecologically permissible lends due to increase in industrial activity. More than 100 million people of West Bengal in India and Bangladesh are affected by drinking ground water contaminated with copper, lead, cadmium and some part of India is also affected by poisoning effects of Copper, Cadmium, Zinc, Lead. Different methods have been evolved to reduce the cadmium concentration in water in a maximum permissible level of 10 µg/L as where various methods are also available today, removal of cadmium and copper by polymeric ion-exchangers has been most effective. While chelating ion-exchange resins having specific chelating groups attached to a polymer have found extensive use in sorption of Cu^{2+} and Cd^{2+} ions.The copolymer resin o-APDF has been synthesized by the condensation of o-amino phenol and dithiooxamide with formaldehyde in 1:1:2 molar ratio in presence of 2 M hydrochloric acid as catalyst. The newly synthesized copolymer resin has been characterised by UV-visible, IR and proton NMR spectral studies. The copolymer o-APDF proved to be a selective chelating ion exchange polymer for certain metals. Chelating ion-exchange properties of this polymer were studied for Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions. A batch equilibrium method has been 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. The polymer showed higher selectivity for Fe^{3+}, Cu^{2+}, Ni^{2+} than for Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{+2} ions. Study of distribution ratio as a function of pH indicates that the amount of metal ion taken by resin increases with the increasing pH of the medium. .

Keywords : Chelating resins, Metal ion uptake, Phenolic copolymer, Ion-exchanger, Distribution ratio.

INTRODUCTION

Ion-exchange resins are used in biotechnology for the purification of biologically active compounds obtained from chemical synthesis, fermentation processes or other biological sources. Specially tailored resins are used for this purpose. They are used as carriers for the immobilization of enzymes, chromatographic separations / adsorptions, depolarization, enzyme carrier, peptide purification. When organic polymers are used as adhesives, coatings, some of them can be infected by microorganisms such as bacteria and fungi. This problem can be solved by the addition of metal ions in the polymeric system[1], which changes the physicochemical as well as biological properties of the polymers. Coordination polymers are also used as biocidal coatings and are widely applied to prevent the growth of microorganism on surface e.g. anti fouling paints[2].

The concentration of toxic metal ions like Cu(II), Cd(II), As(III), As(V), Pb(II), Ni(II) and U(VI) etc. has increased beyond environmentally and ecologically sustainable levels due to natural phenomenon as well as anthropogenic impact. It has resulted in severe contamination of ground and surface water. The poisoning effect of toxic metals from contaminated drinking water has evolved as one of the major health hazards in the 21st century[3,4]. The adverse health effects caused by copper, mercury and arsenic poisoning are far more catastrophic than any other natural calamity through out the world in recent times. Especially

in the developing countries, water and soil degradation generated by industrial effluents has been a serious issue[5]. An estimated 120 million people are at risk of poisoning effect of arsenic in Bengal Delta (parts of Bangladesh, Nepal, and West Bengal), Taiwan, the USA, Chile, and Argentina. Many people are also suffering from different health hazards due to poisoning effect of copper, lead, and mercury[6]. Extraction of these metal ions is a tedious process as they are associated with a variety of complex species present in the natural aquatic systems. Again copper, lead, nickel, cadmium and uranium are present as cations such as Cu^{2+}, Pb^{2+}, Cd^{2+} and UO^{2+} in ground and surface water while arsenic is present as anions like AsO_4^- and AsO_3^-. Therefore different methods and mechanism are required to separate them from water. Chelating ion exchange resins having specific chelating groups attached to a polymer have found extensive use in sorption and pre concentration of metal cations[7-10]. Ion-exchange is process where, an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle[11]. Cation-exchanger resins can also be used as fillers. In general it helps to increase the ion exchange capacity of the basic material and also some specific properties such as alkali resistance, mechanical and chemical properties. It is also found that ion exchangers have positive effects on the water absorption. Therefore, it is recommended to produce more durable and weather-resistant products[12]. An oxyethylene copolymer with phenyl and 4 , 4'- biphenyl structural units in the backbone has been reported in the literature[13]. The effect of annealing on structural changes in a liquid-crystalline copolymer of 6-hydroxy-2-naphthanoic acid, p-hydroxybenzoic acid, terephthalic acid and 4 , 4'- biphenol was investigated by Yoon et at[14]. In a continuation of earlier work on the synthesis and characterization of chelating ion exchangers[15-17].
In this paper, we have tried to combined both the above idea to separate toxic metal cation Cu^{2+} and other metal ions. Because the ground water in some part of India contaminated with both copper and cadmium[18]. Here, we are report the synthesis of three phenol-formaldehyde type resins containing *o*-aminophenol functionalities and their metal ion uptake capacity towards metal ion such as Cu^{2+}, Ni^{2+} and Fe^{3+}. Copper and iron polychelate of the resins are used as polymeric ligand exchanger to remove metal ions from drinking water. A comparative study was done between the iron and other metal ions.

EXPERIMENTAL

Materials

The chemicals were all analytical reagent or chemically pure grade. N, N'- Dimethyl formamide (DMF) and dimethylsulfoxide (DMSO) were used after double distillation. o-Amino phenol (Merck, Mumbai, India), dithiooxamide (S. D. Fine Chemical, Mumbai, India) and 37 % formaldehyde solution (Merck, Mumbai, India) were used.

Synthesis of copolymer resin

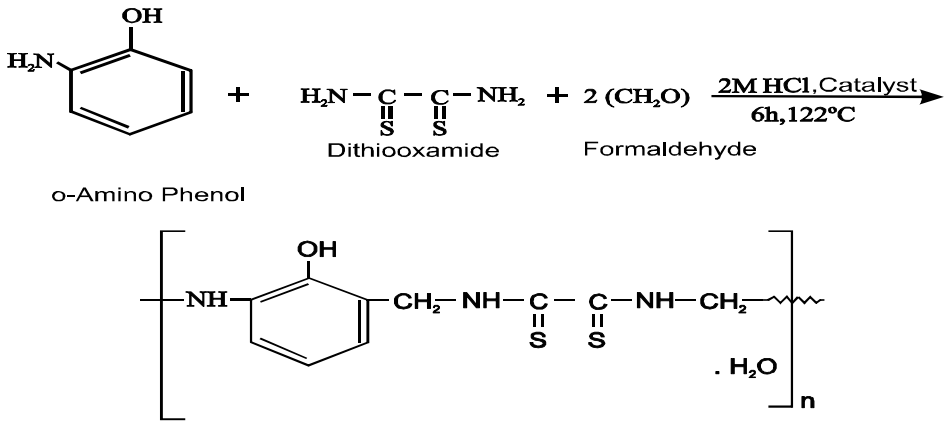
A mixture of o-Amino phenol (1.091 gm, 0.1 mol), dithiooxamide (1.20 gm, 0.1 mol) and formaldehyde (7.50 ml, 0.2 mol) in the presence of 200 ml of 2M hydrochloric acid as a catalyst was heated in an oil bath at 122^0C for 6h with occasional shaking.
The separated brown resinous product was washed with 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 o-amino phenol-formaldehyde copolymer that might be present along with the copolymer. The resin was purified by dissolution in 8% NaOH and by reprecipitation through the dropwise 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 vacuo over anhydrous $CaCl_2$. The reaction and suggested structure of o-APDF copolymer is shown in Scheme-1.

Characterization of copolymer resin

The copolymer resin was subjected to microanalysis for carbon, hydrogen, nitrogen and sulphur on a Cargo Elmer Elemental Analyzer at Central Drug Research Institute (CDRI, Lucknow, India). 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°C.

Electronic absorption spectra of o-APDF copolymer resin was 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 o-APDF was recorded on Cargo 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 Advanced 400 NMR spectrometer using DMSO - d_6 at Central Drug Research Institute, Lucknow.



o-APDF copolymer resin

Scheme-1; Preparation of the o-APDF copolymer resin

Ion-exchange properties

The results of the batch equilibrium study carried out with the copolymer sample of o-APDF are shown in Figure- 6 to 11. From this study of seven metal ions with limited variations of the experimental conditions, a certain generalization may be made about the behaviour of the copolymer sample.

Determination of metal uptake in the presence of various electrolyte and different concentrations

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°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°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:

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

RESULTS AND DISCUSSION

The newly synthesized purified o-APDF copolymer resin was found to be brown in color. The copolymer is soluble in solvents such as DMF, DMSO, 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 418 K.

The composition of o-APDF 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-

Anal . Calcd . for $C_{10}H_{13}O_2S_2N3$ **:** C = 44.28 %, H = 4.79%, N = 15.49 and %, S = 23.61%.
Found **:** C = 43.94%, H = 4.23%, N = 15.01%, and S = 23.14%.

The molecular weight ($\overline{Mn}$) of this copolymer resin was determined by non-aqueous conductometric titration in DMF against ethanolic KOH by using 50 mg of sample. The average degree of polymerization as given by $\overline{DP}$ = (Total Milliequivalents of base required for complete neutralization / Milliequivalents of base required for smallest interval) is found to be 20.74. The number average molecular weight ($\overline{Mn}$) is 5620 as obtained by the formula weight of the repeating unit[19,20]. The conductometric titration curve is depicted in Figure--1.

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

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

Viscosity measurements were carried out in DMF. The resin showed normal behaviour. The viscometric plot is shown in Figure- 2. The plots η_{sp} / C and η_{rel} / C against C were linear giving as slopes K_1 and K_2 respectively. The value of [η] obtained was in good agreement[21].

The UV-visible spectrum of the o-APDF copolymer sample in pure DMF was recorded in the region 200 to 600 nm (Fig.- 3). The spectra exhibits two characteristic bands at 210 to 230 and 250 to 280 nm. The 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) [22]. This observation is in good agreement with the proposed probable structure for the o-APDF copolymer resin.

The IR spectral data are tabulated in Table-2 and IR spectra of o-APDF copolymer is depicted in Figure- 4. A broad band appeared in the region 3407.6 cm^{-1} to 3301.9 cm^{-1} may be assigned to the stretching vibrations of the phenolic -OH groups[23-25]. Presence of >NH is indicated by the sharp band at 2366.2 cm^{-1} which is merged with a broad band due to hydroxyl group[26]. A medium band at 1655.8 cm^{-1} may be due to stretching vibration of the thio (C=S) group. The broad band at

1616.3 cm^{-1} may be due breathing modes of aromatic skeletal ring. The spectra show bands at 1441.2 cm^{-1}, 1303.1 cm^{-1} and 770 cm^{-1} which may be ascribed to methylene groups[27]. 1, 2, 3, – tri substitution are indicated by the peaks at 966.4cm^{-1}, 1027.6 $cm^{-1}$and 1122.1 cm^{-1}.

Proton NMR spectra of copolymer resin are presented in Figure- 5 and NMR spectra data are incorporated in Table-2 and the chemical shift (δ) ppm observed on the basis of data available in literature[28]. In the NMR spectra of o-APDF copolymer, exhibit singlet signal at 1.62 (δ) ppm due to methylene protons of the Ar-CH_2-Ar- bridges[29]. The weak multiplet signal (unsymmetrical pattern) to 6.92 (δ) ppm are due to aromatic protons. The methylene proton of Ar-CH_2-N moiety appears at 3.52 (δ) ppm region[30]. The signal to 6.55 (δ) ppm is attributed to the protons of –NH- bridges. The signal at 8.30 (δ) ppm is attributed to phenolic hydroxyl proton. The signal at 4.05 (δ) ppm is due to proton of Ar-NH_2- group.

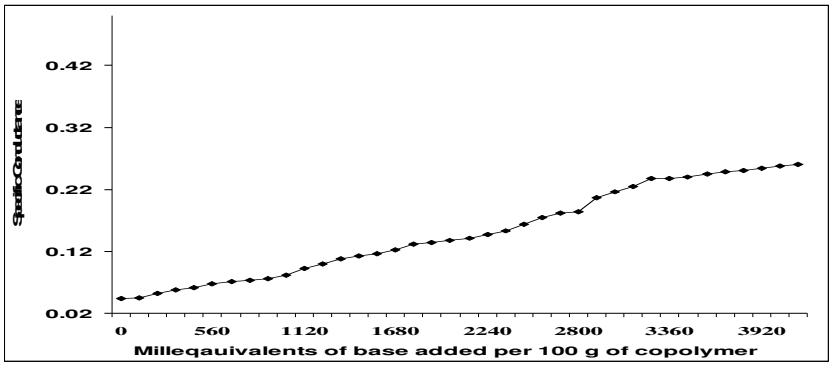


Fig.-1: Conductometric titration curve of o-APDF copolymer resin

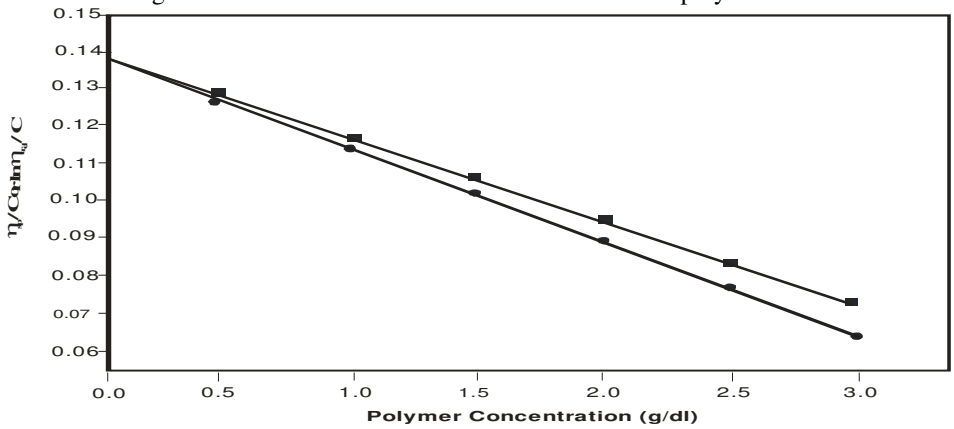


Fig.-2: Viscometric Plots of o-APDF copolymer resin

Ion-exchange properties

The results of the batch equilibrium study carried out with o-APDF copolymer resin sample are shown in Figure-s- 6 to 11. To ascertain the selectivity of the o-APDF copolymer for the selected metal ions the influence of various electrolytes on the selectivity of metal ions. The rate of metal uptake, and the distribution ratio of metal ions between the copolymer and the solution containing metal ions have been studied.

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 have been examined. Figure-s-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. Figure- 6 shows that in the presence of chloride ions, the amount of Fe(III), Cu(II) and Ni(II) ions taken up by the o-APDF copolymer increases with increasing concentrations of the NaCl electrolyte. Where

as the uptake of Co(II), Cd(II), Zn(II) and Pd(II) ions decreases with increasing concentration of the electrolyte. Figure--7 shows that in the presence of Nitrate ions, the uptake of Fe(III), Cu(II) and Ni(II) ions by the o-APDF copolymer increases with increasing concentration of $NaNO_3$ electrolyte. Where as the uptake of Co(II), Cd(II), Zn(II) and Pd(II) ions decreases with increasing concentration of the electrolyte. Figure- 8 shows that in the presence of chlorate ions, the uptake of Fe(III), Cu(II) and Ni(II) ions by the o-APDF copolymer increases with increasing concentration of the $NaClO_4$ electrolyte. Where as the uptake of Co(II), Cd(II), Zn(II) and Pd(II) ions decreases with increasing concentration of electrolyte. Figure- 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 by the o-APDF copolymer decreases with the increasing concentration of the electrolyte. This can be explained on the basis of stability constants of the complexes which Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions form with these anions. SO_4^{2-} is expected to form strong complexes with Fe^{3+}, Cu^{2+}, Ni^{2+}, ions, while ClO_4^-, NO_3^- and Cl^- are expected to form weak complexes and therefore may not influence the position of the Fe^{3+}, Cu^{2+} and Ni^{2+} chelates equilibrium as much as SO_4^{2-} ions. Sulphate, chlorate, nitrate and chloride ions form strong chelates with Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions and therefore might be expected to influence the position of the Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} chelates equilibrium. This type of trend has also been observed by other investigators in this field[31].

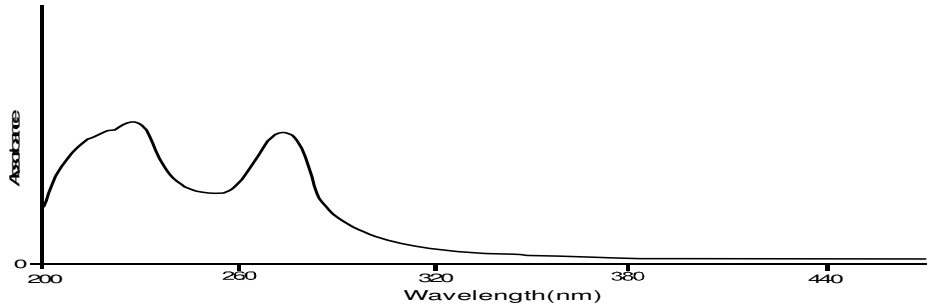


Fig.-3: UV-visible Spectra of o-APDF copolymer resin

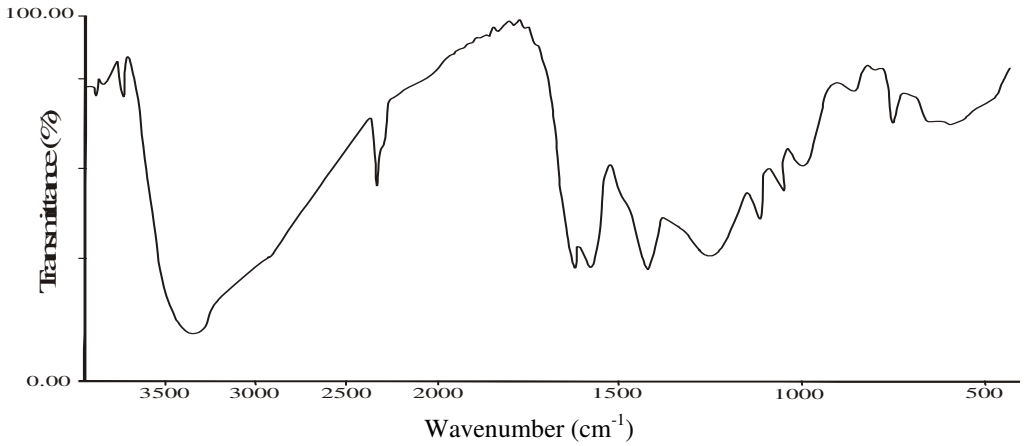


Fig.-4: IR Spectra of o-APDF copolymer resin

Rate of metal uptake

The rate of metal ion uptake depend on the nature of metal. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given polymer. The results in Figure--10 show 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 require about 3 hr for the establishment of the equilibrium, whereas Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} require about 5 h for equilibrium.

Cd^{2+} and Pb^{2+} ions require almost 6 hr for equilibrium. Thus, the rate of metal ion uptake follows the order Fe(III) > Cu(II) > Co(II) > Pb(II) > Cd(II) > Ni(II) > Zn(II).

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 Figure--11. The distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the o-APDF copolymer increases with increasing pH of the medium[32]. The magnitude of increase, however, is different for different metal cations. The study was carried out up to a definite pH value for a particular metal ion to prevent hydrolysis of the metal ions at higher pH values. The results also indicate that the copolymer takes of Fe^{3+} ions more selectively than any other metal ions under study. The lower distribution ratio of Fe^{3+} may be attributed to steric hindrance[33]. Amongst the other metal ions, Cu^{2+} and Ni^{2+} ions are taken up by the copolymer 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 to 6. This could be attributed to the low stability constants, i.e. the weak ligand stabilization energy of the metal complexes. Thus, the order of selectivity of metal ions by the copolymer is found to be $Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+} > Zn^{2+} > Pb^{2+}$.

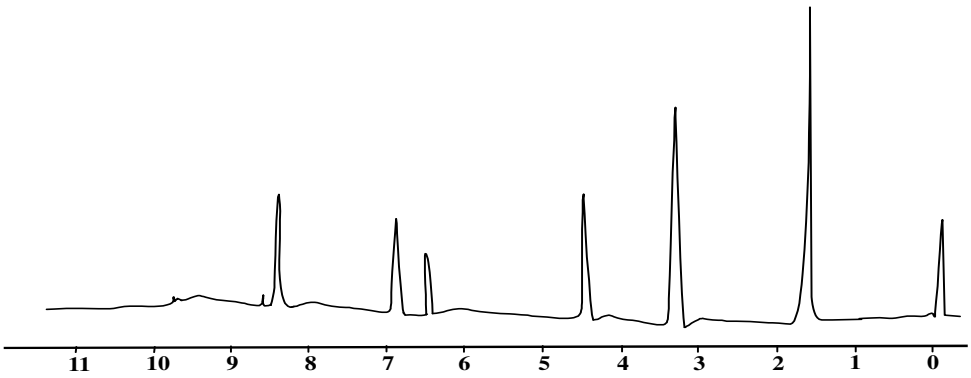


Fig.-5: NMR spectra of o-APDF copolymer resin

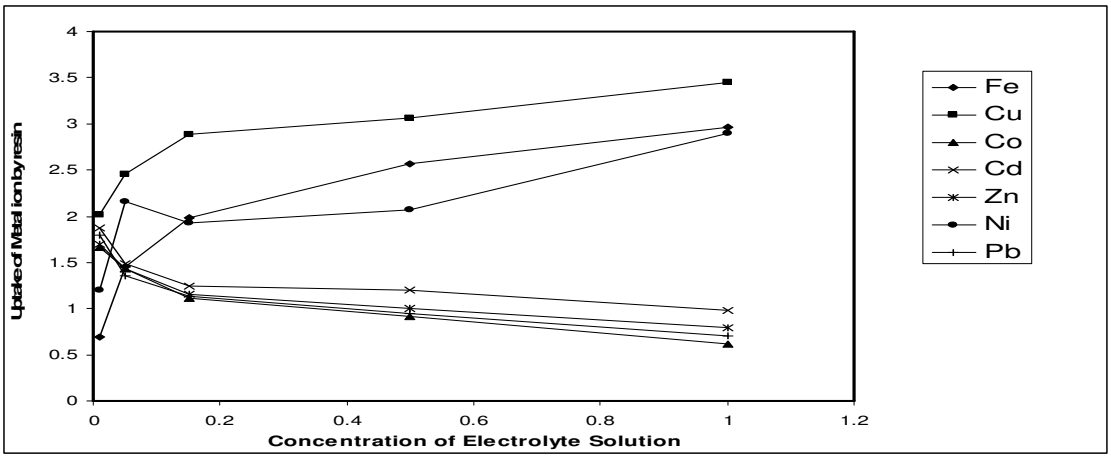


Fig.-6: Uptake of several metal ions by o-APDF copolymer resin at five different concentrations of electrolyte solution NaCl

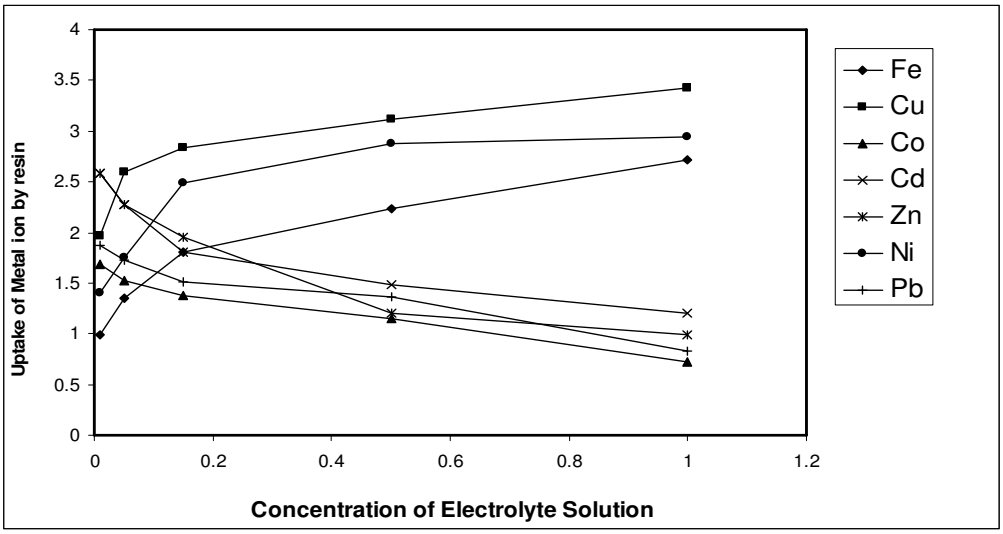


Fig.-7: Uptake of several metal ions by o-APDF copolymer resin at five different concentrations of electrolyte solution $NaNo_3$

Table-1: IR Spectral Data of o-APDF copolymer resin

Observed band frequency (cm^{-1})	Assignment	Expected band frequency
3596.3 to 3322.1 b	-OH phenolic 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

Table-2: ^{1}H-NMR Spectral Data of o-APDF 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

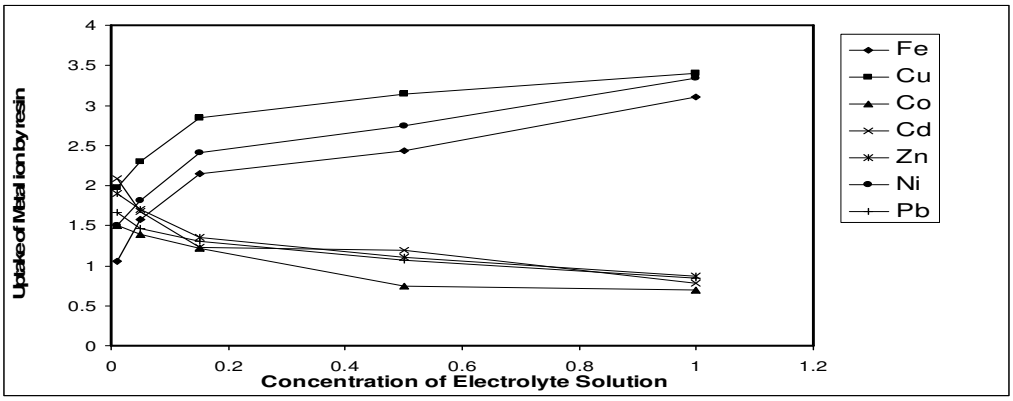


Fig.-8: Uptake of several metal ions by o-APDF copolymer resin at five different concentrations of electrolyte solution $NaClO_4$

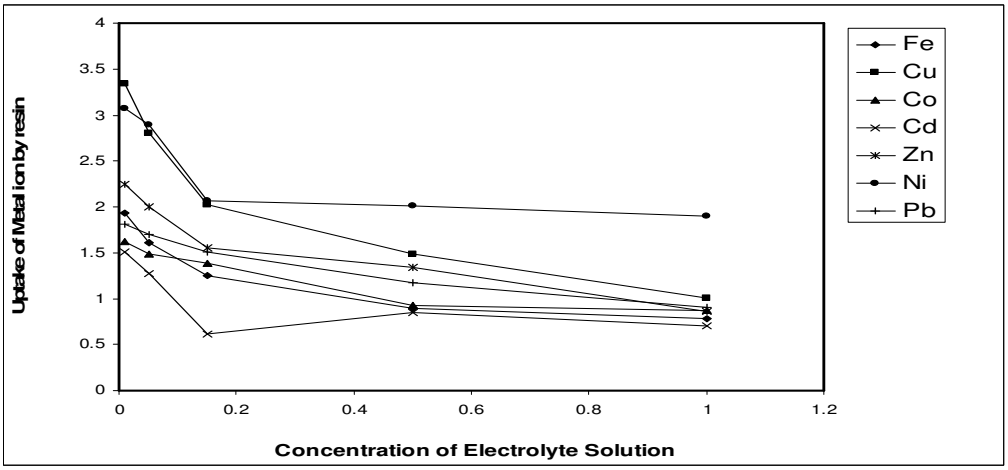


Fig.-9: Uptake of several metal ions by o-APDF copolymer resin at five different concentrations of electrolyte solution Na_2SO_4

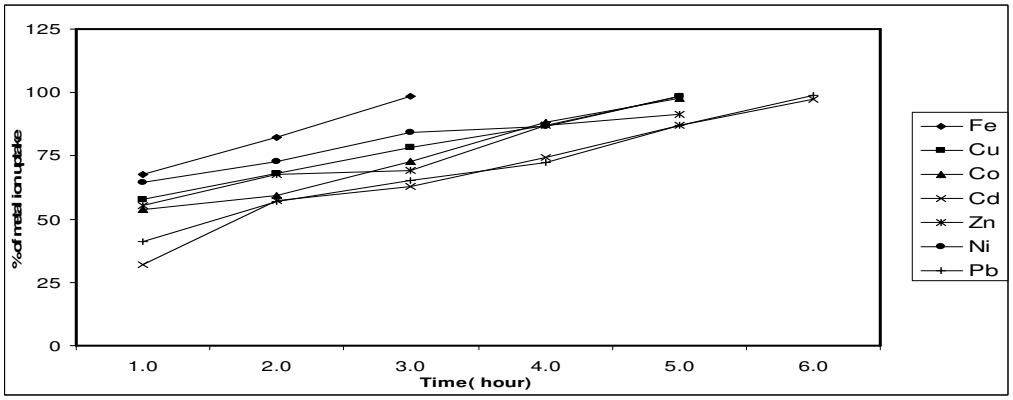


Fig.-10: Comparisons of the rate of metal ion uptake by o-APDF copolymer resin

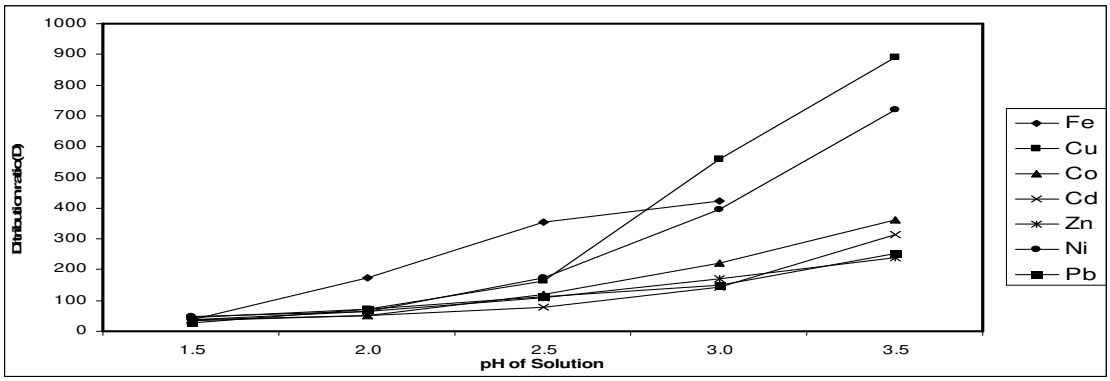


Fig.-11: Distribution ratio (D) of various metal ions as function of different pH by o-APDF copolymer resin

CONCLUSIONS

1. A copolymer, o-APDF based on the condensation reaction of o-amino phenol and dithiooxamide with formaldehyde in the presence of acid catalyst was prepared.
2. o-APDF 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+}, Cd^{2+}, Pb^{2+}.
4. It can be concluded that the phenolic resins containing p-aminophenol are very efficient for uptake of various cations of heavy metals like copper, nickel and iron etc.
5. So by the help of the resin and its polychelate simultaneously the toxic cation Cu(II), Cd(II), Fe(II), Pb(II), Ni(II), Co(II) and Zn(II) can be separated from drinking water.

ACKNOWLEDGEMENTS

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. R. Jayakumar, M. Rajkumar, R. Nagendran and S. Nanjundan, *J. Apply. Poly Sci.*, **85**, 1194, (2002).
2. R.F. Brady, *J. Polym. Paint. Colour*, **18**, 20, (2000).
3. P. Bagla and J. Kaiser, *Science,* **274**, 174, (1996).
4. W. Lepkowski, Arsenic Crisis in Bangladesh*, C & EN News*, **27,** Nov.16, (1998).
5. G.D. Clayton and F.E. Clayton, *Patty's Industrial Hygiene; Toxicology*, Wiley Interscience, New York, Vol. 2C, (1994).
6. J.E. Camuglia, G. Grigoriadis and C.P. Gilfillan, *Med J. Aust*., **189**(6), 339, (2008).
7. Jr.J. Dingman, S. Siggia, C. Barton and K.B. Hiscock, *Anal. Chem.,* **44**, 1045, (1973).
8. C.W. Blount, D.E. Leyden, T.L. Thomas and S.M. Guill, *Anal. Chem*., **44**, 1045, (1973).
9. E.M. Moyer and J. B. Fritz, *Anal. Chem.,* **49**, 418, (1977).
10. S. Bohra, R. Mathur, N.K. Mathur and P.N. Mathur, *J. Polym. Mater.*, **9**, 101, (1992).
11. G.W. Shepherd, W. Klein-schwartz and A.H. Bursein, *Clin Toxicol*, **38**, 4, (2000).
12. P. Soroushian, M. Elzafraney, H. Chowdhury, G. Sarwar and F. Aouadi, *Polym. Compos*, **26**, 679, (2005).
13. K.C. Hong, J. Kim and J.Y. Bae, *Polym. Bull.*, **44**, 115, (2000).
14. D.Y. Yoon, Y. Ando, O.O. Park, T.E. Karis, D. Dowson and T. Huang, *Polym. Prepr.*, **31,** 81, (1996).
15. W.B. Gurnule, P.K. Rahangdale, L.J. Paliwal and R.B. Kharat., *React. Funct. Polym.*, **50**, 95, (2002).
16. M.M. Jadhao, L.J. Paliwal and N.S. Bhave, *J. Appl. Polym. Sci.*, **96,** 1605, (2005).
17. M. M. Jadhao, L. J. Paliwal and N. S. Bhave, *J Appl Polym Sci*, **101,** 227 (2006).
18. S.K. Acharyya, S. Lahiri, B.C. Raymahashay and A. Bhowmik, *Environ Geol*., **39(10)**, 1127, (2000).

19. M.M. Patel and R. Manavalan, *Indian J. Chem.,* **22,** 117, (1983).
20. M.M. Patel and R. Manavalan, *Indian J. Chem. Soc.,* **16,** 490, (1984).
21. R.H. Gupta, A.B. Zade and W.B. Gurnule, *J. Appl. Polym. Sci.,* **109,** 3315, (2008).
22. P.E.P. Michel, J.M. Barde, H.D. Juneja and L.J. Paliwal, *Europ. Polym. J.,* **42,** 4995, (2007).
23. W.B. Gurnule, H.D. Juneja, L.J. Paliwal and R.B. Kharat, *Reac.t Funct. Polym.,* **50,** 95, (2002)
24. P. Savith and D.N. Sathyanarayana, *.J Polym. Sci.,* **43,** 3040, (2005).
25. A. Deshkhun, G. Young and U. Choi, *React. Funct. Polym.,* **67,** 312 ,(2007).
26. M.V. Tarase, A.B. Zade and W.B. Gurnule, *J. Appl. Polym. Sci.,* **108,** 738, (2008).
27. W.B. Gurnule, P.K. Rahangdale, L.J. Paliwal and R.B. Kharat, *Synth. React. Inorg. Met-Org. Chem.,* **33,** 1187, (2003).
28. R.N. Singru, A.B. Zade, and W.B. Gurnule, *J. Appl. Polym. Sci.,* **109 (2),** 859, (2008).
29. M. Sekera, *Synth. React. Inorg. Met-Org. Chem.,* **30,** 191, (2000).
30. S.S. Rahangdale, A.B. Zade and W.B. Gurnule, *J. Appl. Poly. Sci.,* **108,** 747, (2008).
31. B.A. Shah, A.V. Shah and B.N. Bhandari, *Asian J. Chem.,* **15,** 117, (2003).
32. W.B. Gurnule, P.K. Rahangdale, L.J. Paliwal and R.B. Kharat, *React. Func. Polym.,* **55,** 255, (2003).
33. R.C. DeGeiso, L.G. Donaruma and E.A. Tomic, *Analyt. Chem.,* **34**, 845, (1962).

[RJC-952/2012]