

Analytical Applications of Newly Synthesized Copolymer Resin Derived from *p*-Aminophenol, Dithiooxamide, and Formaldehyde

Wasudeo B. Gurnule,¹ Sharayu S. Katkamwar²

¹Department of Chemistry, Kamla Nehru College, Sakkardara, Nagpur 440009, India

²Department of Chemistry, Laxminarayan Institute of Technology, R.T.M Nagpur University, Nagpur 440009, India

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ABSTRACT: A copolymer resin (*p*-APDF) has been synthesized using the monomers *p*-aminophenol, dithiooxamide, formaldehyde in 1 : 1 : 2M proportions in the presence of 2M HCl as catalyst. The structure of *p*-APDF copolymer has been elucidated on the basis of elemental analysis and various physicochemical techniques, i.e., UV-visible, FTIR, and ¹H-NMR spectroscopy. The number average molecular weight of copolymer resin was determined by nonaqueous conductometric titration in DMF. Viscosity measurement were carried out in DMF indicate normal behavior. The prepared resin proved to be a selective ion exchange resin for

some metal ions. The chelating ion exchange properties of this resin was studied for Fe(III) and Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Pb(II) ions. A batch equilibrium method was used to study selectivity of metal ion uptake over a wide pH range and in media of various ionic strength. The resin showed a higher selectivity for Fe(III), Ni(II), Cu(II) ions than for Co(II), Pb(II), Zn(II), and Cd(II) ions. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1421–1427, 2012

Key words: structure; resin; degree of polymerization; synthesis; ion-exchanger

INTRODUCTION

Many polymers with reactive functional groups are now being synthesized, tested and used not only for the macromolecular properties but also for the properties of functional groups. These functional groups provide an approach to a subsequent modification of the polymers for specific end group application.¹ In recent years, some comprehensive work has been published on functional monomers and their polymers.^{2,3}

Ion-exchangers have been used commercially on a worldwide basis for almost a century due to diverse applications in many fields such as water softening and deionization,⁴ extraction of uranium,⁵ isolation and purification of antibiotics,⁶ in hydrometallurgy for separation and purification of waste water treatment⁷ and pollution control.⁸ The presence of heavy metal in environment is a cause of concern due to their acute and long term toxicity. Lead and mercury are the major hazardous metals present in the envi-

ronmental waste water. Thus, removal of trace heavy metal from the environmental area have become an interesting field increasing interest and there is strong need for a reliable analytical procedure that can be applied for the removal and determination of these metals at a very low concentration.⁹ Since long, considerable interest has been developed in the synthesis of ion-exchange resin having selective properties and containing selective functional groups. Various hydroxyl benzoic acid-formaldehyde and 4-hydroxyacetophenone-biure-formaldehyde copolymers have been reported and found to be useful as ion-exchangers.^{10–12}

Copolymers of 8-hydroxyquinoline-formaldehyde-resorcinol/catechol were reported by Shah et al.^{13,14} and chromatographic column separation for various metal ions such as Cu²⁺, Ni²⁺, Zn²⁺, Pb²⁺, and Cd²⁺ have carried out using the quinoline base resins. Mubarak and coworkers¹⁵ have studied the chelation behavior of the phenolic-formaldehyde polymers, poly(2,4-dihydroxybenzoic acid-3,5-dimethylene), poly(2-hydroxybenzoic acid-3,5-dimethylene) and poly(3-hydroxybenzoic acid-4,6-dimethylene) towards the trivalent lanthanide metal ions such as La³⁺, Nd³⁺, Sm³⁺, Gd³⁺, and Tb³⁺ by a static batch equilibrium technique at 25°C as a function of contact time, pH, and concentration. Polymer supported reagents¹⁶ containing various ligands have been studied for their selective complexation towards

Correspondence to: W. B. Gurnule (wbgurnule@yahoo.co.in).

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various metal ions. So far no resin based on *p*-aminophenol-dithiooxamide-formaldehyde in DMF media has been synthesized for the quantitative separation of transition and post-transition metal ions.

As industrial effluents are often rich in transition metal ions, removal of these metal is an important task for industries. Therefore, we have studied the use of ion-exchanger for the removal and separation of heavy trace metal ions. In this article, synthesis and characterization of the above resin are reported together with the conditions for the effective separation of transition and post-transition metal ions. An appreciable higher ion-exchange capacity for heavy metal ions was exhibited by the present resin *p*-APDF which contain more acidic characters of the monomer.

EXPERIMENTAL

Materials

The important chemicals (starting materials) like *p*-aminophenol, dithiooxamide, and formaldehyde, etc., used in the preparation of new *p*-APDF copolymer resin, were procured from Merck, India, and were of analytically or chemically pure grade. The solvent like *N,N'*-dimethyl formamide and dimethyl sulfoxide were purified by distillation and are of Merck, India.

Synthesis of the copolymer resin

The new copolymer resin *p*-APDF was synthesized by condensing *p*-aminophenol (1.39 g) and dithiooxamide (1.20 g) with 37% formaldehyde (7.5 mL) in a mol ratio of 1 : 1 : 2 in the presence of 2M 200 mL HCl as a catalyst at 120°C ± 2°C for 6 h in an oil bath with occasional shaking to ensure thorough mixing. The separated brown copolymer resin was washed with hot water and methanol to remove unreacted monomers. The properly washed resin was dried, powdered, and then extracted with diethyl ether and then with petroleum ether to remove unreacted monomers which might be present along with *p*-APDF copolymer. The reaction and suggested structure of *p*-APDF was shown in Figure 1.

The copolymer was purified by dissolving in 8% aqueous sodium hydroxide solution, filtered, and reprecipitated by gradual drop wise addition of ice cold 1 : 1 (v/v) concentrated hydrochloric acid/distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The copolymer sample *p*-APDF thus obtained was filtered, washed several times with hot water, dried in air, powdered, and kept in vacuum desiccator over silica gel. The yield of the copolymer resin was found to be 87%.

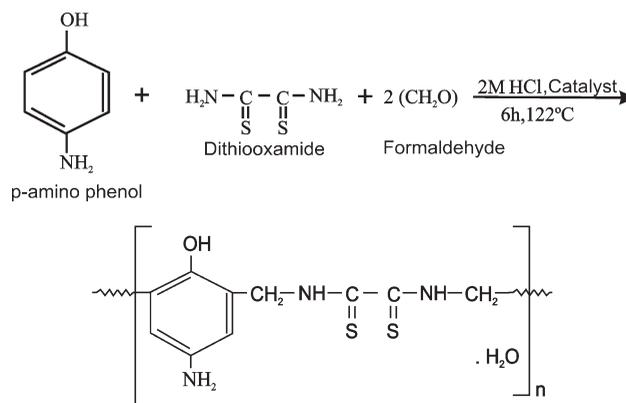


Figure 1 Preparation of the *p*-APDF copolymer resin.

Characterization of the copolymer

The copolymer resin was subjected to elemental analysis for C, H, N on a Colemann C, H, N analyzer. The number average molecular weight \overline{M}_n was determined by conductometric titration in DMF using ethanolic KOH as the titrant by using 25 mg of sample. Plot of the specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of copolymer was made. The viscosity was determined using a Tuan-Fuoss viscometer at six different concentrations ranging from 0.3 to 0.05 wt % of resin in DMF at 30°C.

Electronic absorption spectra of the copolymer in DMSO was recorded with a Shimadzu UV-visible double beam spectrophotometer fitted with an automatic pen chart recorder on thermosensitive paper in the range of 200–600 nm. Infrared spectra of *p*-APDF copolymer resin was recorded in nujol mull with Perkin-Elmer-spectrum RX-I spectrophotometer in the range of 4000–500 cm⁻¹. Proton NMR spectra was recorded with Bruker Avance-II 400 MHz proton NMR spectrophotometer and DMSO-d₆ was used as a solvent.

Ion-exchange properties

The ion-exchange property of the *p*-APDF copolymer resin was determined by the batch equilibrium method and was carried out to investigate the three aspects.

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

The following experimental procedure was applied 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 (25 mg) was suspended in an electrolyte solution (25 mL) of known concentration. The pH of the suspension was adjusted to the required value by using either 0.1M HNO₃ or 0.1M

NaOH. The suspension was stirred for 24 h 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 h and filtered. The solid was washed and the filtrate and washing were combined and the metal ion content was determined by titration against standard ethylene diamine tetra-acetic acid (EDTA). The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments. The experiment was repeated in the presence of 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 NaNO₃. 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 five metal ions [Fe(III), Ni(II), Cu(II), Co(II) and Pb (II)] between the polymer phase and aqueous phase was estimated at 300 K and in the presence of a solution of NaNO₃. 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 *p*-APDF copolymer resin was found to be brown in color. The copolymer is soluble in solvents such as DMF, DMSO, and THF 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 425 K.

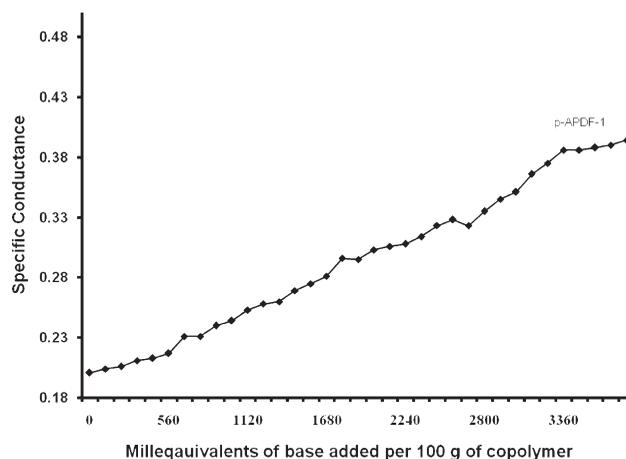


Figure 2 Conductometric titration curve of *p*-APDF copolymer resin.

The elemental analyses of copolymer resin was found to be in agreement with the calculated values [C-46.60% (Found) 46.05% (Calc.), H-5.05% (Found) 5.28% (Calc.), N-10.89% (Found) 10.02% (Calc.)]. The number average molecular weight (\overline{M}_n) of this copolymer has been determined by conductometric titration method in nonaqueous medium and using standard potassium hydroxide (0.05M) in absolute ethanol as a titrant. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 g 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 of each chain was neutralized.¹⁷ From the plot, the first and last breaks were noted. The average degree of polymerization \overline{DP} and, hence, the number average molecular weight \overline{M}_n of all copolymers have been determined using the

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

$$\overline{M}_n = \overline{DP} \times \text{Repeat unit weight}$$

The value of degree of polymerization for *p*-APDF copolymer resin having empirical formula of repeat unit C₁₀H₁₃N₂O₂S₂ (empirical formula weight of repeat unit is 257 g) is found to be 11.92 and number average molecular weight is obtained as 3063.44 g. The conductometric titration curve is depicted in Figure 2.

Viscometric measurements were carried out in DMF at 30°C. All the resins showed normal behavior. The intrinsic viscosity was determined by the Huggin [1] equation.

TABLE I
¹H-NMR Spectral Data of the *p*-APDF Copolymer Resin

Nature of proton assigned	Observed chemical shift (δ) (ppm)	Expected chemical shift (δ) (ppm)
Methylene proton of Ar-CH ₂ -Ar moiety	1.35	1.5–2.5
Methylene proton of Ar-CH ₂ - moiety	2.65	2.0–3.0
Methylene proton of Ar-CH ₂ -N moiety	3.47	3.0–3.5
Proton of Ar-NH ₂ - group	4.25	3.0–5.0
Thioimide proton of -CS-NH-CS- linkage	4.43	4.0–8.5
Aromatic proton (Ar-H) (unsymmetric pattern)	6.82	6.2–8.5
Proton of phenolic -OH	8.52	8.0–12.0

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2.C$$

and Kraemers [2] equation:

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

In accordance with the above relations, the plots of η_{sp}/C and η_{rel}/C against C were found to be linear giving as slopes K_1 and K_2 , respectively. The intercept on the axis of viscosity function gave the $[\eta]$ value in both the plots. The calculated values of constants K_1 and K_2 (Table I) in most of cases satisfy the relation. $K_1 + K_2 = 0.5$ favorably [18–19]. The values of $[\eta]$ obtained from eq. (1) and (2) were in close agreement with each other. It has been observed that the intrinsic viscosity increases with the increase in molecular weight of copolymer.

The UV-visible spectra of *p*-APDF copolymer resin in pure DMSO was recorded in the region 200–600 nm. The UV-visible spectrophotometer was calliberated with 0.005% potassium permanganate and potassium nitrate solution. The spectra of these copolymer exhibit to absorption maxima in the regions of 220–240 nm and 290–330 nm. The bands at 220–240 nm indicate the presence of a C=S group containing a carbon-sulfur double bond in conjugation with the aromatic nucleus, and this is characteristic of the $\pi \rightarrow \pi^*$ transition. The bathochromic shift (the shift toward a longer wavelength) from the basic values (257 nm and 320 nm) may be due to the combined effect of conjugation and the phenolic hydroxyl group (auxochrome) is responsible for hyperchromic effect, i.e., higher ϵ_{max} value (1110).

The IR spectral data are tabulated in Table II. A broad absorption band appeared in the region 3400 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding.¹⁸ A sharp strong peak at 1600 cm^{-1} may be ascribed to aromatic skel-

etal ring. The bands obtained at 1272 cm^{-1} and 1420 cm^{-1} suggest the presence of methylene (-CH₂-) bridge.¹⁹ The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium/weak absorption bands appeared at 903 cm^{-1} , 1050 cm^{-1} , 1105 cm^{-1} , and 1218 cm^{-1} . The presence of sharp and strong band at 3102 cm^{-1} indicates the presence of -NH bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.

The NMR spectrum of *p*-APDF copolymer was scanned in DMSO-d₆ solvent and the spectral data are given in Table I. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature.²⁰ The singlet signal obtained at 3.9 (δ) ppm may be due to the methylene proton of Ar-CH₂-N moiety. The singlet at 1.35 (δ) ppm is due to the methylene proton of Ar-CH₂-Ar moiety. The singlet at 2.61(δ) ppm is due to methylene proton of Ar-CH₂ moiety. The singlet at 3.47(δ) ppm may be due to methylene proton of Ar-CH₂-N moiety. The singlet at 4.25(δ) ppm may be attributed to proton of Ar-NH₂-group. Because of thioimide proton of -CS-NH-CS- a signal appeared in the region 4.43(δ) ppm. The weak multiplied signals (unsymmetrical pattern) in the region 6.74–6.82(δ) ppm may be due to aromatic proton (Ar-H). The signal at 8.52(δ) ppm may be due to phenolic hydroxyl groups. The much downfield chemical shift for phenolic -OH indicates clearly the intramolecular hydrogen bonding on -OH group.

Ion-exchange properties

With a view to ascertain the selectivity of *p*-APDF copolymer for the selected metal ion, we have studied the influence of various electrolyte on the selectivity of metal ions, the rate of metal uptake and the distribution ratio of metal ions between the copolymer and solution containing the metal ions.

TABLE II
IR Spectral Data of *p*-APDF Copolymer Resin

Observed band frequency (cm^{-1})	Assignment	Expected band frequency
3400 St	-OH phenolic intermolecular hydrogen bonding	3750–3200
3102 b	>NH stretching	2800–3500
1595 Sh	>C=S stretching	1600–1400
1600 S	Aromatic ring	1600–1500
1420 m	-CH ₂ - bending	1460
1272 Sh	-CH ₂ - wagging	1280–1370
775 Sh	-CH ₂ - rocking	710–800
903, 1050, 1105, 1218	1,2,3,5 substitution	900, 1000, 1100, 1200

Sh, sharp; b, broad; St, strong; m, medium; w, weak.

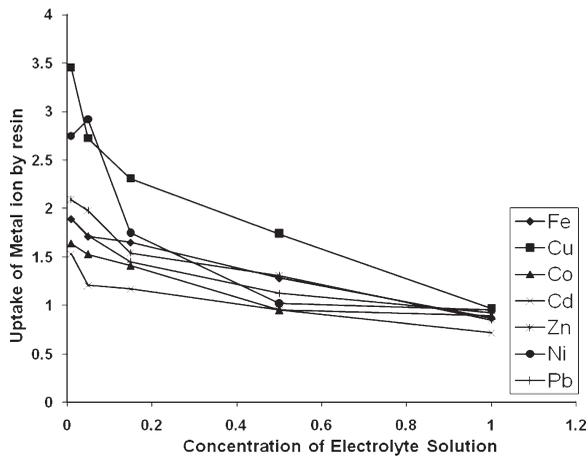


Figure 3 Uptake of several metal ions by *p*-APDF copolymer resin at five different concentrations of electrolyte solution Na₂SO₄.

Batch equilibrium technique developed by Gregor et al. and De Geiso et al. was used to study ion exchange properties of *p*-APDF copolymer resin. The results of the batch equilibrium study carried out with the copolymer *p*-APDF are presented in Figures 3–8. Seven metal ions Fe(III), Cu(II), Ni(II), Co(II), Zn(II), Cd(II), and Pb(II) in the form of aqueous metal nitrate solution were used. The ion exchange study was carried out using three experimental variables (a) Electrolyte and its ionic strength, (b) Rate of metal ion uptake at different time intervals, and (c) pH of the aqueous medium. Among these three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymers.²¹ Ion-exchange mainly depends on various physical properties including particle size distribution, pore size, physical core structure and diffusion of counter ions. Crystal accumulated structure for resin is observed with the particle size almost equal to 1 μm.

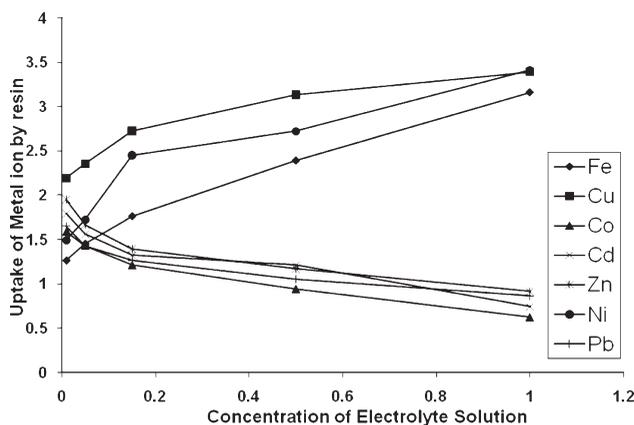


Figure 4 Uptake of several metal ions by *p*-APDF copolymer resin at five different concentrations of electrolyte solution NaClO₄.

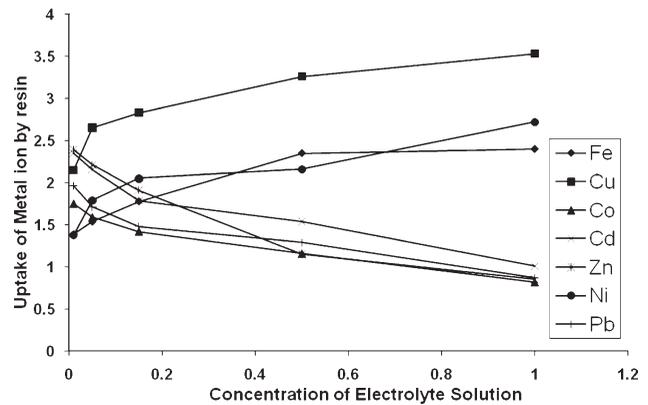


Figure 5 Uptake of several metal ions by *p*-APDF copolymer resin at five different concentrations of electrolyte solution NaNO₃.

Effect of electrolytes and their concentrations on metal ion uptake capacity

We examined the influence of ClO₄⁻, NO₃⁻, Cl⁻, and SO₄²⁻ at various concentrations on the equilibrium of metal-resin interaction. Figures 3–6 show that the amount of metal ions taken up by a given amount of copolymer depends on the nature and concentration of the electrolyte present in the solution. Generally as concentration of the electrolyte increases, the ionization decreases, number of ligands (negative ions of electrolyte) decrease in the solution which forms the complex with less number of metal ions and therefore more number of ions may available for adsorption. Hence on increasing concentration, uptake of metal ions may be increased, which is the normal trend. However, this normal trend disturbed due to the formation of stable complex with more number of metal ions with electrolyte ligands, which decrease the number of metal ions available for adsorption, hence uptake decreases.

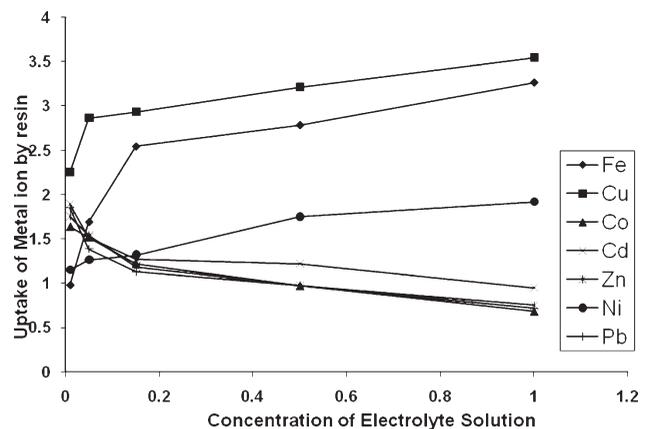


Figure 6 Uptake of several metal ions by *p*-APDF copolymer resin at five different concentrations of electrolyte solution NaCl.

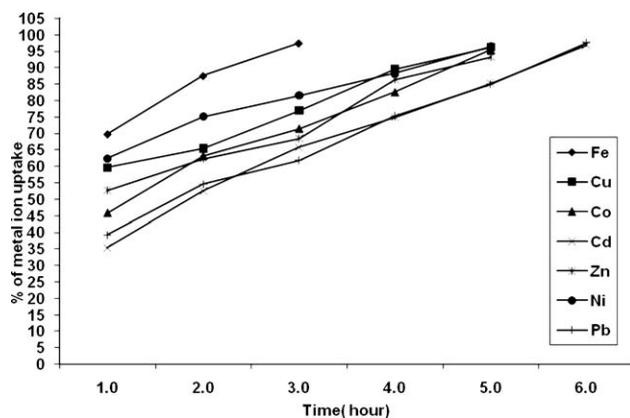
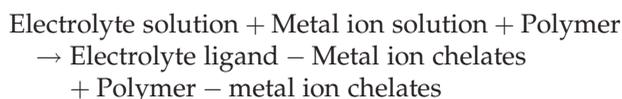


Figure 7 Comparisons of the rate of metal ion uptake by *p*-APDF copolymer resin.



If electrolyte ligand-metal ion complex is weak than polymer metal ion chelates, the more metal ion can form complex with polymer hence uptake of metal ion is more. However, if this complex is strong than polymer-metal ion chelates, more metal ions form strong complex with electrolyte ligand which make metal uptake capacity lower by polymer.

In the presence of perchlorate, chloride, and nitrate ions, the uptake of Fe(III), Cu(II), and Ni(II) ions increase with increasing concentration of the electrolytes, whereas in the presence of sulfate ions the amount of the above-mentioned ions taken up by the copolymer decreases with increasing concentration of the electrolyte.²² Moreover, the uptake of Co (II), Zn (II), Cd (II), and Pb(II) ions increase with decreasing concentration of the chloride, nitrate, perchlorate, and sulfate ions. This may be explained on the basis of the stability constants of the complexes with those metal ions.²² The ratio of physical core structure of the resin is significant in the uptake of different metal ions by the resin polymer. The amount of metal ion uptake by the *p*-APDF copolymer resin is found to be higher when comparing to the other polymeric resins.²³

Rate of uptake for metal ions as a function of time

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried to while operating as close to equilibrium conditions as possible. Figure 7 show the results of rate of uptake of metal ion on *p*-APDF polymer resin. 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. As shaking time increases the polymer gets more time

for adsorption, hence uptake increases on the increasing in the time. The result shows that the time taken for the up take 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 (III) ions require about 3 h for the establishment of the equilibrium, whereas Cu (II), Ni (II), Co (II), and Zn (II) ions required about 5 and 6 h. Thus the rate of metal ions uptake follows the order Cu (II) > Ni (II) > Zn (II) > Co (II) > Pb (II) > Cd (II) for the copolymer.²⁴ The rate of metal uptake may depend upon hydrated radii of metal ions. The rate of uptake for the post transition metal ions exhibit other trend for Cd(II), the rate of uptake is in the comparable that of Pb (II) because of difference in 'd' orbital.

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 8. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ion taken up by the *p*-APDF copolymer increases with increasing pH of the medium. The magnitude of increase, however, is different for different metal cation. The *p*-APDF 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 pH range 2.5 to 6.5 is found to be Fe (III) > Cu (II) > Ni (II) > Co (II) > Zn (II) > Pb (II) > Cd (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.²⁵

The study was carried from pH 2.5 to 6.5 to prevent hydrolysis of metal ions at higher pH. For metal ion Fe³⁺ the highest working pH is 3, where distribution ratio is medium, since Fe³⁺ forms octahedral complex with electrolyte ligand, showing crowding effect (steric hindrance), which may lower

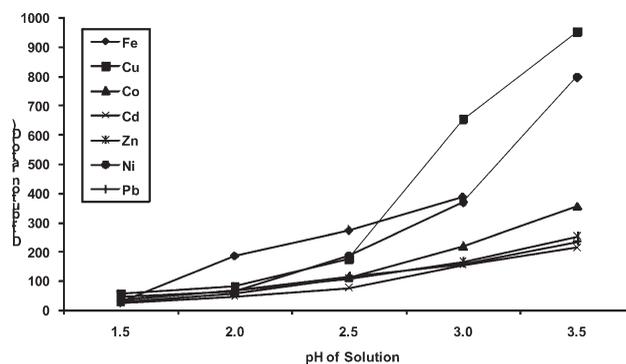


Figure 8 Distribution ratio (*D*) of various metal ions as function of different pH by *p*-APDF copolymer resin.

the distribution ratio of Fe(III) ions. The value of distribution ratio at particular pH thus depends upon the nature and stability of chelates with particular metal ion. The data of distribution ratio show a random trend in certain cases.²⁵ This may be due to the amphoteric nature of the *p*-APDF resin.

From the result it reveals that with decrease in atomic number, the ion uptake capacity is increased. In case of Cd (II) and Pb (II), purely electrostatic factors are responsible. The ion uptake capacity of Cd (II) is lower owing to the large size of its hydrated ion than that of Cu (II). The steric influence of the methyl group and hydroxyl group in *p*-APDF resin is probably responsible for their observed low binding capacities for various metal ions. The higher value of distribution ratio for Cu (II) and Ni (II) at pH 4 to 6.0 may be due to the formation of more stable complex with chelating ligands. Therefore the polymer under study has more selectivity of Cu (II) and Ni (II) ions at pH 4.0 to 6.0 than other ions which form rather weak complex. While at pH 3 the copolymer has more selectivity of Fe³⁺ ions. The order of distribution ratio of metal ions measured in pH range 2.5 to 6.5 is found to be Fe (III) > Cu (II) > Ni (II) > Zn (II) > Co (II) > Pb (II) > Cd (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 [1]. For example, the result suggests the optimum pH 6.0, for the separation of Co (II) and Ni (II) with distribution ratio "D" at 415.4 and 854.4, respectively, using the *p*-APDF copolymer resin as ion-exchanger. Similarly, for the separation of Cu (II) and Fe (III) the optimum pH is 3, at which the distribution ratio "D" for Cu (II) is 66.1 and that for Fe (III) are 341.5. The lowering in the distribution of Fe (III) was found to be small and, hence, efficient separation could be achieved.²³⁻²⁵

CONCLUSIONS

A copolymer *p*-APDF based on the condensation reaction of *p*-aminophenol, dithiooxamide with formaldehyde in the presence of acid catalyst was prepared. The copolymer resin is a selective chelating ion-exchange copolymer resin for certain metals. The copolymer resin showed a higher selectivity for Fe³⁺, Cu²⁺, and Ni²⁺ ions than for Co²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ ions. The uptake of some metal ions by the resin was carried out by the batch technique. The uptake capacities of metal ions by the *p*-APDF copolymer resin were pH dependent. Because of considerable difference in the uptake capacities at different pH and media of electrolyte, the rate of metal ion uptake and distribution ratios at equilib-

rium, it is possible to use for separation of particular metal ions from their admixture.

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