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Metal ion binding properties of a copolymer resin: synthesis, characterization, and its applications

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Abstract A novel chelating copolymer resin has been synthesized through the copolymerization of *o*-aminophenol and melamine with formaldehyde (*o*-APMF) in 1:1:3 mol ratio using hydrochloric acid as a reaction medium by condensation technique. The synthesized copolymer resin was characterized by elemental analysis, FTIR, and ^{1}H NMR spectroscopy. On the basis of the spectral studies, the structure of the copolymer resin was proposed. The physico-chemical parameters have been evaluated for the copolymer resin. Non-aqueous conductometric titration was used to determine the average molecular weight and polydispersity of the *o*-APMF copolymer resin and the intrinsic viscosity was also determined. The semicrystalline nature of the synthesized copolymer was established by scanning electron microscopy (SEM). Batch equilibrium method was employed to study the selectivity and binding capacity of the copolymer resin toward certain trivalent and divalent metal ions such as Fe^{3+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, and Hg^{2+} and in different electrolyte concentrations, wide pH ranges, and time intervals.

Keywords Copolymers · Ion exchangers · Morphology · Resins · Batch equilibrium

Introduction

The heavy metal ion toxicity has increased substantially because of the use of metal ions as catalyst in various industries. Many methods have been developed for the

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preconcentration and removal of metal ions such as electrodeposition, co-precipitation, and solid liquid extraction. However, the metal ion removal by chelating ion-exchange resin using batch equilibration method has gained rapid acceptance because of its wide variety of sorbent phases, high degree of selectivity, high loading capacity, and enhanced hydrophilicity [1–3]. Ion exchangers are widely used for the treatment of radioactive wastes from nuclear power stations [4, 5]. The chelation ion-exchange behavior of poly (2-hydroxy, 4-acryloyloxy benzophenone) resin toward the divalent metal ions was studied by batch equilibration method as a function of contact time and pH [6]. A crosslinked styrene/maleic acid chelating matrix has been reported for its higher ability to remove the metal ions such as Cr, Fe, Ni, Cu, and Pb [7]. Acidic polymers such as poly(methacrylic acid) and poly(acrylic acid) have the tendency to remove the metal ions like Ag^+, Cu^{2+}, Co^{2+}, Ni^{2+}, and Cr^{3+} at different pH and polymer metal ion ratios [8]. Salicylic acid and melamine with formaldehyde copolymer found to have higher selectivity for Fe^{3+}, Cu^{2+}, and Ni^{2+} ions than for Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions [9]. Resin synthesized by the condensation of a mixture of phenol or hydroxybenzoic acid with formaldehyde and various amines have also been reported [10]. The metal ion uptake increases with increasing mole proportions of the copolymer synthesized from substituted benzoic acid [11]. *o*-Nitrophenol and thiourea with paraformaldehyde copolymer was identified as an excellent cation exchanger for Zn^{2+} and Co^{2+} ions [12]. Salicylic acid–formaldehyde–resorcinol resin has been synthesized and explored its use for the removal and separation of heavy metal ions from their binary mixtures [13]. 8-Hydroxyquinoline–formaldehyde–catechol copolymer found to have lower moisture content indicating the high degree of crosslinking in the resin [14]. Phenolic Schiff bases derived from hydroxybenzaldehydes and 4,4′diaminodiphenyl ether has been reported as better chelating resin for Cu (II) leading to its separation from a mixture of Cu (II) and Ni (II) ions [15]. Recently, our research group synthesized a chelating copolymer resin using an ecofriendly technique and reported for its good binding capacity for Ba^{2+} and Zn^{2+} ions [16]. In this article, we describe the synthesis of copolymer derived from *o*-aminophenol and melamine with formaldehyde (*o*-APMF). The synthesized copolymer resin has been characterized by elemental analysis, spectral studies (FTIR, ^{1}H NMR), number average molecular weight determination, and viscometric measurement. The surface features of the copolymer resin were established by SEM. The metal ion uptake capacity of the copolymer resin by batch equilibrium method for Fe^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, and Hg^{2+} ions in different electrolytes, pH ranges, and time intervals were also studied and reported for the first time.

Experimental methods

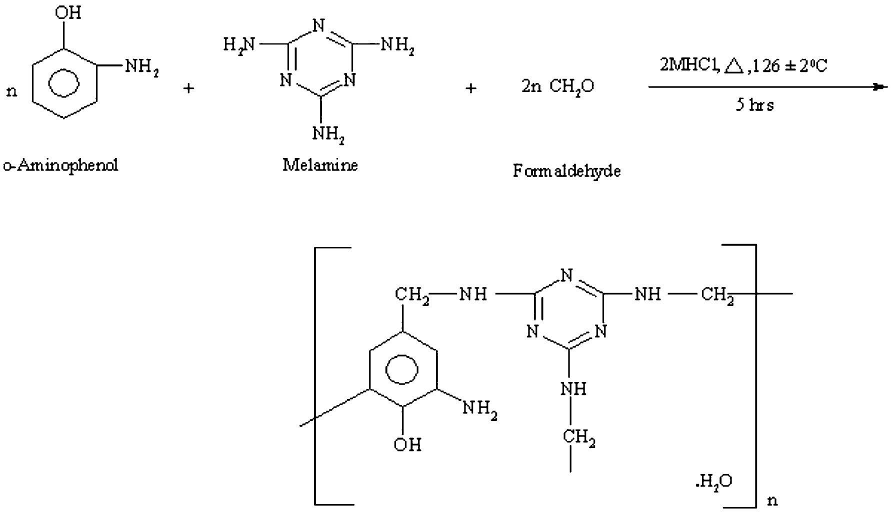
Chemicals and reagent

o-Aminophenol and melamine (Merck, India) were purified by rectified spirit. Formaldehyde (37%), metal chlorides, and nitrates of chosen metals (AR grade, Merck) were used as received. All the other chemicals, solvents, and the indicators such as fast sulphon black F for copper, xylenol orange for cadmium and lead, solochrome black T for zinc, and variamine blue for iron were of the analytical grade procured from Qualigens fine chemicals, Mumbai, India. Standardized disodium salt of EDTA was used as a titrant for all the complexometric titrations. Double-distilled water was used for all the experiments.

Synthesis of *o*-APMF copolymer resin

The *o*-APMF copolymer resin was prepared by the condensation polymerization of *o*-aminophenol (0.1 mol) and melamine (0.1 mol) with formaldehyde (0.3 mol) in hydrochloric acid medium at 126 ± 2 °C in an oil bath for 5 h. The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove excess of *o*-aminophenol–formaldehyde copolymer, which might be present along with the *o*-APMF copolymer.

The dried resin was further purified by dissolving in 8% NaOH and regenerated in 1:1(v/v) HCl/water. This process was repeated twice to separate the pure copolymer. The resulting polymer sample washed with boiling water and dried in vacuum at room temperature. The purified copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in a vacuum over silica gel. The yields of these copolymer resins found to be 87%. The sieved resin was used for further characterization. The reaction sequence of the synthesis of *o*-APMF copolymer resin is shown in Scheme 1.



Scheme1 Formation and suggested structure of *o*-APMF copolymer resin

Characterization of copolymer resin

Physicochemical and elemental analysis

The copolymer resin was subject to micro analysis for C, H, and N on an Elementar Vario EL III Carlo Erba 1108 elemental analyzer. The number average molecular weight $\overline{M}_n$ was determined by conductometric titration in DMSO medium using ethanolic KOH as the titrant by using 25 mg of sample. A plot of the specific conductance against the milliequivalants of potassium hydroxide required for neutralization of 100 g of copolymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot, the first break and the last break were noted. The calculation of $\overline{M}_n$ by this method is based on the following consideration [17, 18]: (1) the first break corresponds to the stage at which the first acidic phenolic hydroxyl group is neutralized, and (2) the last break observed beyond the first break represents the stage at which phenolic hydroxyl group of all the repeating units are neutralized. On the basis of the average degree of polymerization, ($\overline{DP}$) the average molecular weight has to be determined by following Eq. 1:

$$\overline{\mathrm{DP}} = \frac{\text{(Total milliquivalents of base required for complete neutralization)}}{\text{(Milliquivalents of base required for smallest interval)}} \tag{1}$$

$$\overline{M}_n = \overline{DP} \times \text{molecular weight of the repeating unit.}$$

The intrinsic viscosity was determined using a Tuan–Fuoss viscometer [19] at six different concentrations ranging from 0.3 to 0.05 wt% of resin in DMSO at 30 °C. Intrinsic viscosity (η) was calculated by the Huggin's equation (2) [20] and Kraemer's equation (3) [21].

$$\mathrm{In}\eta_{\mathrm{sp}}/\mathrm{C} \; = [\eta] + \mathrm{K}_1[\eta]^2 \times \mathrm{C} \tag{2}$$

$$\mathrm{In}\eta_{\mathrm{r}}/\mathrm{C} \; = [\eta] - \mathrm{K}_2[\eta]^2 \times \mathrm{C} \tag{3}$$

Spectral analysis

Electronic (UV–visible) absorption spectra of the copolymer in DMSO was recorded with a double beam spectrophotometer fitted with an automatic pen chart recorder on themosensitive paper in the range of 200–850 nm.

Infrared spectra of *o*-APMF copolymer resin was recorded in najol mull with Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pallets in the range of 4000–500 cm^{-1} at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Proton NMR spectra was recorded with Bruker Advance—II 400 NMR spectrophotometer using DMSO-d_6 as a solvent, at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. The surface analysis was performed using scanning electron microscope at different magnifications. SEM has been scnanned by JEOL JSM-6380A Analytical Scanning Electron Microscope at VNIT, Nagpur.

Ion-exchange properties

The ion-exchange properties of the *o*-APMF copolymer resin was determined by the batch equilibrium method. We studied the influence of various electrolytes, the rate of metal uptake, and distribution of metal ions between the copolymer and solutions.

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

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 0.1 N HCl or 0.1 N NaOH. The suspension was stirred for a period of 24 h at 25 °C. To this suspension was added 2 mL of a 0.1 M solution of metal ion and the pH was adjusted to the required value. The mixture was again stirred at 25 °C for 24 h and filtered [22, 23]. 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 metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments [24, 25]. The experiment was repeated in the presence of other three electrolyte such as NaCl, $NaClO_4$, and Na_2SO_4.

Evaluation of the rate of metal uptake

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

Evaluation of the distribution of metal ions at different pH

The distribution of each one of the eight metal ions i.e. Fe(III), Cu(II), Hg(II), Cd(II), Zn(II), and Pb(II) between the polymer phase and the aqueous phase was determined at 25 °C and in the presence of a 1 M $NaNO_3$ solution. The experiment were carried out as described earlier at different pH values. The distribution ratio "*D*" is defined by the following relationship:

$$D=\frac{\{\text{Wt. (in mg) of metal ions taken up by 1 g of copolymer}\}}{\{\text{Wt. (in mg) of metal ions present in 1 mL of copolymer}\}}$$

Results and discussion

The resin sample was dark brown in color, insoluble in commonly used organic solvents, but was soluble in dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, pyridine, and concentrated H_2SO_4. The resin synthesized do not show sharp melting point but undergo decomposition above 570 °C. Based on the analytical data, the empirical formula of the copolymer resin is found to be $C_{12}H_{16}N_7O_2$, which is in good agreement with the calculated values of C, H, N, and O. The resin was analyzed for carbon, hydrogen, and nitrogen content. C = 49.65% (Cal) and 49.22% (F); H = 5.51% (Cal) and 5.18% (Cal); N = 33.79% (Cal) and 33.35% (F).

Characterization of copolymer resin

The number average molecular weight ($\overline{M}_n$) could be obtained by multiplying the $\overline{DP}$ by the formula weight of the repeating unit [26]. The molecular weight of copolymer was also estimated by conductometric titration. The calculated molecular weight for *o*-APMF resin is 4129.45.

Viscometric measurement was carried out in DMSO at 30 °C. *o*-APMF resin showed normal behavior. The intrinsic viscosity was determined by the Huggin's equation (2) and Kraemer's equation (3) [20, 21], which is 0.27 and 0.24, respectively. In accordance with the above relations, the plot of $\eta_{sp/c}$ and $\eta_{rel/c}$ against C was linear giving slopes K_1 and K_2 (0.51), respectively. The 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 with each other.

The UV–visible spectra of *o*-APMF copolymer resin shown in Fig. 1. UV–visible spectra of *o*-APMF resin have been recorded in pure DMSO in the region of

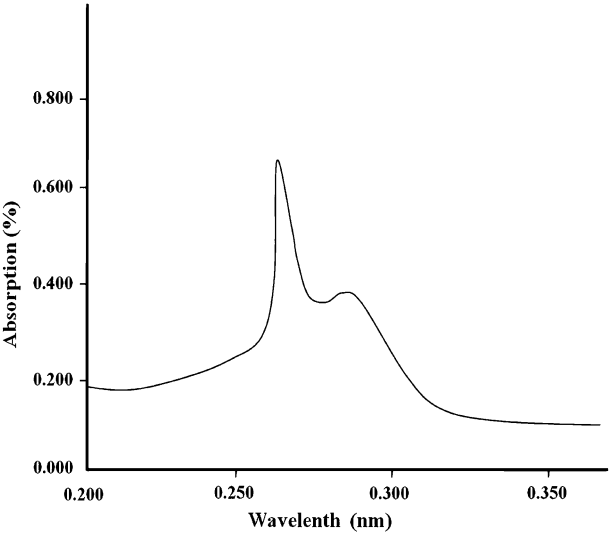


Fig. 1 Electronic spectra of *o*-APMF copolymer resin

200–800 nm at a scanning rate of 100 nm min^{-1} and at a chart speed of 5 cm min^{-1}. The electronic spectra of copolymer exhibit two absorption maxima in the region 258.40 and 286.60 nm. These observed positions of the absorption bands indicate the presence of hydroxy group, which is in conjugation with the aromatic nucleus. The appearance of former band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition, while the later band (less intense) may be due to $n \rightarrow \pi^*$ electronic transition. The presence of phenolic hydroxyl group (auxochromes) is responsible for hyperchromic shift i.e. ε_{max} higher values [27, 28]. This observation is in good agreement with the proposed most probable structures of *o*-APMF copolymer resin.

The IR spectrum of *o*-APMF copolymer resin is presented in Fig. 2 and IR data are specified in Table 1. A broad band appearing in the region 3417.14 cm^{-1} may be assigned to the stretching vibration of the phenolic hydroxyl groups exhibiting intermolecular hydrogen bonding [29]. The band obtained at ~1568.27 cm^{-1} suggest the presence of >NH (amido) group. A band appearing in the region of 1352.57 cm^{-1} show the presence of methylene bridges (>CH_2) in the polymer chain [30]. A sharp band appearing in the region of 1480 cm^{-1} may be due to the aromatic

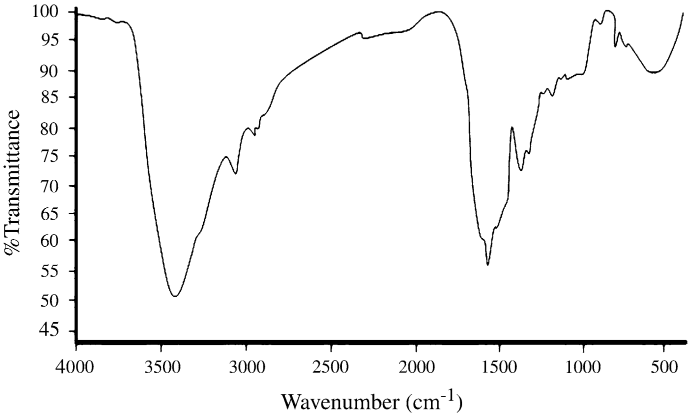


Fig. 2 FTIR spectra of *o*-APMF copolymer resin

Table 1 FT-IR spectral data of *o*-APMF copolymer resin

Assignment	Expected wave number (cm^{-1})	Observed wave number (cm^{-1}) *o*-APMF
OH (phenolic)	3100–3500	3417.14 (b, st)
>NH (amido)	1560	1568.27 (sh, st)
Aromatic ring	1445–1485	1480 (sh, m)
>CH_2 (methylene bridges)	1250–1360	1352.57 (w, m)
1,2,3,4,5 substitution in benzene skeleton	557.9–900	590.86 and 811.52 (b, st)

Sh sharp, *b* broad, *st* strong, *m* medium, *w* weak

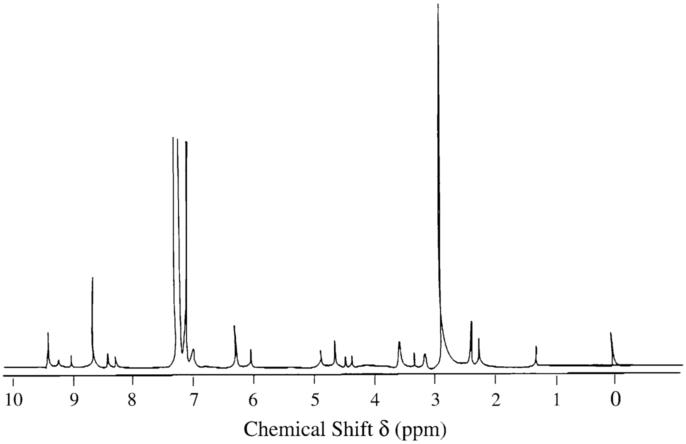


Fig. 3 ^{1}H NMR spectra of *o*-APMF copolymer resin

Table 2 ^{1}H NMR spectral data of *o*-APMF copolymer resin

Chemical shift (δ) ppm of copolymer *o*-APMF	Nature of proton assigned
8.7–9.2	Aromatic proton (unsymm. Pattern)
6.60	Proton of –NH linkage
3.3	Mathelene proton of Ar-CH_2-NH moiety
8.3 and 3.05	Proton of Ar-OH
1.27	Ar-NH_2

ring. 1,2,3,4, and 5 pentasubstitution of aromatic ring is recognized from the bands appearing at ~590.86–811.52 cm^{-1} [31–36].

H^1 NMR spectra of *o*-APMF copolymer is shown in Fig. 3 and the spectral data are presented in Table 2. The NMR spectrum reveals that a weak multiplicity signal (unsymmetrical pattern) in the region 8.33 to 8.72 (δ) ppm may be due to the aromatic protons. The weak multiply signals appearing at 6.12–6.35 (δ) ppm may due to the proton of –NH bridges [30, 31]. A signal that appeared in the region 3.22–3.38 (δ) ppm may be due to proton of methelenic bridges (Ar–CH_2–NH moiety) of polymer chain. The signals in the range of 8.26 – 8.28 (δ) ppm and 3.05–3.1 (δ) ppm is attributed to phenolic –OH proton. A weak signal in the range of 1.27 exhibits the presence of Ar-NH_2 group.

Scanning electron microscopy (SEM)

Surface analysis has found great use in understanding the surface features of the materials. The morphology of the reported resin sample was investigated by scanning electron micrographs at different magnification, which are shown in

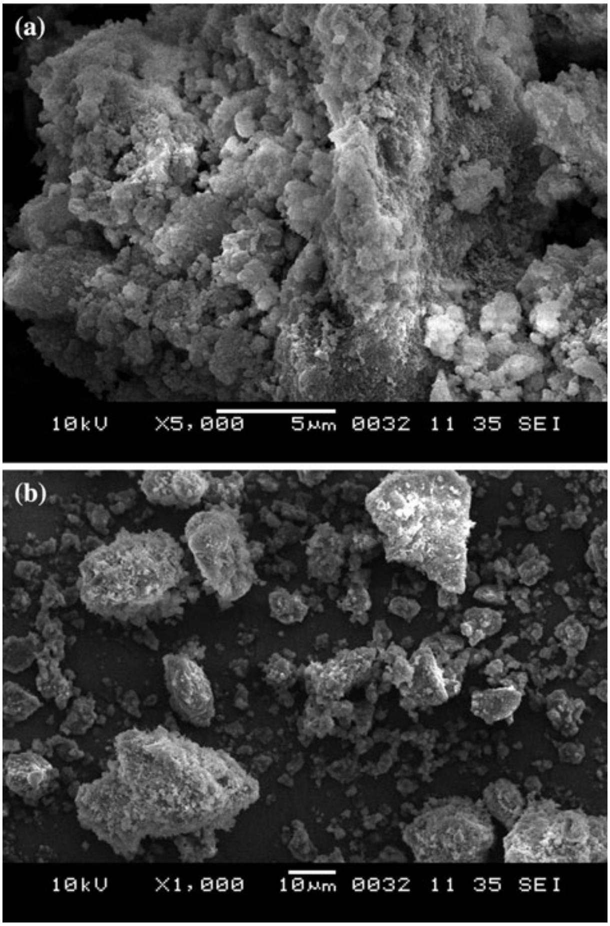


Fig. 4 **a** SEM Micrographs of *o*-APMF coplymer resin at 5000× magnification. **b** SEM Micrographs of *o*-APMF coplymer resin at 1000× magnification

Fig. 4a, b, respectively. It gives the information of surface topology and defect in the structure. The resin appeared to be dark brawn in color. The morphology of copolymer resin shows spherulites and fringed model. The spherulites are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of *o*-APMF copolymer resin sample. The morphology of resin polymer shows also a fringe model of the crystalline amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. However, the photograph showing the fringed and scattered nature having shallow pits represents the transition between crystalline and amorphous. The resin exhibits more amorphous characters with close packed surface having deep pits as shown in Fig. 4a. Thus, SEM micrographs morphology of the resin shows the transition between crystalline and amorphous nature, when compared to the other resin [37, 38], the *o*-APMF copolymer resin is more amorphous in nature, hence shows higher metal ion-exchange capacity.

Ion-exchange properties

With a view to ascertain the selectivity of the copolymer for the selected metal ions, we have studied the influence of various electrolyte on the selectivity of metal ion, the rate of metal uptake and the distribution ratio of metal ions between the polymer and the solution containing the metal ions, by using batch equilibrium method [39–41].

The *o*-APMF copolymer (Scheme 1) shows that the group −OH and −NH contain lone pair of electrons, which can be donated to the metal ion during complex formation. Hence, it shows chelating behavior. When polymer is suspended in metal ion solution, the chelating tendency of copolymer forms the cyclic complex with the metal ion, which absorbs the metal ion from solution to surface of polymer. This mechanism of adsorption of metal ion by polymer ligands is known at metal uptake of polymer. The metal uptake concentration of metal ion in solution decreases, this can be determined by titration with standard EDTA solution. The metal uptake capacity of polymer is different for different metal ion, and is also known as selectivity of polymer toward the uptake of metal ion. The metal uptake of copolymer depends on three variables, concentration of electrolyte solution, shaking time, and pH of the solution. The chelating behavior of *o*-APMF copolymer was studied with these three variables by keeping two variable constant at each time.

$$\text{Polymer} + \text{metal ion solution} + \text{shaking} \rightarrow \text{polymer} - \text{metal ion chelate.}$$

(Metal uptake capacity of polymer depends on stability of polymer – metal ion chelate). The following structure has been proposed for the polychelate (Fig. 5).

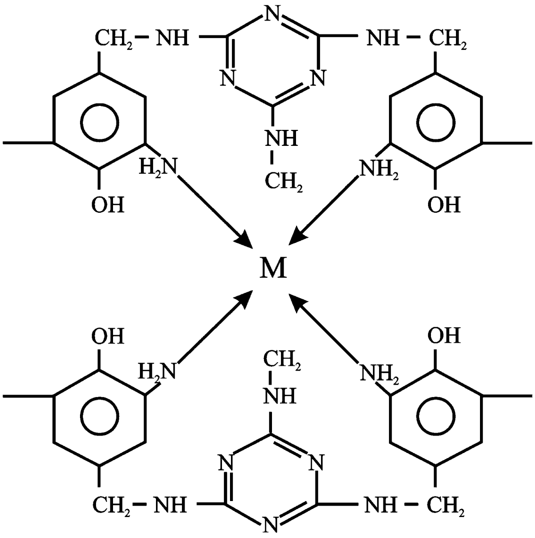


Fig. 5 Proposed structure of the polymeric chelate

Batch equilibrium technique developed by Gregor et al. and DeGeiso et al. was used to study the ion-exchange property of *o*-APMF copolymer resin. The result of the batch equilibrium study carried out with the copolymer resin *o*-APMF is presented in Figs. 6, 7, 8, 9, 10, and 11. Eight metal ions Fe^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} in the form of aqueous metal nitrate solution were used.

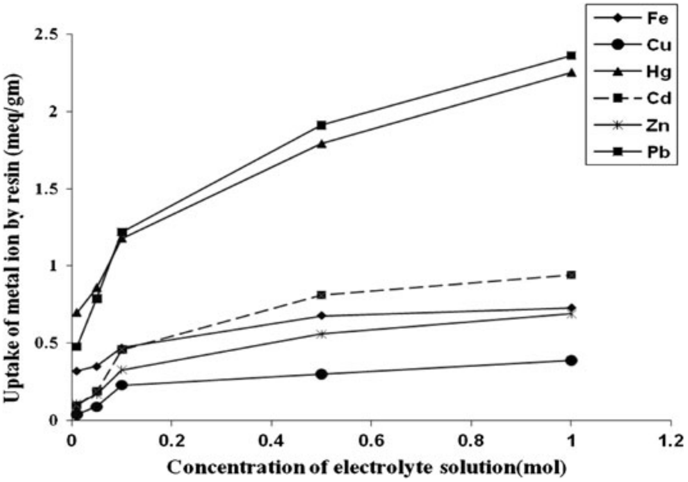


Fig. 6 Uptake of several metal ions by *o*-APMF copolymer resin at five different concentration of electrolyte solution $NaNO_3$. $[M(NO_3)_2] = 0.1$ mol/L; volume = mL; volume of electrolyte solution : 25 mL Weight of resin = 25 mg; time : 24 h: Room temperature. pH : Fe(III) = 2.5; Cu(II) = 4.5; Hg(II) = 6.0; Zn (II) = 5.0; Cd(II) = 5.0; Pb(II) = 6.0

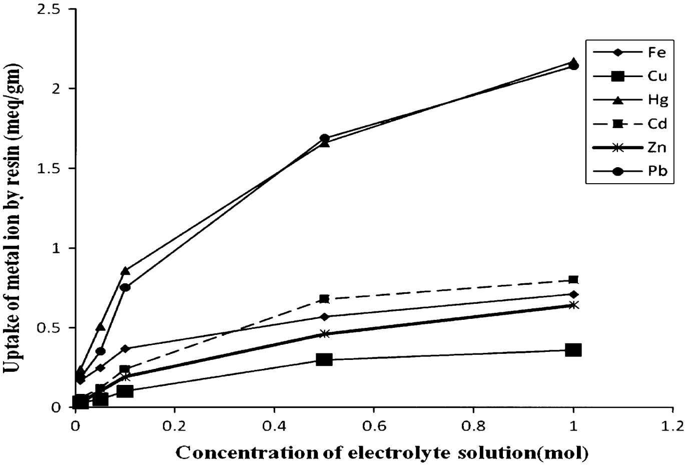


Fig. 7 Uptake of several metal ions by *o*-APMF copolymer resin at five different concentration of electrolyte solution NaCl. $[M(NO_3)_2] = 0.1$ mol/l; volume = mL; volume of electrolyte solution: 25 mL weight of resin = 25 mg; time: 24 h: Room temperature. pH : Fe(III) = 2.5; Cu(II) = 4.5; Hg(II) = 6.0; Zn (II) = 5.0; Cd(II) = 5.0; Pb(II) = 6.0

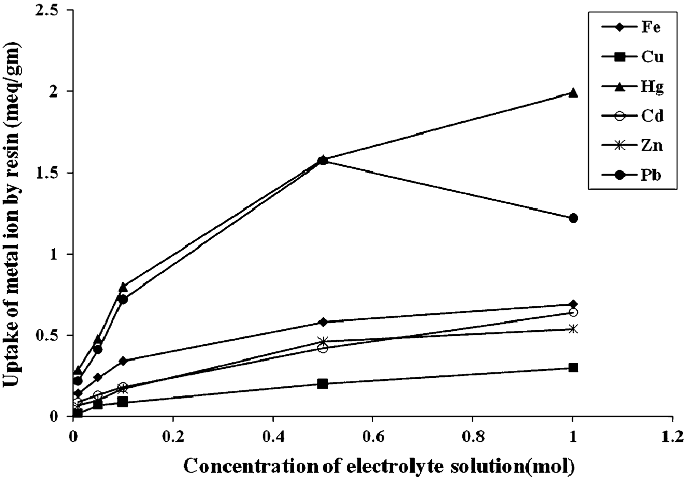


Fig. 8 Uptake of several metal ions by *o*-APMF copolymer resin at five different concentration of electrolyte solution $NaClO_4$. $[M(NO_3)_2] = 0.1$ mol/L; volume = mL; volume of electrolyte solution: 25 mL weight of resin=25 mg; time : 24 h: Room temperature. pH : Fe(III) = 2.5; Cu(II) = 4.5; Hg(II) = 6.0; Zn (II) = 5.0; Cd(II) = 5.0; Pb(II) = 6.0

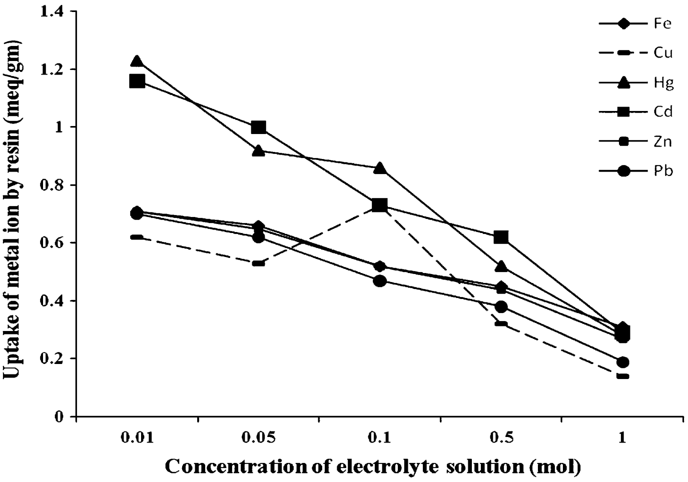


Fig. 9 Uptake of several metal ions by *o*-APMF copolymer resin at five different concentration of electrolyte solution Na_2SO_4. $[M(NO_3)_2] = 0.1$ mol/L; volume = mL; volume of electrolyte solution: 25 mL weight of resin = 25 mg; time: 24 h: Room temperature. pH: Fe(III) = 2.5; Cu(II) = 4.5; Hg(II) = 6.0; Zn (II) = 5.0; Cd(II) = 5.0; Pb(II) = 6.0

The ion-exchange study was carried out using three experimental variables: (a) electrolyte and its ionic strength, (b) shaking time, and (c) pH of the aqueous medium. Among three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymer [22, 24, 25].

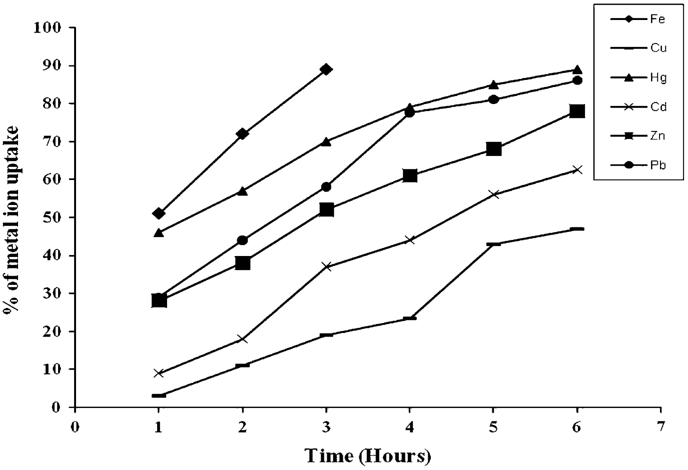


Fig. 10 Comparison of the rate of metal ion uptake by *o*-APMF copolymer resin. [M(NO_3)$_2$] = 0.1 mol/L; volume: 2mL; $NaNO_3$ = 1.0 mol/L; volume: 25 mL, Room temperature. Metal ion uptake = (Amount of metal ion absorbed × 100)/amount of metal ion absorbed at equilibrium). pH: Fe(III) = 2.5; Cu(II) = 4.5; Hg(II) = 6.0; Zn (II) = 5.0; Cd(II) = 5.0; Pb(II) = 6.0

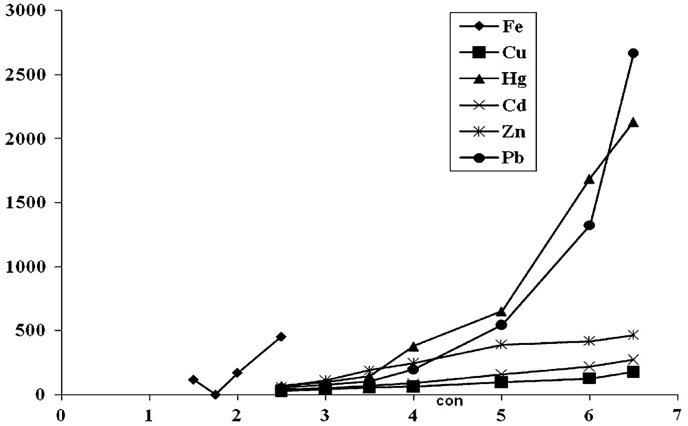


Fig. 11 Distribution ration (*D*) of various metal ions as function of different pH by *o*-APMF copolymer resin. *D* = weight (mg) of metal ions taken up by 1 g of copolymer/weight (mg) of metal ions present in 1 mL of solution. [M(NO_3)$_2$] = 0.1 mol/L; volume: 2mL; $NaNO_3$ = 1.0 mol/L; volume: 25mL, time 24 h (equilibrium state) at Room temperature pH: Fe(III) = 2.5; Cu(II) = 4.5; Hg(II) = 6.0; Zn (II) = 5.0; Cd(II) = 5.0; Pb(II) = 6.0

Effect of electrolytes and their concentration on the metal ion uptake capacity

We examined the effect of NO_3^-, Cl^-, SO_4^{2-}, and ClO_4^- at various concentrations on the equilibrium of metal resin interaction of constant pH. Different metal ions have different pHs in solution, which have been mentioned in Figs. 6, 7, 8, and 9, and the figures show that the amount of metal ions taken up by a given amount of copolymer depends on the nature of concentration of the electrolyte present in the solution. In the presence of nitrates, perchlorates, and chloride ions, the uptake of Fe(III), Cu(II), Hg(II), Cd(II), Zn(II), and Pb(II) ions increases with increasing concentration of electrolytes. Whereas in the presence of sulfate ions, the amount of above-mentioned ions taken up by the copolymer resin decreases with increasing concentration of the electrolyte [42]. NO_3^-, Cl^-, and ClO_4^- ions form weak complex with the above metal ions, while SO_4^{2-} forms stronger complex thus the equilibrium is affected. This may be explained on the basis of the stability constants of the complexes with those metal ions and nature of ligands.

Rate of metal ion uptake 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 out while operating as close to equilibrium condition as possible. During rate of metal ion determination, the concentration of metal ion and electrolyte solution and pH of the solution remain constant and pH of each metal ion is different which is given in Fig. 10. As shaking time increases the polymer gets more time for adsorption, hence uptake of metal ions increases. Figure 10 shows the results of rate of uptake of metal ion on *o*-APMF copolymer 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 copolymer. The figure shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of metal ions under given conditions. It is found that Fe(III) ions required about 3 h for the establishment of the equilibrium, whereas Cu(II), Hg(II), Zn(II), and Pb(II) ions required about 6 h. Thus, the rate of metal ions uptake follows the order Fe(III) $\gg$ Pb(II) $>$ Zn(II) $>$ Hg(II) $>$ Cu(II) for the copolymer [43–50]. The rate of metal uptake may depend on hydrated radii of metal ions. The rate of uptake for the post transition metal ions such as Cd (II) exhibits other trend, the rate of uptake is comparable to that of Pb(II) because of difference in '*d*' orbital.

Distribution ratios of metal ions at different pH

The distribution of metal ion depends upon pH of the solution. By increasing pH, the H^+ ion concentration in the solution decrease and only metal ion in the solution available for adsorption which increase uptake of metal ions.

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 data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the copolymers increase with increasing pH of the medium [24, 42]. The magnitude of increase, however, is different for different metal cations. The study was carried out from pH 2.5 up to pH 6.5 to prevent hydrolysis of metal ions at higher pH (Fig. 10). The selectivity of Fe(III) ion is more for the *o*-APMF copolymer resin as compared to any other metal ions under study. The order of distribution ratio of metal ions measured in the range 1.5 to 6.5 is found to be Fe(III) > Cu(II) > Pb(II) > Hg(II) > Zn(II) [25]. Thus, the result of such type of study is 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 suggests that the optimum pH 2.5 for the separation of Fe(III) and Zn(II) with distribution ratio '*D*' are 4355.6 and 65.7, respectively, using the *o*-APMF copolymer resin as ion exchange. Similarly for the separation of Fe(III) and Hg(II) at the optimum pH is 2.5 with distribution ratio 4355.6 and 72.72, respectively, for *o*-APMF copolymer. The lowering in the distribution ratios of Fe(III) was found to be small, hence efficient separation could be achieved. Thus, the separation of Fe(III) from other metal having combination (1) Fe^{3+} and Cu^{2+}, (2) Fe^{3+} and Hg^{2+}, (3) Fe^{3+} and Zn^{2+}, (4) Fe^{2+} and Pb^{2+} are effectively may separate out.

From the result, it reveals that with decrease in atomic number, the ion uptake capacity is increased. In the 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 *o*-APMF 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^{2+} and Ni^{2+} 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 Fe^{3+} ions.

The strength of ion-exchange capacities of various resins can be studied by comparing their ion-exchange capacity. The ion-exchange capacity (IEC) is a fundamental and important quantity for the characterization of any ion-exchange material. It is defined as the amount of ion that undergoes exchange in a definite amount of material, under specified experimental conditions. The ion-exchange capacity of *o*-APMF copolymer has been calculated, which was found to be 4.5 meq g^{-1} which indicates that *o*-APMF copolymer resin is better ion exchanger than commercial phenolic and some polystyrene commercial ion exchangers.

Some commercially available ion-exchange resins are given below

Trade name	Functional group	Polymer matrix	Ion-exchange capacity (meq g^{-1})
Amberlite IR-120	$–C_6H_4SO_3H$	Polystyrene	5.0–5.2
Duolite C-3	$–CH_2SO_3H$	Phenolic	2.8–3.0
Amberlite IRC-50	–COOH	Methacrylic	9.5
Duolite ES-63	$–OP(O)(OH)_2$	Polystyrene	6.6
Zeocarb-226	–COOH	Acrylic	10.00
Dowex-1	$–N(CH_3)_3$ Cl	Polystyrene	3.5
Amberlite IRA-45	$–NR_2$, –NHR, $–NH_2$	Polystyrene	5.6
Dowex-3	$-NR_3$, −NHR, $-NH_2$	Polystyrene	5.8
Allusion A WB-3	$–NR_2$, $–N^+R_3$	Epoxy-amine	8.2

Conclusion

A copolymer *o*-APMF based on the condensation reaction of *o*-aminophenol and melamine with formaldehyde in the presence of acid catalyst was prepared. The copolymer resin *o*-APMF is a selective chelating ion-exchange copolymer resin for certain metals. The uptake capacity of metal ions by the resin was carried out by the batch equilibrium technique. The uptake capacities of metal ions by the copolymer resin were pH dependent. As the pH of medium increases the polymer should have a higher selectivity for Fe^{3+}, Hg^{2+}, and Pb^{2+} ions than for Zn^{2+} and Cu^{2+}. Due to the considerable difference in the adsorption capacity at different pH media, the rate of metal uptake and distribution ratio at equilibrium, it may be possible to use the polymers for separation of particular metal ions from their admixture.

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