Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Applied Science Research, 2010, 2 (1) 261-276
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Study of chelation ion-exchange properties of new copolymer resin derived from o-aminophenol, urea and formaldehyde

Wasudeo B. Gurnule[1*] and Deepti B. Patle[2]

[1]Department of Chemistry, Kamla Nehru College, Sakkardara, Nagpur, India
[2] Department of Chemistry, Laxminarayan Institute of Technology, Rashtrasant Tukdoji Maharaj, Nagpur University, Nagpur, India

---

Abstract

Copolymer resin (o-APUF) was synthesized by the condensation of o-aminophenol[AP] and urea[U] with formaldehyde[F] in the presence of an acid catalyst and using varied molar ratio of reacting monomers. Copolymer resin compositions have been determined on the basis of their elemental analysis and the number average molecular weight of o-APUF copolymer was determined by conductometric titration in non-aqueous medium. Viscometric measurements in dimethyl sulphoxide have been carried out with a view to ascertain the characteristic functions and constants. UV-VIS, FT-IR and ^1H NMR spectra were studied to elucidate the structure. Ion-exchange properties of these resin were studied by batch equilibrium method for Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} ions over the pH range, 1.5 to 6.5 and in media of various ionic strengths. In the presence of nitrate, perchlorate and chloride ions the uptake of Fe(III), Cu(II), Hg(II), Zn(II), and Pb(II) ions increasing with increasing concentration of electrolytes, whereas in the presence of sulphate ions, the amount of above mentioned ions taken up by the copolymer resin decreases with increasing concentration of electrolyte. The resin shows a higher selectivity for Fe^{3+} ion over any other ions. Study of distribution ratio as a function of pH indicates that the amount of metal ion taken by resin is increases with the increasing pH of medium. The surface morphology of the copolymer resin was examined by scanning electron microscopy and it establishes the transition state between crystalline and amorphous nature.

Keywords: Copolymer resin, Chelating properties, Batch equilibrium, Ion-exchangers, Distribution ratio, Metal ion uptake.

Introduction

Copolymer find very useful applications as adhesives, high temperature flame resistant, fibers, coating materials, semiconductors, catalysis and ion exchange resins [1-5]. Ion exchange resins have been attached much interest in the recent years due to their applications in waste water treatment, metal recovery and for the identification of specific metal ions. Chelating ion-exchange resin involving o-amino-phenol with resorcinol and formaldehyde was reported by Pennington and Williams [6-8]. DeGeiso et. al. studied the chelation ion-exchange properties of the resin synthesized from salicylic acid and thiourea with trioxane copolymer [9-11]. Copolymer involving 2-hydroxyacetophenoneoxime-thiourea-trioxane [12], 2,4-dihydroxy-benzeldehyde and formaldehyde [13] and 4-hydroxyacetophenone-biuret-formaldehyde [14] were reported for its ion-exachange characteristics. Synthesis of o-nitrophenol and thiourea with paraformaldehyde copolymer was reported and its chelation ion- exchange properties were investigated by a static batch equilibrium method [15]. Poly[(2-hydroxy-4-methoxy benzophenone) ethylene] resin has good binding capacity for the Lanthanum (III) at various conditions [16]. The copolymer from 2,4dichlorophenylacrylate/8-quinolinyl methacrylate and acrylic copolymer derived from 8-quinolinyl group have been synthesized [17, 18]. Recently, Shah et. al. reported the chelating ability of the resin synthesized by a microwave irradiation technique involving salicylic acid and formaldehyde with resorcinol [19]. S. G. Pawar et. al studied the conducting properties of the conducting polymer of polyanilines films containing electrical and optical properties [20]. Recently, D Xie et. al. reported the conducting ability of the chemically synthesized polymer by oxidation method at 0^{o}C [21].

The present study deals with the synthesis and characterization of o-aminophenol-urea-formaldehyde [o-APUF] copolymer resin by spectral methods for the first time. The synthesized copolymer was characterized by elemental analysis, UV-VIS, FT-IR, ^{1}H NMR, intrinsic viscosity and number average molecular weight. One of the important applications of chelating and functional polymer is their capability to recover metal ions from waste solutions. Hence, the chelation ion-exchange property of the o-APUF copolymer resin was also reported for specific metal ions.

Materials and Methods

o-Aminophenol, urea and formaldehyde (37%) were of analytical grade and chemically pure, (all from Merck India) and wherever necessary the purity was tested and confirmed by thin layer chromatography using Silica gel as stationary phase and chloroform: methanol (9:1). The metal solutions were prepared by dissolving appropriate amount of the nitrates of the metals in double distilled water and standardized by EDTA titrations. Solvents like N, $N^{'}$- dimethyl formamide and dimethyl sulphoxide were used after distillation.

Synthetic procedure of o-APUF copolymer resin

The o-APUF copolymer was prepared by condensing o-aminophenol (1.09 gm, 0.1 mol) and urea (0.70 gm, 0.1 mol) with formaldehyde (7.5 ml, 0.2 mol) in presence of 2M HCl heated in an oil bath at 126 ± 2ºC for 5 hrs [22]. 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-APUF copolymer. It was further purified by dissolving in 8% NaOH and filtered. It was then precipitated by drop wise addition of 1:1 (v/v) conc. HCl/water with constant stirring and filtered. The process was repeated twice. The resulting polymer sample washed with boiling water and dried in vacuum at room temperature. The purified copolymer resins were 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 86%. The reaction and suggested structure of o-APUF copolymer resin is depicted in Figure 1.

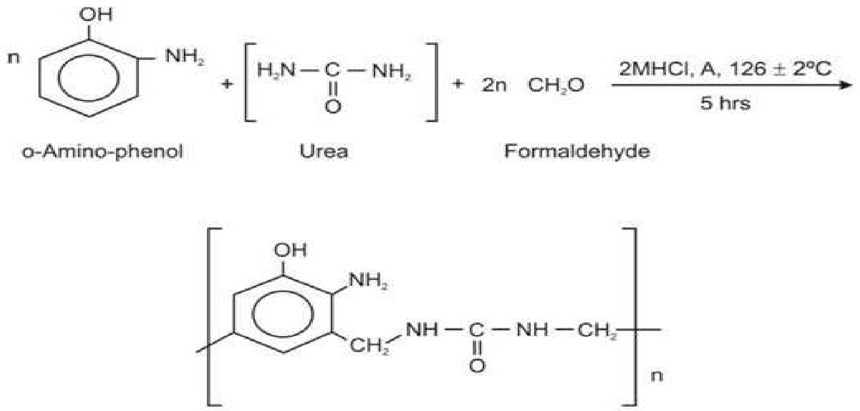


Fig.1. Formation and suggested structure of o-APUF copolymer

Characterization of the copolymer

The copolymer resin was subject to micro analysis for C, H and N on a 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 gm 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 [23-24] : (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 have to be determined by following eq.(1)…

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

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

The intrinsic viscosity was determined using a Tuan-Fuoss viscometer [25] at six different concentrations ranging from 0.3 wt % to 0.05 wt % of resin in DMSO at 30ºC. Intrinsic viscosity (η) was calculated by the Huggin's eq.(2) [26] and Kraemer's eq.(3) [27].

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

$$\text{In } \eta_r/C = [\eta] - K_2[\eta]^2.C \text{ ------------}(3)$$

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

Infrared spectra of o-APUF 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 Adanve – 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.

Ion-exchange properties

The ion-exchange properties of the o-APUF 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 hrs at 25ºC. 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 25ºC for 24 hrs and filtered [28, 29]. 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 [30, 31]. 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 describe above were carried out, in which the metal ion taken up by the chelating resin was determined from time to time at 25ºC (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 hrs. the rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain 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), Co(II), Zn(II), Ni(II) and Pb(II) between the polymer phase and the aqueous phase was determined at 25ºC and in the presence of a 1M $NaNO_3$ solution. The experiment were carried out as described earlier at different pH values. The distribution ratio "D" is defined by the following relationship……..

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

Results and Discussion

The resin sample was dark brown in colour, 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 550ºC**.** The resin was analyzed for carbon, hydrogen, and nitrogen content. C = 46.78% (Cal) and 46.22%(F); H= 5.30%(Cal) and 5.25%(Cal); N = 18.58% (Cal) and 18.03%(F).

Characterisation 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 [32]. The molecular weight of copolymer was also estimated by conductometric titration. The calculated molecular weight for o-APUF resin is 5803.68.

Viscometric measurement was carried out in DMSO at 30ºC. o-APUF resin showed normal behavior. The intrinsic viscosity was determined by the Huggin's [26] eq. (2) and Kraemer's [27], eq. (3) which is 0.28 and 0.26 respectively. In accordance with the above relations, the plots of $\eta_{sp/c}$ and $\eta_{rel/c}$ against C was linear giving as slopes K_1 and K_2(0.54) 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 [33].

The UV-visible spectra of o-APUF copolymer resin shown in Figure 2. UV-visible spectra of o-APUF resin has been recorded in pure DMSO in the region of 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 248.50 and 282.50 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 hyperehromic shift i.e. ϵ_{max} higher values [34-35]. This observation is in good agreement with the proposed most probable structures of o-APUF copolymer resin.

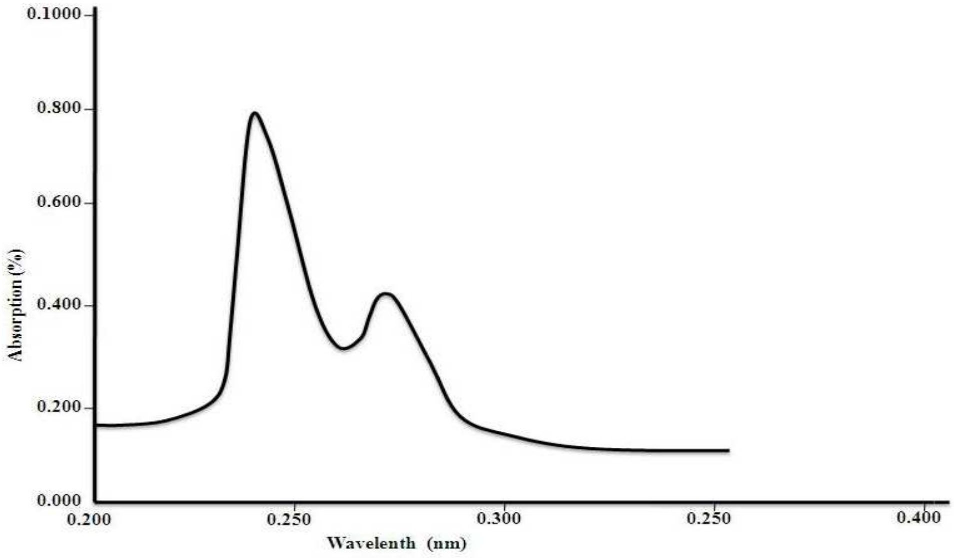


Fig 2. Electronic spectra of o-APUF copolymer resin

The IR spectra of o-APUF copolymer resin is presented in Figure 3 and IR data are specified in Table 1.

Table 1. FT- IR Spectral data of o-APUF Copolymer Resin

Assignment	**Expected wave number (cm^{-1})**	**Observed wave number (cm^{-1-})**
		o-APUF
-OH (phenolic)	3100-3500	3396(b,st)
>C=O(ketonic and urea)	1630-1680	1627.7 (w,sh)
>NH (amido)	1533.6	1533.7 (sh,st)
Aromatic ring	1445-1485	1445.2 (sh,m)
>CH_2 (methylene bridges)	1250-1340	1275.5-1353.9 (w,m)
-OH bending and C-O stretching	1050-1100	1098.7 (w)
1,2,3,4,5substitution in benzene skeleton	557.9	557.9 (b,st)

Sh= sharp; b= broad; st = strong; m = medium; w= weak

A broad band appear in the region 3100 – 3500 cm^{-1} may be assigned to the stretching vibration of the phenolic hydroxyl groups exhibiting intermolecular hydrogen bonding [36]. The sharp band displayed at 1630 – 1680 cm^{-1} may be due to the bending vibration of >C=O group. The bond obtained at ~ 1533 cm^{-1} suggest the presence of >NH (amido) group. A band appear in the reason of 1250 – 1340 cm^{-1} show the presence of methylene bridges (>CH_2) in the polymer chain [37]. 1,2,3,4 and 5 pentasubstitution of aromatic ring is recognized from the bands appearing at ~557.9 cm^{-1} [38-42].

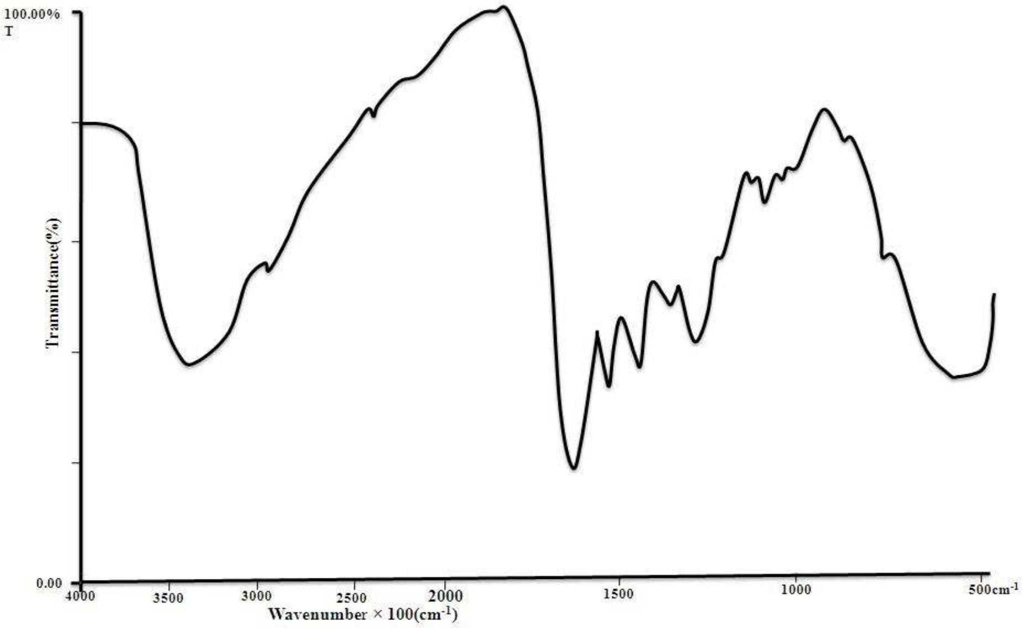


Fig 3. Infrared spectra of o-APUF copolymer resin

H^1 NMR spectra of o-APUF copolymer is shown in Figure 4 and show a weak multiplicity signals (unsymmetrical pattern) in the region 7.77 to 7.88 (δ)ppm may be due to the aromatic protons. The weak multiply signals appearing at 6.62 – 6.75 (δ)ppm may due to the amido –CH_2 -NH-CO linkage [37-38]. A signal appeared in the region 4.07 – 4.98 (δ)ppm may be due to proton of methelenic bridges (Ar – CH_2 – N) of polymer chain. The signal in the range of 8.26 –

8.32 (δ) ppm is attributed to phenolic -OH proton. A weak signal in the range of 1.25 exhibits the present of Ar – NH_2 group.

Table 2. ^{1}H NMR Spectral Data of o-APUF Copolymer Resin

Chemical shift (δ) ppm of copolymer	**Nature of proton assigned**
o-APUF	
7.88	Aromatic proton (unsymm. Pattern)
6.60	Amido proton of –CH_2-NH-CO linkage
4.60	Methelene proton of Ar-CH_2-N moiety
8.26	Proton of Ar-OH
1.2505	Amine Ar-NH_2

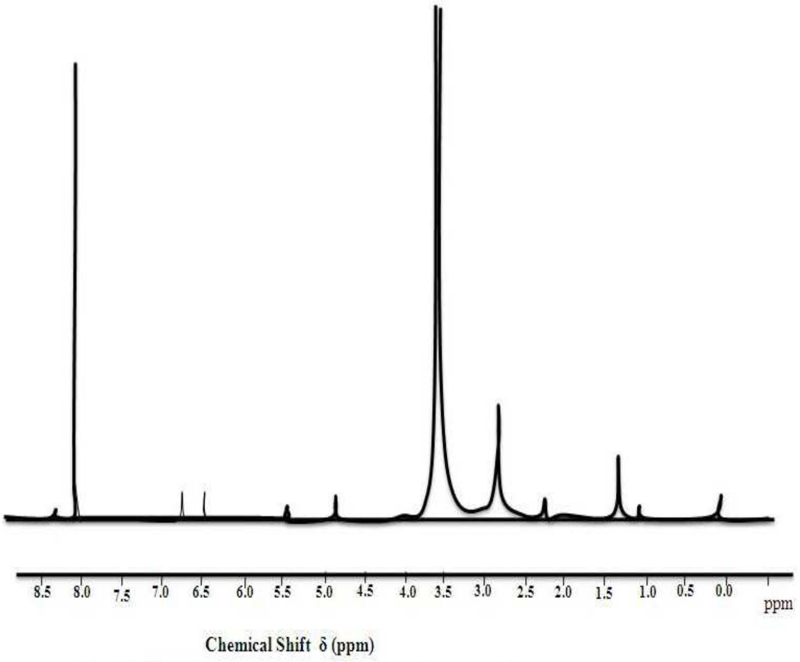


Fig 4. H^1 NMR spectra of o-APUF copolymer resin

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 Figure5(a), 5(b)and 5(c) respectively. It gives the information of surface topology and defect in the structure. The resin appeared to be dark brawn in colour. 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-APUF copolymer resin sample. The morphology of resin polymer shows also a fringes model of the crystalline amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. But the photograph shows the fringed and scatted nature having shallow pits represent the transition between crystalline and amorphous. The resin exhibits more amorphous characters with closed packed surface having deep pits in figure 5(c). Thus by SEM micrographs morphology of the resin shows the transition between crystalline and amorphous nature, when compare to the other resin [43-44], the o-APUF copolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.

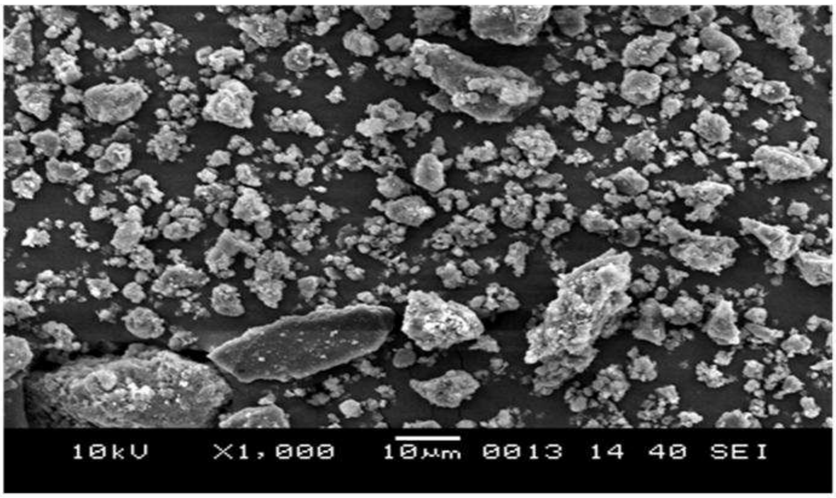


Fig.5(a). SEM Micrographs of o-APUF copolymer resin at 1000x magnification.

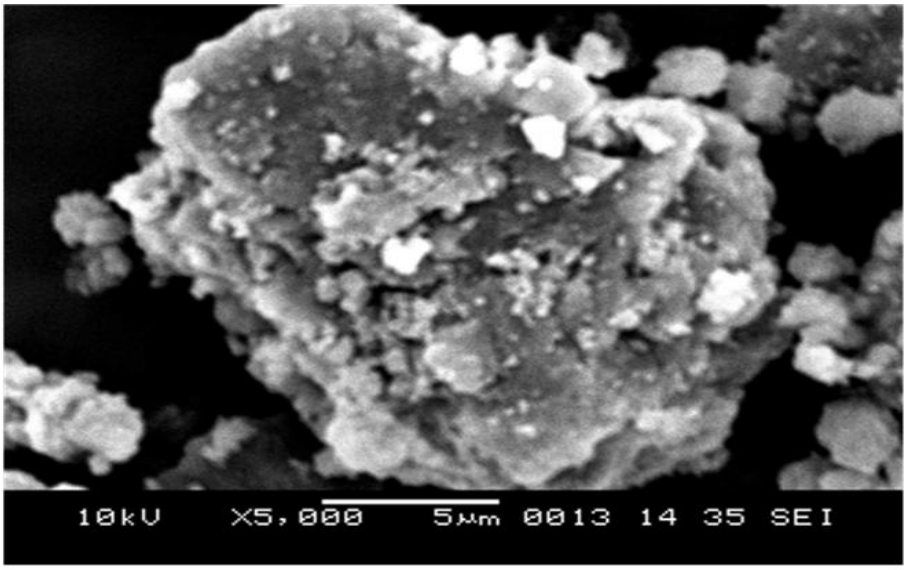


Fig.5(b). SEM Micrographs of o-APUF copolymer resin at 5000x magnification.

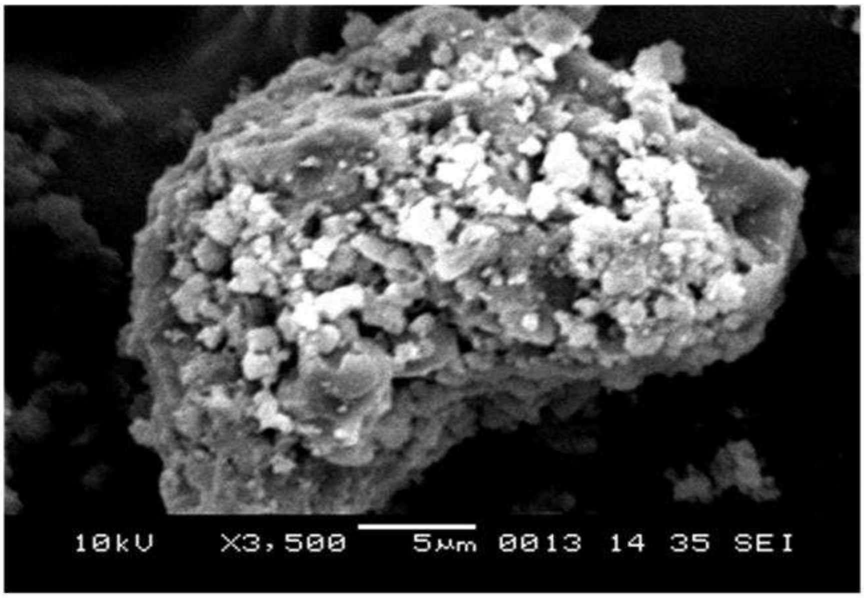


Fig.5(c). SEM Micrographs of o-APUF copolymer resin at 3500x magnification.

Ion-exchange properties

With a view to ascertain the selectivity of the studied 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 solution containing the metal ions, by using batch equilibrium method [45-47].

The o-APUF copolymer **(**Fig.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. Due to 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, is also known as selectivity of polymer towards 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-APUF copolymer was studied with these three variables by keeping two variable constant at each time.

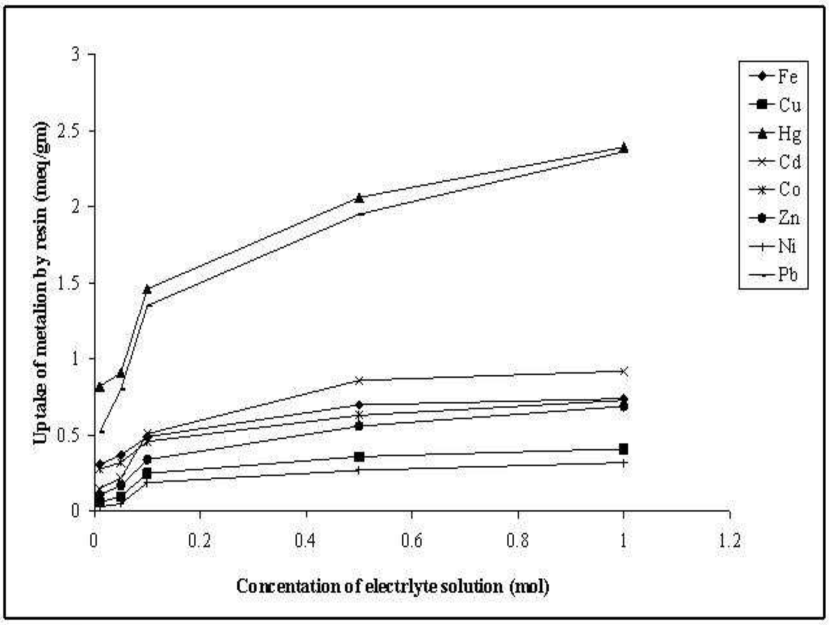
Polymer + metal ion solution + shaking $\longrightarrow$ polymer – metal ion chelate

(Metal uptake capacity of polymer depends on stability of polymer – metal ion chelate)

Batch equilibrium technique developed by Gregor et al. and DeGeiso et al. was used to study of ion exchange property of o-APUF copolymer resin. The result of the batch equilibrium study carried out with the copolymer resin o-APUF is presented in Fig.6-11. Eight metal ions Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} 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) 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 evaluable its effect on metal uptake capacity of the polymer [28, 29, 31].

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

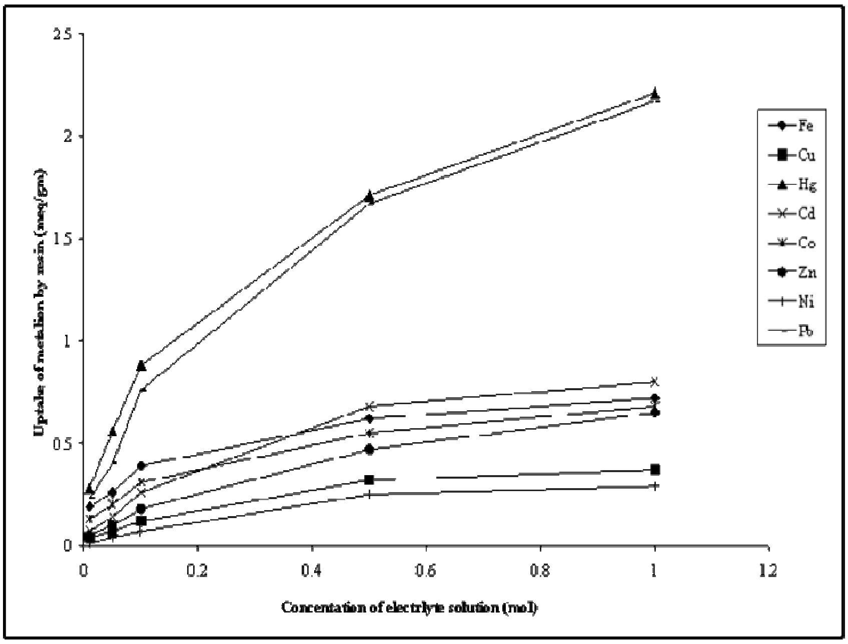
We examined the effect of NO_3^-, Cl^-, SO_4^{2-} and ClO_4^- at various concentration on the equilibrium of metal resin interaction of constant pH. Different metal ions have different pH in solution, has been mentioned in Fig.6-9, which shows that the amount of metal ions taken up by a given amount of copolymer depends on the nature of concentration of the electrolyte present in the solution. In the presence of nitrates, perchlorate and chloride ions the uptake of Fe(III), Cu(II), Hg(II), Zn(II) and Pb(II) ions increasing with increasing concentration of electrolytes. Whereas in the present of sulphate ions, the amount of above maintained ions taken up by the copolymer resin decreases with increasing concentration of the electrolyte [48]. Above NO_3^-, Cl^-, and ClO_4^- ions form weak complex with the above metal ions, while SO_4^{-2} form 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.



[M(NO$_3$)$_2$]=0.1 Mol/l; Volume = ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.

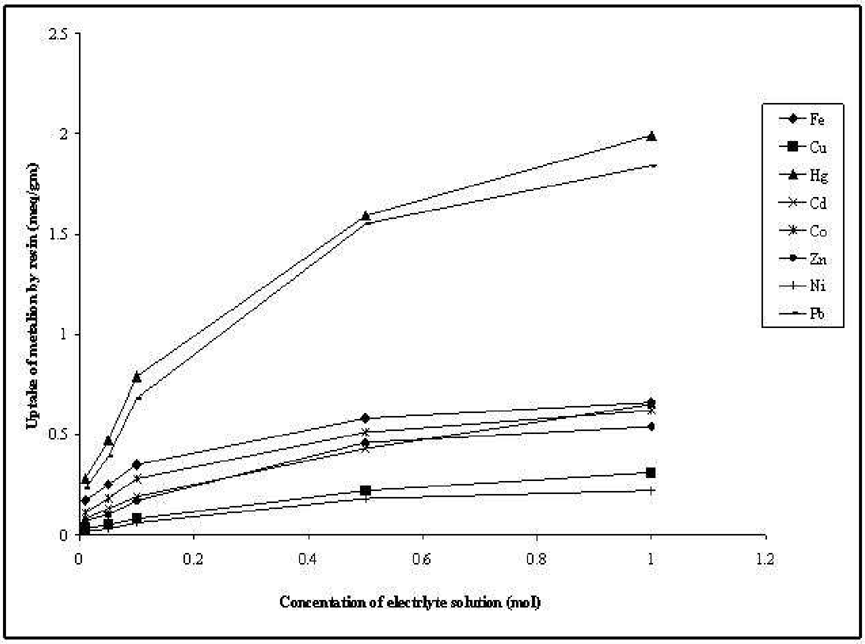
pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0

Figure 6. Uptake of several metal ions by o-APUF Copolymer resin at five different concentration of electrolyte solution NaNO$_3$



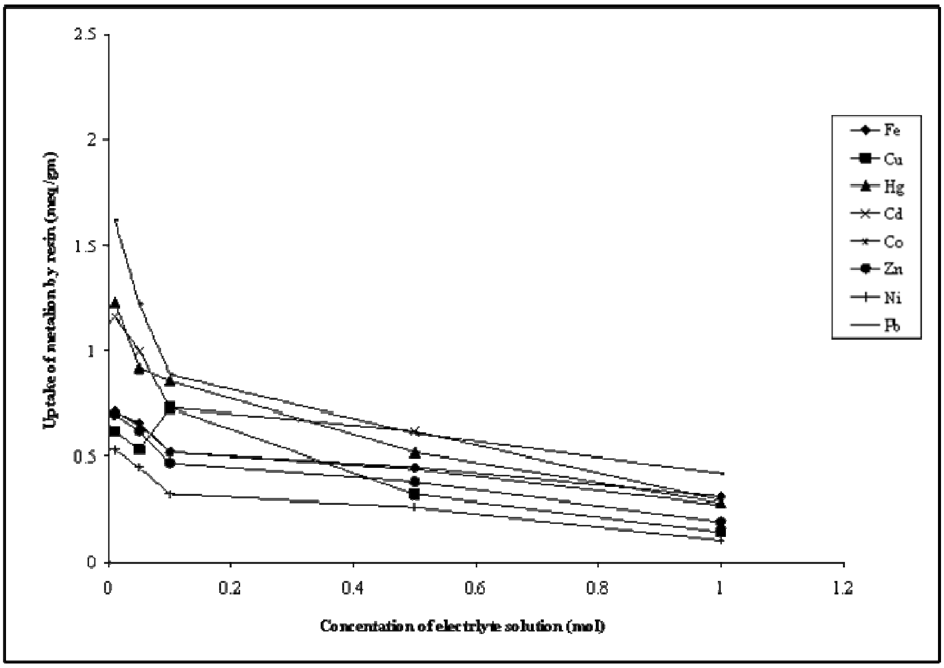
$[M(NO_3)_2]$=0.1 Mol/l. Volume = ml. Volume of electrolyte solution = 25 ml, Weight of resin = 25 mg, time = 24 hrs. at Room temperature
pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0; Hg(II)=6.0

Figure 7. Uptake of several metal ions by o-APUF 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 hrs. Room temperature
pH : Fe(III)=2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0; Hg(II)=6.0

Figure 8. Uptake of several metal ions by o-APUF copolymer resin at five different concentration of electrolyte solution $NaClO_4$

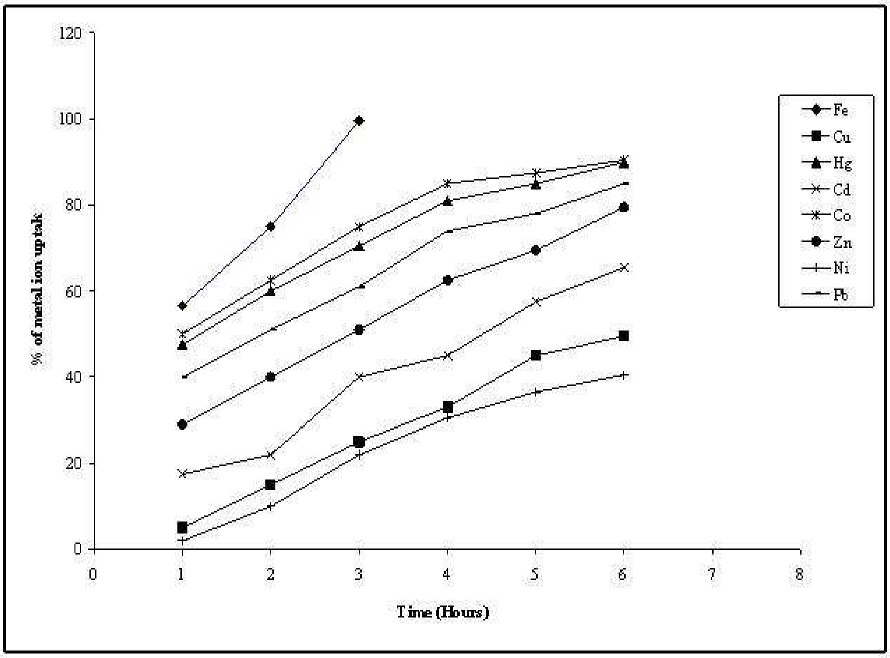


[M(NO$_3$)$_2$]=0.1 Mol l; Volume = ml; Volume of electrolyte solution=25ml; Weight of resin = 25 mg; time=24hrs; Room temperature
pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0; Hg(II)=6.0

Figure 9. Uptake of several metal ions by o-APUF copolymer resin at five different concentration of electrolyte solution Na$_2$SO$_4$

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. Fig 10 shows the results of rate of uptake of metal ion on o-APUF copolymer resin. The rate refer 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 hrs for the establishment of the equilibrium, whereas Cu(II), Hg(II), Zn(II) and Pb(II) ions required about 6 hrs. Thus the rate of metal ions uptake follows the order Fe(III) >> Pb(II) > Zn(II) > Hg(II) > Cu(II) for the copolymer [49-52].



$[M(NO_3)_2]$=0.1 mol/l; volume of metal nitrate=2ml; $NaNO_3$= 1.0 mol/l; volume of electrolyte=25ml, Room temperature

Metal ion uptake = (Amount of metal ion absorbed x 100) / (amount of metal ion absorbed at equilibrium)

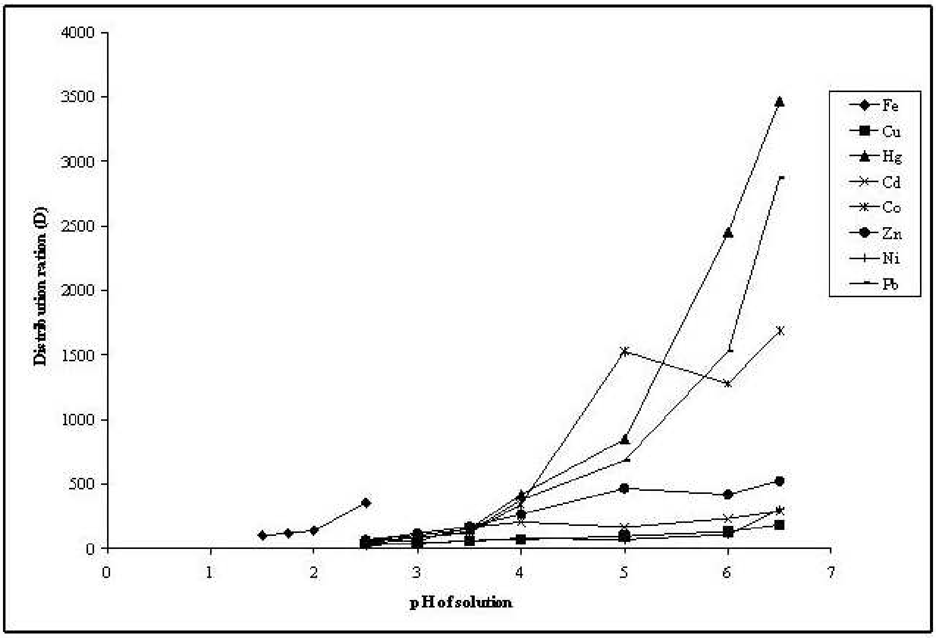
pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0; Hg(II)=6.0

Figure 10. Comparison of the rate of metal ion uptake by o-APUF copolymer resin

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 [22, 31, 48]. The magnitude of increase, however, is different for different metal cations. The study was carried out from 2.5 up to pH 6.5 to prevent hydrolysis of metal ions at higher pH (Fig11). The selectivity of Fe(III) ion is more for the o-APUF copolymer resin as compare to the 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) [31]. Thus the result 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 [22, 29]. For example, the result suggests 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-APUF 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 are 4355.6 and 72.72 respectively for o-APUF 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.



D= weight (mg) of metal ions taken up by 1 g of copolymer/weight (mg) of metal ions present in 1ml of solution.

$[M(NO_3)_2]$=0.1 mol/l; volume of metal nitrate=2ml; $NaNO_3$= 1.0 mol/l; volume of electrolyte= 25ml, time=24hrs (equilibrium state) at Room temperature.
pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Pb(II)=6.0; Hg(II)=6.0

Figure 11. Distribution ration (D) of various metal ions as function of different pH by by o-APUF copolymer resin

Conclusion

A copolymer o-APUF based on the condensation reaction of o-aminophenol and urea with formaldehyde in the presence of acid catalyst was prepared. The copolymer resin o-APUF is a selective chelating ion exchange copolymer resin for certain metals. The uptake capacities 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 increase the polymer should a higher selectively for Fe^{3+}, Hg^{2+} and Pb^{2+} ions than for Zn^{2+} and Cu^{2+}. Due to considerable difference in the uptake capacities at different pH and media of electrolyte, the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to use for separation of particular metal ions from their admixture.

Acknowledgements

Authors are highly thankful to the Director, Laxminarayan Institute of Technology, Nagpur, India, for providing the necessary laboratory facilities. Authors are also thankful to SAIF, Punjab University, Chandigarh for carrying out spectral analysis of the copolymer resin.

References

[1] K.E. Geckeler; Z.W. Rongnang; *Chem Abstr Italian*, **1994**, 121, 10302f.
[2] R. Purohit; S. Devi; *Analyst*, **1992**, 117, 1175-1177.
[3] B.L. Rivas; H.A. Maturana; M.J. Molina; M.R. Gomej-Anoton; M. Rosa; M.J. Prerola; *J Appl Polym Sc*, **1998**, 1109-1118.
[4] W. Jin-Yin; C. Wan-Yuan; **2002**, 1, 20-21.

[5] A.N. Egorov; Y.I. Sukhorukov; G.V. Plotnikova; A.K. Khaliullin; *Rus J Appl Chem*, **2002**, 75, 152-155.
[6] L.K. Drazzhanova; M.G. Vashkarova; L.A. Bimendina; S.D. Kudaibergenov; *J Appl Polym Sci*, **2003**, 87, 759-764.
[7] A.A. Atia; A.M. Donio; K.Z. Elvakeel; *React Funct Polym*, **2005**, 65, 267-275.
[8] L.D. Pennington; M.B. Williams; *Ind Eng Chem*, **1959**, 57, 759-762.
[9] R.C. DeGeiso; L.G. Donaruma; E.A.Tomic; *Anal Chem*, **1962**, 34, 845-847.
[10] R. Manavalan; M.M. Patel; *Macromol Chem*, **1983**, 184, 717-723.
[11] K.S. Siddiqui; N.H. Khan; R.I. Kureshy; S. Tabassum; A.S. Zaidu; *Macromol Chem*, **1987,** 26A, 495-497.
[12] H.B. Pancholi; M.M. Patel; *J Indian Chem Soc*, **1998,** 75, 86-87.
[13] B.K. Patel; M.M. Patel; *Ind Chem Soc*, **1990**, 67, 186-188.
[14] W.B. Gurnule; P.K. Rahangdale; L.J. Paliwal; *React Funct Polym*, **2003**, 55, 255-265.
[15] A. Burkanudeen; M. Karunakaram; *Orient J Chem*, **2002**, 18(1), 65-68.
[16] M.M. Patel; M.A. Kapadia; G.P. Patel; J.D. Joshi; *React Funct Polym*, **2007**, 67, 746-757.
[17] J.M. Patel; M.G. Patel; H.J. Patel; K.H. Patel; R.M. Patel; *J Mac Mol Sci*, **2008**, 45, 281-288.
[18] S.A. Patel; B.S. Shah; R.M. Patel; P.M. Patel; *Iran Polym J*, **2004**, 13(6), 445-453.
[19] Bhavna A. Shah; Ajay A. Shah; *Iran Polym J*, **2008**, 17(1), 3-17.
[20] S.G.Pawar; S.L.Patil; A.T.Mane; B.T.Raut; V.B.Patil; *Archives of Applied Science Research*, **2009**, 1 (2) 109-114.
[21] D Xie; *Sensors and Actuators B*, **2000** ,81, 158.
[22] W.B. Gurnule; P.K. Rahangdale; L.J. Paliwal; R.B. Kharat; *Synthesis and Reactivity in Inorganin and Metal-Organic Chemistry*, **2003,** 33, pp1187-1205.
[23]S.H. Maron; R.B. Reznik; *J. Polym Sci.*, **1969**, 2, 309.
[24]S.K. Chatterjee; *J. Polym Sci.,* **1970**, 18, 1299.
[25] D. E. Tuan; Fouss; *J Phys Chem*, **1963**, 67, 1343.
[26]M.L. Huggins; *J Am Chem Soc*, **1942**, 71, 2715.
[27]E.O. Kraemer; *Ind Eng Chem*, **1938**, 30, 1200.
[28] H.B. Pancholi; M.M. Patel; *High Perform Polym J*, **1991**, 3, 257.
[29] X.Liu; D. Zhu; D. Chan; *Huazheng Nongye Daxue*, **2000**, 19, 15-19.
[30] B.A. Shah; A.V. Shah; P.M. Shah; *E J Chem*, **2008**, 5, 291.
[31] R. Kunin; *Wiley*; London, **1958**, 324-339.
[32] M.R. Lutfor; S. Silong; *Europ Polym J*, **2000**, 36, 2105.
[33] Milan V. Patel; Samir A. Patel; Arbinda Roy; Rajni M. Patel; *Journal of Appl Polym Sc*, Part A : Polymer Chemistry, **2004,** 42, 5227-5224.
[34] E.I. Du Pont de Nemours and Co Netherlands, Patent, 6, 410,**1965**.
[35] I.J. Bigio and J. R. Mourant ; Phys. Med. Biol, **42**, **1997**,803-814.
[36] T.K.Bastia; S. Lenka; P.L. Nayak; *Journal of Appl Polym Sc*, **2003**, 46, 739-744.
[37] R.M. Silverstein; G.C. Basslel; T.C. Mohrill; Spectrometric Identification of Organic Compounds, John Wiley and Sons, 5th Ed, **1999**.
[38] W. Kemp; Organic Spectroscopy, Macmillan, Hong Kong, **1975.**
[39] W.B. Gurnule; H.D. Juneja; L.J. Paliwal; *Ultra Sci*, **2001**, 3, 33.
[40] K. Nakanishi; Infrared Absorption Spectroscopy – Practical, Noldden Day and Nankoto, Tokyo, **1967.**
[41] H. dudly; I. Fleming; spectroscopic methods in organic chemistry; Mc-Graw Hill; UK, **1975.**
[42] A.I. Vogal; Textbook of Practical Organic Chemistry, Longman Scientific and Technical, UK, **1989**.

[43] E. Suzuki; High Resolution Scanning Electron Microscopy of Immunogold Labeled cells by the use of thin plasma coating osmium, J Microscopy, **2002**, 153, 208.
[44] B.A. Shah; A.V. Shah; R.R. Bhatt; *Iran Polym J,* **2007**, 16(3), 173-184.
[45] M. Porter; Handbook of Industrial Membrane Technology, Noyes, Pork Ridge, New York, **1990.**
[46] Walter de Gruyter ; Ion Exchangers (K. Dorfner, ed.), Berlin,**1991.**
[47] C. E. Harland; Ion exchange: Theory and Practice, The Royal Society of Chemistry, Cambridge, **1994.**
[48] D. Muraviev; V. Gorshkov; A. Warshawsky; Ion exchange, M. Dekker, New York**, 2000.**
[49] S. Lenka; A. Parija; P.L. Nayak; *Polymer International,***2007**, 29(2), 103-106.
[50] T.K. Pal; R.B. Kharat; *Angewandte Macromol Chem* **1989**, 173, 55.
[51] F.A. Cotton; G. Wilkinson; Advanced Inorganic Chemistry, 3rd ed., Wiley. NewYork, **1972**, pp 52.
[52] F. Helfferich; Ion Exchange, McGraw Hill, New York, **1962.**