Preparation, characterization and chelating ion-exchange properties of terpolymer resins derived from o-aminophenol, urea and formaldehyde

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ABSTRACT
Terpolymer resins (o-APUF) synthesized by the condensation of o-aminophenol and urea with formaldehyde in the presence of acid catalyst, were proved to be selective chelation ion-exchange copolymers for certain metals. The chelating ion-exchange properties of these terpolymers were studied for Fe(III), Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Pb(II) ions in the form of their metal nitrate solutions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurements of the distribution of a given metal ion between the terpolymer sample and a solution containing the metal ion. The study was carried out over a wide pH range, shaking time and in media of various ionic strengths of different electrolytes. The ion-exchange capacity of metal ions has also been determined experimentally and compared with other commercial resins. Besides ion-exchange properties, the terpolymer resins were also characterized by viscometric measurements in dimethyl sulphoxide (DMSO), UV-visible absorption spectra in non-aqueous medium, infra-red spectra, nuclear magnetic resonance spectra and C13 NMR spectra. The physico-chemical and spectral methods were used to elucidate the structures of o-APUF resins. The morphology of the terpolymers was studied by scanning electron microscopy; showing amorphous nature of the resins therefore can be used as a selective ion-exchanger for certain metal ions.

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Introduction
Many research works has been carried out on the preparation and characterization of urea containing terpolymers. Terpolymer is found very useful application as adhesive, high temperature flame resistant, fibers, coating materials, semiconductors, catalysis and ion exchange resins [1-5]. Ion-exchange resins have attracted much interest in the recent years due to their application in waste water treatment, metal recovery and for the identification of specific metal ions [6-7]. Chelating ion-exchange properties of the resin involving poly[(2,4-dihydroxybenzophenone) butylene] and its polychelates with transition metals are reported [8]. A new chelating sorbent for metal ion extraction under saline conditions has also been studied [9]. Poly (2-hydroxy-4 acryloyloxybenzophenone) resin [10] and resin functionalized with dithiooxamide [11] are found to be chelation ion exchangers. Copolymers involving 2-hydroxyethylmethacrylate and 2-methacryloyl-amidocysteine [12], polyacrylonitrile beads and 2-amino-2-thiazoline [13] and 4-hydroxy acetophenone-biuret-formaldehyde [14] are reported for their ion-exchange characteristics. The purpose of present study is, to explore the adsorption behavior of eight metal ions Fe2+, Cu2+, Ni2+, Co2+, Zn2+, Cd2+, Hg2+ and Pb2+ on the newly synthesized terpolymer resins o-APUF at different pH values, different concentrations of different electrolytes and at different shaking time intervals. The adsorption behavior of these metal ions are based on the affinity differences towards the chelating resins as functions of pH, electrolyte concentrations and shaking time. The terpolymer resins under investigations are found to be cation exchanger having both ion-exchange group and chelating group in the same polymer matrix and the resin can be used selectively for the purpose of purification of waste water. One of the important applications of chelating and functional polymers is their capability to recover metal ions from waste solution. Hence the chelating ion exchange property of the o-APUF terpolymer resin was also reported for specific metal ions. Pollution by toxic heavy metals due to their toxicities in relatively low concentration and tendency to bioaccumulation in the ecosystem, agriculture and human body has received wide spread attention in recent years. Various approaches such as ion-exchange, reverse osmosis, electro dialysis, precipitation and adsorption techniques have been developed for the removal and recovery of the metal ions from sewage and industrial wastewater. Among these techniques, many research works have focused on metal ions removal by adsorption on chelating polymers, because they are reusable, easily separable, and with higher adsorption capacity and selectivity having physical and chemical stabilities [15-16].

The present study deals with the synthesis and characterization of o-aminophenol-urea-formaldehyde [o-APUF] terpolymer resin by spectral methods for the first time. The synthesized terpolymer was characterized by elemental analysis, UV-VIS, FT-IR, H1 NMR, C13 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 terpolymer resin...
was also reported for specific metal ions. Some commercially available ion-exchange resins are given in Table 1.

**Experimental**

**Starting Materials**

The important chemicals (starting materials) like o-aminophenol, urea and formaldehyde used in the preparation of various new o-APUF terpolymer resins were procured from the market and were of chemically pure grade, and wherever necessary the purity was tested and confirmed by thin layer chromatography.

All the reagents were of the analytical grade and metal solutions were prepared by dissolving appropriate amount of the nitrates of the metals in double distilled water and standardized by EDTA titrations.

**Preparation of o-APUF Terpolymer Resin**

A mixture of o-aminophenol (1.09 gm, 0.1 mol), urea (0.70 gm, 0.1 mol), formaldehyde (7.5 ml, 0.2 mol) and 2M HCl (200ml) was taken in a round bottom flask, fitted with water condenser and heated in oil bath at 126 ± 2°C for 5 hrs with occasional shaking. The resinous solid product obtained was immediately remove from the flask as soon as reaction period was over and then purified.

The solid resinous product obtained was repeatedly washed with cold distilled water, dried in air and powdered with the help of mortar and pestle. The powdered sample was washed many times with boiling water to remove unreacted monomers. The air dried powdered then extracted with diethyl ether and then with petroleum ether to remove o-aminophenol-formaldehyde copolymer which might be present along with o-APUF terpolymer resin. It was further purified by dissolving in 8% NaOH solution, filtered and precipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated HCl/distill water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated thrice. The resulting polymer sample was filtered, washed several time with boiling water, dried in air, powdered and kept in vacuum over silica gel.

![Scheme 1. Formation of o-APUF-I terpolymer resin](image)

In the same way the other terpolymer resin viz. o-APUF-II, o-APUF-III and o-APUF-IV, were prepared with the molar proportion ratios of 2:1:3, 3:1:4 and 4:1:5 respectively using o-aminophenol, urea and formaldehyde as starting materials. The reaction and suggested structure of o-APUF-I terpolymer resin is depicted in Scheme 1 and elemental analysis is tabulated in Table 2.

**Characterization of the Terpolymer**

The terpolymer resins were subject to micro analysis for C, H and N on Elementar Vario EL III Carlo Erba 1108 elemental analyzer. The number average molecular weights \( \overline{M_n} \) were determined by conductometric titration in DMSO using ethanolic KOH as the titrant by using 25 mg of sample. A plot of the specific conductance against the milliequivallents of potassium hydroxide required for neutralization of 100 gm of terpolymer was made. Inspection of such a plot revealed that there were several 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 have to be determined.

\[
\text{Total milliquivalents of base required for complete neutralization} = \overline{M_n} = \frac{\text{Milliquivalents of base required for smallest interval}}{\overline{DP} \times \text{molecular weight of the repeating unit}}
\]

The intrinsic viscosities were determined using a Tuan-Fuoss viscometer at six different concentrations ranging from 0.3 wt % to 0.05 wt % of resin in DMSO at 30°C. Intrinsic viscosity (\( \eta \)) was calculated by the Huggin’s eq.(1) [19] and Kraemer’s eq.(2) [20].

In \( \eta_0/C = [\eta] + K_1 [\eta] C \) (1)

In \( \eta/C = [\eta] - K_2 [\eta] C \) (2)

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

Infrared spectra of o-APUF terpolymer resins were recorded in nujol mull with Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pellets in the range of 4000 – 500 cm⁻¹ at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Proton NMR and C¹³ NMR spectra were recorded with Bruker Adance – II 400 NMR spectrophotometer using DMSO-d₆ as a solvent, at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. The surface analysis was performed using scanning electron microscope at different magnifications, which is shown in Figure 6. SEM has been scanned by JEOL JSM-6380A Analytical Scanning Electron Microscope at VNIT, Nagpur (M.S.).

**Ion-exchange properties**

The ion-exchange properties of the o-APUF terpolymer resin was determined by the batch equilibrium method [21]. We studied the influence of various electrolytes, the rate of metal uptake and distribution of metal ions between the terpolymer and solutions. However, only the data for the o-APUF-I terpolymer resin are presented in this paper.

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

The terpolymer 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 using either 0.1 M HNO₃ or 0.1 M NaOH. The suspension was stirred for 24 h at 30°C. To this suspension 2 ml of 0.1 M solution of the metal ion was added and pH was adjusted to the required value. The mixture was again stirred at 30°C for 24 h. The polymer was...
then filtered off and washed with distilled water. The filtrate and the washing were collected and then the amount of metal ion was estimated by titrating against standard EDTA (ethylenediamine tetraacetic acid) at the same pH (experimental reading). The same titration has been carried out without polymer (blank reading). 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 [22-23]. Metal ion, its pH range, buffer and indicator used and colour change are given in Table 3. The metal ion uptake can be determined as:

\[
\text{Metal ion adsorbed (uptake) by resin} = \frac{(X-Y)}{Z} \ \text{mmol/g}
\]

Where \(Z\) (ml) is the difference between actual experimental reading and blank reading; \(X\) (mg) is metal ion in 2 ml 0.1 M metal nitrate solution before uptake; and \(Y\) (mg) is metal ion in 2 ml 0.1 M metal nitrate solution after uptake.

By using this equation the uptake of various metal ions by resin can be calculated and expressed in terms of millimols per gram of the terpolymer.

**Estimation of the Rate of Metal Ion Uptake as a Function of Time**

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 resins was determined from time to time at 30ºC (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 [24]. 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 and it can be defined by the following relationship:

\[
\text{Metal ion taken up at different times (\%) = Metal ion adsorbed / Metal ion adsorbed at equilibrium} \times 100
\]

The percent amount of metal ions taken up at different times is defined as: Percentage of metal ion adsorbed after 1 h = \((100X)/Y\)

Where \(X\) is mg of metal ion adsorbed after 1 h and \(Y\) is mg of metal ion adsorbed after 25 h. Then, by using this expression, the amount of metal adsorbed by polymer after specific time intervals was calculated and expressed in terms of percentage metal ion adsorbed. This experiment was performed using 0.1 M metal nitrate solution of Fe\(^{3+}\), Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\) and Pb\(^{2+}\).

**Evaluation of the Distribution of Metal Ions at Different pH Solutions**

The distribution of each of the seven metal ions i.e., Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Pb(II) and Fe(III) between the polymer phase and the aqueous phase was determined at 30ºC and in the presence of 1 M NaNO\(_3\) solution. The experiments were carried out as described above at different pH values. The distribution ratio, \(D\), is defined by the following relationship [25-26]...

\[
\Delta = \left( \frac{\text{Wt (in mg) of metal ions taken up by 1 gm of terpolymer}}{\text{Wt (in mg) of metal ions present in 1 ml of terpolymer}} \right)
\]

**Results and discussion**

The resin samples were dark brown in colour, insoluble in commonly used organic solvents, but were soluble in dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, and pyridine and concentrated H\(_2\)SO\(_4\). The resins synthesized do not show sharp melting point but undergo decomposition 420-425ºK. These resins were analyzed for carbon, hydrogen, and nitrogen content. The composition of terpolymer (represented in scheme 1) obtained on the basis of the elemental analysis data was found to be in good correlation, which is presented in Table 2.

The molecular weight \((M_n)\) of the terpolymer was determined by nonaqueous conductometric titration in DMSO against KOH in a 50% (v/v) DMSO/alcohol mixture using 100mg of resin sample. A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100g of terpolymer was made. The number average molecular weight \((M_n)\) could be obtained by multiplying the \(\Delta DP\) by the formula weight of the repeating unit. The results are shown in Table 2.

Viscometric measurements were carried out in DMSO at 30ºC. All resins showed normal behaviors. The intrinsic viscosity was determined by the Huggin’s [27] eq. (1) and Kraemer’s [28], eq. (2) are noted in Table 2. In accordance with the above relations, the plots of \(\eta_{splic}^\infty\) and against C were linear giving as slopes \(K_1\) and \(K_2\) respectively (Figure 1). The Intercept on the axis of viscosity function gave the \((\eta)\) value in both the plots. The values of \((\eta)\) obtained from both relations were in good agreement with each other. The values of Huggin’s and Kraemer’s constant \(K_1\) (0.28) and \(K_2\) (0.26) were determined from the slope of the graph and satisfy the condition of the relation \(K_1 + K_2 = 0.54\) favorably [30-31]. It was observed that terpolymer having higher average molecular weight \((M_n)\) shows a higher value of intrinsic viscosity [32].

![Figure 1. Viscometric plots of o-APUF terpolymer resins: (1) o-APUF-I, (2) o-APUF -II, (3) o-APUF -III and (4) o-APUF - IV](image)
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. $\Sigma_{\text{max}}$ higher values [32-33]. This observation is in good agreement with the proposed most probable structures of these terpolymer resins.

### Infrared Spectra

The IR spectra of all four o-APUF terpolymer resins are presented in Figure 3 and IR spectral data are tabulated in Table 4. The IR spectra revealed that all these terpolymers give rise to nearly similar pattern of spectra (Table 4). A broad band appear in the region 3450 – 3250 cm$^{-1}$ may be assigned to the stretching vibration of the phenolic hydroxyl groups exhibiting intermolecular hydrogen bonding [34]. The sharp band displayed at 1630 – 1680 cm$^{-1}$ may be due to the bending vibration of $\text{>C}=\text{O}$ group. The bond obtained at $\sim$ 1533 cm$^{-1}$ suggest the presence of $\text{>NH}$ (amido) group. A band appear in the reason of 1250 – 1340 cm$^{-1}$ show the presence of methlene bridges (<CH$_2$) in the polymer chain [35]. 1,2,3,4 and 5 pentasubstitution of aromatic ring is recognized from the bands appearing at $\sim$ 557.9 cm$^{-1}$

### Nuclear Magnetic Resonance Spectroscopy

The $^1$H NMR spectra of all o-APUF terpolymers are 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 (Table 5). The weak multiply signals appearing at 6.62 – 6.75 (δ)ppm may be due to the amido –CH$_2$ -NH-CO linkage [36-37]. A signal appeared in the region 4.07 – 4.98 (δ) ppm may be due to proton of methelicene 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. Except o-APUF-I and o-APUF-II terpolymer resin all the remaining two terpolymer resins exhibit signals in the region of 2.2 – 2.8 (δ) ppm which may be due to methelicene bridges of Ar – CH$_2$ – Ar linkage.

### 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 is shown in Figure 6 for o-APUF-I. It gives the information of surface topography and defect in the structure. The resin appeared to be dark drawn in colour. The morphology of polymer resin shows spherulites and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of o-APUF terpolymer 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. Thus by SEM micrographs morphology of the resin shows the transition between crystalline and amorphous nature, when compare to the other resin [39-40], the o-APUF terpolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.
presented in Table 6, 7 and 8. Eight metal ions Fe
study carried out with the terpolymer resin o-APUF-I is
APUF terpolymer resin. The result of the batch equilibrium
Batch equilibrium technique developed by Gregor et al. and
Ion-exchange properties
DeGeiso et al. was used to study of ion exchange propert y of o-
Effect of electrolytes and their concentration on the metal
various concentrations on the equilibrium of metal resin
medium. Among three variables, two were kept constant and
concentration of the metal ions in the aqueous solution which is
Table 7. As shaking time increases the polymer gets more time
rate of uptake of metal ion on o-APUF-I for adsorption, hence uptake of metal ions increases. Table 7
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 Table 8. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the
terpolymer resin o-APUF-I (Figure 11) increase with increasing
pH of the medium [22, 28, 31, 43-44]. 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 (Table 8). The selectivity
of Fe(III) ion is more for the o-APUF-I terpolymer resin as
can be compared 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 is helpful in selecting
the optimum pH for a selective uptake of a particular metal ca
tion exchange. Similarly for the separation of Fe(III) and Hg(II) at
the optimum pH is 2.5 with distribution ratio is 4865.6 and 85.62 respectively using the o-APUF terpolymer resin as ion
exchange. Similarly for the separation of Fe(III) and Hg(II) at
the optimum pH is 2.5 with distribution ratio is 4865.6 and 85.62 respectively for o-APUF terpolymer. 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.

On the basis of the nature and reactive, position of the
monomer, elemental analysis, electronic, FT-IR, H NMR, C NMR spectra, SEM and molecular weight, the most probable
structures have been proposed for all o-APUF terpolymer resins, as shown in Fig. 7.
Table 1. Commercially available ion-exchange resins

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Functional group</th>
<th>Polymer matrix</th>
<th>Ion-exchange Capacity (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite IR-120</td>
<td>-CH₂SO₃H, -CH₃SO₃H</td>
<td>Polystyrene</td>
<td>5.0-5.2</td>
</tr>
<tr>
<td>Duolite C-3</td>
<td>-COOH</td>
<td>Phenolic</td>
<td>2.8-3.0</td>
</tr>
<tr>
<td>Amberlite IRC-50</td>
<td>-OP(O)(OH)₂</td>
<td>Methacrylic</td>
<td>6.6</td>
</tr>
<tr>
<td>Dowex-226</td>
<td>-N(CH₃)₂Cl</td>
<td>Acrylic</td>
<td>10.00</td>
</tr>
<tr>
<td>Dowex-1</td>
<td>-N₃, -NHR, -NH₂</td>
<td>Polystyrene</td>
<td>3.5</td>
</tr>
<tr>
<td>Dowex A</td>
<td>-N₃, -NHR, -NH₂</td>
<td>Polystyrene</td>
<td>5.6</td>
</tr>
<tr>
<td>IRA-45</td>
<td>-N₃, -NHR, -NH₂</td>
<td>Epoxy-amine</td>
<td>5.8</td>
</tr>
<tr>
<td>Dowex-3</td>
<td>-N₃, -NHR, -NH₂</td>
<td>Epoxy-amine</td>
<td>8.2</td>
</tr>
<tr>
<td>Allassion A</td>
<td>-N₃, -NHR, -NH₂</td>
<td>Epoxy-amine</td>
<td></td>
</tr>
<tr>
<td>WB-3</td>
<td>-N₃, -NHR, -NH₂</td>
<td>Epoxy-amine</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Elemental analysis data, molecular weight determination and viscometric data of terpolymer of o-APUF terpolymer resins

<table>
<thead>
<tr>
<th>Terpolymers</th>
<th>Elemental analysis (%)</th>
<th>Molecular Weight [n]</th>
<th>Intrinsic Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc. Found</td>
<td>Calc. Found</td>
<td>Calc. Found</td>
</tr>
<tr>
<td>o-APUF-I</td>
<td>47.78</td>
<td>5.30</td>
<td>18.58</td>
</tr>
<tr>
<td>o-APUF-II</td>
<td>46.22</td>
<td>5.25</td>
<td>18.03</td>
</tr>
<tr>
<td>o-APUF-III</td>
<td>52.89</td>
<td>5.23</td>
<td>15.11</td>
</tr>
<tr>
<td>o-APUF-IV</td>
<td>56.30</td>
<td>5.96</td>
<td>15.11</td>
</tr>
<tr>
<td></td>
<td>62.12</td>
<td>5.80</td>
<td>15.42</td>
</tr>
<tr>
<td></td>
<td>64.63</td>
<td>5.92</td>
<td>15.68</td>
</tr>
<tr>
<td></td>
<td>63.20</td>
<td>5.69</td>
<td>15.08</td>
</tr>
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Table 3. Data of experimental procedure for direct EDTA titration

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Buffer used</th>
<th>Indicator used</th>
<th>Colour change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)</td>
<td>Dil.HNO₃/dil.NaOH</td>
<td>Varismine blue</td>
<td>Blue-Yellow</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>Dil.HNO₃/dil.NaOH</td>
<td>Fast sulphon black</td>
<td>Purple-Green</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>Ag.NH₃/Ag.NH₄Cl</td>
<td>Murexite</td>
<td>Yellow-Violet</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Ag.NH₃/Ag.NH₄Cl</td>
<td>Salochrom</td>
<td>Wine Red-Blue</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>Hexamine</td>
<td>Xylenol orange</td>
<td>Red-Yellow</td>
</tr>
<tr>
<td>Co(II)</td>
<td>Hexamine</td>
<td>Xylenol orange</td>
<td>Red-Yellow</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Hexamine</td>
<td>Xylenol orange</td>
<td>Red-Yellow</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>Hexamine</td>
<td>Xylenol orange</td>
<td>Red-Yellow</td>
</tr>
<tr>
<td>Ca⁴⁺</td>
<td>0.01</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.22</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.34</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.58</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Table 4. FT-IR Spectral data of o-APUF terpolymer resins

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Expected wave number (cm⁻¹)</th>
<th>Observed wave number (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH (phenolic)</td>
<td>3100-3500</td>
<td>3396 (b,sh)</td>
</tr>
<tr>
<td>&gt;CeO (ketonic and urea moiety)</td>
<td>1630-1680</td>
<td>1627.7 (w,sh)</td>
</tr>
<tr>
<td>&gt;NH (amido)</td>
<td>1533.6</td>
<td>1533.7 (sh,ct)</td>
</tr>
<tr>
<td>Aromatic ring</td>
<td>1445.2-1485</td>
<td>1445.2 (sh, m)</td>
</tr>
<tr>
<td>&gt;CH₃ (methine bridges)</td>
<td>1250-1340</td>
<td>1275.5-1353.9 (w, m)</td>
</tr>
<tr>
<td>-OH bending and C-O stretching</td>
<td>1050-1100</td>
<td>1098.7 (w)</td>
</tr>
</tbody>
</table>

Table 5. ¹H NMR spectral data of o-APUF terpolymer resins

<table>
<thead>
<tr>
<th>Chemical shift (δ ppm)</th>
<th>o-APUF-I</th>
<th>o-APUF-II</th>
<th>o-APUF-III</th>
<th>o-APUF-IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.88</td>
<td>8.79</td>
<td>8.78</td>
<td>8.78</td>
<td>8.78</td>
</tr>
<tr>
<td>6.60</td>
<td>6.62</td>
<td>6.74</td>
<td>6.74</td>
<td>6.74</td>
</tr>
<tr>
<td>4.60</td>
<td>4.69</td>
<td>4.07-4.98</td>
<td>4.44-4.55</td>
<td>4.55</td>
</tr>
<tr>
<td>8.26</td>
<td>8.32</td>
<td>8.29</td>
<td>8.32</td>
<td>8.32</td>
</tr>
</tbody>
</table>

Table 6. Evaluation of the effect of different electrolytes on the uptake of several metal ions by o-APUF-I terpolymer resin

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>pH</th>
<th>Weight of metal ion (mgs⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe³⁺</td>
<td>2.5</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>4.5</td>
<td>0.08</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>6.0</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>5.0</td>
<td>0.01</td>
</tr>
</tbody>
</table>
of the o-APUF terpolymer resins were confirmed by the SEM studies and reveals that the terpolymers can act as an effective ion exchanger for various trivalent and divalent metal ions such as Fe\(^{3+}\), Cd\(^{2+}\), Cu\(^{2+}\), Hg\(^{2+}\), Zn\(^{2+}\) and Pb\(^{2+}\) ions. Since o-APUF terpolymer contain phenolic (-OH) group and amino (-NH\(_2\)) group, it play a key role in the ion exchange phenomenon, because of its higher tendency of capturing metal ions. Thus o-APUF terpolymer has immense applications as an ion exchange resin in waste water treatment, metal recovery and for the identification of specific metal ions. Due to considerable differences in the uptake capacities at different pH and media of electrolyte, and the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to separate particular metal ions from their admixtures by this technique.

The terpolymer showed higher selectivity for Fe\(^{3+}\), Cd\(^{2+}\) and Co\(^{3+}\) than for Cu\(^{2+}\), Hg\(^{2+}\), Zn\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) ions.

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