ABSTRACT

Chelating Ion-exchange Properties of Copolymer Resins Derived from \( p \)-Cresol, Oxamide and Formaldehyde

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Copolymer resins (\( p \)-COF) synthesized by the condensation of \( p \)-cresol and oxamide 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 copolymers 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 copolymer 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 copolymer showed a higher selectivity for Fe(III), Cu(II) and Ni(II) ions than for Co(II), Zn(II), Cd(II) and Pb(II) ions. Distribution ratios (\( D \)) of metal ions were found to be increased by increasing pH of the solutions; hence the resin can be used to recover certain metal ions from waste solutions and used for the purpose of purification of waste water and removal of iron from boiler water. The ion-exchange capacity of metal ions has also been determined experimentally and compared with other commercial resins. Besides ion-exchange properties, the copolymer resins were also characterized by viscometric measurements in dimethyl sulphoxide (DMSO), UV-visible absorption spectra in non-aqueous medium, infra-red spectra and nuclear magnetic resonance spectra. The physico-chemical and spectral methods were used to elucidate the structures of \( p \)-COF resins. The morphology of the copolymers 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.

INTRODUCTION

Ion-exchange technique can remove traces of ionic impurities from water/process liquors to give a product of ultra pure quality in a simple efficient and techno-economically viable manner. Ion-exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotic purification and separation of radioisotopes and find large applications in water treatment and pollution control \cite{1,2}. Various hydroxyl benzoic acid-formaldehyde and 4-hydroxy-acetophenone-biuret-formaldehyde copolymers have been reported and found to be useful as ion-exchangers \cite{3-5}. In an earlier communication \cite{6-8} from this department a number of such copolymers have been reported. However, no work has been carried...
out on the synthesis, characterization and ion-exchange properties of the copolymer resins from \( p \)-cresol, oxamide and formaldehyde. The purpose of present study, is to explore the adsorption behaviour of seven metal ions \( \text{Fe}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+}, \text{CO}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+} \) and \( \text{Pb}^{2+} \) on the newly synthesized copolymer resins \( p \)-COF-1 at different pH values, different concentrations of different electrolytes and at different shaking time intervals. The adsorption behaviour of these metal ions are based on the affinity differences towards the chelating resins as functions of pH, electrolyte concentrations and shaking time. The copolymer 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 \( p \)-COF copolymer 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 [9,10].

The present paper describes the development of a novel ion-exchanger resin process suitable for the desalination of waste water which is high in \( \text{Fe(III)}, \text{Ni(II)} \) and \( \text{Cu(II)} \) ions, to meet effluent discharge specifications. Ion-exchange column of \( p \)-COF copolymer resin can be used for removal of the iron, nickel and copper metal ions as well as suspended solids in waste water. It can also be used in the removal of iron from boiler water in industries [11]. The resin can also be used for the removal of iron and zinc from brass. There are many useful reports on ion-exchange separation methods in chemical processes [12,13]. Some commercially available ion-exchange resins are given in Table 1.

### EXPERIMENTAL

#### Materials

The chemicals used were all of analytical grades or chemically pure grades and are procured from the market.

#### Synthesis of \( p \)-COF Copolymer Resin

The \( p \)-COF-1 copolymer resin was prepared by condensing \( p \)-cresol (1.08 g, 0.1 mol) and oxamide (0.88 g, 0.1 mol) with formaldehyde (7.4 mL of 37% solution, 0.2 mol) in the presence of 2 M HCl (200 mL) as a catalyst at 130°C in an oil bath for 5 h with occasional shaking to ensure thorough mixing.
Scheme 1. Synthesis of representative \( p \)-COF-1 copolymer resin.

The solid resinous product obtained was removed immediately from the flask. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove unreacted monomers. Then it was extracted with diethyl ether to remove excess of \( p \)-cresol-formaldehyde copolymer which might be present along with \( p \)-COF copolymer resin. The purified copolymer resin was finely ground and kept in a vacuum over silica gel. The yield of the copolymer resin was found to be 80%.

Similarly, the other copolymer resins, \( p \)-COF-2, \( p \)-COF-3 and \( p \)-COF-4 were synthesized by varying the molar proportion of the starting materials i.e., \( p \)-cresol, oxamide and formaldehyde in the ratios of 2:1:3, 3:1:4 and 4:1:5, respectively. The details of the reaction, structure (Scheme 1) and elemental analysis are depicted in Table 2.

Characterization of the Copolymers
The viscosities were determined by using Taun-Fuoss viscometer at six different concentrations ranging from 1.00 to 0.031% of copolymer in DMSO at 30°C. The intrinsic viscosity \([\eta]\) was calculated by relevant plots of the Huggins’ equation and Kraemmer’s equation similar to earlier coworkers [9,10].

The number average molecular weights \( (M_n) \) were determined by conductometric titration in non-aqueous medium such as dimethylsulphoxide (DMSO) using ethanolic KOH as a titrant. From the graphs of specific conductance against milliequivalent of the base, first and last breaks were noted from which the degree of polymerization (DP) and the number average molecular weight \( (M_n) \) have been calculated for each copolymer resins.

Electron absorption spectra of all copolymer resins in DMSO (spectroscopic grade) were recorded on a Shimadzu double beam spectrophotometer in the range of 200 to 850 nm at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh, infrared spectra of four \( p \)-COF copolymer resins were recorded on a Perkin-Elmer-983 spectrophotometer in KBr pellets in the wavenumber region of 4000-400 cm\(^{-1}\) at SAIF, Punjab University, Chandigarh, nuclear magnetic resonance (NMR) spectra of newly synthesized copolymer resins have been scanned on a Bruker Advanced 400 NMR spectrometer using DMSO-d\(_6\) at sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh. SEM has been scanned by a FEI-Philips XL-30 electron microscope.

Ion-exchange Properties
The ion-exchange properties of the \( p \)-COF copolymer resins were determined by the batch equilibrium method [15]. The ion-exchange properties of all the

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### Table 2. Synthesis and physical data of \( p \)-COF copolymer resins.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>( p )-Cresol (mol)</th>
<th>Oxamide (mol)</th>
<th>Formaldehyde (mol)</th>
<th>Catalyst (2 M HCl) (mL)</th>
<th>Yield (%)</th>
<th>Colour</th>
<th>Melting point (K)</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p )-COF-1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>200</td>
<td>80</td>
<td>Yellow</td>
<td>388</td>
<td>59.31</td>
</tr>
<tr>
<td>( p )-COF-2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>200</td>
<td>75</td>
<td>Yellow</td>
<td>391</td>
<td>63.50</td>
</tr>
<tr>
<td>( p )-COF-3</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>200</td>
<td>80</td>
<td>Yellow</td>
<td>394</td>
<td>67.78</td>
</tr>
<tr>
<td>( p )-COF-4</td>
<td>0.4</td>
<td>0.1</td>
<td>0.5</td>
<td>200</td>
<td>80</td>
<td>Yellow</td>
<td>398</td>
<td>70.11</td>
</tr>
</tbody>
</table>
four resins have been studied. However, only the data for the \( p \)-COF-1 copolymer resin are presented in this paper.

**Determination of Metal Uptake in the Presence of Various Electrolytes and 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 using either 0.1 M HNO\(_3\) or 0.1 M NaOH. The suspension was stirred for 24 h at 30\(^\circ\)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\(^\circ\)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 [14,15]. 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:

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

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 copolymer.

**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 30\(^\circ\)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 [15]. 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:

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

The percent amount of metal ions taken up at different times is defined as:

\[
\text{Percentage of metal ion adsorbed after 1 h} = \frac{(100X)}{Y}
\]

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 uptake.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>pH range</th>
<th>Buffer</th>
<th>Indicator</th>
<th>Colour change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)</td>
<td>2-3</td>
<td>Dil. HNO(_3)/dil. NaOH</td>
<td>Varieamine blue</td>
<td>Blue-yellow</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>9-10</td>
<td>Dil. HNO(_3)/dil. NaOH</td>
<td>Fast sulphone black</td>
<td>Purple-green</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>7-10</td>
<td>Aq. NH(_3)/NH(_4)Cl</td>
<td>Murexide</td>
<td>Yellow-violet</td>
</tr>
<tr>
<td>Co(II)</td>
<td>6</td>
<td>Hexamine</td>
<td>Xylenol orange</td>
<td>Red-yellow</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>10</td>
<td>Aq. NH(_3)/NH(_4)Cl</td>
<td>Salochrom black</td>
<td>Wine red-blue</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>5</td>
<td>Hexamine</td>
<td>Xylenol orange</td>
<td>Red-yellow</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>6</td>
<td>Hexamine</td>
<td>Xylenol orange</td>
<td>Red-yellow</td>
</tr>
</tbody>
</table>

Table 3. Data of experimental procedure for direct EDTA titration.
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 [16].

\[
D = \frac{\text{Amount of metal ion on resin}}{\frac{\text{Volume of solution (mL)}}{\text{Weight of resin (g)}}} \times \frac{\text{Amount of metal ion in resin}}{\text{Amount of metal ion in solution}}
\]

Metal ion adsorbed by the resin = \(\frac{ZX}{Y} \times 0.025\)

where \(Z\) is the difference between actual experimental reading and blank reading, \(C\) (g) is the amount of metal ion in 2 mL 0.1 M metal nitrate solution, and \(Y\) (g) is the amount of metal ion in 2 mL of metal nitrate solution after uptake.

RESULTS AND DISCUSSION

The four new copolymer resins \(p\)-COF were synthesized by condensing \(p\)-cresol and oxamide with formaldehyde in the presence of 2 M HCl as catalyst in an oil bath for 5 h in the molar ratios of 1:1:2, 2:1:3, 3:1:4 and 4:1:5. All four \(p\)-COF copolymer resins were found to be yellow in colour. The copolymers are soluble in DMF, DMSO and are insoluble in almost all other organic solvents. The melting points of these resins were found to be in the range of 118-130ºC. These resins were analyzed for carbon, hydrogen and nitrogen content. The \(p\)-COF-I copolymer which has been used in the present investigation was prepared by the reaction given in Scheme I. The details of the copolymer synthesis along with colour test, melting point, yield and elemental analysis are presented in Table 2.

Viscometric Study

Viscometric measurements were carried out in DMSO solutions at 30ºC using a Tuan-Fuoss [9] viscometer fabricated in our research laboratory at different concentrations ranging from 1.00 to 0.031%. Intrinsic viscosity (\(\eta\)) was calculated from relevant plots of Huggins’ eqn (1) and Kraemer’s eqn (2) [10].

\[
\eta / C = [\eta] + k_1 [\eta] C
\]

In:

\[
\eta / C = [\eta] - k_2 [\eta] C
\]

where \(C\) is concentration in g/100 mL; \(\eta_r\) is the ratio between viscosity of solution [\(\eta\)] and viscosity of the solvent [\(\eta_0\)] that is known as relative viscosity: \(\eta_r = \eta / \eta_0\); \(\eta_{sp}\) has been derived from relative viscosity and given by \(\eta_{sp} = (\eta - \eta_0) / \eta_0 = \eta / \eta_0 - 1 = \eta_r - 1\); \([\eta]\) is intrinsic viscosity obtained by extrapolating of a plot of \(\eta_{sp}/C\) or \(\ln \eta_r / C\) against concentration; and \([\eta]\) is \(\lim(\eta_{sp} / C)\). The intrinsic viscosity is characteristics of a polymer.

According to the above relations, the plots of \(\eta_{sp}/C\) and \(\ln \eta_r / C\) against concentration are linear with slopes \(k_1\) and \(k_2\), respectively (Figure 1). Intercepts on the viscosity function axis give \([\eta]\) value in both plots. The calculated values of the constants \(k_1\) and \(k_2\) (Table 4) in most cases satisfy the relation of \(k_1 + k_2 = 0.5\), favourably [15]. It was observed that copolymer having higher average molecular weight (\(M_n\)) shows a higher value of intrinsic viscosity \([\eta]\).

Average Molecular Weight

The number average molecular weight (\(M_n\)) of these copolymers has been determined by conductometric titration method in non-aqueous medium and using standard potassium hydroxide (0.05 M) in absolute ethanol as a titrant. The results are depicted in Table 4. The specific conductance was plotted against milliequivalents of ethanolic KOH required for
neutralization of 100 g of each copolymer. There are several breaks before the complete neutralization of all phenolic hydroxyl groups [18]. The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average of phenolic hydroxy group of each chain was neutralized. From the plot, the first and final breaks were recorded. The average degree of polymerization ($\bar{DP}$) and the number average molecular weight ($M_n$) of all copolymers have been determined as given below:

$$\bar{DP} = \frac{\text{total milliequivalent of base required for complete neutralization}}{\text{milliequivalents of base required for smallest interval}}$$

$$M_n = \bar{DP} \times \text{repeat unit weight}$$

It is observed that the molecular weights of copolymers increase with increase in $p$-cresol content. This observation is in agreement with the trend observed by earlier workers [17,18].

**Electronic Spectra**

The UV-visible spectra (Figure 2) of all $p$-COF copolymer samples in pure DMSO were recorded in the region of 200-850 nm at a scanning rate of 100 nm.min$^{-1}$ and a chart speed of 5 cm.min$^{-1}$. All the four $p$-COF copolymer samples displayed two characteristic broad bands at 325-335 and 260-285 nm. Both of these bands seem to be merged with each other because of their very broad nature. These observed positions for the absorption bands indicate the presence of a carbonyl (C=O; ketonic) group having a carbon-oxygen double bond in conjugating with $-NH$ group. The former band (more intense) can be accounted for by $n \rightarrow \pi^*$ transition while the latter band (less intense) may be due to $\pi \rightarrow \pi^*$ transition [13]. The bathochromic shift (shift towards longer wavelength from the basic values of $>\text{C}=\text{O}$ group viz. 320 and 240 nm, respectively may be due to the combined effect of conjugation of $>\text{C}=\text{O}$ and $NH$
groups and phenolic hydroxyl group (auxochrome) and phenyl ring [17]. It may be observed from the UV-visible spectra of \( p \)-COF copolymers that the absorption intensity gradually increases in the order \( p \)-COF-1 < \( p \)-COF-2 < \( p \)-COF-3 < \( p \)-COF-4. The observed increasing order may be due to the introduction of more chromophore (>\(\text{C}=\text{O}\) groups) and auxochrome (phenolic -\(\text{OH}\)) in the repeat unit structure of the copolymers.

**Infrared Spectra**

Infrared spectra of the \( p \)-COF copolymer resins are shown in Figure 3 and IR spectral data are tabulated in Table 4. From the IR spectral studies, it has been revealed that all the four \( p \)-COF copolymers give rise to nearly similar spectral patterns. Very broad band appeared in the region 3220-3230 cm\(^{-1}\) may be assigned to the stretching vibration of phenolic -\(\text{OH}\) groups exhibiting intermolecular hydrogen bonding between -\(\text{OH}\) and >\(\text{C}=\text{O}\) and NH group of amide [18]. The bands obtained at 1200-1220 cm\(^{-1}\) suggest the presence of methylene (-\(\text{CH}_2\)) bridges. A sharp strong peak at 1502-1503 cm\(^{-1}\) may be ascribed to aromatic skeletal ring breathing modes. The 1,2,3,5-tetrasubstitution of aromatic benzene ring can be recognized from sharp and medium/weak absorption bands appeared at 910-990, 1097-1098, 1148-1149 and 1220-1260 cm\(^{-1}\), respectively. The presence of C-H stretching of aromatic ring may be assigned as a sharp and strong band at 3010-3011 cm\(^{-1}\) which seems to be merged with a very broad band of phenolic hydroxy group.

**Nuclear Magnetic Resonance Spectroscopy**

The NMR spectra of all the four copolymers given in Figure 4 were scanned in DMSO-d\(_6\). The spectral data are given in Table 5. From the spectra, it is revealed that all \( p \)-COF copolymers give rise to different patterns of NMR spectra, since each \( p \)-COF copolymer possesses a set of protons having different electronic environment. The chemical shift
Table 4. Molecular weight determination, viscometric date, and IR frequencies of the p-COF copolymer resins.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Empirical formula of repeat unit</th>
<th>Empirical weight of repeat unit (g)</th>
<th>Average degree of polymerization ((\bar{D}))</th>
<th>Average molecular weight ((\bar{M}_n))</th>
<th>Intrinsic viscosity [(\eta)] (dL/g)</th>
<th>Huggins' constant ((k_1))</th>
<th>Kraemer's constant ((k_2))</th>
<th>(k_1 + k_2)</th>
<th>Important IR frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-COF-1</td>
<td>C_{13}H_{15}N_2O_4</td>
<td>263</td>
<td>23.22</td>
<td>6106</td>
<td>0.44</td>
<td>0.253</td>
<td>0.251</td>
<td>0.504</td>
<td>3220-3230 b,st &gt;OH phenol</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>3010-3011 b,st &gt;CH stretching of aromatic ring.</td>
</tr>
<tr>
<td>p-COF-2</td>
<td>C_{19}H_{23}N_2O_5</td>
<td>359</td>
<td>24.11</td>
<td>8655</td>
<td>0.98</td>
<td>0.258</td>
<td>0.255</td>
<td>0.513</td>
<td>2916-2917 b,st Intramolecular hydrogen bonding</td>
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<td></td>
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<td></td>
<td>1606-1607 sh,st &gt;C=O group of oxamide</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1502-1503 Aromatic ring</td>
</tr>
<tr>
<td>p-COF-3</td>
<td>C_{27}H_{30}N_2O_6</td>
<td>478</td>
<td>25.00</td>
<td>11950</td>
<td>1.50</td>
<td>0.261</td>
<td>0.253</td>
<td>0.514</td>
<td>1480-1482 sh,st &gt;CH_2 bending (scissoring)</td>
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<td></td>
<td></td>
<td></td>
<td>1378-1379 sh,st &gt;CH_2 bending (twisting and wagging)</td>
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<td></td>
<td>1200-1220 sh,st &gt;CH_2, i.e., methyl bridge</td>
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<td></td>
<td></td>
<td>1286-1290 sh,st &gt;CH_2 (plane bending)</td>
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<td></td>
<td></td>
<td></td>
<td>910-990 sh, w 1,2,3,5 substitution in benzene skeleton</td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1097-1098 b,m 1148-1149</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1220-1260</td>
</tr>
</tbody>
</table>

sh: sharp, b: broad, st: strong, m: medium, w: weak.

Table 5. \(^1\)H NMR spectral data of p-COF copolymer resins.

<table>
<thead>
<tr>
<th>Observed chemical shift ((\delta), ppm)</th>
<th>Nature of proton assigned</th>
<th>Expected chemical shift ((\delta), ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-COF-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.20</td>
<td>-CH_2-C=moiety</td>
<td>1.00 to 1.50</td>
</tr>
<tr>
<td>2.16</td>
<td>Methyl proton Ar-CH_3 group</td>
<td>2.00 to 3.00</td>
</tr>
<tr>
<td>2.80</td>
<td>CH_2-N&lt; moiety</td>
<td>2.3 to 3.8</td>
</tr>
<tr>
<td>3.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.59</td>
<td>Methylene proton of Ar-CH_2 moiety</td>
<td>2.00 to 3.00</td>
</tr>
<tr>
<td>3.37</td>
<td>Methylene proton of Ar-CH_2-N moiety</td>
<td>3.00 to 3.5</td>
</tr>
<tr>
<td>4.61</td>
<td>&gt;CH-O</td>
<td>4.00 to 5.00</td>
</tr>
<tr>
<td>5.25</td>
<td>Proton of -NH bridge</td>
<td>5.00 to 8.00</td>
</tr>
<tr>
<td>6.78</td>
<td>Terminal methylene</td>
<td>6.2 to 8.5</td>
</tr>
<tr>
<td>7.31</td>
<td>Aromatic proton (Ar-H)</td>
<td>7.00 to 8.50</td>
</tr>
<tr>
<td>8.80</td>
<td>Proton of phenolic -OH involved in intramolecular hydrogen bonding</td>
<td>8.00 to 12.00</td>
</tr>
</tbody>
</table>

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(δ, ppm) observed is assigned on the basis of data available in literature [19]. All the p-COF copolymer samples show an intense weakly multiplet signals at 2.16-2.17 ppm (δ) may be attributed to methyl proton of Ar-CH₃ group. The medium singlet at 2.53-2.59 ppm (δ) may be due to the methylene proton of Ar-CH₂ bridge. The singlet obtained in the region of 3.47 ppm (δ) may be due to the methylene proton of Ar-CH₂-N moiety. The signals in the region of 5.23 ppm (δ) are attributed to protons and -NH bridge. The weak multiplet signals (unsymmetrical pattern) in the region of 6.93-6.98 ppm (δ) may be due to terminal methylene group. The signals in the range of 7.54-7.92 ppm (δ) may be due to phenolic hydroxy protons. The much downfield chemical shift for phenolic -OH indicates clearly the intramolecular hydrogen bonding on -OH group [20]. The signal at 0 ppm (δ) is due to TMS (tetramethylsilane), the signal at 1.20-1.21 ppm (δ) may due to -CH₃-C moiety. The signal at 2.80-2.81 ppm (δ) and 3.37-3.35 ppm (δ) may be due to CH₂-N< moiety. The signal at 4.60-4.20 ppm (δ) may be due to >CH-O group. The signal at 7.30-7.31 ppm (δ) may be due to aromatic proton (Ar-H).

Scanning Electron Microscopy
Figure 5 shows the SEM [27] micrograph of the pure p-COF-1 copolymer sample at 3000× magnification. The morphology of resin exhibits growth of crystals from polymer solutions corresponding to the most prominent organization in polymers on a large scale such as a size of few millimeters spherulites. The morphology of resin shows a fringed micelle model of the crystalline-amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. The micrograph of pure sample shows the presence of crystalline-amorphous layered morphology which is the characteristic of polymer. The monomers have crystalline structure but during condensation polymerization some crystalline structures are transformed into amorphous morphology.

On the basis of the nature and reactive position of the monomers, elemental analysis, UV-visible, IR, NMR spectral studies and taking into consideration the linear structure of other phenol-formaldehyde and the linear branched nature of urea-formaldehyde polymers, the most probable structure proposed for p-COF-1 copolymer resin, is shown in Scheme I. The morphology of the resin shows the transition between crystalline and amorphous nature. When compared to the other resin [14], the p-COF copolymer resin is more amorphous hence it has higher metal ion-exchange capacity.

Ion-exchange Properties
Batch equilibrium technique developed by Gregor et al. and De Geiso et al. were used to study ion-exchange properties of p-COF-1 copolymer resin. The results of the batch equilibrium study carried out with the copolymer p-COF-1 are presented in Figures 6-15. Seven metal ions Fe³⁺, Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ in the form of aqueous metal nitrate solution were used.

Figure 5. SEM micrograph of p-COF-1 terpolymer resin.

Figure 6. Uptake of Fe³⁺, Cu²⁺, Zn²⁺ metal ions by p-COF-1 terpolymer resin versus concentration of NaNO₃ electrolyte solution.
[M(NO₃)₂] = 0.1 mol/L; volume = 2 mL; volume of electrolyte solution = 25 mL; weight of resin = 25 mg; time = 24 h; room temperature.

**Figure 7.** Uptake of Ni²⁺, Co²⁺, Cd²⁺ and Pb²⁺ metal ions by p-COF-1 terpolymer resin versus concentration of NaNO₃ electrolyte solution.

The experiments were repeated six times and the mean standard deviations were calculated at different concentrations, shaking times and pH of the solutions.

The ion-exchange study was carried out using three experimental variables: (a) electrolyte and its ionic strength, (b) uptake time and (c) pH of the aqueous medium. Among these three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymers similar to the earlier co-workers [4-7]. The details of experimental procedure are given below.

**Effect of Electrolyte and its Ionic Strength on Metal Uptake**

We examined the influence of NO₃⁻ and SO₄²⁻ at various concentrations on the equilibrium of metal-resin interaction. Figures 6-10 show that the amount of metal ions taken up by a given amount of copolymer depends on the nature and concentration of the electrolyte present in the solution. Generally as concentration of the electrolyte increases, the ionization decreases, number of ligands (negative ions of electrolyte) decrease in the solution which forms the complex with less number of metal ions and therefore more ions may be available for adsorption. Hence, upon increased concentration the uptake of metal ions may be increased, which is the normal trend. But this normal trend may be disturbed due to the formation of stable complex with higher number of metal ions with electrolyte ligands, which decrease the number of metal ions available for adsorption, and hence uptake decreases.

Electrolyte solution + metal ion solution + polymer → electrolyte ligand - metal ion chelates + polymer - metal ion chelates

If electrolyte ligand-metal ion complex is weak relative to polymer metal ion chelates, then more metal ion can enter complexation with polymer, hence uptake of metal ion is increased. But if this complex is stronger than polymer-metal ion chelates, then more
metal ions form strong complexes with electrolyte ligand which make metal uptake capacity to be lowered by polymer.

In the presence of nitrate ions, the uptake of Fe(III), Cu(II) and Ni(II) ions increases with increasing concentration of the electrolytes, whereas in the presence of sulphate ions the amount of the above mentioned ions taken up by the copolymer decreases with increasing concentration of the electrolyte [21,22]. Moreover, the uptake of Co(II), Zn(II), Cd(II) and Pb(II) ions increases with decreasing concentration of the nitrate and sulphate ions. This may be explained on the basis of the stability constants of the complexes with those metal ions [21]. The ratio of physical core structure of the resin is significant in the uptake of different metal ions by the resin polymer. The amount of metal ion uptake by the p-COF-1 copolymer resin is found to be higher when comparing to the other polymeric resins [22,23].

**Estimation of the 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 attained to operate as close to equilibrium conditions as possible. As shaking time increases the polymer has more time for adsorption, hence uptake increases at longer time. Figures 11-13 show the dependence of the rate of metal ion uptake on the nature of the metal. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given polymer. The result shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of the metal ion under given conditions. It is found that Fe(III) ions require about 3 h for the establishment of the equilibrium, whereas Cu(II), Ni(II), Co(II) and Zn(II) ions required about 5 or 6 h [7,8]. Thus the rate of metal ions uptake follows the order Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II) > Pb(II) for all the copolymers [21,22]. The rate of metal uptake may depend upon hydrated redii of
metal ions. The rate of uptake for the post transition metal ions exhibits another trend for Cd(II), which is comparable to that of Pb(II) because of difference in 'd' orbital.

Distribution Ratios of Metal Ions at Different pH solutions

The effect of pH on the amount of metal ions distributed between two phases can be explained by Figures 14 and 15. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ion taken up by the p- COF copolymer increases at higher pH of the medium [23,24]. The magnitude of increase, however, is different for different metal cations. The study was carried from pH 2.5 to 6.5 to prevent hydrolysis of metal ions at higher pH. For metal ion Fe3+ the highest working pH is 3, where distribution ratio is medium, since Fe3+ forms octahedral complex with electrolyte ligand, showing crowding effect (steric hindrance), which may lower the distribution ratio of Fe3+ ions. The value of distribution ratio at particular pH thus depends upon the nature and stability of chelates with a particular metal ion. The data of distribution ratio show a random trend in certain cases [22]. This may be due to the amphoteric nature of the p-COF resin.

From the results it is revealed that with decrease in atomic number, the ion uptake capacity is increased. In case of Cd(II) and Pb(II) purely electrostatic factors are responsible. The ion uptake capacity of Cd(II) is lower than that of Cu(II) owing to the larger size of its hydrated ion. The steric influence of the methyl group and hydroxyl group in p-COF 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 higher selectivity towards Cu2+ and Ni2+ ions at pH 4.0 to 6.0 compared to the other ions which form rather weak complexes. While at pH 3 the copolymer has more selectivity towards Fe3+ ions. The order of distribution ratio of metal ions measured at pH range of
2.5 to 6.5 is found to be Fe(III) > Cu(II) > Ni(II) > Zn(II) > Co(II) > Pb(II) > Cd(II). Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions [20]. For example, the result suggests the optimum pH 6.0, for the separation of Co(II) and Ni(II) with distribution ratio, at 415.4 and 854.4, respectively using the \( p \)-COF copolymer resin as ion-exchanger. Similarly, for the separation of Cu(II) and Fe(III) the optimum pH is 3, at which the distribution ratio, for Cu(II) is 66.1 and that for Fe(III) is 341.5. The lowered distribution of Fe(III) was found to be small and, hence, efficient separation could be achieved [23-25].

The strength of ion-exchange capacities of various resins can be studied by comparing their ion-exchange capacities. 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 \( p \)-COF copolymer has been calculated, which was found to be 4.3 mmol.g\(^{-1}\) and it indicates that \( p \)-COF copolymer resin is a better ion-exchanger than commercial phenolic and some polystyrene ion-exchangers.

For the strongly acidic cation exchange resin such as cross-linked polystyrene sulphonic acid resins, the ion-exchange capacity is virtually independent of the pH of the solutions. For weak acid cation exchangers, such as those containing carboxylate groups, ionizations occur only in alkaline solution. Similarly weakly basic cation exchanger does not work above pH 9.

**CONCLUSION**

A terpolymer \( p \)-COF-1 based on the condensation reaction of \( p \)-cresol and oxamide with formaldehyde in the presence of acid catalyst was prepared. \( p \)-COF is a selective chelating ion-exchange terpolymer resin for certain metals. The terpolymer resin showed a higher selectivity for Fe\(^{3+}\), Cu\(^{2+}\) and Ni\(^{2+}\) ions than for Co\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\) and Pb\(^{2+}\) ions. The uptake of some metal ions by the resin was carried out by the batch equilibrium technique. The uptake capacities of metal ions by the terpolymer resin were pH dependent. From the results of distribution coefficients, it can be observed that Cu(II) has higher value of distribution ratio. 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.

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**SYMBOLS AND ABBREVIATIONS**

- \( D \): Distribution ratio
- \( \eta \): Intrinsic viscosity
- \( \overline{DP} \): Degree of polymerization
- \( \overline{M}_n \): Number average molecular weight
- \( I \): Chemical shift
- \( k_1 \): Huggins' constant
- \( k_2 \): Kraemmer's constant
- \( p \)-COF: \( p \)-cresol-oxamide-formaldehyde copolymer

**REFERENCES**
