

Sorption Investigation on the Removal of Metal Ions from Aqueous Solutions using Copolymer Resin

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Abstract-- Copolymer resin (2,4-DHPOF) was synthesized by the condensation of 2,4-dihydroxypropiophenone and oxamide with formaldehyde in the presence of acid catalyst using varied molar ratios of reacting monomers. Copolymer ligand compositions have been determined on the basis of their elemental analysis. Also the number average molecular weight of these copolymers was determined by conductometric titration in non-aqueous medium. IR-spectra were studied to elucidate the structure. The copolymers have been further characterized by absorption spectra in non-aqueous medium and nuclear magnetic resonance spectra. The newly synthesized copolymers (2,4-DHPOF) are proved to be a selective chelating ion exchange polymer for certain metals. Chelating ion exchange properties of these copolymers were studied for Fe (III), Hg (II), Pb (II), Ni (II) and Cu (II) ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurement 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 and a media of various ionic strengths. The copolymers showed a wide higher selectivity for Fe (III), Hg (II) and Pb (II) ions than for Ni (II) and Cu (II) ions.

Keywords: Copolymer; Degree of polymerization; Polycondensation; Ion-exchanger; Synthesis, Resin.

I. INTRODUCTION

The treatment of industry wastes has been a strong concern as it continues to grow day by day. One category of such industrial pollutants includes heavy metals, often contained in the wastewater. When released into the environment, these metals can cause severe damage to the human body, including accumulative poison. The treatment of industry wastes has been a strong concern as it continues to grow day by day. One category of such industrial pollutants includes heavy metals, often contained in the wastewater. When released into the environment, these metals can cause severe damage to the human body, including accumulative poison, brain damage, and cancer [1]. Several processes were accessible for heavy metal removal, including chemical precipitation, membrane, and retention technique [2]. An effective technique to separate the selective metal ions from wastes was greatly found to be ion-exchange process. Ion-exchange resins are polymers that can reversibly interchange the counter ions. The resins are organized into two main types depending upon the charge of the counter ions with which they can exchange. The cationic exchangers contain the negatively ionisable group which is capable of interchanging the positively charged or cationic counter ion. The anionic exchange resin interchanges the negatively charged or anionic counter ion due to the existence of the positively ionisable group. Polymeric resin was synthesized and reported for its ion-exchange characteristics towards selective metal ions

The literature survey reveals that copolymers based on 4-hydroxybenzophenone and its derivatives have received attention due to their application in various areas such as in waste water treatment, for metal recovery, in protective coating and in biological activity [3].

Ion-exchangers are widely used for the treatment of radioactive wastes from nuclear power stations [4,5]. The chelation ion-exchange behavior of poly (2-hydroxy, 4-acryloyloxybenzophenone) resin towards the divalent metal ions were studied by batch equilibrium method as a function of time and pH [6]. A cross linked styrene/meleic acid chelating matrix has been reported for its higher ability to removes the metal ions such as Cr^{3+} , Fe^{3+} , Ni^{2+} , Cu^{2+} and Pb^{2+} [7]. Acidic polymers such as poly (methacrylic acid) and poly (acrylic acid) have the tendency of removes the metal ions like Ag^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Cr^{3+} at different pH and polymer-metal ion ratios [8]. Salicylic acid melamine with formaldehyde terpolymer found to have higher selectivity for Fe^{3+} , Cu^{2+} and Ni^{2+} ions then for Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions [9]. Resin synthesized by the condensation of a mixture of phenol or hydroxybenzoic acid with formaldehyde and various amines have also been reported [10]. The metal ion uptake increases with increasing mole proportions of the terpolymer synthesized from substituted benzoic acid [11]. o-Nitrophenol and thiourea with p-formaldehyde terpolymer was identified as an excellent ion-exchanger for Zn^{2+} and Co^{2+} ions [12]. Salicylic acid – formaldehyde – resorcinol resin has been synthesized and explored its use for the removal and separation of heavy metal ions from their binary mixture [13]. 8-hydroxyquinoline formaldehyde – catechol copolymer found to have lower moisture content indicating the high degree of cross linking in the resin [14].

However no work seems to have been carried out on synthesis and chelation ion-exchange studies of the terpolymer resins synthesized from 2,4-dihydroxypropiophenone and oxamide and formaldehyde. The purpose of present study, is to explore the adsorption behavior of eight metal ions Fe^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+} on the newly synthesized copolymer resins 2,4-DHPOF 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. 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 2,4-DHPOF 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 [15-16].

II. EXPERIMENTAL

All the materials and chemicals (Aldrich, USA) were used as received with analytical grade.

Synthesis of 2,4-DHPOF copolymer resin

The 2,4-DHPOF copolymer resin was prepared by the condensation polymerization of 2,4-dihydroxypropiophenone (0.1mol) and oxamide (0.1mol) with formaldehyde (0.2 mol) in hydrochloric acid medium at 120 ± 2 °C in an oil bath for 4 hrs. 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 2,4-dihydroxypropiophenone - formaldehyde copolymer, which might be present along with the 2,4-DHPOF copolymer. The dried resin was further purified by dissolving in 8% NaOH and regenerated in 1:1(v/v) HCl/water. The purified copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in a vacuum over silica gel. The yields of these copolymer resins found to be 89% and the melting point is between 410-430°K. The sieved resin was used for further characterization.

Instruments Analysis

The copolymer resin was subject to micro analysis for C, H and N on an Elementar Vario EL III Carlo Erba 1108 elemental analyzer. The number average molecular weight \overline{M}_n was determined by conductometric titration in DMSO medium using ethanolic KOH as the titrant by using 25 mg of sample. A plot of the specific conductance against the milliequivalents 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 [17]: (1) the first break corresponds to the stage at which the first acidic phenolic hydroxyl group is neutralized, and (2) the last break observed beyond the first break represents the stage at which phenolic hydroxyl group of all the repeating units are neutralized. On the basis of the average degree of polymerization, (\overline{DP}) the average molecular weight has to be determined by following eq. (1)...

$$\overline{DP} = \frac{\text{(Total milliequivalents of base required for complete neutralization)}}{\text{(Milliequivalents of base required for smallest interval)}} \dots\dots\dots(1)$$

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

The intrinsic viscosity was determined using a Tuan-Fuoss viscometer [18] at six different concentrations ranging from 0.3 wt % to 0.05 wt % of resin in DMSO at 30°C. Intrinsic viscosity (η) was calculated by the Huggin's eq.(2) [19] and Kraemer's eq.(3) [20].

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

$$\ln \eta_r/C = [\eta] - K_2[\eta]^2.C \dots\dots\dots(3)$$

Electronic absorption spectra of the copolymer in DMSO was recorded on UV-1800 spectrophotometer of Shimadzu, Japan in the range of 200 – 850 nm at Dept. of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur. Infrared spectra of 2,4-DHPOF copolymer resin was recorded in nujol mull with IR Affinity, FT-IR spectrophotometer in KBr pallets in the range of 4000 – 500 cm^{-1} at kamla Nehru Mahavidyalaya, Nagpur. Proton NMR spectra and

Carbon NMR spectra were recorded with Bruker Avance – II 400 NMR spectrophotometer using DMSO-d₆ as a solvent, at STIC Kochi,. The surface analysis was performed using scanning electron microscope at different magnifications. SEM has been scanned by JEOL JSM-6380A Analytical Scanning Electron Microscope at STIC, Kochi..

Ion-exchange properties

The ion-exchange properties of the 2,4-DHPOF copolymer resin were 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.

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 25°C. To this suspension was added 2 ml of a 0.1 M solution of metal ion and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24 hrs and filtered [21, 22]. 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 [23]. The experiment was repeated in the presence of other three electrolyte such as NaCl, NaClO₄ and Na₂SO₄.

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 25°C (in the presence of 25 ml of 1 M NaNO₃ 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.

The percent amount of metal ions taken up at different time is defined as.

$$\text{Percentage of amount of metal ion taken up at different time} = \frac{\text{Amount of metal ion adsorbed}}{\text{Amount of metal ion adsorbed at equilibrium}} \times 100$$

The distribution of each one of the eight metal ions i.e. Fe²⁺, Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺, Hg²⁺ and Pb²⁺ between the polymer phase and the aqueous phase was determined at 25°C and in the presence of a 1M NaNO₃ solution.

The experiments were carried out from 1.5 to 6 pH for Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺. In case of Fe³⁺ the study was carried out from 1.5 to 3.0 pH. After 24 hrs the mixture was filtered, the filtrates and washing were collected. Amount of the metal ion which remained in the aqueous phase was estimated by back titration with standard EDTA solution using appropriate indicator. Similarly blank experiment was carried out without adding polymer sample. The amount of metal adsorbed by the polymer was calculated from the difference between sample and blank reading. The original metal ion concentration is known and the metal ion adsorbed by the polymers was estimated. The distribution ratio 'D' is calculated from the following equation-

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

If we consider

‘Z’ is the difference between actual experiment reading and blank reading,

‘C’ gm is the amount of metal ion in 2ml 0.1M metal nitrate solution,

‘Y’ gm of metal ion in 2ml of metal nitrate solution after uptake.

$$\text{Metal ion adsorbed [uptake] by the resin} = \frac{ZX}{Y} \frac{2}{0.025} = \left(\frac{ZX}{Y} \right) 133.33$$

III. RESULTS AND DISCUSSION

The resin sample was light brown in color, insoluble in commonly used organic solvents, but was soluble in dimethyl formamide, dimethyl sulphoxide, tetrahydrofuran, pyridine and concentrated H₂SO₄. The resin synthesized do not show sharp melting point but undergo decomposition 410-430°K. Based on the analytical data, the empirical formula of the copolymer resin is found to be C₁₂H₁₂N₄ SO₅, which is in good agreement with the calculated values of C, H, N and O. The resin was analyzed for carbon, hydrogen, and nitrogen content. C =44.48% (Cal) and 44.17% (F), H=3.76% (Cal) and 3.49% (F), N =17.25%(Cal), and 17.73% (F), O= 24.65% (Cal) and 26.22%(F). The number average molecular weight (\bar{M}_n) could be obtained by multiplying the \bar{DP} by the formula weight of the repeating unit [24, 25]. The calculated molecular weight for 2,4-DHPOF resin is 8329.

Viscometric measurement was carried out in DMSO at 30°C. 2,4-DHPOF resin showed normal behavior. The intrinsic viscosity was determined by the Huggin’s eq. (2) and Kraemer’s, eq. (3) which is 0.29 and 0.27 respectively. In accordance with the above relations, the plot of $\eta_{sp/c}$ and $\eta_{rel/c}$ against C was linear giving as slopes K₁ and K₂ (0.55) respectively. The intercept on the axis of viscosity function gave the (η) value in both the plots [26, 27]. The values of (η) obtained from both relations were in good agreement with each other.

Spectral Analysis

The UV-visible spectrum of 2,4-DHPOF copolymer resin is shown in Fig. 1. UV-visible spectrum of 2,4-DHPOF resin has been recorded in pure DMSO in the region of 200 – 800 nm at a scanning rate of 100 nm min⁻¹. The spectra of these copolymers exhibit two absorption maxima in the region 280 nm and 320 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) processing double bond, which is in conjugation with the aromatic nucleus [28, 29]. 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 shift from the basic value (viz. 240 nm and 310 nm respectively) may be due to conjugation effect, and presence of phenolic hydroxyl group (auxochromes) is responsible for hyperchromic effect i.e. ϵ_{max} higher values.

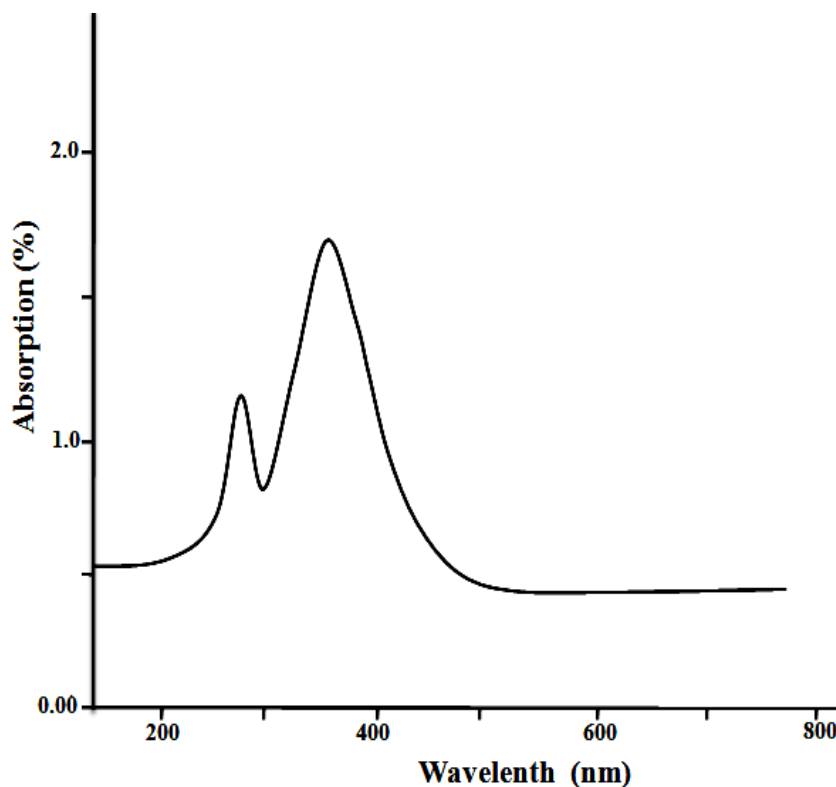


Fig.1. Electronic spectra of 2,4-DHPOF copolymer resin

The IR spectrum of 2,4-DHPOF copolymer resin is presented in Fig. 2 and IR data are specified in Table 2. [30-31]. A broad absorption band appeared in the region $3450-3200\text{ cm}^{-1}$ may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding. The peak at $1390-1270\text{ cm}^{-1}$ (-CH₂ plane bending), indicate the presence of methylene (-CH₂) group and $1367-1369\text{ cm}^{-1}$ methylene bridge in copolymer chain. The bands appeared at 1441 cm^{-1} (Aryl C-H stretching) and $950-1125\text{ cm}^{-1}$ (substituted aromatic ring) may be ascribed to aromatic ring. The band at $600-800\text{ cm}^{-1}$ indicates the presence of tetra substituted aromatic ring. 1,2,3,5 substitution in aromatic ring was confirmed by the bands appeared at $\sim 950, 1058, 1125$. The band of -NH stretching ($3200-3000\text{ cm}^{-1}$) seems to be merged with very broad band of phenolic hydroxyl group.

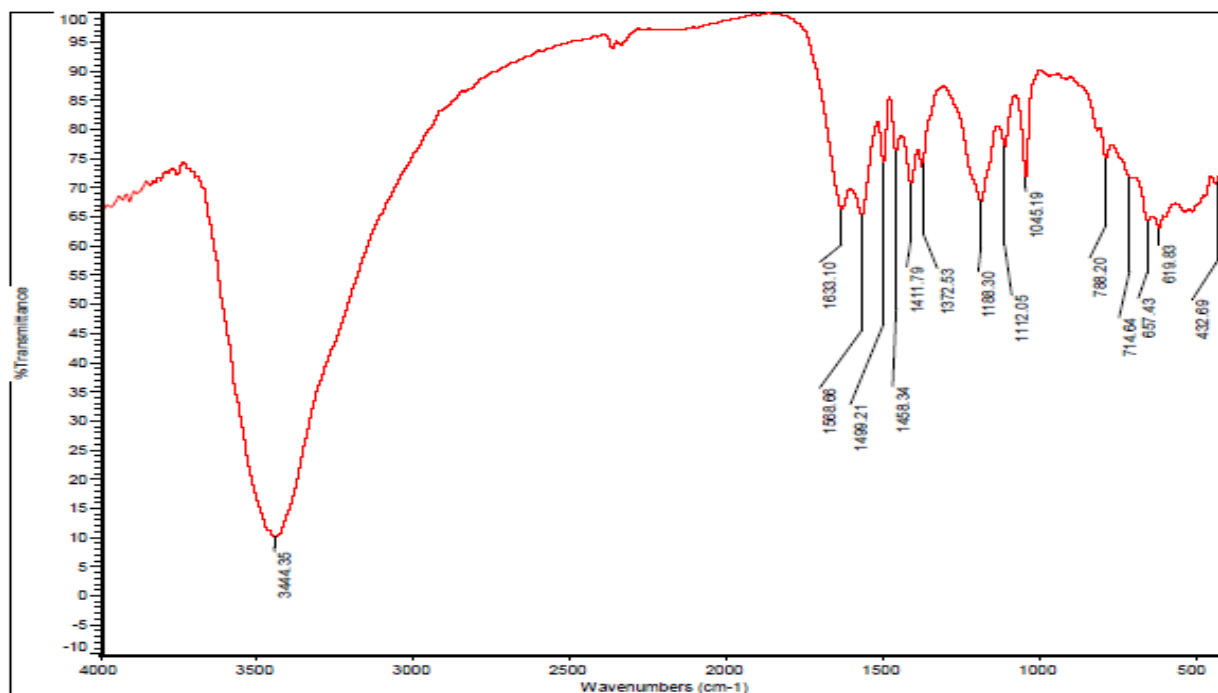


Fig. 2. FTIR Spectra of 2,4-DHPOF Copolymer Resin

Table 2. FT-IR Frequencies of 2,4-DHPOF Copolymer Resin

Observed band frequencies (cm ⁻¹)	Assignment	Expected band frequencies (cm ⁻¹)
8-QSSF		
3445(b,st)	-OH Phenolic intermolecular hydrogen bonding	3450-3200
1544.1(m)	>C=O (Aromatic ketone and semicarbazide moiety)	1600-1500
1441.6(sh,st)	Aromatic ring (substituted)	1500-1400
1510(sh,st)	-NH Bending of secondary amide	1570-1450
1320(sh,st)	-CH ₂ Methylene bridge	1390-1270
1280(m)	-CH ₂ - Bending (wagging & twisting)	1300-1280
920(m)	1,2,3,5 Substitution in aromatic ring	950
1067(m)		1058
1128(m)		1125

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

The NMR spectrum (Fig. 3) of 2,4-DHPOF polymer was scanned in DMSO- d_6 solvent. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature [32,33]. The singlet obtained in the region 3.89 - 3.94(δ) ppm may be due to the methylene proton of Ar-CH₂- moiety. The weak multiple signals (unsymmetrical pattern) in the region of 8.23-8.18(δ) ppm may be attributed to aromatic proton (ArH). The signals in the range at 9.11 to 9.16(δ) ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic -OH indicates clearly the intermolecular hydrogen bonding of -OH group [34,35]. The signals in the range of 9.96 – 9.92(δ) ppm are attributed to proton of -SO₃H groups.

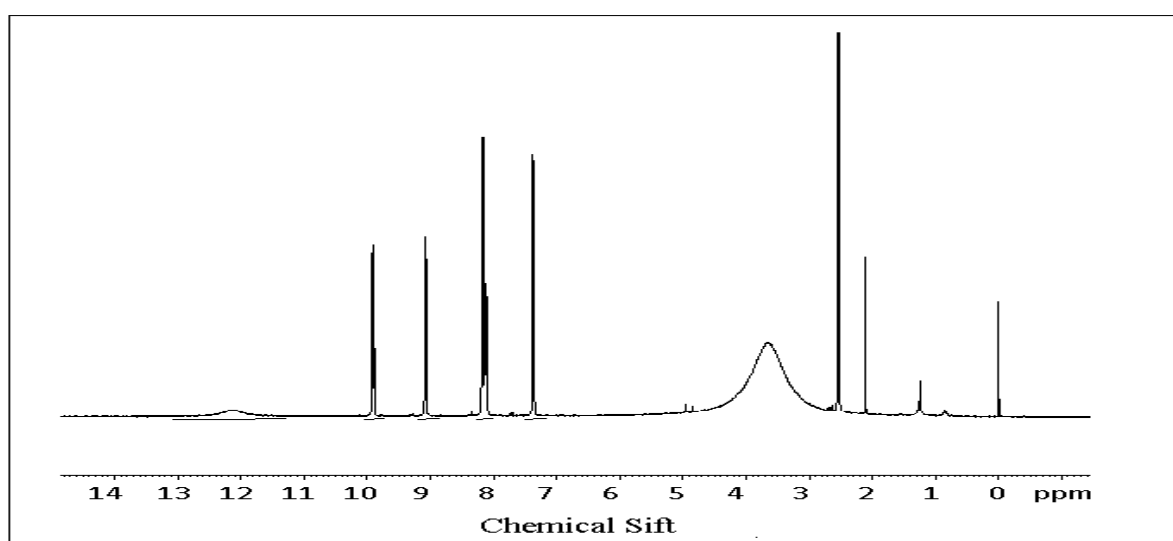


Fig.3. Proton NMR spectrum of 2,4-DHPOF copolymer resin

Scanning electron micrographs

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 Fig.4. It gives the information of surface topology and defect in the structure. The resin appeared to be dark drawn in colour. The morphology of polymer resin is shown spherule and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of 2,4-DHPOF 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, which is shown Fig.5. Due to the deep pits, resin exhibits higher exchange capacity for Pb²⁺ ions (as well as other many metal ions). This could be the reason of bigger nitrated Pd²⁺ ions, which can easily penetrate in to the deep pits. Thus by SEM

micrographs morphology of the resin shows the transition between crystalline and amorphous nature. When compare to the other resin [35, 36], the 2,4-DHPOF copolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.

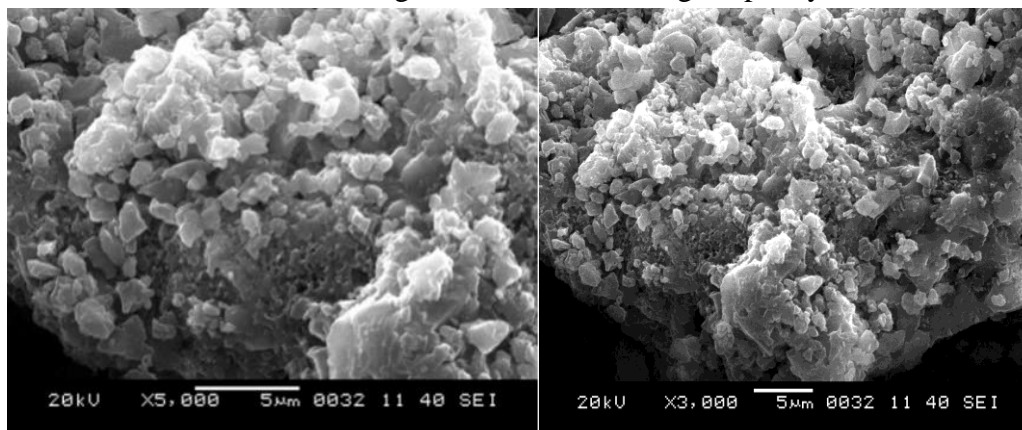


Fig.4. SEM of 2,4-DHPOF Copolymer resin

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 [37,38]. Data of experimental procedure for direct EDTA titration is presented in Table 4.

The 2,4-DHPOF copolymer 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 as 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 2,4-DHPOF copolymer was studied with these three variables by keeping two variable constant at each time.

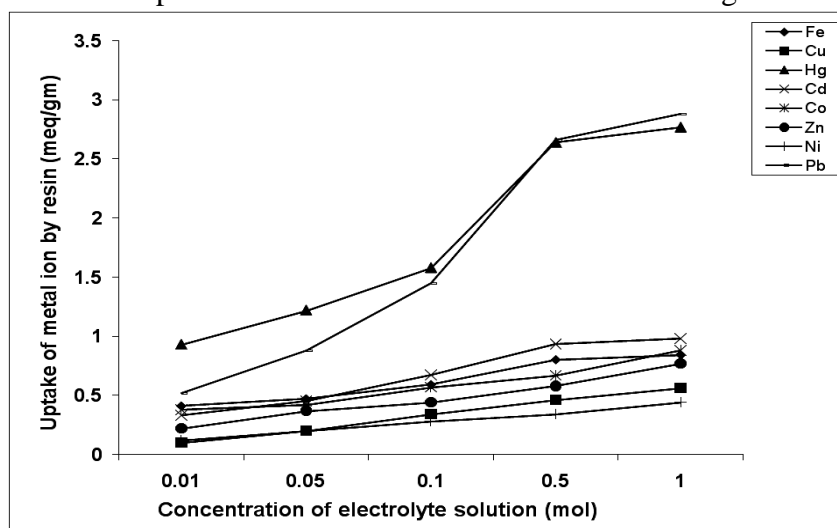
Polymer + metal ion solution + shaking \longrightarrow polymer – metal ion chelate
(Metal uptake capacity of polymer depends on stability of polymer – metal ion chelate)

Batch equilibrium technique developed by Gregor et al. and DeGeiso et al. was used to study of ion exchange property of 2,4-DHPOF copolymer resin. The result of the batch equilibrium study carried out with the copolymer resin 2,4-DHPOF is presented in Fig. 5-10 eight metal ions Fe^{3+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Co^{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 evaluate its effect on metal uptake capacity of the polymer [20, 22, 36].

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

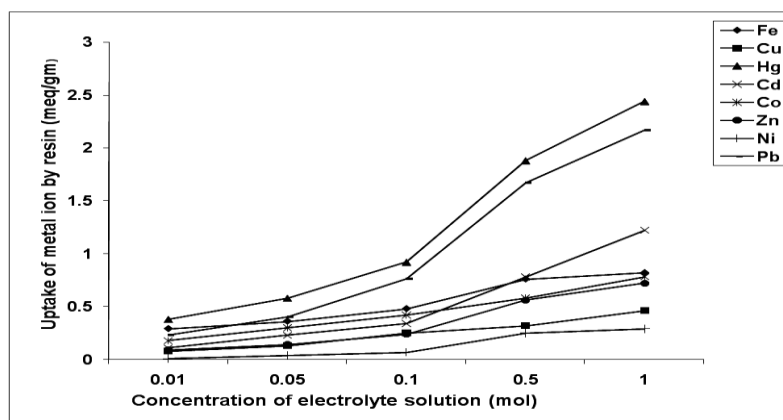
We examined the effect of NO_3^- , Cl^- , SO_4^{2-} and ClO_4^- at various concentrations on the equilibrium of metal resin interaction of constant pH. Different metal ions have different pH in solution, has been mentioned in [Fig.5-8], which shows that the amount of metal ions taken up by a given amount 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^{3+} , Cu^{2+} , Zn^{2+} and Pb^{2+} 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 the electrolyte [39]. 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.



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

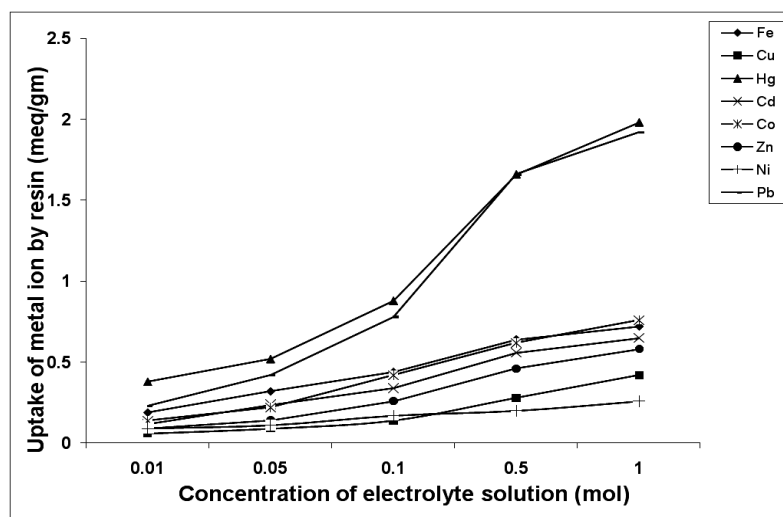
pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Hg(II)=6.0; Pb(II)=6.0

Fig. 5. Uptake of several metal ions by 8-QSSF copolymer resin at five different concentration of electrolyte solution NaNO_3



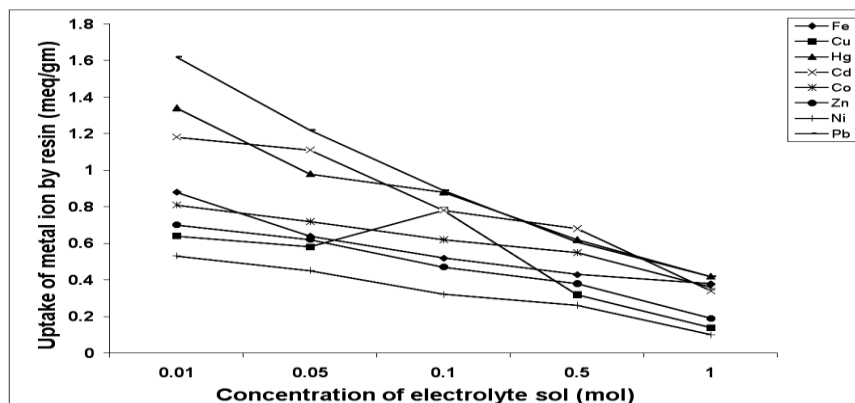
$\text{M}(\text{NO}_3)_2 = 0.1 \text{ Mol/l}$; Volume = ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.
 pH : Fe(III) = 2.5; Cu (II) = 4.5; Ni(II) = 4.5; Co(II) = 5.0; Zn (II) = 5.0; Cd(II) = 5.0; Hg(II) = 6.0; Pb(II) = 6.0

Fig. 6. Uptake of several metal ions by 8-QSSF copolymer resin at five different concentration of electrolyte solution NaCl



$\text{M}(\text{NO}_3)_2 = 0.1 \text{ Mol/l}$; 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; Hg(II) = 6.0; Pb(II) = 6.0

Fig. 7. Uptake of several metal ions by 2,4-DHPOF copolymer resin at five different concentration of electrolyte solution NaClO_4



$\text{M}(\text{NO}_3)_2]=0.1 \text{ Mol/l}$; 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; Hg(II)=6.0; Pb(II)=6.0

Fig. 8. Uptake of several metal ions by 2,4-DHPOF copolymer resin at five different concentration of electrolyte solution Na_2SO_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.9 shows the results of rate of uptake of metal ion on 2,4-DHPOF copolymer resin. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given copolymer. The figure shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of metal ions under given conditions. It is found that Fe^{3+} ions required about 3 hrs for the establishment of the equilibrium, whereas Cu^{2+} , Zn^{2+} and Pb^{2+} ions required about 6 hrs. Thus the rate of metal ions uptake follows the order $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Hg}^{2+} \approx \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+}$ for the 2,4-DHPOF copolymer [40].

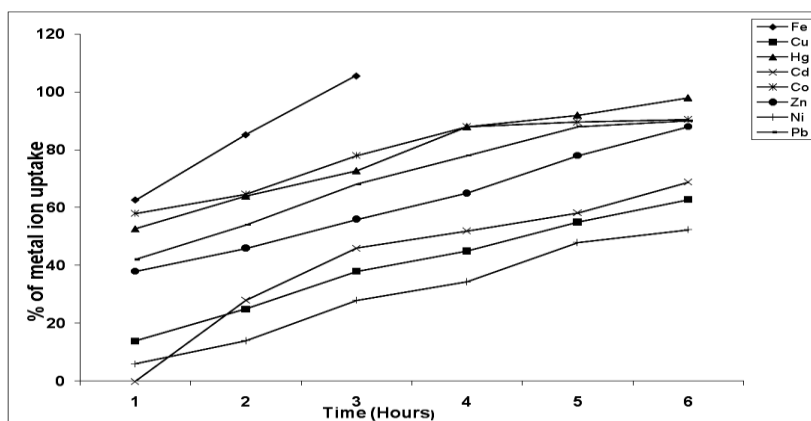


Fig. 9. Comparison of the rate of metal ion uptake by 2,4-DHPOF copolymer resin

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.10]. 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 [40]. 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. The selectivity of Fe^{3+} ion is more for the 2,4-DHPOF 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 $Fe^{3+} > Cu^{2+} > Ni^{2+} > Zn^{2+}$ [38]. 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 [40]. For example, the result suggests the optimum pH 2.5 for the separation of Fe^{3+} and Zn^{2+} with distribution ratio 'D' is 480.2 and 685.7 respectively using the 2,4-DHPOF copolymer resin as ion exchange. Similarly for the separation of Fe^{3+} at the optimum pH is 2.5 with distribution ratio is 480.2 for 2,4-DHPOF copolymer. The lowering in the distribution ratios of Fe^{3+} was found to be small hence, efficient separation could be achieved. The order of distribution ratio of metal ions measured in pH range 2.5 to 6.5 is found to be $Fe^{2+} > Cu^{2+} > Ni^{2+} > Cd^{2+} > Zr^{2+} > Co^{2+} > Pb^{2+}$.

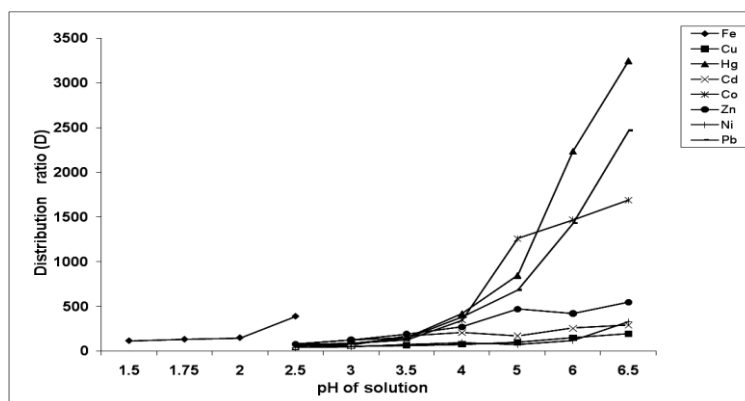


Fig.10. Distribution ratio (D) of various metal ions as function of different pH by 2,4-DHPOF Copolymer resin

IV. CONCLUSIONS

Copolymer resin (2,4-DHPOF) was prepared from 8-hydroxyquinoline 5-sulphonic acid and semicarbazide with formaldehyde in acetic acid medium by condensation technique. The amorphous nature of the 8-QSSF copolymer resins were confirmed by the SEM studies and reveals that the copolymer can act as an effective ion exchanger for trivalent and divalent metal ions such as Fe^{3+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Hg^{2+} and Pb^{2+} ions. This study of ion-exchange reveals that 2,4-DHPOF copolymer resin is proved to be an eco-friendly cation exchange resin and can be used for the removal of hazardous metal ions from the environmental area, for the purification of industrial waste solution and for the purpose of purification and desalination of water.

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