Synthesis, Characterisation and Ion-Exchange properties of new terpolymer resin derived from 2, 4-Dihydroxybenzaldehyde, Adipamide and Formaldehyde.

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***Abstract*- Terpolymer resins (2,4-DHBAF) were synthesized by condensation of 2,4-Dihydroxybenzaldehyde and Adipamide with formaldehyde in presence of acid catalyst with using varied molar ratios of reacting molecules. Terpolymer resins composition have been determined on the basis of their elemental analysis & number average molecular weight of these resins were determined by conductometric titration in non aqueous medium. The viscosity measurement in dimethyl sulphoxide (DMSO) has been carried out with a view to ascertain the characteristics functions and constants. UV-Visible, IR &^{1}H NMR spectra were studied to elucidate the structure. The surface morphology of the terpolymer resin was examined by scanning electron microscopy. Ion-exchange properties of the resin was studied for Fe^{3+}, Cu^{2+}, $Ni^{2+,}$ Zn^{2+}, Cd^{2+} and Pb^{2+} ions in the form of metal nitrate solutions. A batch equilibrium method was employed in the study of selectivity of metal ion uptake involving the measurements of the distribution of a given metal ion between the terpolymer sample and the solution containing the metal ion. The study was carried out over a wide range of pH, shaking time and in media of various ionic strengths of different electrolytes. The terpolymer shows higher selectivity for Fe^{3+} Cu^{2+} and Ni^{2+}than for Co^{2+},Cd^{2+},Zn^{2+} and Pb^{2+}.**

***Keywords*- Resin, Synthesis, Ion-exchanger, Distribution ratio**

I. INTRODUCTION

Terpolymer is found very useful application as adhesives high temperature flame resistant, fibres, coating materials, semiconductors, catalysts and ion exchange resins[1-3]. Ion exchange resins have attracted much interest in the recent years due to their application in waste water treatment, metal recovery and for identification of specific metal ions[4-6]. A new chelating sorbent for metal ion extraction under saline conditions has also been studied [7].Chelating ion exchange properties of resin involving poly [(2, -hydroxy-4 acryoxybenzophenone)] are reported[8]. Copolymers involving 4-hydroxyacetophenone-biuret-formaldehyde[9] are reported for their ion –exchange characteristics. Thepurpose of present study is to explore the adsorption behavior of seven metal ions Fe^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} on the newly synthesized terpolymer resins 2,4-DHBAF at different pH values, different concentrations of different electrolytes and at different shaking time intervals. The terpolymer resins under investigation 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 thechelating ion exchange property of the2,4-DHBAFterpolymer resin was also reported for specific metal ions.

The present study deals with the synthesis and characterization of like 2,4-dihydroxybenzaldehyde, adipamide and formaldehyde [2,4-DHBAF] terpolymer resin by spectral methods for the first time. The synthesized terpolymer was characterized by elemental analysis, UV-VIS, FT-IR,^{1}H-NMR, intrinsic viscosity and number average molecular weight.

II. EXPERIMENTAL

The important chemicals like 2,4-dihydroxybenzaldehyde, adipamide and formaldehyde used in the preparation of various new 2,4-DHBAF terpolymer resins were procured from the market and were of chemically pure grade.

A. Synthesis of 2,4-DHBAF Terpolymer resin

The 2,4-DHBAF-Iterpolymer resin was prepared by condensing 2,4-dihydroxybenzaldehyde(1.3812gm, 0.1mol), adipamide(1.4418gm, 0.1mol), formaldehyde(7.5ml, 0.2mol) in the mole ratio of 1:1:2 in the presence of 2MHCl as a catalyst at 122+2^{o}C for 6h in an oil bath with occasional shaking to ensure through mixing. The separated cream colourterpolymer resin was washed with hot water to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powered and then extracted with diethyl ether to remove 2,4-dihydroxybenzaldehyde - formaldehyde copolymer which might be presentalong with 2,4-DHBAF terpolymer. The terpolymer resin was purified further by dissolving in 8% aqueous sodium hydroxide solution, filtered and reprecipited by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid/distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. Theterpolymer sample 2,4-DHBAF-I thus obtained was filtered, washed several times with hot water, dried in air, powered and kept in vaccumdesicator. The reaction and suggested structure of 2,4-DHBAF-I is given in Fig. 1.

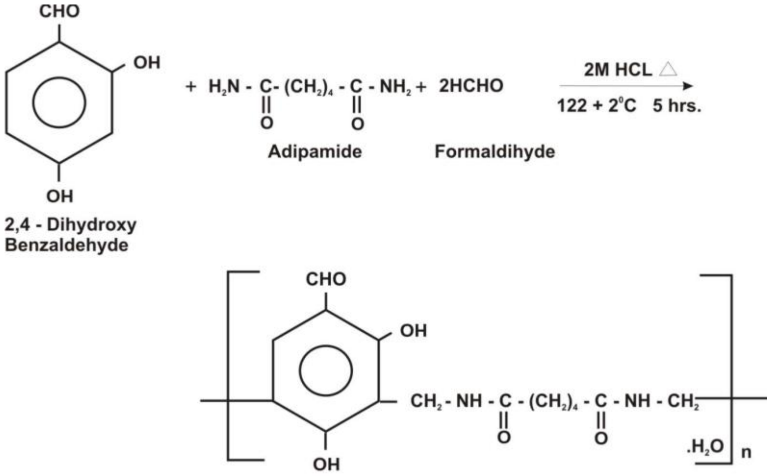

Fig.1Preparation of2, 4-DHBAF-1 Copolymer Resin.

In the same way the other terpolymer resin viz. 2,4-DHBAF-II, 2,4-DHBAF -III, 2,4-DHBAF -IV were prepared with the molar ratios 2:1:3, 3:1:4, 4:1:5.

III. CHARACTERIZATION OF 2,4-DHBAF TERPOLYMER RESIN

A. Physicochemical and Element Analysis

The terpolymer resin was subjected to micro analysis for C, H and N on an ElementalVario EL III Carlo Erba- 1108 elemental analyzer. The number average molecular weight 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 miliequivalents of KOH required for neutralization of 100 gm of terpolymer resin was made. Inspection of such plot revealed that there were many breaks in the plot. From this plot first break and last break were noted. On the basis of average degree of polymerization theaverage molecular weight has to be determined by following eq.

$$\overline{DP} = \frac{\text{Total milleequivalents of base required for complete}}{\text{Miliequivalent of base required for smallest interval}}$$

$$\overline{Mn} = \overline{DP} \text{ x Repeat unit weight}$$

The intrinsic viscosity was determined using a Tuan-Fuoss viscometer at six different concentrations ranging from 0.3% to 0.05% wt % of resin in DMSO at 30^{o}c. Intrinsic viscosity was calculated by the Huggins eq. and Kramer’s eq.

$$\eta_{sp} / C = [\eta] + K[\eta]^2 C$$

$$In\eta_{sp} / C = [\eta] + K' [\eta]^2 C$$

B. Spectral and surface analysis

Electronic (UV-Visible) spectra of terpolymer resin in DMSO was recorded with a double beam spectrophotometer in the range of 200-850 nm at Kamla Nehru Mahavidyalaya, Nagpur.FT-IR spectra of 2,4-DHBAFterpolymer resin was recorded in najol mull with Perkin –Elmer Spectrum RX-I,FT-IR spectrophotometer in KBr pallets in the range of 4000-500 cm-I at SAIF , Punjab University, Chandigarh.1H NMR spectra was recorded with Bruker Advance-II 400 NMR spectrophotometer using DMSO as solvent at SAIF , Punjab University, Chandigarh.The surface analysis was performed using scanning electron microscope at different magnification at VNIT Nagpur.

C. Ion-exchange property

The ion-exchange property of the2,4-DHBAFterpolymer resin was determined by the batchequilibrium method.

1) *Determination of metal uptake in the presence of electrolyte of different concentrations:*The terpolymer sample (25mg) was suspended in an electrolyte solution (25ml) of knownconcentration. The pH of the suspension was adjusted to the required value by using either 0.1mHNO$_3$ or 0.1M NaOH. The suspension was stirred for 24H at 30ºC. To this suspension 2 ml of0.1M solution of the metal ion was added and the pH was adjusted to the required value. Themixture was again stirred at 30ºC for 24 hrs and filtered. The solid was washed and the filtrateand washing were combined and the metal ion content was determined by titration againststandard EDTA (ethylene diamine tetra-acetic acid). The amount of metal ion uptake of thepolymer was calculated from the difference between a blank experiment without polymer and thereading in the actual experiments. The experiment was repeated in the presence of severalelectrolytes. The results are presented in Fig. 6 to 10.

2) *Evaluation of rate of metal uptake:*In order to estimate the time require to reach the state of equilibrium under the givenexperimental conditions, a series of experiments of the type described above were carried out, inwhich the metal ion taken up by the chelating resins was determined from time to time at 30ºC.(in the presence of 25ml of 1M NaNO$_3$ solution). It was assumed that, under the givenconditions, the state of equilibrium was established within 24 hrs. The rate of metal uptake isexpressed as percentage of the amount of metal ions taken up after a certain time related to thatat the state of equilibrium. The results are presented in Fig. 11.

*3)Distribution of metal ion at different pH:*The distribution of each one 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 30ºCand in the presence of 1M NaNO$_3$ solution. The experiments were carried out as described aboveat different pH values.

IV. RESULTS AND DISCUSSION

A) Spectral and surface studies

The UV-Visible spectrum of all four 2,4-DHBAF terpolymer resin has been shown in Fig. 2. All the four 2,4-DHBAFterpolymer resin displayed two broad bands at 270-290 nm and 320-360 nm. The observed position of the absorption bands indicates the presence of a carbonyl group and hydroxyl group which is in conjugation with the aromatic nucleus. Theband at 320-360 nm is more intense which is accounted for a π-π* transition while the less intense band at 200-300 may be due to n-π*transition[10,11]

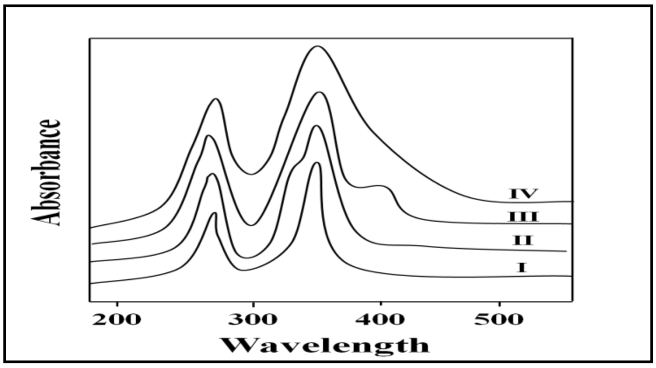

Fig. 2UV-visible Spectra of 2,4-DHBAF Terpolymer Resins.

B) Infrared Spectra

The IR spectra of all four 2,4-DHBAF terpolymer resins are presented in fig 3. IR spectrarevealed that all four 2,4-DHBAF terpolymer resin give rise to nearly same pattern of spectra. A broad band appeared at the region 3338-3339 cm^{-1} may be assigned to stretching vibration of phenolic –OH group exhibiting intramolecular hydrogen bonding[12]. A peak at 1542-1548 cm-1 may be ascribed to aromaticskeletal ring. The band at 1440-1443 cm^{-1} is due to –NH bending of secondary amide. The band at 1381-1383cm^{-1} may be due to -CH_2- bridge. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium/weak absorption bands appeared at 94445-947cm^{-1}, 1064-1065cm^{-1} and 1186-1192cm^{-1} respectively.

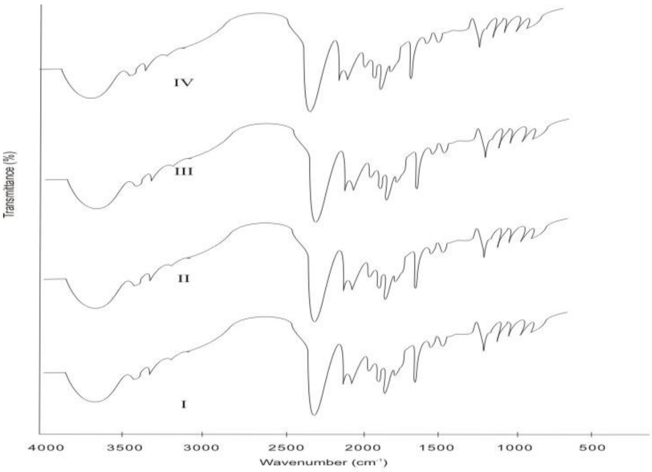

Fig. 3 Infra Red Spectra of 2,4-DHBAF Terpolymer Resins

C) Nuclear Magnetic Resonance spectroscopy

^{1}H NMR spectra of all 2,4-DHBAF terpolymer resin are shown in fig 4. The medium signal at 2.4-2.54 ppm may be due to methylene proton of Ar-CH_2bridge. The signal in the region of 3.26-3.33 ppm may be due to methylene proton of Ar-CH_2-N. The signal in the region 5.14-5.22 ppm may be due to proton of –NH bridge. The weak multiplate signal in the region signal in the range of 7.33-7.36 ppm may be due to aromatic proton(Ar-H). The signal in therange of 9.51-9.58 may bedue to phenolic hydroxyl group[12].

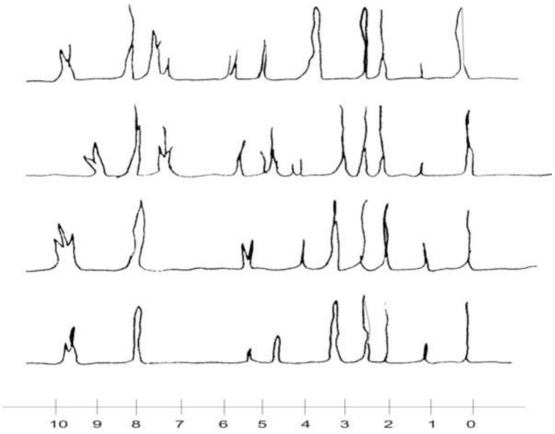

Fig. 4^{1}H NMR Spectra of 2,4-DHBAF Terpolymer Resin.

D) Scanning electron microscopy (SEM)

Surface analysis has found great use in understanding the surface features of the materials. The morphology of the reported sample was investigated by scanning electron micrograph at different magnification which is shown in fig 5.for 2,4-DHBAF. It gives the information of surface topography and defects in the structure. The morphology of polymer resin shows spherulites and fringed and scattered model. The spherulites are complex polycrystalline formation having as good as smooth surface and having deep pits in the photograph. This indicates the crystalline nature of 2,4-DHBAF terpolymer resin sample. Thus by SEM micrograph morphology of the resin shows the transition between crystalline and amorphous nature, when compared to other resin, the 2,4-DHBAFterpolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.

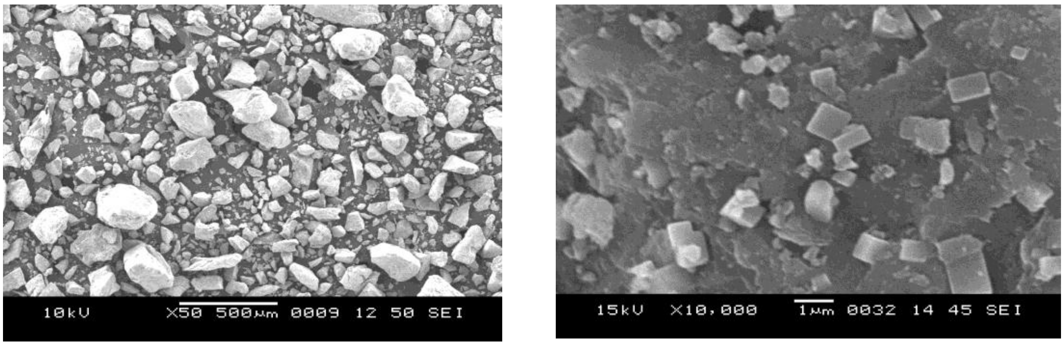

Fig. 5 SEM Micrograph of 2,4-DHBAF-I Terpolymer resin.

E) Ion- exchange properties

Batch equilibrium technique developed by Gregor et al and De Geiso et al. was used to study ionexchange properties of 2,4-DHBAF terpolymer resins. The results of the batch equilibrium studycarried out with the terpolymer2,4-DHBAF are presented in Fig. 6 to 11. Seven metal ionsFe$^{3+,}$ Cu$^{2+,}$ Ni^{2+}, Co$^{2+,}$ Zn$^{2+,}$ Cd^{2+} and Pb^{2+} in the form of aqueous metal nitrate solution wereused. The ion exchange study was carried out using three experimental variables : a) Electrolyteand its ionic strength b) Shaking time and c) pH of the aqueous medium, Among these threevariables, two were kept constant and only one was varied at a time to evaluate its effect onmetal uptake capacity of the polymers[13-15].

1) Effect of Electrolytes and their concentrations on metal ion uptake capacity:

We examined the influence of ClO_4^{-}, NO_3^{-}, Cl^{-} and SO_4^{2-} at various concentrations on theequilibrium of metal-resin interaction. Fig. 6,7,8,9 shows that the amount of metal ions taken up by agiven amount of terpolymer depends on the nature and concentration of the electrolyte present inthe solution. In the presence of perchlorate, chloride and nitrate ions, the uptake of Fe(III), Cu(II)and Ni(II) ions increase with increasing concentration of the electrolytes, whereas in the presenceof sulphate ions the amount of the above mentioned ions taken up by the terpolymer decreaseswith increasing concentration of the electrolyte. Moreover, the uptake of Co(II), Zn(II), Cd(II)and Pb(II) ions increase with decreasing concentration of the chloride, nitrate, perchlorate andsulphate ions. This may be explained on the basis of the stability constants of the complexeswith those metal ions.

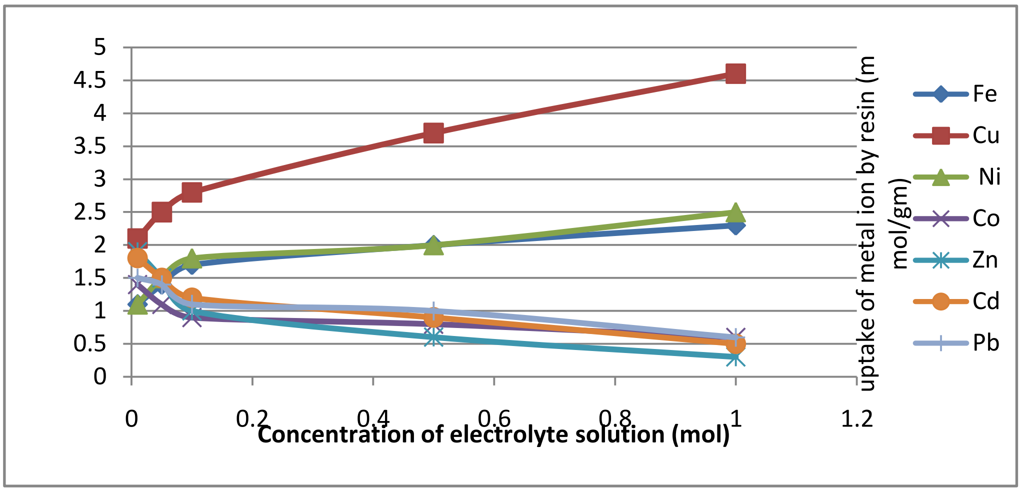

Fig. 6Uptake of Several Metal Ions by2, 4-DHBAF - I Terpolymer Resin at five different concentration of Electrolyte Solution $NaNO_3$

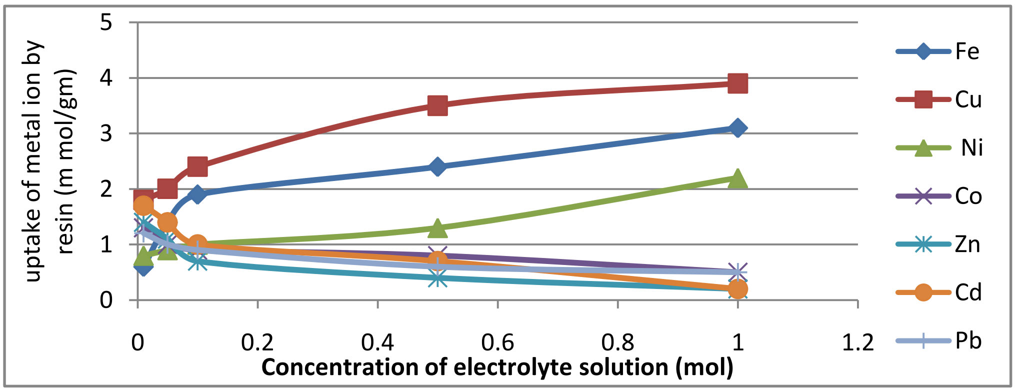

Fig. 7 Uptake of Several Metal Ions by 2 4- DHBAF -I Terpolymer Resin at five different concentration of Electrolyte Solution NaCl

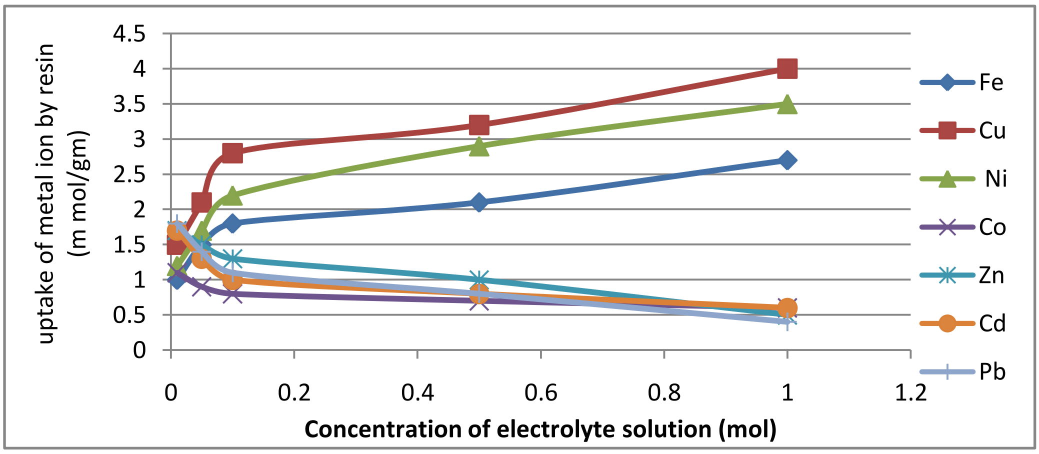

Fig. 8 Uptake of Several Metal Ions by 2,4- DHBAF -I Terpolymer Resin at five different concentration of Electrolyte Solution $NaClO_4$.

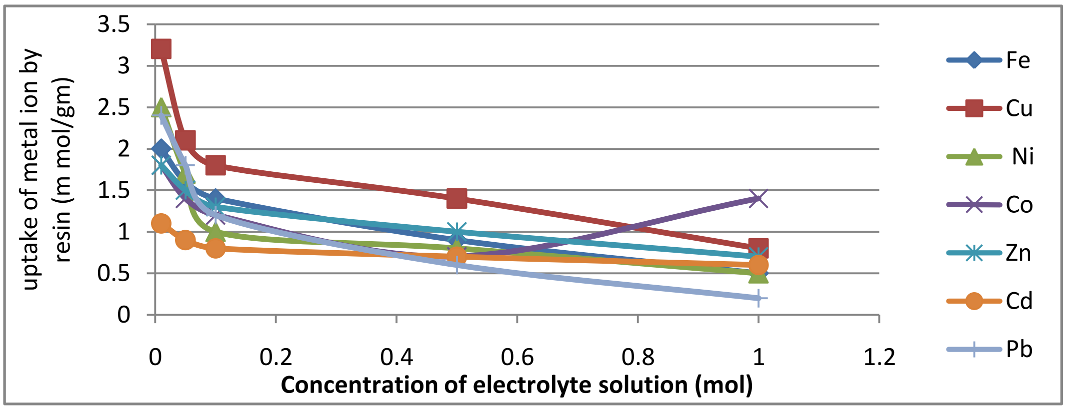

Fig. 9Uptake of Several Metal Ions by 2,4- DHBAF -I Terpolymer Resin at five different concentration of Electrolyte Solution Na_2SO_4.

2) Evaluation of rate of metal ion uptake

The data presented in Fig 10 indicates that the rate of metal ion uptake depends on the nature of metal ion.[16]. The rate of metal ion means the change in concentration of metal ion in aqueous solution containing polymer sample. Fe^{3+} requires 3hrs and rest of metal requires 5 hrs for establishing equilibrium.

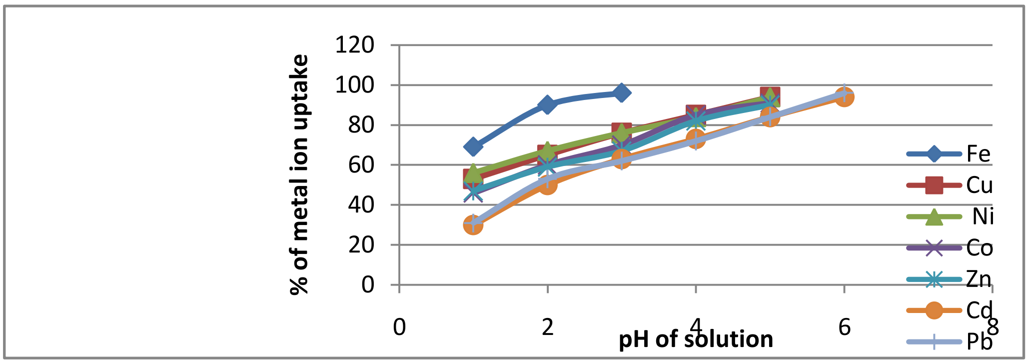

Fig. 10Comparison of the Rate of Metal Ion uptake by 2,4-DHBAF-I Terpolymer Resin

3) Distribution ratios of metal ions at different pH:

The effect of pH on the amount of metal ions distributed between two phases can be explainedby the results given in Fig. 11. The data on the distribution ratio as a function of pH indicatethat the relative amount of metal ion taken up by 2,4-DHBAF terpolymer increases withincreasing pH of the medium. The magnitude of increase, however, is different for differentmetal cations. The2,4-DHBAF terpolymer resin take up Fe (III) ion more selectively than anyother metal ions under study. The order of distribution ratio of metal ions measured in pH range2.5 to 6.5 is found to be Fe (III) > Cu (II) > Ni (II) > Co (II) > Zn (II) > Cd (II) >Pb (II) [17-19]. Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake ofa particular metal cation from a mixture of different metal ions.

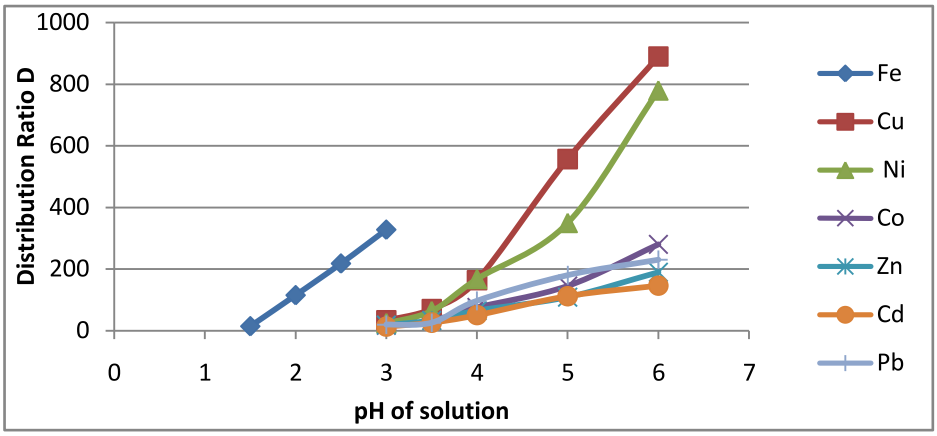

Fig.11Distribution Ratio (D) of various metal ion as a function of different pH by 2,4-DHBAF Terpolymer Resins.

V. CONCLUSIONS

1. A terpolymer2,4-DHBAF, based on the condensation reaction of 2,4-Dihydroxybenzaldehyde and adipamidewithformaldehyde in the presence of acid catalyst was prepared.
2. The 2,4-DHBAF terpolymer resin is a selective chelating ion-exchange terpolymer resin forcertain metals.
3. 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.
4. This study of ion–exchange reveals that2,4-DHBAF polymer resin is proved to be eco-friendly cation exchange resin and can be used for the removal of hazardous metal ions from environmental area, for purification of industrial waste solution and for the purpose of purification and desalination of water.

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