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Removal of heavy metal ions using eco-friendly synthesized terpolymer

Jiwatode Manisha M[1], Kariya Kiran P[2]* and Berad Baliram N[1]

[1]Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, India
[2]Department of Chemistry, VMV Commerce JMT Arts & JJP Science College, Nagpur, India
*Corresponding author Email: manisha.jiwatode186@gmail.com

Manuscript details:	ABSTRACT
  Cite this article as: Jiwatode Manisha M, Kariya Kiran P and Berad Baliram N (2018) Removal of heavy metal ions using eco-friendly synthesized terpolymer, *Int. J. of. Life Sciences*, Special Issue, A12: 9-16. 	A novel chelating resin synthesized from phthalic acid, 1,5-naphthalene diamine with formaldehyde by condensation in glacial acetic acid. The structure of chelating resin was clearly elucidated by use of variety of spectral techniques, for example FTIR, 1HNMR and UV-Visible spectroscopy. The average molecular weight of terpolymer resin was determined by non-aqueous conductometric method. The empirical formula and empirical formula weight of the resin were determined by elemental analysis. Scanning electron microscopy was used to established surface features of the chelating resin. The ion exchange behavior of heavy metals, viz. Pb^{+2}, Co^{+2}, Cd^{+2} and Hg^{+2} was evaluated by batch equilibrium method. The study was extended to three variations evaluation of metal ion uptake in the presence of different electrolytes at different concentrations; evaluation of metal ion uptake at different pH; and evaluation of metal ion uptake at different times. **Keywords:** Synthesis; Characterization; Metal ion uptake; Distribution coefficient; Batch equilibrium

INTRODUCTION

Ion exchangers have been used commercially on a worldwide basis for almost a century due to diverse applications in many fields such as water softening and deionization (Singh and Saraf, 2009). The presence of heavy metals in environment is a cause of concern due to their acute and long-term toxicity. Lead and mercury are the major hazardous metals present in the environmental wastewater. Thus, removal of trace heavy metals from the environmental area have become of increasing interest and there is a strong need for a reliable analytical procedure that can be applied for the removal and determination of these metals at very low concentrations (Patel *et al.*, 2007). Synthesized a chelating terpolymer resin using an eco-friendly technique and reported for its good binding capacity for Fe^{+2} and Cu^{+2} ions (Hiwase *et al.*, 2010).

Chelating terpolymer resin synthesized from 2,4-di-hydroxy-acetophenone –oxamide –formaldehyde (Butolia *et al.*, 2009) selective for Cu^{+2}, Hg^{+2}, Cd^{+2}, Co^{+2}, Zn^{+2}, Ni^{+2}, Pb^{+2} and Fe^{+3}. Ion exchange resin synthesized from 2,4-dihydroxyacetophenone –dithiooxamide – formaldehyde (Rahangdale *et al.*, 2008) Phenolic Schiff bases derived from hydroxybenzaldehyde and 4,4' di-amino-di-phenyl ether have been reported as better chelating resin for Cu(II) leading to its separation from a mixture of Cu(II) and Ni(II) ions (Gurnule *et al.*, 2003). Salicylic acid and melamine with formaldehyde terpolymer was found to have higher selectivity for Fe^{+3}, Cu^{+2} and Ni^{+2} ions than for Co^{+2}. Zn^{+2}, Cd^{+2} and Pb^{+2} ions. An ecofriendly synthesis of ion exchange resin (Patel and Gurnula, 2016) selective for Fe^{+3}, Cu^{+2}, Cd^{+2}, Zn^{+2} Ni^{+2} and Pb^{+2}.

MATERIALS AND METHOD

1. Chemicals and reagents
The important chemicals like phthalic acid (Chemocart), 1,5-naphthalenediamine and formaldehyde (S.D. Fine chemicals) used in preparation of PANDF terpolymer resin were procured from the market and were chemically pure grade and wherever necessary the purity was tested and confirmed by thin layer chromatography.

2. Synthesis of PANDF terpolymer resin
A mixture of phthalic acid (0.2 mol), and 1,5-naphthalene diamine (0.1 mol) and formaldehyde (0.3 mol) in molar ratio of 2:1:3 in the presence of glacial acetic acid medium was refluxed in an oil bath at 140 ^{0}C ± 2 for 6 h with occasional shaking to ensure thorough mixing. The temperature of electrically heated oil bath was controlled with the help of dimmer stat. The resulting mixture was then cooled, poured into crushed ice with constant stirring and left overnight. The brown coloured resin obtained. The separated terpolymer resin was washed with hot water and ethanol to remove unreacted starting materials and acid monomers. The product so obtained was further purified by reprecipitation technique. For this purpose, the terpolymer resin was dissolved in 8% aqueous sodium hydroxide solution, stirred well, filtered, and reprecipitated 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 re-precipitation was repeated twice. The purified resin was finally ground well to pass

through resin 300 mesh size sieve and kept in a vacuum over silica gel. The yield of these terpolymer resin were found to be 83 %. and the melting point found to be in the range of 383-388 K. The sieved resin was used for further characterization. The reaction sequence of the synthesis of PANDF terpolymer resin is shown in Fig. 1 and the composition determination of terpolymer was examined by elemental analysis. Since PANDF terpolymer resin contains (COOH) group it plays a key role in the ion exchange phenomenon, because of its higher tendency of capturing metal ions.
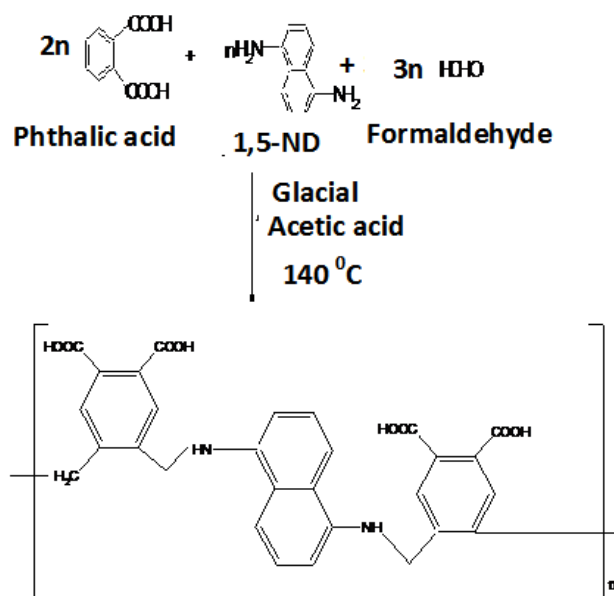

Fig.1. Reaction and suggested structure for PANDF terpolymer resin

3. Characterization of terpolymer resin

a. Physiochemical and Elemental Analysis
The terpolymer resin was subject to microanalysis for C, N and H present in the PANDF were determined by Perkin Elmer elemental analyser. The number average molecular weight $\overline{Mn}$ was determined by conducto-metric 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 g of terpolymer 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 calculations of $\overline{Mn}$ by this method is based on the following consideration. The first break corresponds to neutralization of the more acidic carboxylic group is neutralize and second break in the plot beyond which a continuous increase in conductance is observed

represents the stage at which carboxyl group of repeating units are neutralized completely. On the basis of the average degree of polymerization ($\overline{DP}$) is given by the following relation.

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

...(1)

$\overline{Mn}$ = $\overline{DP}$ x molecular weight of repeating unit

The intrinsic viscosity was determined by using a Tuan-Fuoss viscometer at six different concentration ranging from 3.0 % to 0.5 wt % of resin in DMSO at 32^0C. The intrinsic viscosity [η] was determined by using following Huggin's and Kramer's relation:

$$\eta rel = \eta_{sp}/C = [\eta] + K_1[\eta]^2 \cdot C \quad ....(2).$$

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

b. Spectral and surface analysis

Electronic (UV-Visible) absorption spectra of the terpolymer was recorded at room temperature in the range 185-2600 nm using UV-Visible-NIR Spectrometer Hitachi 330, Perkin Elmer Spectrometer was used for recording FTIR spectrum of the terpolymer resin to identify the linkage and functional groups. The proton NMR spectrum of the PANDF terpolymer resin was recorded in DMSO- d6 solvent using BRUKER AVANCE II 400 NMR Spectrometer. Surface morphology of the terpolymers were studied by Scanning Electron Microscopy (SEM) Jeol 6390LV at Sophisticated Analytical Instrument Facility, STIC Cochin.

4. Ion-exchange properties

The ion-exchange properties of PANDF terpolymer resin was determined by the batch equilibrium method. We studies the influence of various electrolytes, the rate of metal uptake and distribution of metal ions between the terpolymer and solutions.

1. Determination of effect of different electrolytes on Metal ion uptake:

The ion exchange properties of PANDF resin was determined by batch equilibrium method. 25 mg offinely powdered resin was suspended in an electrolyte solution (25ml) of known concentration. The pH of the Solution was adjusted to required value by using either 0.1M HCl or 0.1M NaOH. The suspension was stirred for a period of 24 hours at room temperature. To this suspension 2ml of 0.1M solution of metal was added and the pH was adjusted to the required value. The mixture was again stirred at 25^0C for 24 hour and filtered. The polymer was washed and the filtered and washing were combined and estimated for the metal ion content by titrating against standard ethylene diaminetetra acetic acid. A blank experiment was also carried out in the same manner without adding the polymer sample to estimate the metal ion content. The amount of metal ion taken up by the resin in the presence of given electrolyte of known concentration was determined from the difference between the blank reading and the reading in the actual experiments. The experiment was repeated in the presence of several electrolytes of known concentration with four different metal ions such as Co^{2+}, Hg^{2+}, Cd^{2+} and Pb^{2+}.

2. Evaluation of the rate of metal ion uptake:

In order to estimate the time required to reach the state of equilibrium under given experimental conditions, a series of experiments of the type described above were carried out. The metal ion uptake by the chelating resins was estimated from time to time at room temperature at 25^0C. It was assumed that under given conditions, the state of equilibrium is established in the 24 hrs. The rate of metal ion uptake is expressed as percent of the amount of metal ion taken up after a certain time related to that in the state of equilibrium.

3. Evaluation of distribution of metal ion at different pH values:

The distribution of each of the metal ions Co^{2+}, Hg^{2+}, Cd^{2+} and Pb^{2+} between the resin phase and aqueous phase was estimated at 25^0C using 1M NaNO$_3$solution. The experiment was carried out as described above at different pH values.

4. Distribution ratios of metal ions at different pH :

The distribution of each one of four metal ions i.e. Co^{2+}, Hg^{2+}, Cd^{2+} and Pb^{2+} between the polymer phases and the aqueous phase was determined at 25 ^{o}C and in presence of 1 M NaNO$_3$ solution. The experiment was carried out as described earlier at different pH values. The distribution ratio "D"is defined the following relationship.

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

RESULTS AND DISCUSSION

1. Physicochemical studies

The brown coloured resin obtained. The terpolymer resin are found to be soluble in N, N-dimethylsulphoxide (DMSO), concentrated aqueous NaOH and KOH. The synthesized terpolymer was analysed for the % of Carbon, Hydrogen and nitrogen content. Based on the analytical data, the empirical formula of the terpolymer resin was found to be $C_{29}N_2O_8H_{23}.2H_2O$, which is in good agreement with the calculated values of C, H and N. The resin was analyzed for carbon, Hydrogen and nitrogen content C = 60.24 % (F) and 61.81% (cal); H = 4.11 % (F) and 4.79 % (cal); N = 4.20 % (F) and 4.79 % (cal).

The number average molecular weight $\overline{Mn}$ could be obtained by multiplying the $\overline{DP}$ by formula weight of repeating unit (Katkamwar *et al.*, 2009). The calculated molecular weight for PANDF resin is 6851.

Viscometric measurement was carried out in DMSO at 32°C. The intrinsic viscosity of PANDF resins determined from both the plots is found to be identical. The intrinsic viscosity [η] was determined by using following Huggin's Eq. (2) and Kramers Eq. (3) which is 0.082 and 0.080, respectively. In accordance with the above relations, the plots of η_{sp}/C and $\ln\eta_r/C$ Vs C were found to be linear giving as slopes K_1 and K_2, respectively. Intercept on the axis of viscosity function gave the [η] value in both the plots (Kushwaha *et al.*, 2012)). viscosity obtained from both the plots have been found to be in close agreement with each other.

2 Spectral and surface studies

The UV-visible spectrum of the PANDF [Fig. 2]. UV-Visible spectra of PANDF resins have been recorded in pure DMSO in the region of 200-800 nm. The spectra depicted two characteristic bands in the region of 260-290 band which may be accounted for a π→π* transition and 300 -320 nm may be due to n→π* transition. π→π* transition indicates the presence of aromatic nuclei and n→π* transition indicates presence of –COOH group. The allowed and forbidden transition of π→π* and n→π* transition.

FTIR spectra of PANDF is depicted in (Fig. 3). A band appeared in the region of 3237 cm^{-1} is assigned to the hydroxyl group of –COOH group present in aromatic ring which is involved in an intramolecular hydrogen bonding. The band obtained in the range of 2926 cm^{-1},1499 cm^{-1}, 606 cm^{-1} may be due to –NH- stretching, bending and deformation out of plane vibration of the amine moiety in resins respectively. The presence of methylene bridge (-CH$_2$-) in polymer chain may be assigned due to presence band at 1474 cm^{-1} ,1371 cm^{-1} and 790 cm^{-1} bending, wagging and rocking mode of vibration respectively. The sharp band displayed at 1623 cm^{-1} may be due to the stretching vibration of carbonyl group. The 1,2,4,5 tetra substitution of aromatic benzene ring confirmed by sharp/ medium/ weak absorption bands appeared between 1283-914 cm^{-1}. The >C-O stretch in phenol is ascribed due to the presence of band at 1430 cm^{-1}. ^{1}HNMR spectra of newly synthesized PANDF resins [Fig. 4]. The signal in the region of 7.2-7.76(δ) ppm is assigned to all the protons of aromatic ring.
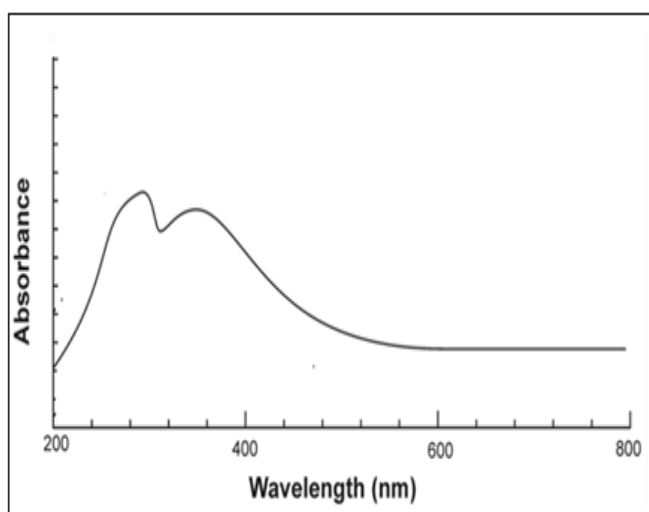

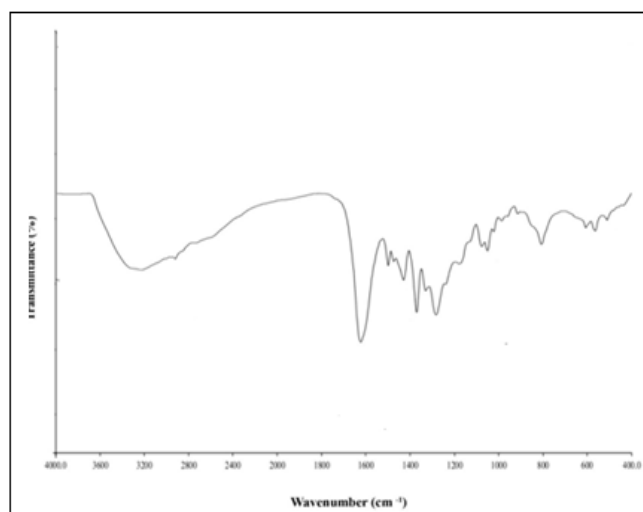**Fig 2.** Electronic spectra of PAND terpolymer resin

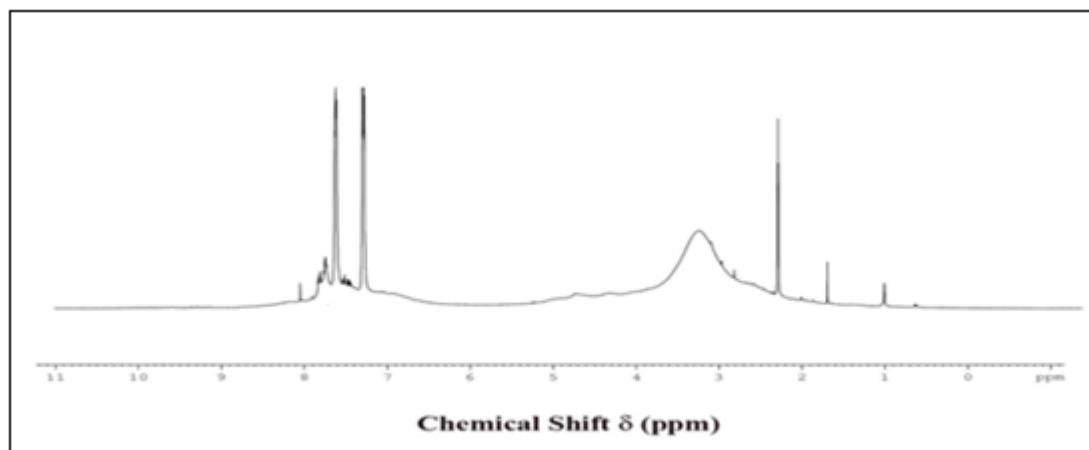**Fig. 3 :** IR-spectral data of PANDF terpolymer resin
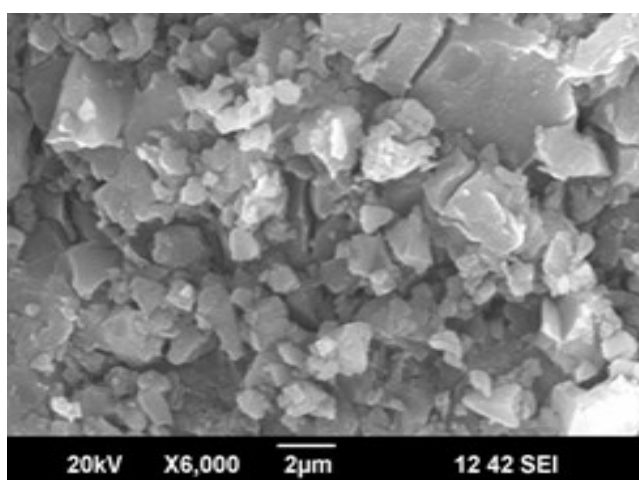
Fig. 4 : NMR-spectral data of PANDF terpolymer resin

Fig. 5 : SEM image of PANDF terpolymer resin

The signal appeared in the region of 7.9-8.05 (δ) ppm is due to the –NH bridge present in the resin. The methylenic protons of Ar-CH$_2$-NH- moiety may be recognized as signal appearing in the region 2.51 (δ) ppm.

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.5). It gives the information of surface topology and defect in the structure. 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 PANDF- shows the presence of crystalline-amorphous layered morphology which is the characteristic of polymer. The monomer have crystalline structure but during condensation polymerization of some crystalline lost into amorphous nature, hence shows higher metal ion exchange capacity.

3. Ion Exchange Properties

With a view to ascertain the selectivity of the terpolymer resin for the selected metal ions, we have studied, the influence of various electrolyte on the selectivity of metal ions, the rate of metal uptake and distribution ratio of metal ions between the terpolymer and solution containing metal ions , are analyzed by using the batch equilibrium method. Data of experimental procedure for EDTA titration is presented in Table.1.

The PANDF terpolymer (Fig. 1.) shows that the group –COOH and –NH contain lone pair of electrons, which can be donated to the metal ion during complex formation. Hence it shows chelating behavior. When the polymer is suspended in metal ion solution, the chelating tendency of terpolymer forms the cyclic complex with metal ion, which absorb the metal ion from the solution to the surface of the polymer. This mechanism of adsorption of metal ion by polymer ligands is known as metal uptake of polymer. As the 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 known as selectivity of polymer towards the uptake of metal ion. The metal uptake of terpolymer depends on three variables, concentration of electrolyte solution, time and pH of the solution. The chelating behavior of PANDF terpolymer was studies with these three variables by keeping two variable constant at each time.

Polymer + metal ion solution + shaking $\longrightarrow$
   Polymer –metal ion chelate
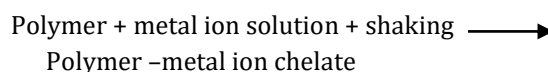
Batch equilibrium technique developed by Gregor and DeGeiso was used to study of ion exchange property of PANDF terpolymer resin. The result of batch equilibrium study carried out with the terpolymer resin PANDF is presented in Table.2-4. Four metal ions Co^{2+}, Hg^{2+}, Cd^{2+} and Pb^{+2} in the form 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.

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

The effect of different concentrations of chloride (Cl^-), nitrate (NO_3^-) and sulfate (SO_4^{2-}) ions in the electrolytes under equilibrium metal–resin interaction conditions were studied. The amount of metal ion taken up by a given amount of terpolymer resin depends on the nature and concentrations of the electrolyte present in (Table.2.). The anions present in the electrolyte are also of vital importance in the metal ion adsorption process. If the electrolyte ligand is capable of forming strong chelates with the metal ions, the availability of metal ions in the solution will decrease (Jadhao *et al.*, 2006), Azarudeen and Burkanudeen., 2012). Hence metal ion uptake by the terpolymer decreases. If the anion forms weak chelates with the metal ions, the availability of the metal ions increases in solution. Furthermore, the polymer is capable of breaking the electrolyte ligand–metal chelate bond which leads to increased availability of the metal ions for adsorption. Among the three electrolytes, the sulfate ($SO4^{2-}$) has the capacity to donate more electrons during the complex formation.

Therefore, the sulfate ($SO4^{2-}$) ion-containing electrolyte forms strong and stable complexes, hence the number of metal ions available for polymer adsorption decreases.

Compared with the sulfates, the other anions form weak complexes, therefore metal ion uptake increases. However, uptake of other metal ions, for example Co^{2+}, Hg^{2+}, Cd^{2+} and Pb^{+2} decreases on increasing the concentrations of chloride (Cl^-) and nitrate (NO_3^-) electrolytes at higher pH. At higher pH, these ligands form strong complexes with the Co^{2+}, Hg^{2+}, Cd^{2+} and Pb^{+2} metal ions.

3.2 Evaluation of metal ion uptake at different pH

The distribution of each of the metal ions between the polymer phase and the aqueous phase was determined at room temperature in the presence of 1 M $NaNO_3$ at pH ranging from 1.5 to 6 (Table. 3.). The study was limited to a maximum pH of 6 to avoid any hydrolysis of the metal ion. The metal hydroxide, if formed, will interfere withthe ion-exchange process. The amount of metal ion uptake by the terpolymer at different pH was calculated to optimize the exact pH at which the terpolymer takes most metal ion. The metal ions, for example Co^{2+}, Hg^{2+}, Cd^{2+} and Pb^{+2} have low distribution ratios. The distribution ratio for all the metal ions depends on the stability constants of their complexation during the ion-exchange process. At higher distribution ratios of the metal ions, the stability constants of the ligand and metal complexation will be higher. metal ions Hg^{2+} and Pb^{+2} form weak chelates over a wide range of pH. The order of the distribution ratios of the metal ions with the PANDF terpolymer was $Co^{2+}>Cd^{2+}>Pb^{2+}>Hg^{2+}$.

3.3. Rate of metal ion uptake as a function of time

The study was carried out to determine the time at which a state of equilibrium between the polymer and the metal ion solution is attained. Generally, the rate of metal ion uptake depends upon the ionic size of the metal ions (Table.4.). It is found that Cd^{2+} and Pb^{2+} ions required almost 6 h, Co^{2+} required 5 h and Hg^{2+} required 7 h. Thus, the rate of metal ion uptake follows the order $Co^{2+}>Cd^{2+}>Pb^{2+}>Hg^{2+}$.

Table 1: Data of experimental procedure for direct EDTA titration.

Metal Ion	Type of titration	pH	Buffer	Indicator	Colour change
Pb^{2+}	Direct	5.5	Hexamine	Xylenol orange	Red-yellow
Co^{2+}	Direct	5.0	Hexamine	Xylenol orange	Red-yellow
Hg^{2+}	Direct	6.0	Hexamine	Xylenol orange	Red-yellow
Cd^{2+}	Direct	5.5	Hexamine	Xylenol orange	Red-yellow

Table 2: Evaluation of the influence of different electrolyte on the uptake of several metal ions of PANDF Terpolymer resins

Metal Ion	Electrolyte Conc. (mol/lit)	Weight of the metal ion (mg) taken up in presence of		
		NaCl	NaNO$_3$	Na$_2$SO$_4$
		PANDF	PANDF	PANDF
Co^{2+}	0.01	1.99	1.79	1.70
	0.05	1.19	1.22	1.40
	0.1	1.10	1.50	1.02
	0.5	0.39	0.92	0.79
	1.0	0.35	0.41	0.32
Cd^{2+}	0.01	1.82	1.69	1.62
	0.05	1.40	1.29	1.34
	0.1	0.84	1.20	1.20
	0.5	0.57	0.99	0.70
	1.0	0.34	0.59	0.25
Pb^{2+}	0.01	1.30	1.62	-
	0.05	1.19	1.00	-
	0.1	1.10	0.97	-
	0.5	0.82	0.67	-
	1.0	0.49	0.29	-
Hg^{2+}	0.01	0.70	0.99	-
	0.05	0.21	0.89	-
	0.1	0.19	0.81	-
	0.5	0.14	0.61	-
	1.0	0.12	0.19	-

[a][M(NO$_3$)$_2$] = 0.1 mol/L, Volume electrolyte solution = 25 mL
Volume of metal ion solution =2 mL, weight of resin, Time = 24 h, Room temperature,
pH value : Co^{2+} = 5, (Cd^{2+} ,Pb^{2+}) = 5.5, Hg^{2+} = 6.

Table 3 : Distribution Ratio D[a] Of Different Metal Ions As Function Of The pH Of PANDF Terpolymer Resins

Metal Ion	Terpolymer	Distribution ratio of metal ions [b] at various pH								
		1.5	1.75	2.0	2.5	3	3.5	4	5	6
Co^{2+}	PANDF	-	-	-	39.45	121.40	182.72	219.10	240.74	284.50
Cd^{2+}	PANDF	-	-	-	29.40	40.21	110.26	184.00	212.24	230.40
Pb^{2+}	PANDF	-			31.40	40.00	90.10	130.12	201.01	201.24
Hg^{2+}	PANDF	-	-		-	-	10.43	21.04	41.19	112.2

[a]D = weight (in mg) of metal ions taken up by 1g of terpolymer/ weight (in mg) of metal ions present in 1 mL of solution.
[M(NO$_3$)$_2$] = 0.1 mol/L; volume : 2 ml; NaNO$_3$ = 1.0 mol/L, volume =25, time 24 h (equilibrium state) at Room temperature.

Table 4 : Comparision Of the Rate Of Metal Ion Uptake Of PANDF Terpolymer

Metal Ion	Terpolymer	Percentage of the amount of metal ion uptake at different (hr)						
		1	2	3	4	5	6	7
Co^{2+}	PANDF	34.0	50.2	60.3	79.2	92.3	-	-
Cd^{2+}	PANDF	19.4	24.4	42.4	66.2	72.1	76.2	-
Pb^{2+}	PANDF	19.4	29.4	39.4	66.4	74.8	75.0	-
Hg^{2+}	PANDF	-	-	30.6	51.2	61.3	80.5	92.4

[a][M(NO$_3$)$_2$] = 0.1 mol/lit, NaNO$_3$ = 1.0 mol/L, Volume NaNO$_3$ = 25 mL, Volume of metal ion solution =2 mL

CONCLUSION

An eco-friendly terpolymer resin PANDF has been synthesized. The structure of the resin was clearly elucidated by use of a variety of spectral techniques. Empirical formula and average molecular weights were also determined. The surface of the terpolymer resin was found to be more amorphous than crystalline in nature, clearly indicating the suitability of the synthesized resin for ion-exchange applications.

Conflicts of interest: The authors stated that no conflicts of interest.

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