

STUDY OF CHELATION ION-EXCHANGE PROPERTIES OF NEW POLYMER RESIN DERIVED FROM 4-HYDROXYACETOPHENONE AND CATECHOL

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ABSTRACT

A polymer was synthesized for the detoxification of harmful metal ions using a synthesized resin involving 4-hydroxyacetophenone and catechol with formaldehyde (4-HACF-I) in 1:1:2 molar ratio condensation technique. The average molecular weight of resin was determined by non. aqueous conductometric titration method. The synthesized polymer resin was characterized by elemental analysis, UV-Visible absorption spectra, IR spectra and ¹H NMR spectra. The morphology of polymer was studied by scanning electron microscopy. To study the selectivity and binding capacity of the polymer resin toward certain metal ions such as Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺ and Pb²⁺ in different electrolyte concentrations, wide pH ranges and time intervals was carried by batch equilibrium method.

Keywords Spectra, Resin, Ion exchange, pH range and Batch equilibrium.

I.

INTRODUCTION

Ion exchange technique can remove traces of ion impurities from water process liquors and given out a product of ultra pure quality in a single efficient and techno economically viable manner. A resins which contain both cation and an anion as exchangeable ions, is said to be ampholytic ion exchanger resin. Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotics, purification and separation of radioisotopes and find large application in water treatment and pollution control [1]. The chelating poly (amidoxime) resin was characterized by FT-IR spectra, TG and DSC analyses. Samir et. al. [2]

synthesized ion exchange resin from 8-quinolinyl methacrylate and characterized by conventional methods. The metal ion uptake capacities of synthesized copolymers were estimated by batch equilibration method using different metal ion solutions under different experimental conditions. Three phenol-formaldehyde chelating resins, poly (8-hydroxyquinoline-5, 7 diylmethylene) and poly (2- aminophenol-5,7 diylmethylene) were synthesized and characterized by Ebraheem [3]. The chelating characteristics of these polymers were studied by a batch equilibrium technique. The ion exchange capacity, effect of electrolyte on metal ion up take, rate of metal uptake and distribution of metal ion at different pH with resin copolymer derived from thiosemicarbazone derivatives of phenol compound shows higher order than the resin copolymer derived from semicarbazone derivatives [4]. Gurnule et al [5] studied the ion exchange properties of polymer derived from o-aminophenol, urea and formaldehyde Recently much work has been carried out to study the ion exchange properties of anchoring functional chelating groups on the polymeric network. Lutfor et. al. [6] prepared a chelating ion exchange resin containing amidoxime functional group.

The synthesized polymer resins showing versatile applications and properties attracted the attention of scientists and introduce the recent innovations in the polymer chemistry. These polymers can be used as high energy material [7], ion-exchanger [8], semiconductors [9], antioxidants [10], fire proofing agent [11]. One of the important application of this chelating and functional polymer is its capability to recover metal ions from waste solution. Hence the chelating ion-exchange property of the 4-HACF polymer resin was also reported for specific metal ions.

A. Experimental

- ***Materials***

The reagents 4-hydroxyacetophenone and catechol were procured from Merck, India and purified by rectified spirit. Formaldehyde (37%) were of AR grade, Merck and used as received. Solvents like N,N-dimethyl formamide and dimethylsulphoxide were used after distillation. Standardized disodium salt of EDTA was used as a titrant for all the complexometric titrations.

• *Synthesis of 4-HACF polymer resin*

The resin 4-HACF was synthesized by the condensation polymerization reaction of 4-hydroxyacetophenone and catechol with formaldehyde in 1:1:2 mole ratio by using hydrochloric acid as the reaction medium at $124\pm 2^\circ\text{C}$ in an oil bath for 5 hrs under refluxed condition with occasional shaking. 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 dried resin was further purified by dissolving in 8% NaOH and regenerated in 1:1 (v/v) HCl/H₂O. The resulting polymer resin washed with boiling water and dried in vacuum at room temperature. The yield of the polymer was found to be 87 % and the reaction route for the synthesis is shown in Fig. 1.

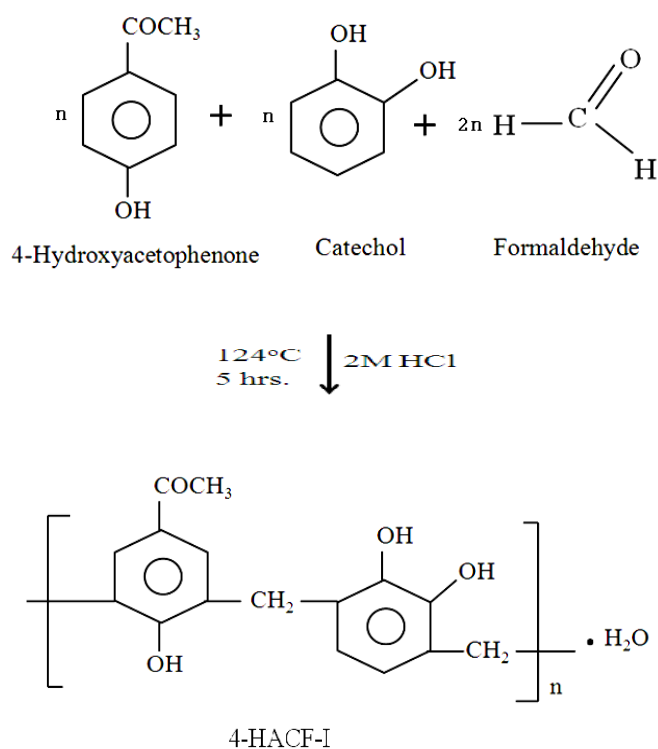


Figure 1: Reaction and suggested structure of 4-HACF-I polymer resin

B. Ion-exchange properties

The purpose of ion exchange study is to explore the adsorption behavior of seven metal ions Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} on the newly synthesized resin 4-HACF at different pH

values, different concentrations of different electrolytes, and at different shaking time intervals. The adsorption behaviour of these metal ions is based on the affinity differences towards the chelating resins as a function of pH, electrolyte concentrations and rate of uptake time. The ion-exchange property of the 4-HACF polymer resin was determined at three different variations given below.

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

The resin 25 mg was taken in glass bottles and each of the electrolytes such as NaClO₄, NaCl, Na₂SO₄ and NaNO₃ in different concentrations. The pH of the suspension was adjusted to the required value either by adding 0.1 M HCl or 0.1 M NaOH and mechanically stirred for 24 h at 25 °C for swelling of the polymer. Then exactly 0.1 M of the metal ion solution (2 mL) was added and stirred for 24 h. The mixture was then filtered off and washed with distilled water. The filtrate and the washings were collected and then the amount of metal ion adsorbed was estimated by titrating against standard Na₂EDTA solution. A blank experiment was also performed following the same procedure without the polymer sample. The metal ions taken up by the polymer in the presence of a given electrolyte can be calculated from the difference between the actual and blank value.

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

The distribution of each of the metal ions i.e Cu(II), Co(II), Ni(II), Zn(II) and Pb(II) at various pH ranging from 1.5 to 6 between the polymer phase and the aqueous phase were determined in the presence of 1 M KNO₃ at 25 °C. The experiment was carried out as described earlier at different pH values.

- ***Evaluation of Rate of Metal Ion Uptake***

The time required for attain the state of equilibrium under the experimental conditions was evaluated by a series of experiments carried out to determine the amount of metal ion adsorbed by the polymer at specific time intervals. 25 mg of the polymer sample was mechanically stirred with 25 mL of 1 M KNO₃ to allow the polymer to swell. It was observed that under the given experimental conditions the state of equilibrium established

within 24 h at 25 °C. The rate of metal ion uptake is expressed as the percentage of the metal ion uptake after the specific time related to the state of equilibrium. It is given as,

Metal ion uptake = Amount of metal ion adsorbed / Amount of metal ion adsorbed at equilibrium × 100

C. Physicochemical and elemental analysis

The polymer resin was subject to micro analysis for C, H and N on an Elementer Vario EL III Carlo Ebra 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 KOH requires for neutralization of 100 g of polymer was made. On the basis of average degree of polymeration, \overline{DP} the average molecular weight has to be determined by following equation.

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

$$\overline{M}_n = \overline{DP} \times \text{Repeat unit weight.}$$

The intrinsic viscosity was determined using a Tuan-Fuoss viscometer [12] at six different concentrations ranging from 0.3 to 0.05 wt% of resin in DMF at 30°C. Intrinsic viscosity (η) was calculated by the Huggin's equation [13] and Kraemer's equation. [14].

$$[\eta_{sp}/c] = [\eta] + K_1[\eta]^2.C$$

$$\ln [\eta_r/c] = [\eta] - K_2[\eta]^2.C$$

D. Spectral Analysis

UV-visible spectra of polymer 4-HACF were recorded in 200 to 800 nm range by using Shimadzu automatic recording double beam spectrophotometer (UV-VIS-NIR Spectrometer) UV-240 at SAIF, Punjab University, Chandigarh. An infra-red spectrum of 4-HACF polymer resin was recorded in the region 4000 to 400 cm^{-1} were scanned in KBr pellet on Perkin Elmer Model 983 spectrophotometer at SAIF, Panjab University, Chandigarh. A ^1H NMR spectrum of newly synthesized polymer resin has been scanned on

90 MHz for proton using Bruker Avance II 400 NMR Spectrometer in deuterated dimethyl sulphoxide (DMSO-d₆) at SAIF Panjab University, Chandigarh. Scanning electron micrograph of polymer has been scanned and magnification by SEM at Sophisticated Test and Instrumentation Centre, STIC, Cochin University, Cochin.

II. RESULTS AND DISCUSSION

The polymer sample was dark brown in color and soluble in solvents like DMF, THF, DMSO, aqueous sodium and potassium hydroxide solutions and insoluble in alcohol, chloroform and carbon tetrachloride. The melting point of resin is 487K and empirical formula of the polymer resin is found to be C₁₆H₁₄O₄ which is in good agreement with the calculated values of C, H and O. The molecular weight of polymer resin was also determined by conductometric titration. The calculated molecular weight for 4-HACF resin is 1350.

A. Electronic Spectral Analysis

The UV-Visible spectra (Fig. 2) of the 4-HACF-II polymer sample in pure DMSO was recorded in the region 200-800 nm at a scanning rate of 100 nm min⁻¹ and a chart speed of 5 cm min⁻¹. The 4-HACF-II polymer sample gave two characteristics bands at 260-260nm and 300-370 nm. These observed positions for the absorption bands have different intensities. These observed positions for the absorption bands clearly indicate the presence of carbonyl group in the sample belonging to 4-dihydroxyacetophenone moiety. The more intense appeared as a result of $\pi \rightarrow \pi^*$ transition while the less intense may be due to $n \rightarrow \pi^*$ [15] electronic transition indicates presence of -OH group.

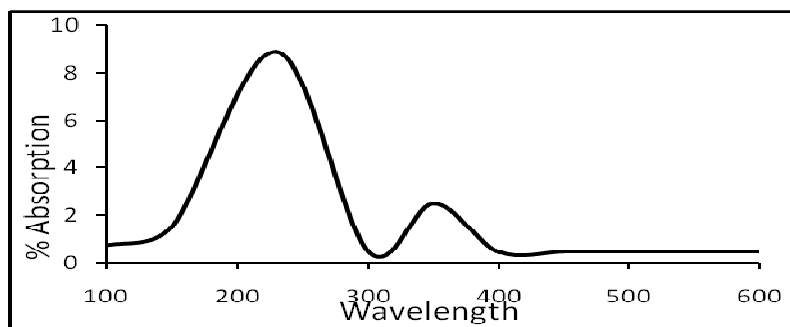


Fig. 2: Electronic spectra of 4-HACF polymer resin

B. *Infra-Red Spectral Analysis*

The IR spectra of 4-HACF polymer resin are presented in Fig. 3. A broad band appeared in the 3262 (b) cm^{-1} may be assigned to the stretching vibration of phenolic hydroxyl (-OH) group exhibiting intermolecular hydrogen bonding [16]. The sharp and weak band obtained at 1279 (w) cm^{-1} suggests the presence of Ar-CH₂-Ar bridge in polymer. The sharp strong peak at 1436 (s) cm^{-1} may be ascribed to aromatic skeletal ring. The bands obtained at 1279 cm^{-1} suggest the presence of methylene (-CH₂) bridge [17]. The sharp band displayed at 1657 cm^{-1} may be due to stretching vibration of carbonyl group attached to acetophenone moiety. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption and appeared at 562 (st) , 800 (s) , 979 (s) and 1018 (m) cm^{-1} respectively. This band seems to be merged with very broad band of phenolic hydroxyl group.

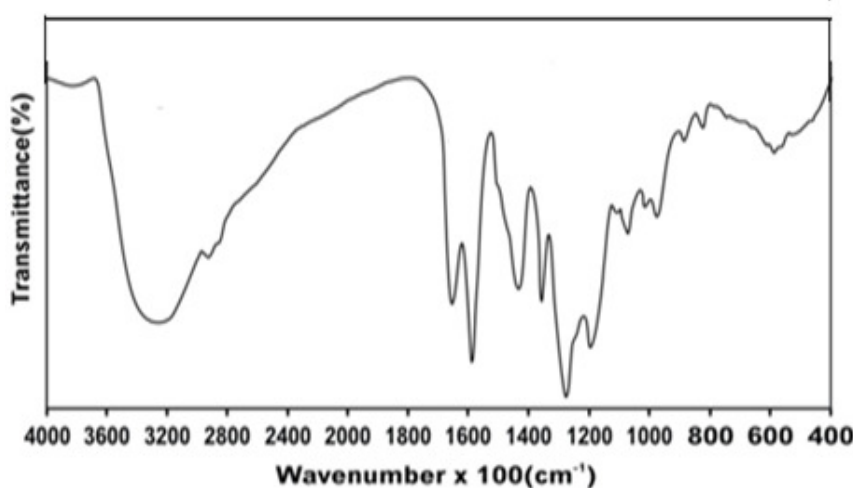


Fig. 3: Infra-red spectra of 4-HACF polymer resin

C. *¹H NMR Spectral Analysis*

The NMR spectra of 4-HACF is presented in Fig. 4. The singlet obtained in the region 2.13 (δ) ppm may be due to the methylene proton of Ar-CH₂-Ar bridge. The weak multiple signals (unsymmetrical pattern) in the region of 7.56 (δ) ppm may be attributed to aromatic proton (Ar-H). The signals in the 8.12 (δ) ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic-OH indicates clearly the intramolecular

hydrogen bonding of -OH group. The signal appeared in the region at 3.84(δ) ppm is due to the methylene proton of Ar-CH₂ bridge. The methyl protons of the Ar - CO - CH₃ moiety may be identified by the intense peak at 3.24(δ) ppm [18,19].

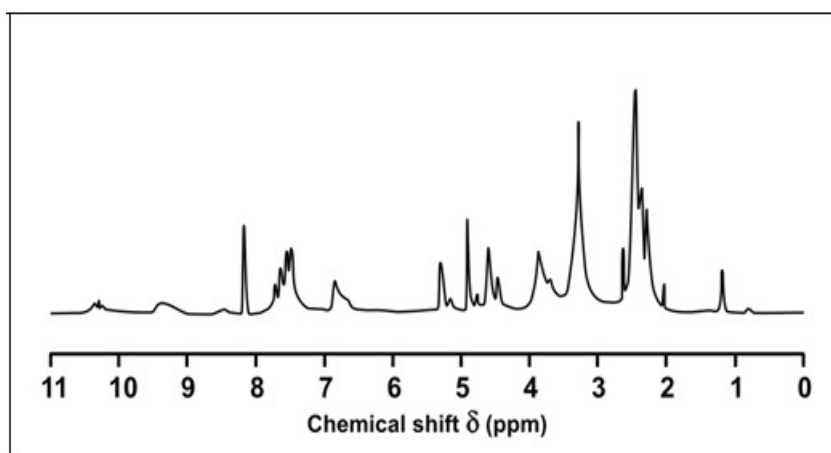


Fig. 4: ¹H NMR spectral data of 4-HACF polymer resin

D. Scanning electron microscopy (SEM)

The scanning electron micrograph of 4-HACF polymer resin have been scanned and magnification by analytical scanning electron microscope at Sophisticated Test and Instrumentation Centre, STIC, Cochin University, Cochin as shown in the Fig.5. Surface analysis has found great use in understanding the surface features of the polymers. SEM gives the information of surface topology and defect in the structure. The semi crystalline nature of 4-HACF copolymer resin was established by scanning electron microscopy. The morphology of resin sample thus identified by SEM as crystalline as well as amorphous or transition between crystalline and amorphous, showing more or less good ion capacity. The polymerization reaction proceeds by introducing amorphous character in the polymer sample [20].

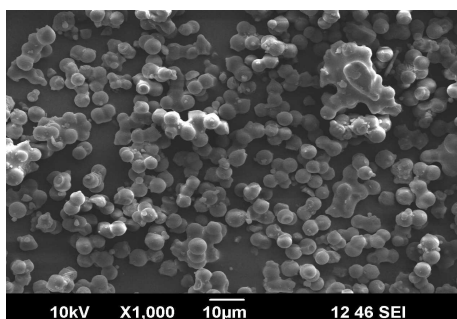


Fig 5: Scanning electron microscopy of 4-HACF polymer resin

E. Ion-exchange properties

The results of the batch equilibrium study carried out with the polymer 4-HACF are presented in Tables 1–3. Five metal ions Cu(II), Co(II), Ni(II), Zn(II) and Pb(II) in the form of aqueous metal nitrate solution were used. The ion-exchange properties was carried out using three experimental variables such as a) electrolyte and its ionic strength b) uptake time and c) pH of the aqueous medium [21].

- *Effect of Electrolytes on Metal Ion Uptake*

Examination of the data given in Table 1 reveals that the amount of metal ions taken up from a given amount of polymers depends on the nature and concentration of the electrolyte. In presence of perchlorate, chloride and nitrate ions, the uptake of Cu^{2+} and Ni^{2+} ions increases with increasing concentration of the electrolytes, whereas in presence of sulphate ions the amount of the above mentioned ions taken up by the polymers decreases with increasing concentration of the electrolytes [22]. Moreover, the amount of Co^{2+} , Zn^{2+} and Pb^{2+} ions taken up by the polymer resin decreases with increasing concentration of the chloride, nitrate, perchlorate and sulphate ions [22]. This may be explained in terms of the stability constants of the complexes which Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} ions form with these anions. SO_4^{2-} might form rather strong complexes with Ni^{2+} and Cu^{2+} ions, while ClO_4^- , NO_3^- and Cl^- might form weak complexes and, therefore, might not be expected to influence the position of the Ni^{2+} and Cu^{2+} chelates equilibrium as much as SO_4^{2-} . Sulphate, perchlorate, nitrate and chloride might form rather strong chelate with Co^{2+} , Zn^{2+} and Pb^{2+} .

Table 1. Evaluation of the uptake of metal ions by 4-HACF resin

Metal ions	Concentration of electrolytes (mol/L)	Weight of metal ion uptake in presence of electrolytes (mg)			
Cu^{2+}	0.01	2.18	2.42	1.68	3.59
	0.05	2.49	2.67	1.94	2.47
	0.10	2.89	2.88	2.65	2.26
	0.50	3.21	3.49	3.11	1.44
	1.00	3.39	3.81	3.44	0.83

Ni^{2+}	0.01	1.85	1.22	1.25	2.93
	0.05	2.61	1.31	1.76	2.21
	0.10	3.07	1.42	2.16	1.65
	0.50	3.54	1.87	2.31	0.87
	1.00	4.17	2.24	2.55	0.64
Co^{2+}	0.01	1.56	1.62	1.76	1.71
	0.05	1.34	1.31	1.55	1.53
	0.10	1.24	1.19	1.31	1.37
	0.50	0.83	0.91	0.94	1.16
	1.00	0.56	0.63	0.72	0.92
Zn^{2+}	0.01	1.71	1.55	2.35	1.93
	0.05	1.46	1.26	2.14	1.66
	0.10	1.25	1.06	1.64	1.29
	0.50	0.89	0.87	1.17	1.16
	1.00	0.64	0.43	0.64	0.83
Pb^{2+}	0.01	1.48	1.76	1.79	2.14
	0.05	1.32	1.46	1.60	1.81
	0.10	1.16	1.23	1.39	1.34
	0.50	0.96	0.91	1.15	0.95
	1.00	0.72	0.52	0.67	0.63

• ***Evaluation of the Rate of Metal Ion Uptake***

The data of metal ion uptake at various shaking time intervals is given in Table 2. These results indicate that the time taken for the uptake of the different metal ions at a given stage depends on the nature of metal ion under given conditions. It is found that Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} ions require about 5h for the establishment of the equilibrium where as Pb^{2+} ions required almost 6h for equilibrium. Thus, the rate of metal ion uptake follows the order Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} > Pb^{2+} for the polymer 4-HACF. The trend is good agreement with earlier workers [23].

At the equilibrium condition metal has the highest percentage rate of uptake, which is acquired due to 24 hrs staking. The sequence of rate of metal ion uptake indicates that the rate may depend on size of the ion. The rate is directly proportional to the size of the metal

ion. For example first transition ions Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} have nearly equal cationic size, having same charges, therefore required 5 hrs to attain equilibrium, while Pb^{2+} have large atomic size, therefore requiring 6 hrs to attain equilibrium. This trend is good agreement with earlier workers [23].

Table 2 Evaluation of rate metal ion uptake by 4-HACF resin

Metal ions	Equilibrium attainment (%)					
	Time (h)					
	1	2	3	4	5	6
Cu^{2+}	54.5	68.7	81.5	89.4	94.3	-----
Ni^{2+}	61.7	70.2	81.4	86.5	96.2	-----
Co^{2+}	48.3	67.3	76.6	86.4	97.3	95.2
Zn^{2+}	50.4	62.2	71.3	89.2	94.2	
Pb^{2+}	27.2	48.3	66.2	75.4	85.4	

• ***Distribution Ratio of Metal Ions at Different pH***

The effect of pH on the amount of metal ion distributed between two phases can be explained by the result shown in the Table 3. The study was carried out up to definite pH value for the particular metal ion to prevent hydrolysis of the metal ions at higher pH. Cu^{2+} and Ni^{2+} have highest distribution ratio at pH 2.5 to 6, therefore these ions can be taken up more selectively between the ranges of pH 2.5-6. The other three ions Co^{2+} , Zn^{2+} and Pb^{2+} have lower distribution ratio over pH range of 2.5 to 6. The high distribution ratio may be due to higher stability constant of metal ligand complexes and vice versa. Cu^{2+} and Ni^{2+} may form more stable complex, indicate that these ions adsorbed more selectively to the higher extent, rather than Co^{2+} , Zn^{2+} and Pb^{2+} which may form rather weak complexes with ligand during the course of time, therefore these ions adsorb to a least extent over an entire pH range study. Thus, the order of selectivity of metal ions by the polymer is found to be $\text{Cu (II)} > \text{Ni (II)} > \text{Co (II)} > \text{Zn (II)} > \text{Pb (II)}$. The result is in good agreement with earlier co-workers [24].

Table 3 Evaluation of distribution ratio D, at different pH

Metal ions	Distribution ratio(KD) of the metal ions							
	pH of the medium							
	1.5	2	2.5	3	3.5	4	5	6
Cu ²⁺	-	-	64.6	87.4	192.2	343.4	769.1	1044.3
Ni ²⁺	-	-	59.1	68.3	91.3	237.1	452.3	741.3
Co ²⁺	-	-	43.4	55.2	89.4	126.1	264.5	452.3
Zn ²⁺	-	-	46.3	54.6	82.3	94.4	182.4	249.2
Pb ²⁺	-	-	34.2	55.3	74.7	96.1	145.3	233.3

III.CONCLUSIONS

The polymer 4-HACF resin is a selective chelating cation exchange polymer resin for certain metals. The uptake capacities of metal ions by the polymer resin were pH dependent. The uptake capacities of metal ions by the polymer resin were carried out by batch equilibrium technique. Due to the considerable difference in the adsorption capacity at different pH media, the rate of metal uptake and distribution ratio at equilibrium, it may be possible to use the polymer for separation of particular metal ions. Also from the FTIR and ¹H NMR spectral studies the proposed structure of the 4-HACF polymer resin has been determined.

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