Synthesis, Characterization, Chelatio n and Ion-Exchange Studies of a Resin Copolymer-II Derived From 2,4-Dihydroxyacetophenone-Formaldehyde-Adipamide

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Abstract-- Copolymer resin 2,4-DHAFA-IIwas synthesized by condensation of 2,4dihydroxyacetophenone and adipamidewith formaldehyde in presence of 2M HCl acid ascatalyst. Different techniques like elemental analysis, conductometric, viscosity measurements, UV-visible, IR and ¹H-NMR were used to characterized the resin. Using different metal ions Fe^{+3} , Cu^{+2} , Pb^{+2} , $Cd^{+2}and Co^{+2}$ ions the chelation cation exchange properties of this copolymer were studied .The selectivity distribution of a given metal ions for polymer sample and a solution containing metal ion was studied by a batch equilibrium method over a wide pH range using different electrolytes of various ionic strength. It was observed that among the different metal ionslike Fe^{+3} , Cu^{+2} , Pb^{+2} , Cd^{+2} and Co^{+2} ions a higher selectivity was shown by Fe^{+3} ion.

Keywords--2,4-DHAFA-II, Synthesis, characterization, ion-exchangers, batch equilibrium, distribution ratio.

I. INTRODUCTION

Over the past years, there has been a growing concern for theimmobilization of metal ions introduced into bodies of water andwastewater by increasing human technological activities. It hasbeen established beyond doubt that the ions of heavy metals in the environment

(air, soil and water) pose a serious threat to humanhealth. With the exponential growth of the population, it is necessary to control the release of toxic heavy metal ions before entering the complex ecosystem. Separation, removal, and the enrichment of metals in trace amountsin aqueous solutions, have an important role in wastewater, industrial or geological sample analysis. The quality of the water is get affected by discharge of heavy metals which poses a serious environmental problem as well as severehealth hazards because of their toxicity, persistence in nature, and nonbiodegradability, particularly when they exceed the permissible limits[1]. Using static batch equilibrium method chelationion exchange properties were investigated for tercopolymer. Heavy toxic metal ions are generally found together in a hydrometallurgical, recycling or wastewater process, preliminary separation of those metals ions are very essential at this juncture.Synthesis of o-nitrophenol and thiourea with p-formaldehyde terpolymerhas been reported and its by [2]. Lutfor et al [3] prepared a chelating ion exchange resin containing amidoxime functional group and was characterized by FT-IR spectra, TG and DSC analyses and chelating behaviorof prepared resin was studied with Cu (II), Zn (II), Ni (II), Cd (II) and Pb (II) metal ions. Synthesis and characterization of ion exchange resin prepared from 8-quinolinyl methacrylate was carried out by Samir et al [4]. Thermal analysis was carried out using TGA and DSC.Batch equilibration method was used to find out metal ion uptake capacity of synthesized copolymersfor different metal ions under different experimental conditions.

Ebraheemhave been synthesized and characterized three different phenol-formaldehyde chelating resins which are poly(8-hydroxyquinoline-5,7-diylmethylene), poly(8-hydroxyquinoldine-5,7-diyl-methylene) and poly(2-aminophenol-5,7-diylmethylene) [5]. At various conditionsa good binding capacity for lanthanum (III) was shownby Poly[(2-hydroxy-4methoxybenzophenone)ethylene] resin[6]. Recently much work has been carried out to study ion exchange properties of anchoring functional chelating groups on polymeric network.Because of good stability and flexibility in working conditions synthesizedresinwere found to be moreadvantageousthan anchored resins.

Rivas [7] have been synthesized cross linked poly [3-(methacryloylamino)-propyl]-dimethyl(3-sulfopropyl)ammoniumhydroxide-co-2-acrylamid glycolicacid [PCMAAPDSA-co-AGCO] by radical polymerization and tested the synthesized polymer as an absorbent under competitive and noncompetitive conditions for Cu(II), Cd(II), Pb(II), Zn(II), Pb(II) and Cr(III) by batch and column equilibrium procedures. From their work they concluded that resin metal ion equilibrium was achieved within 1 hrand resin showed amaximum retention capacity value of 1.084 m.equ g⁻¹ for Pb(II) at pH 2.

Anather type of copolymer resin wassynthesized by Rahangdale et. al. [8] using chemicals like 2,2'-dihydroxybiphenyl and formaldehyde in presence of acid catalyst and studied chelating ion exchange properties for different metal ions. The selectivity of metal ion uptake and the distribution of mal ionwas studiedby batch equilibriummethod. The study was carried out over a wide pH range in media of various ionic strengths and reported that the polymer showed a higher selectivity for Fe (III), Cu (II) and Ni (II) than for Co (II), Zn (II) Cd (II) and Pb (II) ions.

The present article describes the synthesis of 2.4dihydroxyacetophenone-adipamide-formaldehyde copolymer resin using solution condensation technique in the presence of acid medium. The synthesized resin have been characterized by various spectral techniques and confirmed. The surface features of the copolymer resin were examined by scanning electron microscopy. The ion exchange capacity of the copolymer resin was studied by batch separation technique for the selective metal ions and the results were compared with the commercially available ion-exchange resins.

II. EXPERIMENTAL

Materials

The chemicals required for the experiments were 8-hydroxyquinoline 5-sulphonic acid, formaldehydeand semicarbazide. All these chemicals were of A. R. grade chemically pure and purchased from Merck, India. Distillation process for the solvents like N, N-dimethyl formamide and dimethylsulphoxide was carried out before their utilization.

Preparation of 2,4-DHAFA-II Copolymer

The 8-HQ5-SASF-III copolymer resin was prepared by condensing 2,4-dihydroxyacetophenone(0.2mol) and adipamaide (0.1 mol) with formaldehyde (0.3 mol) in presence of 2M HCl as a catalyst at temperature 124 ± 2 ⁰C in an oil bath for 5 hr. Brown coloured solid product obtained was

immediately removed and extracted with diethyl ether to remove excess of 8hydroxyquinoline 5-sulphonic acid-formaldehyde copolymer, which may be present along with the 2,4-DHAFA-IIcopolymer. It was further purified by dissolving in 8 %NaOH and then filtered. The copolymer was then reprecipited by dropwiseaddition of 1:1 (v/v) conc. HCl/water with constant stirring and filtered. The process was repeated twice. The resulting polymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified copolymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of copolymer was found to be about 85 % (Table 1).



2,4-DAAF-II

Fig. 1.Synthesis of 2,4-DHAFA-IIcopolymer

Analytical studies

Newlysynthesized copolymer were analysed and studied spectroscopicallyat STIC Analysis, Kochi.Intrinsic viscosities were determined at six different concentrations ranging from 0.3 wt % to 0.05 wt % of resin in DMF at 30^{0} C. The viscometer used for that purpose was a Tuan-

Fuoss viscometer [9].Huggin'seq (1)[9] and Kraemer eq (2) [9] were used to calculate Intrinsic viscosity (η).

Perkin Elmer 2400 elemental analyser instrument was used to carried out Elemental analysis. Using Shimadzu UV-VIS Spectrophotometer in the range 200-800 nm UV–visible study was done. Infrared spectrum was recorded in the region of 500–4000 cm⁻¹ on Shimadzu IR-Affinity Spectrophotometer. ¹H-NMR studied using BrukerAvance-II FT-NMR Spectrometer in DMSO-d₆ solvent. All analytical and spectral studies for *Ion exchange properties*

The influence of various electrolyteshaving different concentrations at different pH have been studied to decide the selectivity of 2,4-DHAFA-II copolymer as an ion exchanger.

Determination of metal ion uptake in the presence of electrolytes of different concentrations

The suspension of copolymer sample (25 mg) was prepared using 25 ml of NaNO₃ electrolyte solution of known concentration . The pH was adjusted to required value by using either 0.1 N HCl or 0.1 N NaOH. The suspension was stirred for a period of 24 hrs attemperatutre 25° C. 2 ml of 0.1M solution of the metal ion was added to this suspensionwith the adjacementof pHvalue. The mixture was again stirred at 25° C for 24 hr and filtered. The solid was washed and the filtrate and washings were combined and the metal ion content was determined by titration against standard EDTA [8]. The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in actual experiments. Experiment was repeated in presence of other three electrolytes such as NaCl and NaClO₄,Na₂SO₄ at different concetration.

Evaluation of the Rate of Metal Uptake

From series of experiments it is estimated that the time required to reach the state of equilibrium is 24 hrs. In these experiments the rate at which metal ion taken up by chelating resins was determined from time to time at 25 0 C in the presence of 25 ml of 1M NaNO₃ solution and this rate is expressed as percentage of the amount of metal ions taken up after a certain time.

Evaluation of the Distribution of the Metal Ions at Different pH

Distribution of each one of the five metal ions i.e. Fe^{+3} , Cu^{+2} , Pb^{+2} , Cd^{+2} and Co^{+2} between polymer and aqueous phase was determined at $25^{0}C$ in presence of 1M NaNO₃ solution. The experiments were carried out as described above at different pH values. The distribution ratio 'D' is defined by eq. (3).

 $D = \frac{Wt.(mg.) of metal ions taken up by 1 gm. of terpolymer}{Wt.(mg.) of metal ion present in 1 ml. of terpolymer} ----(3)$

III. RESULTS AND DISCUSSION

Copolymer which has been used in present investigation as ionexchanger was prepared as shown in reaction scheme. Resin sample was brown in color, insoluble in commonly used solvents but was soluble in DMF, DMSO and THF solvent. No precipitation and degradation of resin occurred in all these solvents. This resin wasthen purified and analyzed for carbon, hydrogen and nitrogen content and found to be in agreement with calculated value.

- Calculated for C₃₀H₂₆N₆O₁₃: C: 48.12%; H: 3.25%; N: 10.52%., O: 26.06%, S: 12.03%
- Found for C₃₂H₂₆N₆O₁₃: C: 48.90 %; H: 3.03 %; N: 10.17 %. O: 26.45%, S: 12.12%

Viscometric Study

Viscometric measurements were carried out in DMF solution at 30^{0} C using a Tuan-Fouss viscometer [9]. Reduced viscosity versus concentration (0.3 % - 0.05 %) was plotted for each set of data. Intrinsic viscosity [η] was then determined by extrapolating linear plots as shown in Fig.2. The following equations were used to determine Huggin's [9] and Krammer's [9] constant, respectively:

$\eta_{sp}/C = [\eta] + k_1$	$[\eta]^2.C$	(1)
$ln\eta_{rel}/C = [\eta] - 1$	$k_{2.}[\eta]^{2}.C$	(2)
Where,		
$[\eta] = intrinsic v$	iscosity;	C = concentration of solution;
$k_1 = Huggin's c$	onstant;	k ₂ = Kraemer's constant;

 $ln\eta_{rel}/C$ = inherent viscosity; η_{sp}/C = reduced viscosity.

According to above relations, a plots of η_{sp}/C and η_{rel}/C against C were linear with slopes of k_1 and k_2 respectively. Intercepts on the viscosity function axis have been taken [η] as intrinsic viscosity in both plots. Calculated values of the constants k_1 and k_2 for intrinsic viscosities (Table 1) satisfy the relation $k_1 + k_2 = 0.5$ favourably [10]. It was observed that copolymer having higher \overline{Mn} have shown a higher value of [η].



Fig.2. Viscometric plots of 2,4-DHAFA-IIcopolymer

UV-visible spectrum

The UV-visible spectrumwas recorded in pureDMSO in region 190 nm–800 nm for2,4-DHAFA-IIcopolymer sample (fig.3). Two characteristics broad bands at 245 nm and 290 nm were observed for terpolymer sample whichindicate the presence of a carbonyl (>C=O) group having a carbon-oxygen doublebondwhich is in conjugation with aromatic nucleus. More intense band at 290 nm can be accounted for $\pi \rightarrow \pi^*$ transition while the less intense band at 245 nm may be due to $n \rightarrow \pi^*$ transitions [11].

Due to the combine effect of conjugation and phenolic hydroxyl group (auxochrome) [12, 13] the bathochromic shift (shift towards longer

wavelength) from basic values of C=O group viz. 310 and 245 nm respectively was observed.



Fig.3.Electronic Spectra of 3 of 2,4-DHAFA-IIcopolymer

Infra Red-spectrum

IR-spectrum of 2,4-DHAFA-II copolymer is presented in Fig 4 and data reported inTable 2. Due to the stretching vibration of phenolic hydroxy groups exhibiting intermolecular hydrogen bondinga broad band appeared in the region 3442 cm⁻¹[12]. Due topresence of the –NH- group in biuret moiety of copolymericchaina weak peak at 2917 cm⁻¹ was found [12, 13]. Thesharp and weak peaks at 2847 cm⁻¹may be due to presence of methyl and methylene vibrations. Sharp band displayed at 1633 cm⁻¹ may be due to stretching vibration of carbonyl group of both, ketonic as well as adipamidemoiety [14-15]. The presence of –CH₂- methylene bridgesin copolymer chain can be confirmed from sharp and weak bond obtained at 1373 cm⁻¹–1382 cm⁻¹[15].



Fig.4.Infrared spectrum of 2,4-DHAFA-IIcopolymer

¹H-Nuclear Magnetic Resonance Spectrum

¹H-NMR spectrum of 2,4-DHAFA-IIcopolymer was scanned in DMSO-d₆ and the spectrum isas shown in Fig.5. Weak multiplet signals (unsymmetrical pattern) in the region 7.42 ppmare due to aromatic protons. The methylenic protons of the Ar-CH₂-N moiety may be recognized as signal appearing in the region 4.25 ppm [12, 13]. The signal in the region 7.66 ppm are attributed to the protons of -NH- bridges. A medium singlet peaks appeared at 9.51ppm may be assigned to adipamide protons of [12, 13]. The signals in the range of 8.65 ppm are attributed to presence of phenolic hydroxyl protons. This significant downfield in chemical shift of proton of phenolic -OH group clearly indicates intramolecular hydrogen bonding of - OH with carbonyl group present at the adjacent *ortho* position [12, 13].



Fig. 5.Proton NMR Spectrum of 2,4-DHAFA-IIcopolymer

On the basis of the nature and reactive position of the monomer elemental analysis, electronic, IR, ¹H-NMR spectrum and molecular weight, the most probable structures have been proposed for this copolymer as shown in the reaction.

Ion-Exchange Properties

The results of the batch equilibrium study carried out with the copolymer sample 8-2,4-DHAFA-IIare presented in Table 1-3. From the study with five metal ions under limited variation of experimental conditions, certain generalization may be made about the behavior of the copolymer sample.

Effect of Electrolytes on Metal Uptake

The amount of metal ions taken up by a given amount of copolymer depends on the nature and concentration of the electrolyte present in the solution. The different electrolytes which were which were used are NO_3^- , CI^- , CIO_4^- and SO_4^{-2} at various concentrations which affects the metal-resin interactions. It is found that the uptake of metal ions like Fe⁺³, Cu⁺², Pb⁺², Cd⁺² and Co⁺² ionsincreases with increasing concentration of NO₃⁻, Cl⁻, ClO₄⁻ electrolytes while the capacity decreases with rise in concentration of SO₄⁻² ions. (Table 1) This is because equilibrium is get affected as nitrate, chloride and perclorate ionsform weak complex with the above metal ions while sulphate ions form stronger complex, this can be explained on the basis of the stability constants of the complexes with those metal ions. This type of trends has been observed by other investigator in this field [16-18].

Rate of Metal Ion Uptake

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. Table 2 show the dependence of the rate of metal ion uptake on nature of the metal. Rate refers to change in concentration of metal ions in aqueous solution, which is in contact with the given polymer. The results showed that the time taken for the uptake of different metal ions at a given stage depends on nature of the metal ion under given conditions. It is found that Fe⁺³ ions required near about 3 hrs for establishment of the equilibrium, whereas Cu⁺², Pb⁺², Cd⁺²and Co⁺² ions required about 6 hrs. Thus, rate of metal ion uptake follows the order Fe⁺³ >> Cd⁺² >Co⁺²>Pb⁺² >Cu⁺² for the copolymer [16-18]. *Distribution Ratios of Metal Ions at Different pH*

Table 3 shows the effect of pH on the amount of metal ions distribution .It is clear from the data that the relative amount of metal ions taken up by copolymers increases with increasing pH of the medium [16-18]. The magnitude of increase, however, is different for different metal ions. As compare to the any other metal ions under study, Fe (III) ion is having highest selectivity for the 2,4-DHAFA-II copolymer resins. The order of distribution ratio of metal ions is found to be $Fe^{+3} >> Cd^{+2} \approx Co^{+2} > Cu^{+2} > Pb^{+2}$ measured in the pH range 1.5 to 6.5. From this studyit is possible to select the optimum pH for a selective uptake of a particular metal ion from a mixture of different metal ions [16-18].

In case of Fe^{+3} ion the lowering in the distribution ratio was found to be small thus Fe^{+3} ion can be effectively separate out from other metals having combination of (1) Fe^{+3} and Cu^{+2} (2) Fe^{+3} and Pb^{+2} (3) Cu^{+2} and Cd^{+2} .

Weight of metallion (in ma) taken up in the									
Metal ion	Electrolyte	nH	presence of						
	(mol./l)	P11	NaClO ₄	NaCl	NaNO ₃	Na ₂ SO ₄			
Fe ⁺³	0.01		0.16	0.17	0.18	0.68			
	0.05		0.23	0.24	0.26	0.63			
	0.10	2.5	0.34	0.35	0.36	0.49			
	0.50		0.55	0.56	0.57	0.43			
	1.00		0.72	0.72	0.72	0.34			
Cu^{+2}	0.01		0.09	0.10	0.08	0.58			
	0.05		0.27	0.27	0.11	0.49			
	0.10	4.5	0.44	0.46	0.38	0.42			
	0.50		0.58	0.61	0.55	0.32			
	1.00		0.65	0.68	0.74	0.20			
Co ⁺²	0.01		1.19	1.28	0.25	2.38			
	0.05		1.41	1.48	0.65	2.12			
	0.10	6.0	1.54	1.68	1.01	1.62			
	0.50		1.64	1.79	1.72	1.43			
	1.00		1.95	1.97	2.20	1.12			
Cd^{+2}	0.01		0.19	0.17	0.21	0.64			
	0.05		0.34	0.27	0.33	0.50			
	0.10	5.0	0.43	0.37	0.44	0.41			
	0.50		0.50	0.50	0.66	0.37			
	1.00		0.59	0.64	0.79	0.26			
Pb ⁺²	0.01		0.81	0.92	0.84	1.80			
	0.05		1.17	1.07	1.42	1.47			
	0.10	6.0	1.43	1.54	1.72	1.23			
	0.50		1.82	1.97	2.03	0.98			
	1.00		2.33	2.40	2.56	0.71			

Table 1.

Evaluation of the effect of different electrolytes on the uptake of several metal ions^aby 2.4-DHAFA-II copolymer.

^a[M(NO₃)₂] = 0.1 mol./lit.; Volume = 2 ml.; Volume of electrolyte solution:

25 ml.; Weight of resin = 25 mg.; Time = 24 hrs, at room temperature.

Table 2.

Comparison of the rates of metal (M) ion uptake^a by 2,4-DHAFA-II copolymer.

Metal ion	% of metal ion uptake ^b at different time (hrs.)						
	1	2	3	4	5	6	
Fe ⁺³	37	60	99	-	_	-	
Cu^{+2}	32	38	48	55	73	84	
Co^{+2}	19	37	49	59	82	87	
Cd^{+2}	35	52	64	75	86	91	
Pb^{+2}	51	61	69	76	94	98	

^a[M(NO₃)₂] = 0.1 mol./lit.; Volume = 2 ml.; Volume of electrolyte solution: 25 ml.; Weight of resin = 25 mg.; Time = 24 hrs, at room temperature.

^bMetal ion uptake = (amount of metal ion absorbed x 100)/ amount of metal ion absorbed at equilibrium.

Table 3.

Distribution ratio D^a of various metal ion as a function of the pH^b by 2,4-

Metal	Distribution ratio of metal ion at different pH									
ion	1.5	1.75	2.0	2.5	3.0	3.5	4.0	5.0	6.0	6.5
Fe ⁺³	53	113	404	8800	-	-	-	-	-	-
Cu^{+2}	-	-	-	37.3	52.3	90.8	259.8	1886	2874	8801
Co^{+2}	-	-	-	45.8	60.5	74.2	145.0	344	846	8800
Cd^{+2}	-	-	-	37.2	38.1	40.9	94.4	212	484	4355
Pb^{+2}	-	-	-	55.7	64.5	78.9	148.3	345	1277	8801

DHAFA-II -III copolymer

^aD = Weight (mg.) of metal ion taken up by 1 gm. of copolymer/ Weight

(mg.) of metal ions present in 1 ml. of solution.

^b[M(NO₃)₂] = 0.1 mol./lit.; Volume = 2 ml.; Volume of electrolyte solution:

25 ml.; Weight of resin = 25 mg.; Time = 24 hrs (equilibrium state), at room temperature.

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IV. CONCLUSION

Using acid catalyst the 2,4-DHAFA-II copolymer has been synthesized by the condensation polymerization of 2,4-dihydroxyacetophenone and adipamide with formaldehyde,the structure of the which was clearly confirmed by spectral and elemental analysis. The 2,4-DHAFA-II Copolymer is a selective chelating ion exchange polymer which showed a higher selectivity for Fe⁺³, Cd⁺² and Co⁺² than for Cu⁺² and Pb⁺² ions.

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