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Retension and Reusable Capacities of Adipamide based Copolymer against some Toxic Metal Ions by Batch Equilibrium Technique

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Abstract-- Currently, wastewater treatment is one of the most important issues related to the toxic effectsof the pathogens and hazardous water pollution impact on human beings, agriculture andanimals. In this study, we synthesized polymeric resin by the condensation of 2-hydroxy 4-methoxy benzophenone and adipamide with formaldehyde(2:1:3) in the presence of acid catalyst at 120 ºC was proved to be a selective chelating ion-exchange copolymer for certain metal ions. A copolymer composition has been determined on the basis of their elemental analysis and the number average molecular weight of this copolymer was determined by conductometric titration in non-aqueous medium. The viscosity measurements in dimethylsulphoxide (DMSO) has been carried out with a view to ascertain the characteristic functions and constants. The newly synthesized copolymer resin was characterized by electronic spectra, FTIR spectra ^{1}H NMR and ^{13}NMR spectra. The copolymer has been further characterized by absorption spectra in non-aqueous medium and XRD to elucidate the structure. Ion-exchange properties of this resin was studied by batch equilibrium method for Fe^{3+}, Cu^{2+}, Co^{2+}, Cd^{2+} and Pb^{2+} ions over the pH range, 1.5 to 6.5 and in media of various ionic strengths. The resin shows a higher selectivity for Fe^{3+} ion over any other ions. Study of distribution ratio as a function of pH indicates that the amount of metal ion taken by resin is increases with the increasing pH of medium. The surface morphology of the copolymer resin was examined by scanning electron microscopy and it establishes the transition state between crystalline and amorphous nature.

***Keywords*--**Ion exchanger, Polycondesation, Resin, Toxic metal ions, Batch equilibrium, Metal ion uptake

I. INTRODUCTION

Wastewater contains varieties of pollutant depending on their sources. The major pollutants in wastewater could be heavy metals (Ag, Pb, Cd, Hg, Cr, etc.), organics (phenoliccompounds, dyes, halogenated compounds, oils, etc.), as well as biodegradable, volatile andrecycled organic compounds, pathogens, suspended solids and parasites[1-2]. The removal of these pollutants from wastewater through an efficient and appropriatetreatment process is an important issue for both environmental and ecological balance as wellas sustainable industrial development.Many copolymers with reactive groups are now being synthesized, tested and used not only for the macromolecular properties but also for the properties of functional groups. These functional groups provide an approach to a subsequent modification of the copolymers for specific end application [3]. Chelation ion-exchange properties and thermal properties of copolymer resins derived from oxamide, melamine, p-cresol and formaldehyde reported [4]. Resin functionalized with dithiooxamide is found to be chelation ion exchangers [5]. In recent years, some comprehensive work has been published on functional monomers and their copolymers [6]. The interaction of heavy metal [7] ions and chelating ion-exchange resin containing 8-hydroxyquinoline (8-HQ), The resin has good selectivity to exchangeable adsorption of heavy metal ions indicating Cu (II), Hg (II), Pb (II) and Mg (II) under pH 5.0 and also suggested that the chelating ion-exchange resin containing 8-HQ could be used to enrich heavy metals in water and their analysis. The adsorption behaviour of these metal ions are based on the affinity differences towards the chelating resins as functions of pH, electrolyte concentrations and shaking time. The copolymer resin under investigations 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. A chelating Copolymer resin synthesized using an eco-friendly technique and reported its good binding capacity for Ba^{2+} and Zn^{2+} ions [8]. The chelating ability of the resin synthesized by a microwave irradiation technique by involving salicylic acid and formaldehyde [9]. Hence the chelating ion exchange property of the 2,4- DBPHF-II copolymer resin was also reported for specific metal ions. 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. A batch equilibrium method was used to study the selectivity of metal ion uptake by measuring the distribution of a metal ion between the resin sample and solution containing the metal ion. The study was carried out at different pH ranges and in medium of different ionic strengths. 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 [10]. The copolymer showed higher selectivity for Fe (III), Cu (II) and Ni (II) ions than Co (II), Zn (II), Cd (II) and Pb (II) ions.

In this study, a simple and cost-effective condensation method was used to synthesize copolymer resin. The synthesized copolymer resin was characterized using UV-Visible, NMR, FT-IR and SEM spectroscopy and an application of chelating ion-exchange property of the 2-H4-MBAF copolymer resin and functional polymers is their capability to recover metal ions from waste solutions. Evaluation of the Distribution of the Metal Ions at Different pH: The distribution of each one of the seven metal ions i.e. Fe^{3+} , Cu^{2+} , Co^{2+} , Zn^{2+}, Cd^{+2} and Ni^{2+} between the polymer phase and the aqueous phase was estimated at 25°C and in the presence of a 1 M $NaNO_3$ solution. The distribution ratio ‘D’ is defined by the following relationship: D = Weight (mg) of metal ions taken up by 1 g of Copolymer / Weight (mg) of metal ions present in 1 ml of solution.

II. MATERIALS AND METHOD

Materials: The chemicals 2-dihydroxy 4-methoxy benzophenone, adipamide and formaldehyde (37 %) used are of analytical grade and chemically pure which is purchased from Merck, India.

***Synthesis of Copolymer Resin*:**

The 2-H4-MBAF Copolymer resin was prepared by condensing 2-hydroxy4-methoxy benzophenone (0.2 mol) and adipamide(0.1mol) with formaldehyde (11.25ml, 0.3 mol) in the presence of 2M HCl as a catalyst at 124 ± 2°C in an oil bath for 6hrs [10]. The brown coloured solid product was washed with hot water and ether to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove 2-hydroxy 4-methoxy benzophenone-formaldehyde copolymer which might be present along with the 2-H4-MBAF Copolymer. It was further purified by dissolving in 10 % NaOH and then filtered. The Copolymer was then reprecipitated by dropwise addition of 1:1 (v/v) conc. HCl / water with constant stirring and filtered. The process was repeated thrice. The resulting polymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified Copolymer wash finely ground to pass through 300 mesh size sieve and kept in a vacuum over silica gel. The yield of the Copolymer was found to be about 86%. The suggested structure of copolymer resin is as given in Fig. 1.

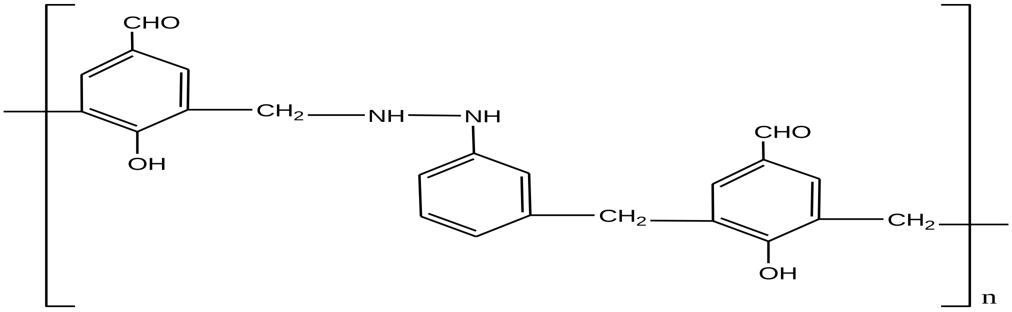

Fig.1. Structure of 2-H4-MBAF Copolymer resin

Characterization:The Copolymer resins were subject to micro analysis for carbon, hydrogen and nitrogen on Elemental Vario Elemental Analyzers at Sophisticated Analytical Instrumentation Facility, Kochi. The number average molecular weights ($\overline{M_n}$) were determined by conductometric titration in DMF using ethanolic KOH as the titrant. The molecular weight ($\overline{M_n}$) of the Copolymer resin was determined by non-aqueous conductometric titration in DMF against ethanolic KOH by using 25 mg. of sample. Electronic absorption spectra of the Copolymers in DMSO were recorded on UV-1800 (Shimandzu) spectrophotometer. Infrared spectra of 2-H4-MBAF Copolymers were recorded on IR affinity 1 spectrophotometer in KBr pallets in the wave number region of 4000-400 cm ^{1}at Kamla Nehru Mahavidyalaya. ^{1}H-NMR spectra were recorded on Bruker Advance-II 400 MHz proton NMR spectrometer DMSO-d_6 was used as a solvents at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh.

Ion-Exchange Properties: The ion-exchange properties of the 2-H4-MBAF Copolymer resins were determined by the batch equilibrium method [8]. The ion-exchange properties of all the four resins have been studied. However, only the data for the 2-H4-MBAF copolymer resins have been presented in this report.

Determination of Metal Uptake in the Presence of Various Electrolytes and Different Concentrations:

The Copolymer sample (25 mg) was suspended in an electrolyte solution (25 ml) of known concentration. The pH of suspension was adjusted to the required value by using either 0.1M HNO_3 or 0.1 M NaOH. The suspension was stirred for a period of 24 h at 25°C. To this suspension 2 ml of a 0.1 M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24 h and filtered [11]. The Copolymer was washed and the filtrate and washings were combined and estimated for the metal ion content by titration against standard ethylene diaminetetraacetic acid. A blank experiment was also carried out in the same manner without adding the polymer sample. The blank was again estimated for the metal ion content. The amount of metal ion taken up by the polymer in the presence of the given electrolyte of known concentrations results from the difference between the blank reading and the reading in the actual experiment. The experiment was repeated in the presence of several electrolytes. The results with seven different metal ions are reported in Table 1.

Evaluation of the Rate of Metal Uptake: 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 described above were carried out, in which the metal ion up taken by the chelating resins was estimated from time to time at 25°C (in presence of 25 ml of 1M $NaNO_3$ solution). It was assumed that under the given conditions, the state of equilibrium was established within 24 h. The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after certain time related to that in the state of equilibrium (Table 2).

Evaluation of the Distribution of the Metal Ions at Different pH: The distribution of each one of the seven metal ions i.e. Fe^{3+} , Cu^{2+} , Co^{2+} , Zn^{2+}, Cd^{+2} and Ni^{2+} between the polymer phase and the aqueous phase was estimated at 25°C and in the presence of a 1 M $NaNO_3$ solution. The experiments were carried out as described above at different pH values. The results are presented in Table 3. The distribution ratio 'D' is defined by the following relationship: D = Weight (mg) of metal ions taken up by 1 g of Copolymer / Weight (mg) of metal ions present in 1 ml of solution.

III. RESULTS AND DISCUSSION

The newly synthesized purified 2-H4-MBAF copolymer resin was found to be cream in colour and soluble in DMF, DMSO, THF and conc. H_2SO_4. Analytical data for $C_{37}H_{36}O_8N_2.H_2O$as per numerical calculations and experimental evidence are mentioned below respectively. Experimentally found C=67.54%, H=5.72% and N=4.15%. Theoretically calculated C=67.89%, H=5.81% and N=4.28%.

The molecular weight ($\overline{M_n}$) of the Copolymer resin was determined by non- aqueous conductometric titration in DMF against ethanolic KOH by using 50 mg of sample. A plot of the specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of Copolymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot the first break at 58 milliequivalent of base and the last break at 1456 milliequivalent of base were noted. The calculation of ($\overline{M_n}$) by this method is based on the following consideration [12], (1) the first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units; and (2) the last break in the plot beyond which a continuous increase is observed represents the stage at which phenolic hydroxy group of all the repeating units are neutralized.On the basis of the average degree of polymerization, $\overline{DP}$ is given by the following relation: $\overline{DP}$ = (Total meq. of base required for complete neutralization) / (meq. Of base required for smallest interval) , found to be 25.10. The number average molecular weight $\overline{M_n}$ is 7959 as obtained by multiplying the $\overline{DP}$ by the formula weight of the repeating unit [2].

The UV-Visible spectra of 2-H4-MBAF Copolymer samples in pure DMF were recorded in the region 190-700 nm at a scanning rate of 100 nm min^{-1} and at a chart speed of 5 cm min^{-1}. The perusal of the UV-Visible spectra of Copolymers showed almost similar nature. The spectra of these Copolymers exhibit two absorption maxima in the region 280 nm and 330 nm. The more intense band may be due to $\pi\rightarrow\pi^*$ transition and less intense may be due to $n\rightarrow\pi^*$ transition. The transition due to $\pi\rightarrow\pi^*$ is the allowed transition of aromatic benzene ring which readily attains co-planarity and shoulder merging. The transition $n\rightarrow\pi^*$ may be due to auxochromer -NH, -OH groups. The bathochromic shift from the basic values viz., 240 and 280 nm may be due to combined effect of conjugation (due to chromophore) and phenolic hydroxyl group or azo group (auxochrome) is responsible for hyperchromic effect i.e. ε_{max} higher values [10-13].

From the IR spectral studies it has been revealed that a band appeared in the region 3390 cm^{-1} may be assigned to the stretching vibration of the phenolic hydroxy groups exhibiting intermolecular hydrogen bonding . The peak at 2917 may be due to presence of Carboxylic Acid C=O & O-H Stretch. The presence of weak peak at 2850 cm^{-1} describes the –NH- stretching in may be ascribed in the copolymeric chain. A peak at 1614 cm^{-1} may be ascribed to aromatic skeletal ring [13]. The presence of peak appears at 1231 cm^{-1} may be ascribed to (C–N) stretching of $Ar–NH_2$. The sharp and weak bond obtained at 1308 cm^{-1} suggests the presence of $–CH_2$- methylene bridges in the copolymer chain. The presence of medium band at 760 cm^{-1} indicates the presence of $> CH_2$ bending (rocking). The presence of 1, 2, 3, 4, 5-

pentasubstitution of aromatic ring is recognized from the weak bond appearing at 1094 cm^{-1} and 813 cm^{-1}[14].

The NMR spectrum of Copolymer was scanned in DMSO-d_6. From the spectra it is reveal that 2-H4-MBAF Copolymer gave rise to different patterns of ^1H NMR spectra. 2-H4-MBAF exhibit the medium singlet peaks appeared at 11 ppm may be assigned to Carboxylic protons of Ar-COOH [15]. A weak singlet signals in the region 6.48 – 7.48 ppm which due to aromatic proton (Ar-H) [16]. Also the weak singlet signal appearing at 5 ppm may be due to proton of Ar-OH (phenolic –OH) [16]. The medium signal at 4 ppm may be due to proton of Ar -NH bridge. The medium triplet signal appeared at 2.35 – 2.59 ppm may be due to a methylene proton of Ar-CH_2 moiety [14-16]. The medium signal at 2 ppm may be due to proton of - CH_2-NH- amines. Also the medium doublet signal in the range of 3.91 ppm is attributed to the protons of methylenic proton of Ar-CH_2-N moiety.

Effect of Electrolytes on Metal Uptake: We examined the influence of ClO_4^-, NO_3^-,Cl^- and SO_4^{2-} at various concentrations on the position of the equilibrium of metal-resin interactions. Examination of the data given in Table 1 reveals that the amount of Fe^{3+}, Cu^{2+} and Co^{2+} ions taken up by the 2-H4-MBAF Copolymer sample increases with increasing concentrations of ClO_4^-, $NO_3^-$and Cl^- and decreases with increasing concentrations of, SO_4^{2-} whereas the uptake of Pb^{2+} and Cd^{2+} ions by above Copolymer increases with decreasing concentrations of ClO_4^-, NO_3^- ,Cl^- and SO_4^{2-}. This may be explained in terms of the stability constants of the complexes which these ions form with these anions. SO_4^{2-} might form rather strong complexes with Fe^{3+}, Cu^{2+} and Co^{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 Fe^{3+} , Cu^{2+} and Co^{2+} chelates equilibrium as much as SO_4^{2-}. ClO_4^-, NO_3^-,Cl^- and SO_4^{2-} might form rather strong chelates withPb^{2+} and Cd^{2+} and, therefore, might be expected to influence the position of the $Pb^{2+}$and Cd^{2+} chelates equilibrium. This type of trend has also been observed by other investigators in this field [17].

Table 1.

Evaluation of the effect of different electrolytes on the uptake of several metal ions[a] by 2-H4-MBAF **copolymer**.

Metal ion	Electrolyte (mol./l)	pH	Weight of metal ion (in mg.) taken up in the presence of			
			$NaClO_4$	NaCl	$NaNO_3$	Na_2SO_4
Fe^{+3}	0.01	2.5	0.16	0.17	0.18	0.68
	0.05		0.23	0.24	0.26	0.63
	0.10		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	4.5	0.09	0.10	0.08	0.58
	0.05		0.27	0.27	0.11	0.49
	0.10		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	6.0	1.19	1.28	0.25	2.38
	0.05		1.41	1.48	0.65	2.12
	0.10		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	5.0	0.19	0.17	0.21	0.64
	0.05		0.34	0.27	0.33	0.50
	0.10		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	6.0	0.81	0.92	0.84	1.80
	0.05		1.17	1.07	1.42	1.47
	0.10		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

[a] $[M(NO_3)_2]$ = 0.1 mol./lit.; Volume = 2 ml.; Volume of electrolyte solution: 25 ml.; Weight of resin = 25 mg.; Time = 24 hrs, at room temperature.

Rate of Metal 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 conditions as possible. Table 2 shows the dependence of the rates of metal ion uptake on the nature of the metal. Fe^{3+} ion required almost 3 h for the establishment of equilibrium, while Cu^{2+}, Co^{2+} and Cd^{2+} ions required about 5 h for equilibrium. Pb^{2+} ion required almost 6 h for equilibrium. The rate of metal uptake follows the order Fe^{3+}> Cu^{2+}, Co^{2+}, Cd^{2+}>Pb^{2+}.

Table 2.

Comparison of the rates of metal (M) ion uptake[a] by 2-H4-MBAF 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] $[M(NO_3)_2]$ = 0.1 mol./lit.; Volume = 2 ml.; Volume of electrolyte solution: 25 ml.; Weight of resin = 25 mg.; Time = 24 hrs, at room temperature.

Distribution Ratios of Metal Ions at Different pH: The effect of pH on the amount of metal ions distributed between two phase can be explained by the results shown in Table 3. The results indicate that the relative amount of metal ions taken up by the Copolymer increases with increasing pH of the medium. The study was carried out up to a definite pH value for the particular metal ion to prevent hydrolysis of the metal ions at higher pH. The Fe^{3+} ion is taken up more selectively than any other metal ions under study. This could be attributed to the low stability constant, i.e. weak ligand stabilization energy, of the metal complexes [18]. The results of this study are helpful in selecting the optimum pH for the selective uptake of a metal ion from a mixture of different ions [19].

Table 3.

Distribution ratio D[a] of various metal ion as a function of the pH[b] by 2-H4-MBAF copolymer

Metal ion	Distribution ratio of metal ion at different pH									
	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

[a] D = Weight (mg.) of metal ion taken up by 1 gm. of copolymer/ Weight (mg.) of metal ions present in 1 ml. of solution.

[b] $[M(NO_3)_2]$ = 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.

IV. CONCLUSIONS

A Copolymer 2-H4-MBAF based on the condensation reaction of 2-hydroxy 4-methoxy benzophenone andadipamide with formaldehyde in the presence of acid catalyst has been prepared. Since 2-H4-MBAF copolymer contain phenolic (-OH) group and methoxy group, it play a key role in the ionexchange phenomenon, because of it higher tendency of capturing metal ions. Thus 2-H4-MBAF copolymer has immense applications as an ion exchange resin in waste water treatment, metal recovery and for the identification of specific metal ions. Due to considerable differences in the uptake capacities at different pH and media of electrolyte, and the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to separate particular metal ions from their admixtures by this technique. The copolymer shows higher selectivity for Fe^{3+}, Cu^{2+} and Co^{2+} than for Cd^{2+} and PB^{+2}ions.

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