STUDIES OF RETENSION AND REUSABLE CAPACITIES OF SEMICARBAZIDE FORMALDEHYDE BASED COPOLYMER AGAINST SOME TOXIC METAL IONS BY BATCH EQUILIBRIUM TECHNIQUE

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ABSTRACT

Copolymer has been synthesized by the condensation of 2-hydroxy 4-methoxy benzophenone and adipamide with formaldehyde(1:1:2) in the presence of acid catalyst at 122 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. The resin was analyzed by TGA to assess the thermal stability, in which the resin could be used in high temperature aqueous solutions for the elimination of harmful metal ions. Ion-exchange properties of this resin was studied by batch equilibrium method for Cu $^{2+}$, Ni^{2+}, Co^{2+}, Zn^{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, Polycondensation, Resin, Toxic metal ions, batch equilibrium, metal ion uptake.

Introduction :

Copolymer is found very useful application as adhesive, high temperature flame resistant, fibers, coating materials, semiconductors, catalysis and ion exchange resins .Ion-exchange resins have attracted much interest in the recent years due to their application in waste water treatment, metal recovery and for the identification of specific metal ions.[1-2] The purpose of present study, is to explore the adsorption behaviour of five metal ions Cu (II) ,Fe (III) ,Zn (II), Cd(II), Mg(II) and Ni(II), and Ag (I) on the newly synthesized copolymer resin 4-HBPHF at different pH values, different concentrations of different electrolytes and at different shaking time intervals. 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.[3-6] Hence the chelating ion exchange property of the 4-HBPHF copolymer resin was also reported for specific metal ions. 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[7].

The present study deals with the synthesis and characterization of 4-HBPHF copolymer resin by spectral methods for the first time. The synthesized copolymer was characterized by UV-VIS, FT-IR, ^{1}HNMR. One of the important applications of chelating and functional polymer is their capability to recover metal ions from waste solutions.

Experimental

Preparation of Copolymer Resin

A mixture 2-hydroxy 4-methoxy benzophenone and adipamide with formaldehyde and 2M HCl (200ml) was taken in a round bottom flask, fitted with water condenser and heated in on oil bath at 127 ± 2ºC for 5 hrs with occasional shaking. The resinous solid product obtained was immediately remove from the flask as soon as reaction period was over and then purified. The solid resinous product obtained was repeatedly washed with cold distilled water, dried in air and powdered with the help of mortar and pestle. The powdered sample was washed many times with boiling water to remove unreacted monomers. The air dried powdered then extracted with diethyl ether and then with petroleum ether to remove o-aminophenol-formaldehyde copolymer which might be present along with 2H4MBAF Copolymer resin. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated HCl/distill water with constant and repid stirring to avoid lump formation. The process of reprecipitation was repeated thrice. The resulting polymer sample was filtered, washed several time with boiling water, dried in air, powdered and kept in vacuum over silica gel.

The reaction and suggested structure of 2H4MBAF Copolymer resin is depicted in Scheme 1.

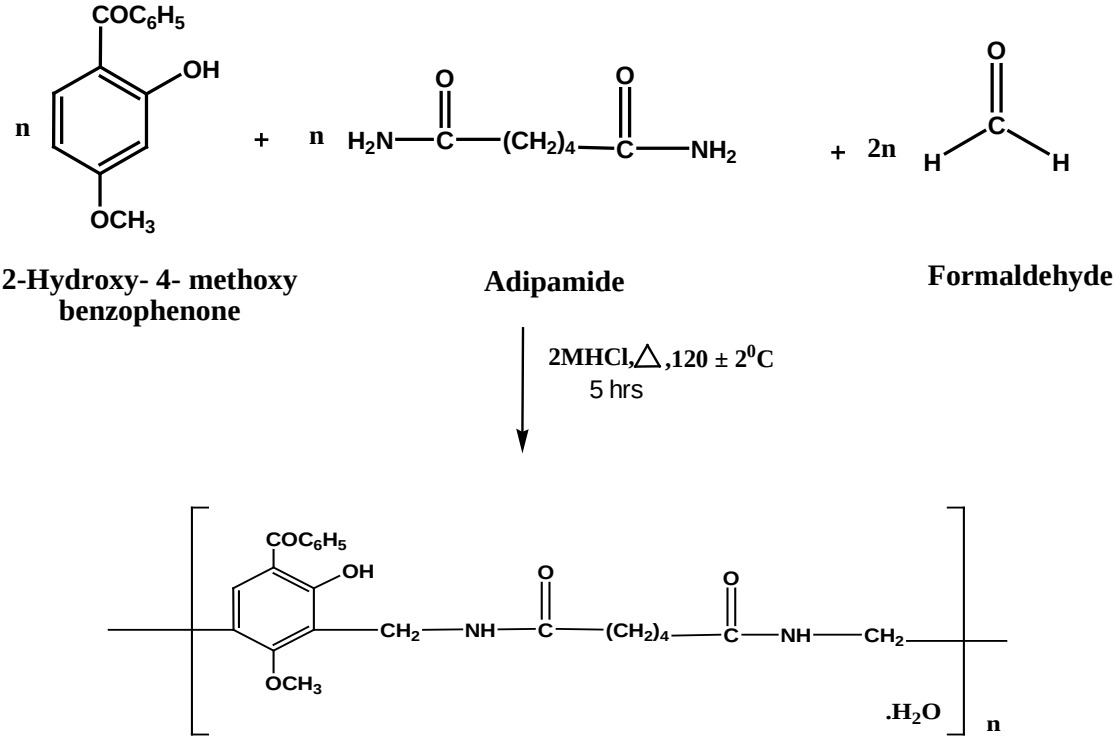

Fig.1: Synthesis of Copolymer Resin (2H4MBAF**)**

Results and Discussion: The copolymer resin is brown in colour and soluble in DMF, SMSO THF and insoluble in common organic solvents.

The UV-visible spectra of all the 2H4MBAF copolymer samples in pure DMSO were recorded in the region 200-800 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 Fig. 5. The spectra of these copolymers exhibit two absorption maxima in the region 290-330 nm and 340-400 nm. These observed positions of the absorption bands indicate the presence of carbonyl group having a carbon-oxygen double bond and azo group which is in conjugation with the aromatic nucleus. The appearance of former band can be accounted for π→π* transition while the later bond may be due to n→π* electronic transition. The shift from the basic value may be due to conjugation effect, and presence of phenolic hydroxy group (auxochromes) is responsible for hyperchromic effect i.e. ε_{max} higher values[7]. This observation is in good agreement with the proposed most probable structures of these copolymer resins.

Infrared spectrum of the 2H4MBAF Copolymer resin has been shown in Fig.2. Very broad band appeared in the region 3399 cm−1 may be assigned to the stretching vibration of phenolic –OH groups exhibiting intermolecular hydrogen bonding between –OH .The band obtained at 2826 cm−1 attributed to the Aromatic ring with aldehydic group. The sharp medium band obtained at 1273 cm−1 may be due to the various –(C–N) stretching of Ar–NH2. A sharp strong peak obtained at 1501 cm−1 suggests the presence of substituted aromatic ring. A sharp strong peak at 858 cm−1 may be due to –NH bending vibration of secondary amide. The 1,2,3,5 tetrasubstitution of aromatic benzene ring can be recognized from sharp and medium/weak absorption bands appeared at 621 cm−1 respectively. The band obtained at 831 cm−1 suggests the presence of tetra substituted ring. The presence of C–H stretching of aromatic ring may be assigned as a sharp and strong band at 3096 cm−1 which seems to be merged with very broad band of phenolic hydroxyl group [7].

The proton NMR spectrum of 2H4MBAF Copolymer resin was scanned in DMSO-d6 solvent. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature [8]. The medium signal at 2.25-2.59 (δ) ppm may be due to methylene proton of Ar–CH2 moiety [7,8]. The signal at 3.91 (δ) ppm may be due to the methylene proton of Ar–CH2–N moiety [8]. The intense singlet signal appeared in the region 4.5 - 5.5 ppm can be assigned to phenolic proton of Ar-OH. The weak multiplate signal (unsymmetrical pattern) in the region of 6.48-7.25(δ) ppm may be attributed to aromatic proton (Ar–H) [8]. A medium singlet peaks appeared at 9.51 ppm may be assigned to aldehydic protons of Ar-CHO12,13. A peaks appeared at 2 ppm may be assigned to Proton of amines - CH2-NH . A peaks appeared at 4 ppm may be assigned to Proton of Ar–NH bridge.

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 Figure 4 for 2H4MBAF. It gives the information of surface topography and defect in the structure. The resin appeared to be dark brawn in colour. The morphology of polymer resin shows spherulites and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of 2H4MBAF copolymer resin sample. The morphology of resin polymer shows also a fringes model of the crystalline amorphous structure.(Fig. 3).

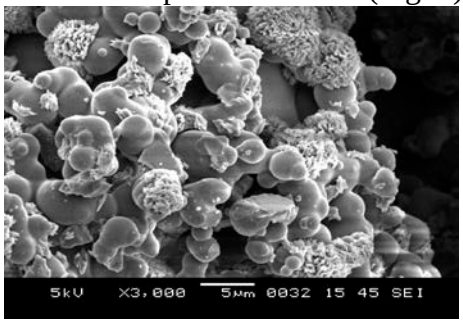

Fig. 3 SEM of 2H4MBAF Copolymer Resin

Batch equilibrium technique developed by Gregor et al. and DeGeiso et al. was used to

study of ion exchange property of 2H4MBAF copolymer resin. The result of the batch equilibrium study carried out with the copolymer resin 2H4MBAF is presented in Table 1. Eight metal ions Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{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 evaluable its effect on metal uptake capacity of the polymer [22]. The details of experimental procedure are given below.

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

We examined the effect of NO_3^-, Cl^-, SO_4^{2-} and ClO_4^- at various concentrations on the equilibrium of metal resin interaction of constant pH. Different metal ions have different pH in solution, has been mentioned in Table 1, which shows that the amount of metal ions taken up by a given amount of copolymer 2H4MBAF depends on the nature of concentration of the electrolyte present in the solution. In the presence of nitrates, perchlorate and chloride ions the uptake of Fe(III), Cu(II), Hg(II), Zn(II) and Pb(II) ions increasing with increasing concentration of electrolytes. Whereas in the present of sulphate ions, the amount of above maintained ions taken up by the copolymer resin decreases with increasing concentration of the electrolytes [9]. Above NO_3^-, Cl^-, and ClO_4^- ions form weak complex with the above metal ions, while SO_4^{-2} form stronger complex thus the equilibrium is affected. This may be explained on the basis of the stability constants of the complexes with those metal ions and nature of ligands.

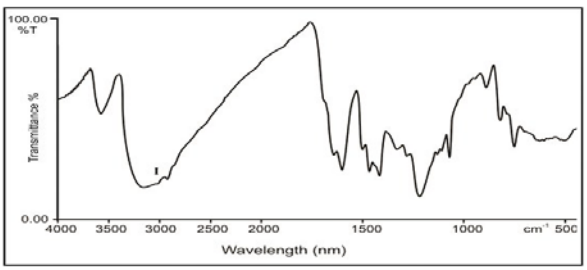

Fig. 2: IR Spectrum of 2H4MBAF Copolymer Resin

Rate of metal ion uptake as a function of time

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. During rate of metal ion determination, the concentration of metal ion and electrolyte solution and pH of the solution remain constant and pH of each metal ion is different. As shaking time increases the polymer gets more time for adsorption, hence uptake of metal ions increases. Table 2 shows the results of rate of uptake of metal ion on 2H4MBAF copolymer resin. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given copolymer. The data's of Table 2 shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of metal ions under given conditions. It is found that Fe(III) ions required about 3 hrs for the establishment of the equilibrium, whereas Cu(II), Hg(II), Zn(II) and Pb(II) ions required about 6 hrs. Thus the rate of metal ions uptake follows the order Fe(III) >> Pb(II) > Zn(II) > Hg(II) > Cu(II) for the copolymer [9].

Distribution ratios of metal ions at different pH

The distribution of metal ion depends upon pH of the solution. By increasing pH, the H^+ ion concentration in the solution decrease and only metal ion in the solution available for adsorption which increase uptake of metal ions.

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results given in Table 8. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the copolymer resin increase with increasing pH of the medium [9]. The magnitude of increase, however, is different for different metal cations. The study was carried out from 2.5 up to pH 6.5 to prevent hydrolysis of metal ions at higher pH. The selectivity of Fe(III) ion is more for the 2H4MBAF copolymer resin as compare to the any other metal ions under study. The order of distribution ratio of metal ions measured in the range, 1.5 to 6.5 is found to be Fe(III) > Cu(II)

> Pb(II) > Hg(II) > Zn(II) [9]. Thus the result of such type of study is helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions [9]. For example, the result suggests the optimum pH 2.5 for the separation of Fe(III) and Zn(II) with distribution ratio 'D' are 4865.6 and 69.6 respectively using the 2H4MBAF copolymer resin as ion exchange. Similarly for the separation of Fe(III) and Hg(II) at the optimum pH is 2.5 with distribution ratio is 4865.6 and 85.62 respectively for 2H4MBAF copolymer. The lowering in the distribution ratios of Fe(III) was found to be small hence, efficient separation could be achieved. Thus the separation of Fe(III) from other metal having combination (1) Fe^{3+} and Cu^{2+}, (2) Fe^{3+} and Hg^{2+} (3) Fe^{3+} and Zn^{2+} (4) Fe^{2+} and Pb^{2+} are effectively may separate out.

Conclusions

2H4MBAF copolymer resins were prepared from 4-hydroxybenzaldehyde and phenyl hydrazine with formaldehyde in hydrochloric acid medium by condensation technique. The semi crystalline nature of the 2H4MBAF copolymer resins were confirmed by the SEM studies and reveals that the copolymers can act as an effective ion exchanger for various trivalent and divalent metal ions such as Fe^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Zn^{2+} and Pb^{2+} ions. This study of ion-exchange reveals that 2H4MBAF copolymer resin is proved to be an eco-friendly cation exchange resin and can be used for the removal of hazardous metal ions from the environmental area, for the purification of industrial waste solution and for the purpose of purification and desalination of water.

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Table 1.
Evaluation of the effect of different electrolytes on the uptake of several metal ions[a] by 2H4MBAF 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
Cu^{+2}	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
Ni^{+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
Zn^{+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.

Table 2
Comparison of the Rate of Metal Ion Uptake[b] of
2H4MBAF copolymer Resins

Metal ions	**pH**	**Resins**	**Percentage of the amount of metal ion[a] taken up[b] at different time (hrs)**					
			1	**2**	**3**	**4**	**5**	**6**
Cu^{2+}	4.5	I	58.3	67.5	74.7	83.6	92.3	-
		II	62.6	72.7	81.4	86.3	94.1	-
		III	69.4	78.4	87.6	89.4	95.2	-
		IV	76.1	81.2	90.2	91.3	97.4	-
Ni^{2+}	4.5	I	62.3	71.6	79.5	86.6	93.7	-

		II	69.4	75.3	83.3	89.4	95.3	-
		III	78.7	82.2	86.7	92.2	96.4	-
		IV	81.2	84.3	89.3	96.1	98.5	-
Co^{2+}	5	I	42.5	58.6	73.4	84.4	93.4	-
		II	47.4	63.4	77.3	85.5	95.9	-
		III	56.3	68.3	79.7	87.8	97.4	-
		IV	59.8	71.7	82.2	91.8	98.7	-
Zn^{2+}	5	I	46.4	61.6	69.4	82.5	92.4	-
		II	53.2	63.2	72.2	85.3	94.2	-
		III	56.3	66.7	77.6	87.8	96.7	-
		IV	58.4	70.6	81.5	90.2	98.8	-
Pb^{2+}	6	I	27.3	42.4	62.8	73.3	84.6	94.5
		II	32.4	49.1	65.2	75.1	85.4	95.2
		III	39.7	55.7	68.4	78.6	87.5	97.7
		IV	44.2	60.3	70.2	82.4	89.1	98.9

[a] $[M(NO_3)_2] = 0.1$ mol/l; volume : 2ml; $NaNO_3 = 1.0$ mol/l; volume: 25ml, Room temperature.

[b] Metal ion uptake = (Amount of metal ion absorbed x 100) / amount of metal ion absorbed at equilibrium.

Table 3
Distribution Ratio 'D'[a] of Different Metal Ions[b] as a Function of Different pH of 2H4MBAF copolymer Resins

Metal ions	**Resins**	**Distribution ratios of different metal ions at different pH**							
		1.5	**2**	**2.5**	**3**	**3.5**	**4**	**5**	**6**
Cu^{2+}	I	-	-	68.2	87.4	196.6	467.3	834.7	1056.3
	II	-	-	74.8	92.5	212.3	489.7	865.4	1134.4
	III	-	-	79.5	98.3	245.7	534.5	935.3	1248.7
	IV	-	-	94.7	105.4	265.6	587.4	965.6	1336.6
Ni^{2+}	I	-	-	59.2	72.5	124.5	318.5	532.3	788.5
	II	-	-	63.4	79.3	145.3	356.1	567.1	874.3
	III	-	-	78.6	87.2	168.4	387.6	612.7	934.2
	IV	-	-	82.5	94.1	187.3	435.3	629.3	989.4
Co^{2+}	I	-	-	45.5	49.5	87.3	132.5	254.7	434.6
	II	-	-	48.2	57.4	93.4	143.1	268.5	453.3

	III	-	-	57.4	63.7	98.1	168.3	283.3	495.4
	IV	-	-	68.4	82.5	108.2	192.5	367.2	523.2
Zn^{2+}	I	-	-	49.6	58.8	85.5	134.4	216.4	294.1
	II	-	-	57.4	62.4	89.3	165.5	244.6	343.2
	III	-	-	63.3	68.6	93.6	212.6	272.2	376.5
	IV	-	-	69.7	75.4	97.3	232.2	285.1	412.3
Pb^{2+}	I	-	-	37.3	54.5	74.7	91.6	144.8	256.7
	II	-	-	42.4	62.4	79.8	112.3	156.2	278.4
	III	-	-	48.6	71.3	87.4	134.4	167.4	293.5
	IV	-	-	52.7	83.5	93.3	143.1	173.5	311.3

a D = weight (in mg) of metal ions taken up by 1g of copolymer/weight (in mg) of metal ions present in 1ml of solution.

b $[M(NO_3)_2]$ = 0.1 mol/l; volume : 2ml; $NaNO_3$ = 1.0 mol/l; volume: 25ml, time 24h (equilibrium state) at Room temperature.