SYNTHESIS, CHARACTERIZATION AND MATHEMATICAL MODELING OF CHELATIONION-EXCHANGE APPLICATIONS OF COPOLYMER RESIN

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ABSTRACT

p-Hydroxybenzaldhyde and Oxamide with Formaldehyde (BOF) Copolymer was synthesized by the condensation polymerization technique. The elemental analysis and physico-chemical parameters of the copolymer were measured. This chelation copolymer was characterized by infrared, electronic and nuclear magnetic resonance (^{1}H &^{13}C NMR) spectral studies. The molecular weight of the copolymer was determined by gel permeation chromatography (GPC). Surface analysis of the copolymer was analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD) method. The thermal stability of the copolymer was analyzed by thermogravimetric analysis (TGA). The cation-exchange property of the copolymer was determined by batch equilibrium method with the effect of pH, contacttime and electrolytes. The reusability of the resin was also studied to estimate the effectiveness of the copolymer resin.

An attempt has been done to present the metal ion selectivity of the resins with respect to time in the form of mathematical model. The model consists of two straight-line equations, involves all dependent and independent parameters. Graph obtained from actual experimental data is very much comparable to the graph plotted from the data provided by the model. This has been clearly shown by the reliability of the model, which is 94.6%.

Key words: Synthesis, Chelation, Resin, Copolymer, Characterization, Batch equilibrium Method.

INTRODUCTION

The term copolymerization refers to the simultaneous polymerization of three monomers together.Ion exchange may be defined as the reversible exchange of ions between the substrate and surrounding medium. 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. 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

The discharge of heavy metals into watercourses is a serious environmental problem that significantly affects the quality of the water supply. Increasing concentrations of these metals in the wastewater constitute a severe health hazard because of their toxicity, persistence in nature, and non-biodegradability, particularly when they exceed the permissible limits [1]. 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 terpolymer has been reported and its chelation ion exchange properties were investigated by static batch equilibrium method [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 behaviour of prepared resin was studied with Cu (II), Zn (II), Ni (II), Cd (II) and Pb (II) metal ions. Samir et al [4]

synthesized ion exchange resin from 8-quinolinyl methacrylate and characterized by conventional methods. Thermal analysis was carried out using TGA and DSC. Metal ion uptake capacity of synthesized copolymers has been estimated by batch equilibration method for different metal ions under different experimental conditions.

Three phenol-formaldehyde chelating resins, poly(8-hydroxyquinoline-5,7-diylmethylene), poly(8-hydroxyquinoldine-5,7-diyl-methylene) and poly(2-aminophenol-5,7-diylmethylene) were synthesized and characterized by Ebraheem [5]. Poly[(2-hydroxy-4-methoxybenzophenone)ethylene] resin and have shown good binding capacity for lanthanum (III) at various conditions [6]. Recently much work has been carried out to study ion exchange properties of anchoring functional chelating groups on polymeric network. As compared to anchored resins, synthesized resins were found to be more advantageous because the synthesized insoluble functionalized polymer can provide good stability and flexibility in working conditions.

Rivas [7] have been synthesized cross linked poly [3-(methacryloyl-amino)-propyl]-dimethyl(3-sulfopropyl)ammoniumhydroxide-co-2-acryl-amid glycolicacid [PCMAAPDSA-co-AGCO] by radical polymerization and tested the synthesized polymer as an absorbent under competitive and non-competitive conditions for Cu(II), Cd(II), Pb(II), Zn(II), Pb(II) and Cr(III) by batch and column equilibrium procedures. They reported that resin metal ion equilibrium was achieved within 1 hr and resin showed a maximum retention capacity value of 1.084 m.equ g^{-1} for Pb(II) at pH 2.

Rahangdaleet. al. [8] synthesized a copolymer resin by condensation of 2,2'-dihydroxybiphenyl and formaldehyde in presence of acid catalyst and studied chelating ion exchange properties for Fe (III), Cu (II), Ni (II), Zn (II), Cd (II) and Pb (II) ions. A batch equilibrium method was employed for studying the selectivity of metal ion uptake involving the measurement of distribution of al ions. 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 p-Hydroxybenzaldhyde and Oxamide with 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.

EXPERIMENTAL

Materials

The chemicals p-Hydroxybenzaldhyde, Oxamide and Formaldehyde (37 %) used were of A. R. grade chemically pure and purchased from Merck, India. Solvents like N, N-dimethyl formamide and dimethylsulphoxide were used after distillation

Preparation of BOF Copolymer

The BOFcopolymer resin was prepared by condensing p-Hydroxybenzaldhyde(0.2 mol) and Oxamide(0.1mol) with formaldehyde (0.3mol) in presence of 2M HCl as a catalyst at temperature 124 ± 2 ^{0}C in an oil bath for 5 hr. Brown coloured solid product obtained was immediately removed and extracted with diethyl ether to remove excess of p-Hydroxybenzaldhyde- Formaldehyde copolymer, which may be present along with the BOFcopolymer. It was further purified by dissolving in 8 % NaOH and then filtered. The copolymer was then reprecipited by dropwise addition 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).

Analytical and physicochemical studies

Intrinsic viscosity was determined using a Tuan-Fuoss viscometer [9] at six different concentrations ranging from 0.3 wt % to 0.05 wt % of resin in DMF at 30^{0}C. Intrinsic viscosity (η) was calculated by using Huggin'seq (1) [9] and Kraemer eq (2) [9].

Elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyser instrument. UV–visible study was carried out using Shimadzu UV-VIS Spectrophotometer in the range 200-800 nm. Infrared spectrum was recorded in the region of 500–4000 cm^{-1} on Shimadzu IR-Affinity Spectrophotometer. ^{1}H-NMR studied using BrukerAvance-II FT-NMR Spectrometer in DMSO-d$_6$ solvent. All analytical and spectral studies for newly synthesized copolymer were carried out at STIC Analysis, Kochi.

Ion exchange properties

To decide the selectivity of BOF copolymer as an ion exchanger we have studied the influence of various electrolytes using different concentration and at various pH, the rate of metal ion uptake and distribution of metal ion between the terpolymer and solution. The results of the batch equilibrium study carried out with the copolymer sample.

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

Copolymer sample (25 mg) was suspended in an electrolyte solution of NaNO$_3$ (25 ml) of known concentration. The pH of the suspension 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 at temperatutre 25^{0}C. To this suspension 2 ml of 0.1M solution of the metal ion was added and the pH was adjusted to the required value. The

mixture was again stirred at 25 ^{0}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 NaClO$_4$,Na$_2$SO$_4$ at different concetration.

Evaluation of the Rate of Metal 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 in which the 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 NaNO$_3$ solution). It was assumed that under given conditions, the state of equilibrium was established within 24 hrs. Rate of metal ions uptake 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 NaNO$_3$ solution. The experiments were carried out as described above at different pH values. The distribution ratio 'D' is defined by eq. (3).

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

RESULTS AND DISCUSSION

Copolymer which has been used in present investigation as ion-exchanger 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 was then purified and analyzed for carbon, hydrogen and nitrogen content and found to be in agreement with calculated value.

- Calculated for C$_{32}$H$_{26}$N$_6$O$_{13}$S$_3$: C: 48.12%; H: 3.25 %; N: 10.52 %., O: 26.06%, S: 12.03%
- Found for C$_{32}$H$_{26}$N$_6$O$_{13}$S$_3$: 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.1. The following equations were used to determine Huggin's [9] and Krammer's [9] constant, respectively:

$$\eta_{sp}/C = [\eta] + k_{1.}[\eta]^2.C \ldots\ldots\ldots\ldots..(1)$$
$$\ln\eta_{rel}/C = [\eta] - k_{2.}[\eta]^2.C \ldots\ldots\ldots..(2)$$

Where,

[η] = intrinsic viscosity;
C = concentration of solution;
k$_1$ = Huggin's constant;
k$_2$= Kraemer's constant;

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

According to above relations, a plots of $\eta_{sp.}/C$ 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 $[\eta]$ 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 $[\eta]$.
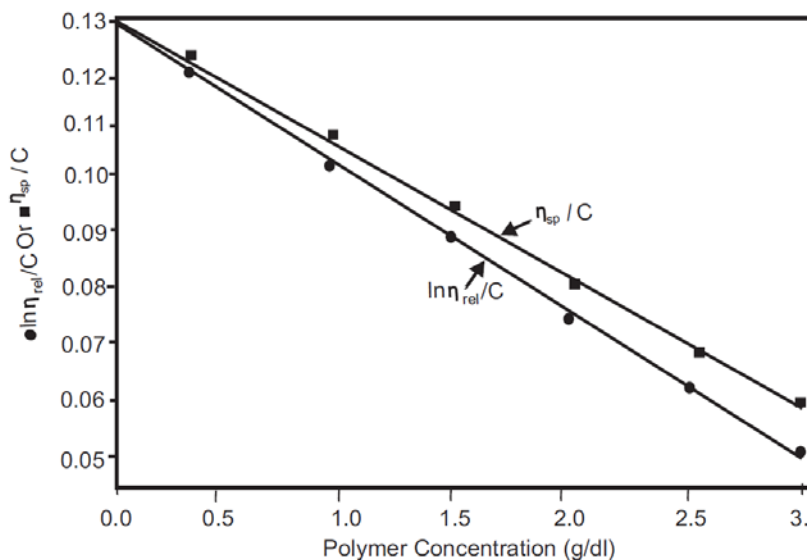

Fig.1. Viscometric plots of BOFcopolymer

UV-visible spectrum

UV-visible spectrum shown in Fig. 2 of BOFcopolymer sample in pure DMSO was recorded in region 190 nm–800 nm. Terpolymer sample displayed two characteristic broad bands at 245 nm and 290 nm. These observed position for absorption bands indicate the presence of a carbonyl (>C=O) group having a carbon-oxygen double bond which is in conjugation with aromatic nucleus. Later band can be accounted for $\pi\rightarrow\pi^*$ transition while the former band (less intense) may be due to $n\rightarrow\pi^*$ transitions [11].

The bathochromic shift (shift towards longer wavelength) from basic values of C=O group viz. 310 and 245 nm respectively, may be due to the combine effect of conjugation and phenolic hydroxyl group (auxochrome) [12, 13].
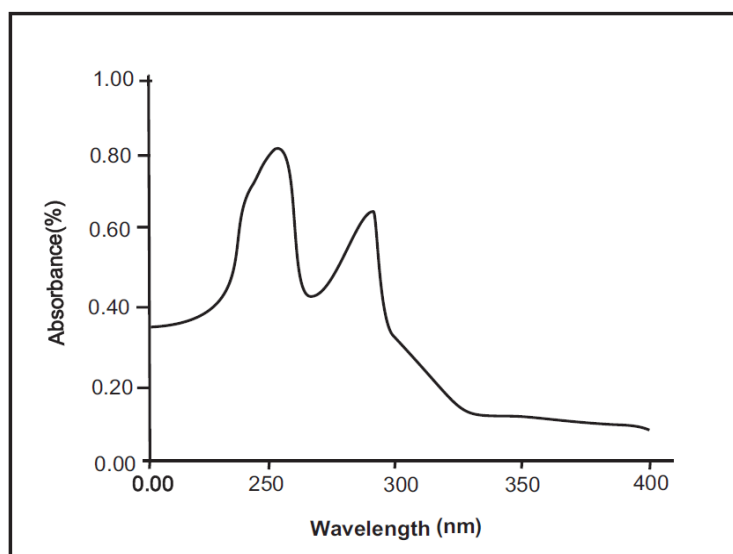

Fig.2. Electronic Spectra of 3 of BOFcopolymer

Infra Red-spectrum

IR-spectrum of BOFcopolymer is presented in Fig 3 and data reported in Table 2. A broad band appeared in the region 3442 cm^{-1} may be assigned to the stretching vibration of phenolic hydroxy groups exhibiting intermolecular hydrogen bonding [12]. The presence of weak peak at 2917 cm^{-1} describes the –NH- in biuret moiety may be ascribed in copolymeric chain [12, 13]. The presence of methyl and methylene vibrations at 2847 cm^{-1} gives sharp and weak peaks. Sharp band displayed at 1633 cm^{-1} may be due to stretching vibration of carbonyl group of both, ketonic as well as semicarbazide moiety [14-15]. The sharp and weak bond obtained at 1373 cm^{-1}– 1382 cm^{-1} suggests the presence of –CH$_2$-methylene bridges [15] in copolymer chain.
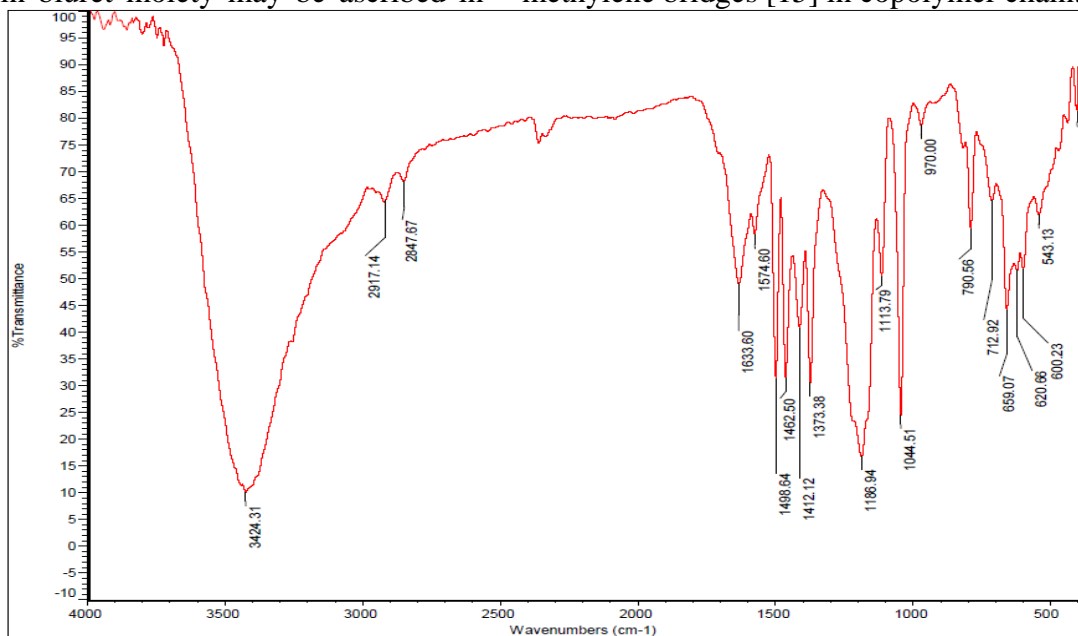

Fig.3. Infrared spectrum of BOFcopolymer

^{1}H-Nuclear Magnetic Resonance Spectrum

^{1}H-NMR spectrum of BOFcopolymer was scanned in DMSO-d$_6$ and the spectrum is as shown in Fig.4. Weak multiplet signals (unsymmetrical pattern) in the region 7.42 ppm are due to aromatic protons. The methylenic protons of the Ar-CH$_2$-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 sulphonic acid protons of SO$_3$H [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].
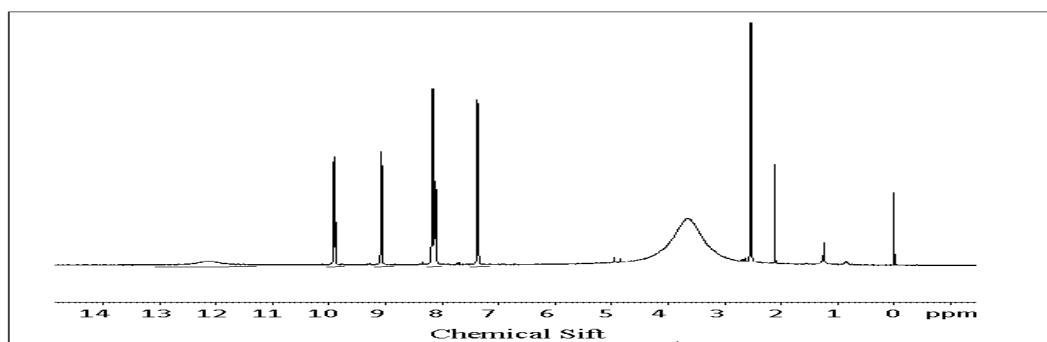

Fig. 4.Proton NMR Spectrum of BOFcopolymer

On the basis of the nature and reactive position of the monomer elemental analysis, electronic, IR, ^{1}H-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 BOFare 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

We have examined the effect of NO_3^-, Cl^-, ClO_4^- and SO_4^{-2} at various concentrations on the equilibrium of metal-resin interaction. Table 1 shows that 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. In presence of nitrate, chloride and perchlorate ions the uptake of Fe^{+3}, Cu^{+2}, Pb^{+2}, Cd^{+2} and Co^{+2} ions increases with increasing concentration of electrolytes. However in the presence of sulphate ions the uptake capacity decreases with rise in concentration. Moreover the uptake of Fe^{+3} and Pb^{+2} ions increases with increasing concentration of nitrate, chloride and perchlorate ions [16-18] as compare to Cd^{+2}, Co^{+2} and Cu^{+2} ions whereas decreases in presence of sulphate ions. Above nitrate, chloride and perchlorate ions form weak complex with the above metal ions while sulphate ions 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 as reported earlier. 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^{+2} and 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

The effect of pH on the amount of metal ions distribution between two phases is given in Table 3. The data on the distribution ratio as a function of pH indicate 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. The selectivity of Fe (III) ion is more for the BOFcopolymer resins as compare to the any other metal ions under study. The order of distribution ratio of metal ions measured in the pH range 1.5 to 6.5 is found to be $Fe^{+3} >> Cd^{+2} \approx Co^{+2} > Cu^{+2} > Pb^{+2}$. Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different metal ions [16-18]. The lowering in the distribution ratio of Fe^{+3} was found to be small and hence, efficient separation could be achieved. Thus the separation of Fe^{+3} from other metals having combination (1) Fe^{+3} and Cu^{+2} (2) Fe^{+3} and Pb^{+2} (3) Cu^{+2} and Cd^{+2} can effectively may separate out.

Table 1.Evaluation of the effect of different electrolytes on the uptake of several metal ions[a]by BOFcopolymer.

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		0.17	0.18	0.19	0.69
	0.05		0.24	0.25	0.27	0.64
	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	4.5	0.09	0.10	0.08	0.58

	0.05		0.27	0.27	0.11	0.49
	0.10		0.45	0.47	0.39	0.43
	0.50		0.58	0.61	0.55	0.32
	1.00		0.65	0.68	0.74	0.20
	0.01		1.19	1.28	0.25	2.38
	0.05		1.41	1.48	0.65	2.12
Co^{+2}	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
	0.01		0.19	0.17	0.21	0.64
	0.05		0.34	0.27	0.33	0.50
Cd^{+2}	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
	0.01		0.81	0.92	0.84	1.80
	0.05		1.17	1.07	1.42	1.47
Pb^{+2}	0.10	6.0	1.43	1.54	1.72	1.23
	0.50		1.82	1.97	2.03	0.98
	1.00		2.34	2.41	2.57	0.72

[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 rates of metal (M) ion uptake[a] by BOFcopolymer.

Metal ion	% of metal ion uptake[b] at different time (hrs.)					
	1	2	3	4	5	6
Fe^{+3}	38	61	90	-	-	-
Cu^{+2}	33	38	48	55	73	84
Co^{+2}	18	37	49	59	82	87
Cd^{+2}	36	52	64	75	86	91
Pb^{+2}	52	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.
[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 various metal ion as a function of the pH[b] by BOF 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}	54	114	405	8801	-	-	-	-	-	-
Cu^{+2}	-	-	-	37.3	52.3	90.8	259.8	1886	2874	8802
Co^{+2}	-	-	-	45.8	60.5	74.2	145.0	344	846	8801
Cd^{+2}	-	-	-	37.2	38.1	40.9	94.4	212	484	4356
Pb^{+2}	-	-	-	55.7	64.5	78.9	148.3	345	1277	8802

[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.

Mathematical modeling: - An attempt has been done to present the metal ion selectivity of the resins with respect to time in the form of mathematical model. The model consists of two straight-line equations, involves all dependent and independent parameters. Graph obtained
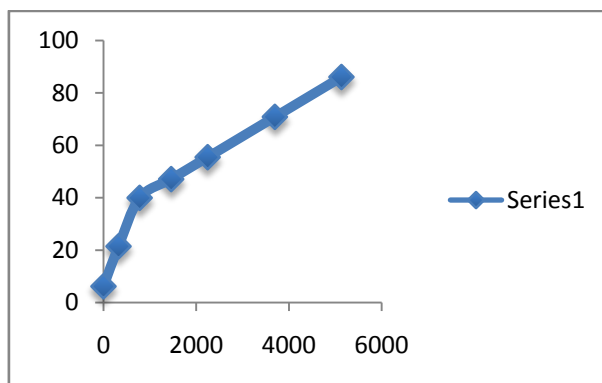
from actual experimental data is very much comparable to the graph plotted from the data provided by the model. This has been clearly shown by the reliability of the model, which is 95.6%.
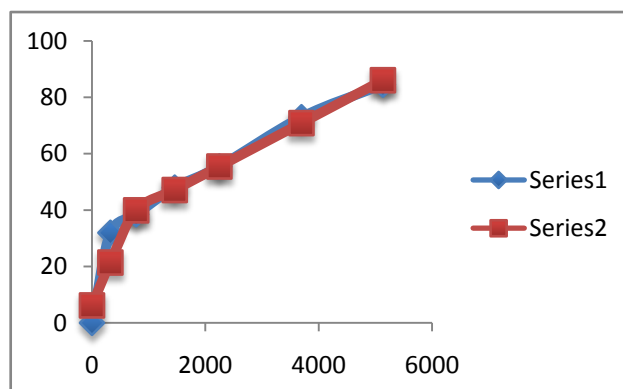
Graph from experimental data
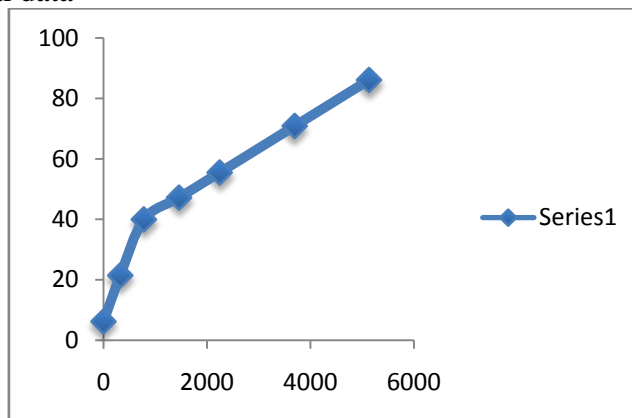
Graph from model

Comparision of graphs

CONCLUSION

The BOFcopolymer based on the condensation polymerization of p-Hydroxybenzaldhyde and Oxamidewith formaldehyde in the presence of acid catalyst has been prepared. The structure of the resin was clearly confirmed by spectral and elemental analysis.The BOFCopolymer is a selective chelating ion exchange polymer for certain metals. The copolymer showed a higher selectivity for Fe^{+3}, Cd^{+2} and Co^{+2} than for Cu^{+2} and Pb^{+2} ions.

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