Original Article

Thermal and ion-exchange studies of 4-aminosalicylic acid-oxamide- formaldehyde-II copolymer resin

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Abstract : Copolymer resin 4-ASAOF-II was synthesized by the condensation of 4-Aminosalicylic acid (4-ASA) and Oxamide (O) with Formaldehyde (F) in the presence of hydrochloric acid catalyst with 2:1:3 molar ratios of reacting monomers. The structure of the resin was characterized by various spectral techniques like infra-red (FTIR) and nuclear magnetic resonance (^{1}H and ^{13}C-NMR) spectroscopy. The empirical formula and empirical weight of the resin were determined by elemental analysis. The morphological feature of the 4-ASAOF-II copolymer resin was established by Scanning electron microscopy (SEM). Thermal study of the resin was carried out to determine its mode of decomposition and relative thermal stability. The Friedman and Change methods have been used in the present investigation to calculate thermal activation energy (Ea), order of reaction (n) and frequency factor (z). The chelating ion-exchange property of this copolymer was studied for eight metal ions viz. Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions by using batch equilibrium method. The chelating ion-exchange study was carried out over a wide pH range at different time intervals using different electrolyte of various ionic strengths. **© Global Scientific Inc.**

Keywords : Copolymer; Thermogravimetry; Ion-exchange; Activation energy.

INTRODUCTION

Ion-exchange has been widely used to treat heavy metal-containing wastewater and most of the ion-exchangers currently being used are commercially mass-produced organic resins. Analysis of trace elements presents as complex mixtures in natural and waste water, and in biological, industrial, and geological samples, are a challenging problem in analytical chemistry. The rapid development of electronic instrumentation has created powerful analytical tools but these can give erroneous results because of the presence of matrix elements. To obtain reliable data, the best course is to separate the analytes of interest from the matrix constituents and to determine them in the isolated state. Thus, preconcentration and separation by batch equilibration is mandatory, particularly when analytes are present at trace levels[1,2]

Ion-exchangers are widely used for the treatment of radioactive wastes from nuclear power stations[3,4].

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The chelation ion-exchange behavior of poly (2-hydroxy, 4-acryloyloxybenzophenone) resin towards the divalent metal ions were studied by batch equilibrium method as a function of time and pH[5]. A cross linked styrene/meleic acid chelating matrix has been reported for its higher ability to removes the metal ions such as Cr^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Pb^{2+} by Roy, Rawat and Rai[6].

The chemically modified silica gel N-(1-carboxy-6 hydroxy) benzylidenepropylamine was used as an ion-exchanger for the removal and pre concentration of hazardous metal ion such as: Cr, Mn, Cd, Pb etc. in natural water samples using batch equilibrium method and Atomic Absorption Spectroscopy (AAS) technique[7]. Poly (HPMA-co-IA) and poly (HPMAco-CA) copolymer gel metal absorption increases with pH. The study proved that poly (HPMA-co-IA) and poly (HPMA-co-CA) could be used as metal absorbents for Cd^{2+} and Pb^{2+} ions[8]. The chelation ion-exchange properties of 2, 4- dihydroxyacetophenone–biuret–formaldehyde terpolymers[9] and resin prepared from 2, 4-dihydroxybenzaldehyde, oxamide and formaldehyde[10] were investigated by Rahangdale and Tarase respectively. The chelation ion-exchange properties of copolymer resin derived from 8-hydroxyquinoline 5-sulfonic acid, oxamide, and formaldehyde indicated that the copolymer had greater selectivity for Fe^{2+}, Cu^{2+},and Ni^{2+} ions than for Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions[11]. The metal ion-binding properties of a copolymer resin derived from o-aminophenol, melamine, and formaldehyde has been reported for the metal ions Fe^{3+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, and Hg^{2+}[12]. Gurnule et al[13] reported that a copolymer prepared from salicylic acid, melamine, and formaldehyde was more selective for Fe^{3+}, Cu^{2+}, and Ni^{2+} ions than for Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions.

Thermal stability is one of the properties that can determine processing and application of materials. The practical use of polymeric material requires knowledge of thermal resistance power corresponding to certain end point criterion and the operating temperature. Terpolymer materials are used for the synthesis of functional nanostructures because of their excellent thermal characteristics. Thus, thermal stability and thermal degradation kinetics may be significant for the production and application of terpolymer based materials. TGA data have been used to determine the thermal degradation kinetics and thermal stability of terpolymer[14,15].

The study of thermal behaviors of terpolymers in different environment and temperature provides useful information about the nature of the species produced at various temperatures due to degradation[16]. Zhao Hong et al studied the thermal decomposition behaviour of phosphorous containing copolystar[17]. Varieties of researches regarding the thermal studies of polymer are emerging out to investigate their renewed application for the betterment of mankind. Area of polymer reaction kinetics is enhanced by applying various models fitting kinetic equation in order to study its kinetic and thermodynamic aspects[18-20]. Thermal degradation of ethylene propylene diene terpolymer and thermal studies of self-crosslinked terpolymer studied by T. Naruse et al. and N.P.S. chauhan respectively[21,22].

EXPERIMENTAL

Starting materials

4-Aminosalicylic Acid and oxamide is of analytical grade purity which is purchased from Acros Chemicals, Belgium. Formaldehyde (37%) was purchased from S. D. Fine Chemicals, and metal nitrates, indicators and disodium salt of ethylenediaminetetraacetic acid (EDTA) perches from S. D. Fine Chemicals India. All the solvents like N, N-dimethylformamide, dimethyl sulphoxide, tetrahydrofuran, acetone, diethyl ether were procured from Merck, India. Double distilled water was used for all the experiments.

Synthesis

4-ASAOF-II copolymer was prepared by condensing 4-Aminosalicylic Acid (0.2 mol) and Oxamide (0.1 mol) with formaldehyde (0.3 mol) in presence of 2 M HCl as a catalyst in the molar proportion of 2:1:3 at 125 °C in an oil bath for 5 h. The dark reddish brown resinous solid product was immediately removed, filtered and repeatedly washed with cold-distilled water, dried in air and powdered with the help of mortar and pestle. The product obtained was extracted with diethyl ether to remove excess of 4-Aminosalysilic Acid -formaldehyde copolymer which might be present along with 4-ASAOF-II copolymer. Dried resin sample was dissolved in 8 % NaOH and regenerated using 1:1 HCl/water (v/v) with constant stirring and filtered. This process was repeated twice. Resulting copoly-
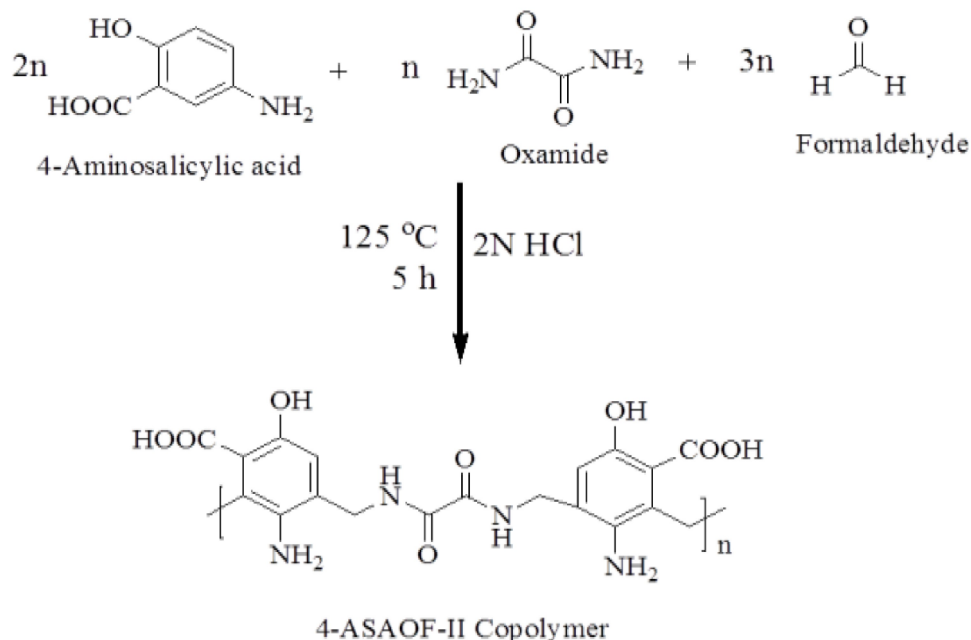
Figure 1 : Chemical reaction of 4-ASAOF-II copolymer resin

mer sample was washed with boiling water and dried in a vacuum at room temperature. Purified copolymer resin was finely ground to pass through 200-mesh size sieve and kept in a vacuum over silica gel[20]. The purity of newly synthesized and purified copolymer resin sample has been tested and confirmed by thin layer chromatography technique. Dimethylsulphoxide (DMSO) was used as a solvent for developing chromatogram and was allowed to run for about 20 min, when the chromatogram was exposed to iodine chamber then we get single colour spot for resin sample. This indicates that the synthesized and purified polymer resin sample has no impurities and used for further studies only after the confirmation of 100% purity of the sample. The Chemical reaction of above synthesis is given in Figure 1.

Spectral and thermal studies

Copolymers were subject to elemental analysis for carbon, hydrogen and nitrogen on Perkin Elmer 2400 Elemental Analyzer. Infrared spectra were recorded in Frontier transform Infrared Spectrophotometer in the range of 4000-500 cm^{-1}. ^{1}H-NMR studies were performed in DMSO-d$_6$ solvent on Bruker Advance-II 400 MHz & ^{13}C-NMR spectrum was also recorded using Bruker 100 MHz. The non-isothermal thermogravimetric analysis carried out using Perkin Elmer, Pyris1 Thermogravimetric Analyzer, in air atmosphere with a heating rate 10 ^{0}C.min^{-1} in the temperature range 50-1000 ^{0}C.

Ion-exchange property

The ion-exchange property of the 4-ASAOF-II copolymer resin was studied by using batch equilibrium method for various metal ion viz. Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} under three different experimental conditions[4,23].

(a) Determination of metal uptake in the presence of four different electrolytes and their different concentrations

Copolymer sample (25 mg) was placed in cleaned glass bottles and each of the electrolytes (25 ml) NaCl, NaNO$_3$, NaClO$_4$ and Na$_2$SO$_4$ at different concentrations, viz. 0.01, 0.05, 0.1, 0.5, and 1 M, was added into the bottles. The suspensions were adjusted to pH 2.5 for Fe^{3+}, pH 4.5 for Cu^{2+} and Hg^{2+}, pH 5.0 for Co^{2+}, Cd^{2+}, Ni^{2+}and Zn^{2+} and pH 6 for Pb^{2+} by adding either 0.1 M HCl or 0.1 M NaOH. The suspensions were mechanically stirred for 24 h at room temperature. After 24 h, 0.1 M of the chosen metal ion solution (2 ml) was added to each bottle and these were again vigorously stirred at room temperature for 24 h. The copolymer was then isolated by filtration and washed with distilled water. The filtrate and the washings were collected and the amount of metal ion was estimated by

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titrating against standard disodium EDTA solution using an appropriate indicator. A blank experiment was also performed by following the same procedure without the copolymer sample. The amount of metal ions taken up by the copolymer in the presence of a given electrolyte can be calculated from the difference between the actual titration reading and that of the blank reading.

(b) Estimation of rate of metal ion uptake as a function of time

In order to estimate the time require 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 taken up by the chelating resins was determined from time to time at room temperature (in the presence of 25 ml of 1 M $NaNO_3$ 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 a certain time related to that at the state of equilibrium and it can be defined by the following relationship. The percentage amount of metal ions taken up at different time is defined as.

$$\text{Percentage of metal ion taken up at equilibrium} = \frac{\text{Amount of metal ion adsorbed}}{\text{Amount of metal ion adsorbed at equilibrium}} \times 100$$

Percentage of metal ion adsorbed after 1 h = (100X)/Y

Where, 'X' mg of metal ion adsorbed after 1 h and 'Y' mg of metal ion is adsorbed after 24 h, then by Using this expression, the amount of metal adsorbed by copolymer after specific time intervals was calculated and expressed in terms of percentage metal ion adsorbed. This experiment was performed using 0.1 M metal nitrate solution of Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}.

(c) Evaluation of the distribution of metal ions at different pH

The distribution of each one of the eight metal ions i.e., Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} between the polymer phase and the aqueous phase was determined at room temperature and in the presence of 1 M $NaNO_3$ solution. The experiments were carried out as described above at different pH values. The distribution ratio, D is defined by the following relationship.

$$D = \frac{\text{Amount of metal ion on resin}}{\text{Amount of metal ion in solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of resin (g)}}$$

$$\text{Metal ion adsorbed (uptake) by the resin} = \left(\frac{ZX}{Y}\right)\frac{2}{0.025}$$

Where, 'Z' is the difference between actual experiment reading and blank reading; 'X' gram is the amount of metal ion in 2 ml 0.1 M metal nitrate solution before uptake and 'Y' gram of metal ion in 2 ml of metal nitrate solution after uptake.

RESULTS AND DISCUSSION

Spectral studies of 4-ASAOF-II copolymer

(a) Elemental analysis

Composition of copolymer obtained on the basis of elemental analysis data and was found to be in good correlation to that of calculated values and yield of resin was found to be 84% as given in TABLE 1.

(b) FT-IR spectra

The FTIR-spectrum of 4-ASAOF-II copolymer is represented in Figure 2 and the data is reported in TABLE 2. Broad band appeared at 3271.27 cm⁻¹, which may be assigned to the stretching vibration of the phenolic -OH groups exhibiting intermolecular hydrogen bonding[24,25]. The presence of a weak peak at 3003.17 cm⁻¹ describes the –NH- in oxamide moiety which might be present in copolymeric chain[25]. The broad band appearing in the spectrum at 3480.1 cm⁻¹ is assigned to the hydroxyl group of –COOH present in the aromatic ring and involves intramolecular hydrogen bonding with the –NH of $Ar-NH_2$[24]. This band

TABLE 1 : Elemental analysis data of 4-ASAOF-II copolymer

Copolymer	Monomer empirical formula	Empirical formula weight	Elemental Analysis (%)					
			C		H		N	
			Found.	Cal.	Found.	Cal.	Found.	Cal.
4-ASAOF-II	$C_{19}H_{18}N_4O_8$	430.37	53.03	53.81	4.22	4.24	13.02	13.42

seems to be merged with the band arising from –NH stretching vibrations of the Ar-NH$_2$ group, and this is further confirmed by the –NH bending vibrations appearing at 1587.4 cm^{-1}[26]. A sharp and weak peak obtained at 2852.0-2895.0 cm^{-1}, indicates the presence of stretching vibrations of methylene group (–CH$_2$-) in the copolymer chain[25,27]. A medium band, displayed between 1450.6 –1580.4 cm^{-1}, may be due to stretching vibration of >C=C< in aromatics. Broad and strong bands displayed at 1267.23 cm^{-1} for confirm the presence of >C=O stretching vibration of carboxylic acid group in the polymer chain[25]. >C=O stretch in phenol is represented at 1197.79 cm^{-1}. The presence of pentasubstitution of aromatic ring[25] is recognized from the weak band appearing at 786.53 - 850cm^{-1}.

(c) ^{1}H- NMR spectra

^{1}H-NMR spectral data is given in TABLE 3 and spectrum is presented in Figure 3. Spectra reveal different patterns of peaks, since each of them possesses a set of protons having different proton environment. A significant downfield in chemical shift of proton of phenolic -OH group, observed at δ 5.05 ppm, is due to intermediate proton exchange reaction of phenolic –OH group[28-30]. A weak singlet is observed at δ 6.30 - 7.13 ppm and is due to the protons of phenol. In oxamide moiety, the singlet observed in the region δ 8.02 is due to CH$_2$-NH-C=O and singlet observed in the region δ 4.32 ppm due to methylene proton of Ar-CH$_2$-NH. A broad

singlet observed at δ 4.10 ppm may be assigned to proton of Ar –NH$_2$. Singlet observed at δ 2.55 ppm and δ 11.51 ppm due to the proton of Ar-CH$_2$ and Ar-COOH respectively[25,28]

TABLE 2 : IR frequencies of 4-ASAOF-II copolymer

Observed band frequencies (cm^{-1})	Vibrational mode	Expected band frequencies (cm^{-1})
3271.27 b,st	-OH (Phenolic)	3200-3400
3003.17 st,w	–NH- (amido)	>3000
2852.0-2895.0 m,st	–CH$_2$- stretching methylene Bridge	2800-2950
1450.6 –1580.4 m	>C=C< in aromatics	1400-1600
1267.23 st	Carboxylic acid –COOH	1250-1300
1587.4 st	Ar-NH$_2$ (Amine)	1560-1640
1197.79 sh,m	C-O str. in phenol	1200
786.53 sh,w 850.4 sh,w	Pentasubstituted benzene ring	700-950

sh- sharp; b- broad; st- strong; m- medium; w- weak

TABLE 3 : ^{1}H-NMR spectral data of 4-ASAOF-II copolymer

Nature of protons assigned	Expected chemical shift (δ) ppm	Observed chemical shift (δ) ppm of terpolymer
1H, Phenolic -OH (S)	3.5-9	5.05
1H, Ar-H (S)	6-9	6.30 - 7.13
2H, Ar- NH$_2$ (S)	3.2-6	4.10
1H, Ar-COOH (S)	10-13	11.51
1H, CH$_2$-NH-C=O (S)	5-8	8.02
2H, Ar-CH$_2$-NH (S)	2.5-4.5	4.32
2H, Ar-CH$_2$ (S)	1.5-3.5	2.55

(S) Stand for singlet
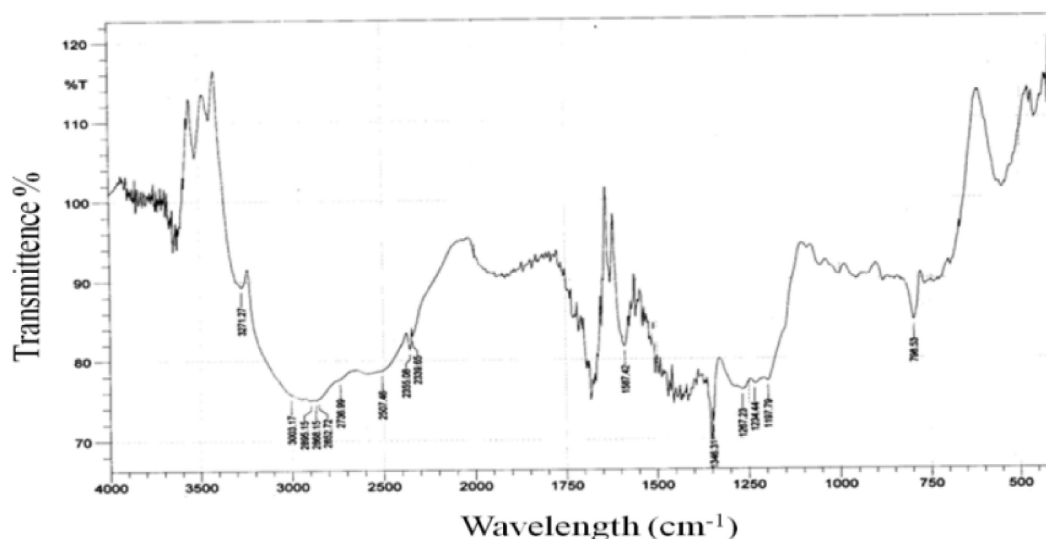
Figure 2 : FT-IR spectra of 4-ASAOF-II copolymer
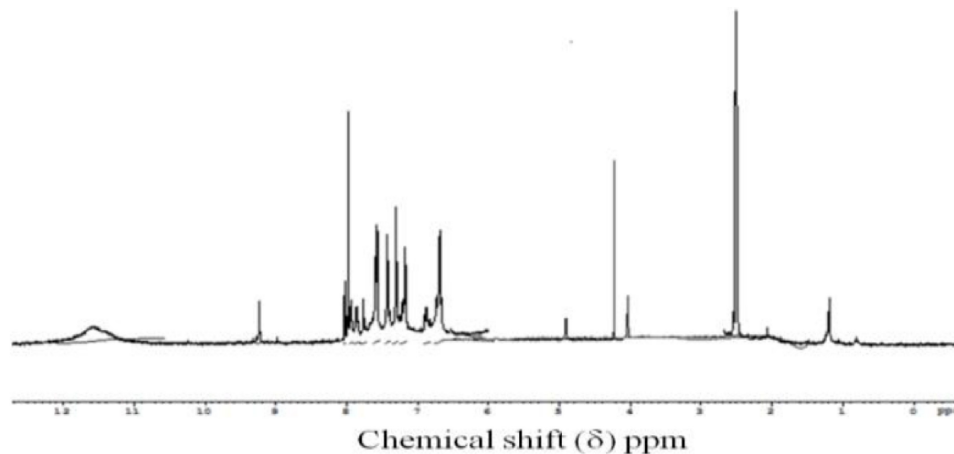
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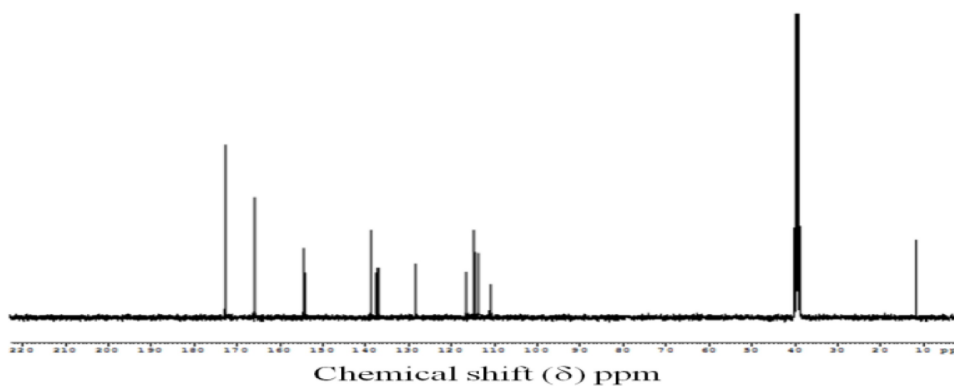**Figure 3 : ¹H-NMR spectrum of 4-ASAOF-II copolymer**

Figure 4 : ¹³C NMR spectrum of 4-ASAOF-II copolymer
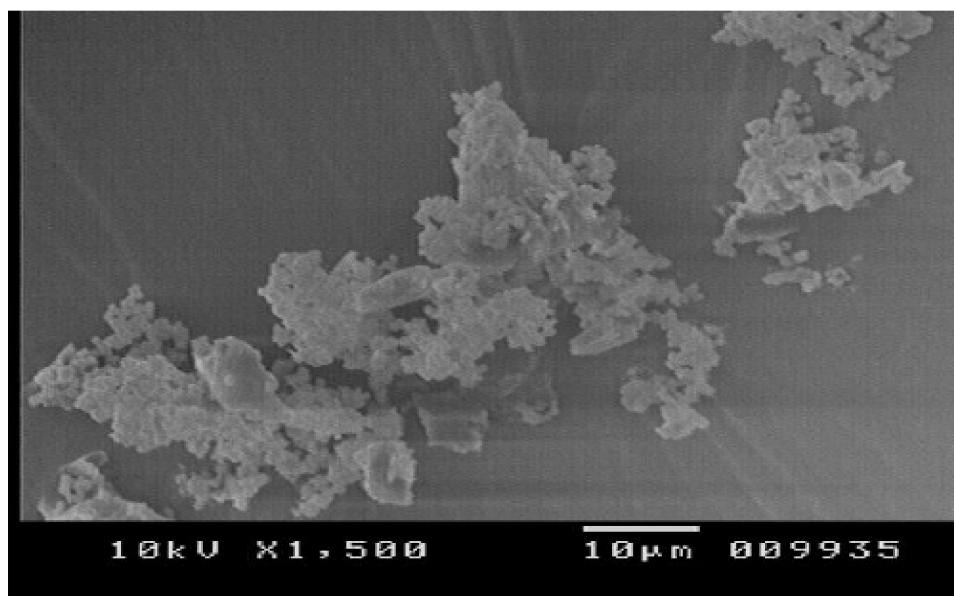
Figure 5 : SEM image of 4-ASAOF-II copolymer

(d) ¹³C-NMR spectra

The ¹³C-NMR spectrum of 4-ASAOF-II copolymer is shown in Figure 4 and observed chemical shift assigned on the basis of the literature[24,28]. The C_1 to C_6 of the first aromatic ring shows the peaks at 152.0, 113.3, 135.8, 136.5, 115.9 and 114.2 ppm respectively and the peaks appeared at 35.3 ppm is assigned to the methylene carbon of Ar-CH_2-NH linkage[23]. The

Figure 6 : Decomposition pattern of 4-ASAOF-II copolymer

Figure 7 : Activation energy plot of Friedmen and Chang

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TABLE 4 : Thermal degradation behavior of 4-ASAOF-II copolymer
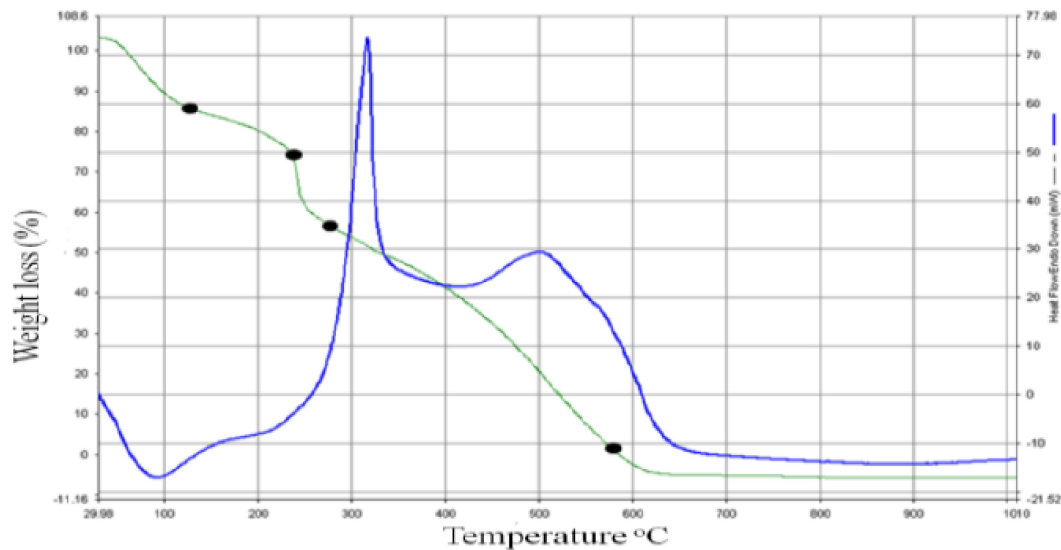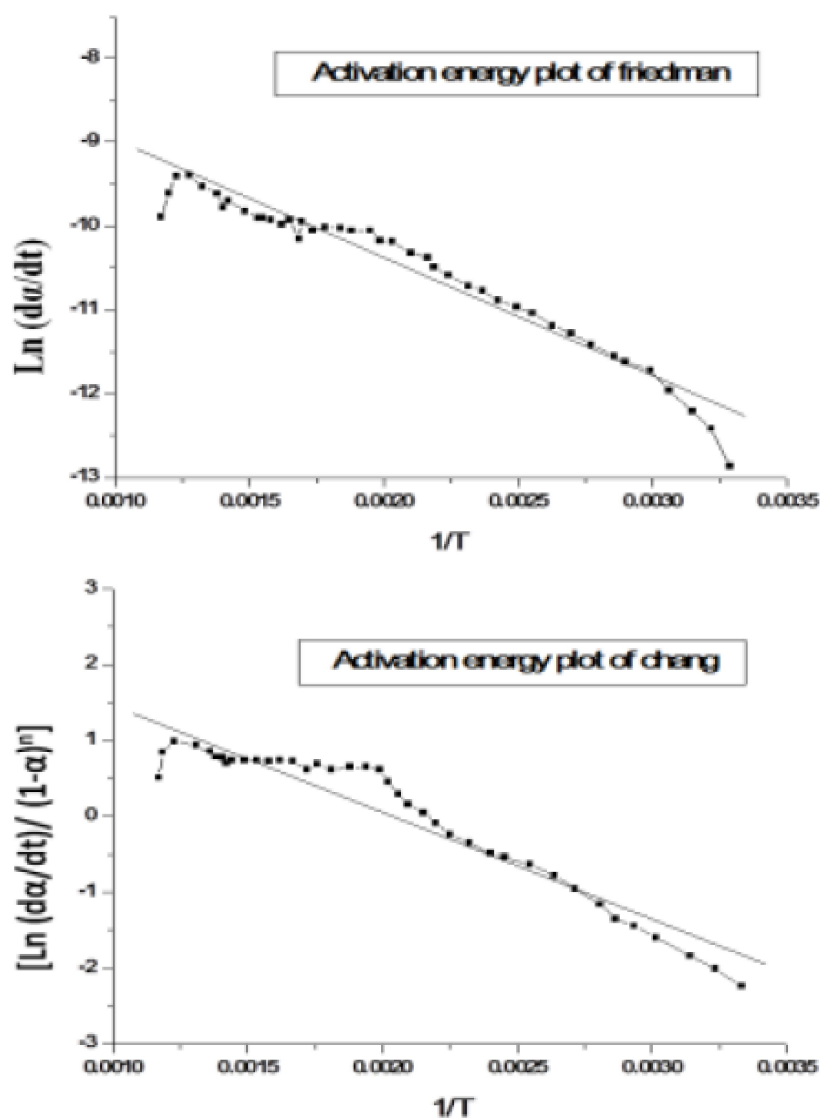
Decomposition Steps	Temp. Range (^{0}C)	Wt. Loss (%) Found	Wt. Loss (%) Calc.	Species Degraded
I	102-227	21.07	21.72	Two (–OH), one (-CH$_2$) groups
II	227-258	39.66	40.23	Two (-COOH), and two (-CH$_2$) groups
III	258-580	100	100	Two benzene rings with two(-NH$_2$), two (-CH$_2$) and complete oxamide moiety

TABLE 5 : Thermoanalytical data for degradation of 4-ASAOF-II copolymer

Kinetic Models	Activation Energy (Ea)	Order of reaction (n)	Frequency factor (z)
Friedman	10.59	1.45	8.95
Chang	10.61	1.45	1.44

peaks appeared at 169.4 ppm is due to the carbon of the carboxylic acid group and at 151.9, 113.7, 127.1, 135.3, 135.7 and 110.3 ppm with respect to C$_1$ to C$_6$ of second aromatic ring of copolymer resin resins[31]. The peaks appeared at 162.7 ppm is due to carbonyl carbon of oxamide moiety.

(e) SEM analysis

The typical microphotograph at 1,500 magnifications from SEM of 4-ASAOF-II is shown in Figure 5. The SEM image shows the surface future of the sample. The image of the 4-ASAOF-II is clearly indicative of a loosely close packed structure with high porosity or voids. The voids presents in the copolymer ligands may be responsible for the swelling behavior and reactivity of active sites buried in the polymer matrix. The image also showed a transitions state between the amorphous and crystalline states. However, more predominantly the copolymer is amorphous, because of the polycondensation reaction[32]
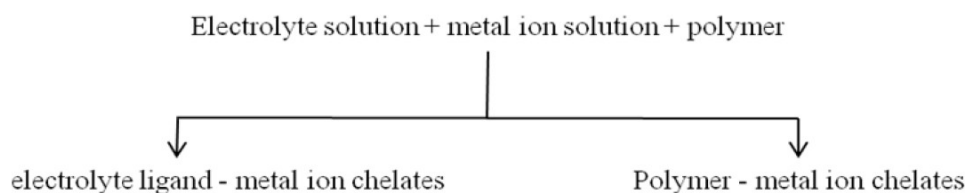
Thermogravimetric analysis

Thermogravimetric analysis is found to be very useful method to determine the thermal stability of copolymer resin. Thermal degradation behavior and kinetic data of copolymer is recorded in TABLE 4 and thermogram is shown in Figure 6. The resin 4-ASAOF-II exhibit three stages of decomposition with initial loss of water molecule. When temperature was raised from 40 to 102 ^{0}C, it showed the weight loss about 11.15 % and is corresponding to the moisture entrapped in molecule or water of crystallization associated with this copolymer[33]. This is in agreement with the weight loss calculated theoretically which is about 11.48 %. First step is slow decomposition in temperature range 102-227 ^{0}C, corresponding to 21.07 % mass loss which may be attributed to loss of two hydroxyl and one methylene groups against calculated value of 21.72 % loss present per repeat unit of copolymer. The second step of decomposition starts from temperature 227 to 258 ^{0}C, corresponding to 39.66 % loss which may be attributed to the two –COOH groups against calculated weight loss of 40.23 %. The third step of decomposition start from 258 to 580 ^{0}C, corresponding to 100 % loss which may be attributed to complete remaining moiety having two benzene ring, two –NH$_2$, two –CH$_2$ groups and oxamide moiety against calculated weight loss of 100 %.

Thermogram expresses the dependence of change in mass on the temperature which gives information about sample composition, product formed after heating and kinetic parameters. Kinetics parameters have been determined using Friedman[34,35] and Chang[36] techniques as follows:

Kinetics of thermal decomposition by Friedman and Chang techniques

In the present investigation Friedman and Chang techniques have been used to determine the kinetic parameters of 4-ASAOF-II copolymer.

Electrolyte solution + metal ion solution + polymer

electrolyte ligand - metal ion chelates   Polymer - metal ion chelates

(a) Friedman technique

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(Z) + n\ln(1-\alpha) - \frac{Ea}{RT} \qquad (1)$$

Where, α is the conversion at time t; R is the gas constant (8.314 J/mol/K) and T is the absolute temperature (K). From the slope of the linear plot of $\ln(1-\alpha)$ vs. $1/T$, n can be obtained. The plot of $\ln(d\alpha/dt)$ vs. $1/T$ should be linear with the slope E_a/R, from which E_a can be obtained (Figure 7).

(b) Chang technique

$$\ln\frac{\left(\frac{d\alpha}{dt}\right)}{(1-\alpha)^n} = \ln(Z) - \frac{Ea}{RT} \qquad (2)$$

Figure 7 has shown Chang method (2) gives plots between $[\ln(d\alpha/dt)/(1-\alpha)^n]$ vs. $(1/T)$ which is used to calculate E_a and $\ln(z)$ of respective degradation reaction for best fitted value of n (from Friedman equation), which corresponds to correct reaction order for thermal decomposition.

A plot of percentage mass loss vs temperature is shown in Figure 6 for a representative 4-ASAOF-II copolymer. From the TG curves, the thermoanalytical data in TABLE 5 and decomposition temperature has been determined for different stages as given in TABLE 4. This kinetic analysis should be a starting point to obtain the useful information on the behavior of samples. Fairly comparable results in the kinetic parameters i.e. E_a, n and $\ln(z)$ are obtained by Friedman and Chang may be due to analogy in mathematical model.

From the above discussion, it is therefore concluded that for each technique, the values of kinetic parameters depend on calculation technique used. Total calculations obtained from different kinetic models demonstrated that the numerical value of kinetic parameters depends on the mathematical model used to analyze the experimental data and level of degradation[37]. Due to complex phenomena of copolymer degradation process in non-isothermal thermogravimetry, the computed kinetic parameters are in fact only parameters of given

TABLE 6 : Evaluation of the effect of different electrolytes and their concentrations on the uptake of 4-ASAOF-II copolymer resin.

Metal ion	Electrolyte (mol/l)	pH	Weight of Metal uptake (mmol g⁻¹) in the presence of				Metal ion	Electrolyte (mol/l)	pH	Weight of Metal uptake (mmol g⁻¹) in the presence of			
			$NaNO_2$	Na_2SO_4	NaCl	$NaClO_4$				$NaNO_2$	Na_2SO_4	NaCl	$NaClO_4$
Fe^{3+}	0.01	2.5	1.54	2.63	1.63	1.45	Co^{2+}	0.01	5.0	1.36	1.86	0.96	0.7
	0.05		1.83	1.42	1.94	1.84		0.05		1.68	1.62	1.36	1.11
	0.10		2.32	1.12	2.32	2.16		0.10		1.92	0.91	1.68	1.62
	0.50		2.74	0.73	2.74	2.54		0.50		2.32	0.54	1.98	1.91
	1.00		3.28	0.33	3.31	2.92		1.00		2.52	0.38	2.12	2.16
Cu^{2+}	0.01	4.5	1.54	2.96	1.42	0.68	Zn^{2+}	0.01	5.0	0.38	1.86	0.78	0.71
	0.05		1.73	2.46	1.86	1.18		0.05		0.63	1.45	1.16	0.94
	0.10		1.95	1.92	2.13	1.52		0.10		1.21	1.16	1.54	1.43
	0.50		2.26	1.32	2.54	1.94		0.50		1.56	0.88	1.86	1.86
	1.00		2.53	0.82	3.12	2.24		1.00		1.90	0.42	2.29	2.12
Hg^{2+}	0.01	4.5	1.16	2.75	1.23	0.86	Ni^{2+}	0.01	5.0	1.28	2.76	1.32	1.48
	0.05		1.62	2.18	1.64	1.18		0.05		1.46	2.34	1.54	1.69
	0.10		1.78	1.76	2.14	1.76		0.10		1.91	1.73	1.91	1.91
	0.50		1.99	1.28	2.67	2.17		0.50		2.37	1.32	2.39	2.32
	1.00		2.32	0.61	3.23	2.42		1.00		2.89	0.86	2.78	2.76
Cd^{2+}	0.01	5.0	0.42	1.64	1.42	0.64	Pb^{2+}	0.01	6.0	0.46	1.32	0.85	0.63
	0.05		0.68	1.32	1.68	0.86		0.05		0.71	0.98	1.16.	0.98
	0.10		0.98	1.07	1.82	1.28		0.10		1.12	0.76	1.46	1.34
	0.50		1.18	0.76	2.11	1.72		0.50		1.54	0.46	1.84	1.69
	1.00		1.54	0.51	2.36	1.94		1.00		1.86	0.29	1.93	1.91

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Metal ion	Fe^{3+}	>	Cu^{2+}	$\approx$	$Ni2^+$	>	Co^{2+}	$\approx$	Hg^{2+}	$\approx$	Zn^{2+}	>	Cd^{2+}	$\approx$	Pb^{2+}
Ionic size	0:55		0:57		0:69		0:90		0:90		0:90		1:10		1:19

TABLE 7 : Comparison of the rates of metal (M) ions[a] uptake by 4-ASAOF-II copolymer resin

Metal ion	pH	Percentage of metal ion uptake[b] at different times (h)						
		1	2	3	4	5	6	7
Fe^{3+}	2.5	54	79.5	97	-	-	-	-
Cu^{2+}	4.5	5	31.5	51.5	63.5	94	-	-
Hg^{2+}	4.5	18	31.5	47	59	82	-	-
Cd^{2+}	5	13	20	35.5	51	76	93	-
Co^{2+}	5	14	30	47.5	66	82	-	-
Zn^{2+}	5	7.5	21.5	41	56	71	-	-
Ni^{2+}	5	0	12.5	34.5	63.5	85	-	-
Pb^{2+}	6	6.5	19	36.5	62	70.5	86	-

[a] $[M(NO_3)_2]$ = 0.1 mol/l; volume = 2 ml; $NaNO_3$ = 1.0 mol/l; volume= 25 ml, room temperature; [b] Metal ion uptake = (amount of metal ion absorbed×100)/amount of metal ion absorbed at equilibrium.

mathematical equation which has the form of kinetic rate equation and which is used to fit the weight loss curves accompanying the thermal degradation of polymers in non-isothermal conditions. Low values of frequency factor revealed that decomposition reaction of copolymer may be slow and no other possible reason can be given[38,39]. As a consequence these kinetic parameters are fictive from the point of view of chemical kinetics.

Ion-exchange properties

Batch equilibrium technique developed by De Geiso et al.[40] and Gregor et al.[41]. This technique was used to study ion-exchange properties of 4-ASAOF-II copolymer resin and results are presented in TABLES 6-8. Eight metal ions Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Zn^{2+}, Cd^{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 such as a) electrolyte and its ionic strength b) uptake time and c) pH of the aqueous medium. Among these three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake of the polymer similar to the earlier co-workers[4,23].

(a) Determination of metal uptake in the presence of four different electrolytes and their different concentrations

We examined the influence of nitrate (NO_3^-), chloride (Cl^-), chlorate (ClO_4^-), and sulfate (SO_4^{2-}) at various concentrations on the equilibrium of metal–resin in-

teraction. The aim of this study is to investigate the effect of the various electrolytes with different concentrations on the amount of the metal ions taken up by copolymer sample which might be used in the purification of waste solution. The results are presented in TABLE 6. This revels 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. Generally as concentration of the electrolyte increases, the ionization decreases, number of ligands (negative ions of electrolyte) decrease in the solution which forms the complex with less number of metal ions and therefore more number of ions may available for adsorption on copolymer. Hence on increasing concentration, uptake of metal ions may be increased, which is the normal trend. But the trend is different in different electrolytes and their different concentrations due to the formation of more or less stable complex of elecrtolyte ligand or copolymer with metal ions.

If electrolyte ligand–metal ion complex is weaker than polymer metal ion chelates, the more number of metal ions can form complex with polymer hence uptake of metal ion is more. But if this complex is stronger than polymer metal ion chelates, more number of metal ions form strong complex with electrolyte ligand which make metal uptake capacity lower by polymer.

In the presence of nitrate (NO_3^-), chloride (Cl^-), chlorate (ClO_4^-), the uptake of Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions increases with increasing concentration of the electrolyte, whereas in the pres-

TABLE 8 : Distribution ratio D^a of various metal ions^b as function of the pH by 4-ASAOF-II copolymer resin

Metal ion	P^H	Distribution ratio of metal ion at different P^H								
		1.5	2	2.5	3	3.5	4	5	6	6.5
Fe^{3+}	2.5	53.63	91.74	168.59	372.18	-	-	-	-	-
Cu^{2+}	4.5	-	-	42.62	51.28	59.36	87.54	147.36	658.53	1156.56
Hg^{2+}	4.5	-	-	35.27	75.36	87.78	298.45	358.54	396.85	557.35
Cd^{2+}	5	-	-	112.34	135.43	186.42	243.12	311.56	407.25	627.54
Co^{2+}	5	-	-	14.84	23.37	47.66	76.14	127.64	214.13	335.18
Zn^{2+}	5	-	-	23.38	38.42	47.90	76.49	123.78	211.23	286.34
Ni^{2+}	5	-	-	1.56	23.23	51.48	96.45	205.42	511.66	1086.14
Pb^{2+}	6	-	-	17.78	23.39	33.26	51.32	84.24	137.41	217.16

^{a} D = weight (in mg) of metal ions taken up by 1 g of copolymer/weight (in mg) of metal ions present in 1 ml of solution; ^{b} [M(NO$_3$)$_2$] = 0.1 mol/l; volume = 2 ml; NaNO$_3$ = 1.0 mol/l; volume = 25 ml, time 24 h (equilibrium state) at room temperature.

ence of sulfate (SO_4^{2-}) ions the amount of the above mentioned ions taken up by the copolymer decreases with increasing concentration of the electrolyte[23].

The ratio of physical core structure of the resin is significant in the uptake of different metal ions by the resin copolymer. The rate of metal ion uptake for NO_3^-, Cl^-, ClO_4^- and SO_4^{2-} electrolytes at various concentrations follows the order as:

$Fe^{3+} > Cu^{2+} \approx Ni^{2+} > Co^{2+} \approx Hg^{2+} \approx Zn^{2+} > Cd^{2+} \approx Pb^{2+}$. The amount of metal ion uptake by the 4-ASAOF-II copolymer resin is found to be higher when comparing to the other tercopolymer resins[2,13,43]. The uptake of metal ions by the copolymer resin was calculated by use of the formula and expressed in mmol g^{-1}.

Metal ion adsorbed (uptake) by resin = (X"Y) Z mmol/ g^{-1}.

Where, 'Z' ml is the difference between actual experimental reading and blank reading; 'X' mg is metal ion in the 2 ml 0.1 M metal nitrate solution before uptake and 'Y' mg is metal ion in the 2 ml 0.1 M metal nitrate solution after uptake.

By using this equation the uptake of various metal ions by resin can be calculated and expressed in terms of millimols per gram of the copolymer. Thus the metal intake of resin was analyzed by mass balance calculation.

(b) Estimation of 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 achieved while operating as close to equilibrium conditions as possible. As shaking time increases the copolymer gets more time for adsorption,

hence uptake increases (TABLE 7). It shows the data of dependence of the rate of metal ion uptake on the nature of the metal ions. 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 results show that the rate of metal uptake may depend upon the nature of the metal ions and their ionic size. Thus the rate of metal ion uptake follows the order

The sequence of rate of metal ion uptake indicates that the rate is directly proportional to the size of the metal ion. For example Fe^{3+} has more charge and small size, therefore equilibrium is attained within three hours, while other four transition ions Cu^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Zn^{2+} have nearly equal cationic size, having same charges, therefore required 5 h to attain equilibrium, while Cd^{2+} and Pb^{2+} have large atomic size, therefore requiring 6 h to attain equilibrium. The trend is in good agreement with earlier workers[23,43,44].

(c) Evaluation of the distribution of metal ions at different pH

The effect of pH on the metal binding capacity of the synthesized copolymers shows that relative amount of metal ion adsorbed by the copolymer resin increase with increasing pH of the medium (TABLE 8). The study was carried from pH 1.5 to 6.5 to prevent absorption or hydrolysis or precipitation of the metal ions at higher pH. The data on the distribution ratio as a function of pH indicates that the distribution of each metal between the polymer phase and aqueous phase increase with increasing pH of the medium. The magnitude of increase, however, is different for different metal ions.

It is observed that Fe^{3+} ion has highest working pH

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is 3 because above this pH Fe^{3+} found to be absorb in the resin and it has lower distribution ratio, since Fe^{3+} forms complex with electrolyte, which shows crowding effect. This steric hindrance may be lower the distribution ratio of Fe^{3+} ion. Cu^{2+} and Ni^{2+} have higher distribution ratio over pH range of 2.5 to 6.5 which may be due to the less steric hindrance. Thus the value of distribution ratio for given pH depends upon the nature and stability of chelate formation for particular metal ion[23,44]. In case of Cd^{2+} and Pb^{2+} purely electrostatic factors are responsible, the ion uptake capacity of Cd^{2+} is lower owing to the large size of its hydrated ion than that of Cu^{2+}. The steric influence of the amine group and hydroxyl group in 4-ASAOF-II resin is probably responsible for their observed low binding capacities for various metal ions. The higher value of distribution ratio for Cu^{2+} and Ni^{2+} at pH 2.5 to 6.5 may be due to the formation of most stable complex with chelating ligands. Therefore the copolymer under study has more selectivity of Cu^{2+} and Ni^{2+} ions in the range of pH 2.5 to 6.5 then other ions which from rather weak complex. While from pH 1.5 to 3 the polymer has more selectivity of Fe^{3+} ions. The order of distribution ratio of metal ions measured in pH range 1.5 to 6.5 is found to be $Fe^{3+} > Cu^{2+} > Ni^{2+} > Hg^{2+} > Zn^{2+} > Co^{2+} > Pb^{2+} > Cd^{2+}$[23,44]. The 4-ASAOF-II copolymer resin is a cation exchange resin and in cation exchange resin the equilibrium may be expressed in terms of mass action law and the relative amount of metal ions in the resin phase and can be determined by the relative concentrations of these ions in the bulk of the solution.

$(Resin\ OH^-)H^+ + M^+$ (in solution) $\rightarrow$ $(Resin\ OH^-)\ M^+ + H^+$ (in solution)
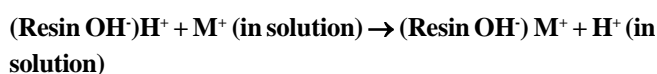
$K = [H^+]\ [(Resin\ OH^-)\ M^+]/\ [(Resin\ OH^-)\ H^+]\ [H^+]$

Equilibrium constant (K) of this type are useful for comparing the relative affinities for a resin towards various ions. The cations are arranged in an affinity scale according to the numerical value of K. For the metal ions under investigation, the relative affinity is $Fe^{3+} > Cu^{2+} \approx Ni^{2+} > Cd^{2+} \approx Hg^{2+} > Co^{2+} \approx Zn^{2+} \approx Pb^{2+}$. The strength of electrolyte and dielectric constant also affect the metal distribution or accumulation of resin.

CONCLUSION

Synthesis of targeted copolymer (4-ASAOF-II) has been confirmed which is supported by the results obtained by the elemental analysis and spectral data. Friedman, Chang methods show nearly similar values of kinetic parameters may be due to resemblance in mathematical model. The values of kinetic parameters are significantly controlled by level of degradation and calculation technique used to analyze the experimental data. It is observed that the metal complexes taken in the present study are pH dependent and each has a definite pH for optimum chelation, and it is useful property to separate a particular metal ion from a solution of different metal ions using this copolymer. The surface of the copolymer resin was found to be more amorphous, clearly indicating the suitability of the synthesized resin for ion-exchange applications.

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