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Synthesis, Characterization, Metal Ion Binding Capacities and Applications of a Terpolymer Resin of Anthranilic acid/Salicylic acid/Formaldehyde

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ABSTRACT

A novel chelating terpolymer resin has been synthesized by terpolymerization of anthranilic acid, salicylic acid and formaldehyde (ASF) in 1/1/2 molar ratios by condensation technique using glacial acetic acid as a reaction medium. The synthesized terpolymer resin was characterized by elemental analysis, FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy. On the basis of spectral studies, the structure of the terpolymer resin was proposed. The physicochemical parameters have been evaluated for the terpolymer resin. Gel permeation chromatography was used to determine the average molecular weight and polydispersity of the ASF terpolymer resin and the viscosity-average molecular weight was also determined to compare molecular weights of the resins obtained. The thermal stability of the terpolymer was analyzed by thermogravimetric analysis. Kinetic parameters such as activation energy and the order of the reaction was determined using Freeman-Caroll method. The electrical property of the terpolymer was also evaluated at various concentrations and temperatures. The surface feature of the synthesized terpolymer was established by scanning electron microscopy. Batch equilibrium method was employed to explore the selectivity and binding capacity of the terpolymer resin towards certain divalent metal ions such as Pb^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+} and Ba^{2+} in different electrolyte concentrations, wide pH ranges and different time intervals.

Key Words:

terpolymers;
ion-exchangers;
morphology;
gel permeation chromatography;
thermal studies.

INTRODUCTION

The heavy metal ion toxicity has increased substantially because of the use of metal ions as catalyst in various industries. Many methods such as electrodeposition, co-precipitation and solid-liquid extraction have been developed for pre-concentration and removal of metal ions. However, the metal ion removal by chelating ion-exchange resin using batch equilibration method has gained rapid acceptance because of its wide variety of sorbent phases, high degree of selectivity, high loading capacity and enhanced hydrophilicity [1-3].

Ion-exchangers are widely used for the treatment of radioactive wastes from nuclear power stations [4,5]. The chelation ion-exchange behaviour of poly(2-hydroxy-4-acryloyloxybenzophenone) resin towards the divalent metal ions were studied by batch equilibration method as a function of contact time and pH [6]. A cross-linked styrene/maleic acid chelating matrix has been reported for its

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higher ability to remove the metal ions such as Cr^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Pb^{2+} [7]. Acidic polymers such as poly(methacrylic acid) and poly(acrylic acid) have the tendency to remove the metal ions, e.g., Ag^{+}, Cu^{2+}, Co^{2+}, Ni^{2+} and Cr^{3+} at different pH and polymer/metal ion ratios [8]. Salicylic acid and melamine with formaldehyde terpolymer found to have higher selectivity for Fe^{3+}, Cu^{2+} and Ni^{2+} ions rather than Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions [9].

Resins synthesized by condensation of mixtures of phenol or hydroxybenzoic acid with formaldehyde and various amines have also been reported [10]. The metal ion uptake capacity increases with increasing mole proportions of the terpolymer synthesized from substituted benzoic acid [11]. *o*-Nitrophenol and thiourea with paraformaldehyde terpolymer was identified as an excellent cation exchanger for Zn^{2+} and Co^{2+} ions [12]. Salicylic acid/formaldehyde /resorcinol resin has been synthesized and explored its use for the removal and separation of heavy metal ions from their binary mixtures [13]. 8-Hydroxyquinoline/formaldehyde/catechol copolymer is found to have lower moisture content, an indication of high degree of cross-linking in the resin [14]. Phenolic schiff bases derived from hydroxybenzaldehydes and 4,4′-diaminodiphenyl ether have been reported as better chelating resins for Cu (II) leading to its separation from mixtures of Cu (II) and Ni (II) ions [15]. Recently, our research group has synthesized a chelating terpolymer resin using an eco-friendly technique and reported its good binding capacity for Ba^{2+} and Zn^{2+} ions [16].

In this article, we describe the synthesis of a terpolymer derived from anthranilic acid, salicylic acid and formaldehyde (ASF). The synthesized terpolymer resin is characterized by elemental analysis, spectral studies (FTIR, ^{1}H NMR and ^{13}C NMR), TGA, GPC and viscometric determinations. The electrical conductivity of the terpolymer resin has also been estimated at different concentrations and temperatures. The surface features of the terpolymer resin are established by SEM. The metal ion uptake capacity of the terpolymer resin by batch equilibrium method for Pb^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+} and Ba^{2+} ions in different electrolytes, pH range and time intervals are also examined and reported for the first time.

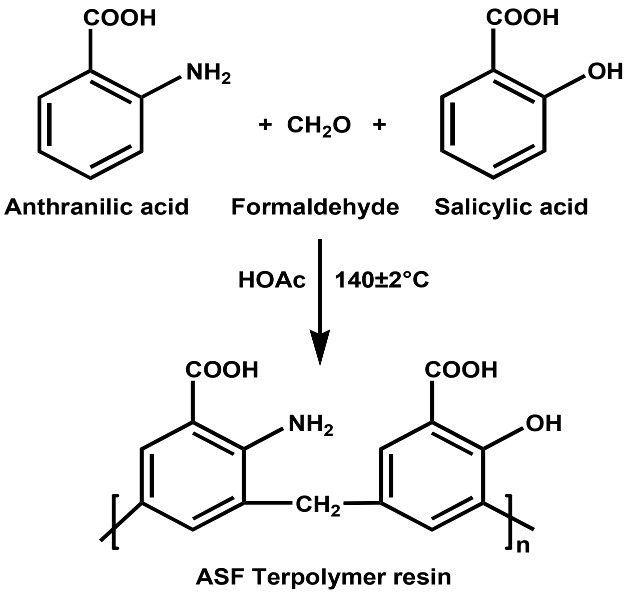
EXPERIMENTAL

Materials

Anthranilic acid (SRL, Mumbai) and salicylic acid (Merck, India) were purified by rectified spirit. Formaldehyde (37%), metal chlorides and nitrates of selected metals (AR grade, Merck) were used as received. All the other chemicals, solvents and the indicators such as fast sulphon black F for copper, methyl thymol blue for barium, xylenol orange for lead, solochrome black for zinc and magnesium were analytical grades procured from Qualigens Fine Chemicals, Mumbai, India. Standardized Na_2EDTA was used as a titrant for all complexometric titrations. Double distilled water was used in all the experiments.

Synthesis of Anthranilic acid/Salicylic acid/Formaldehyde Resin

The ASF terpolymer resin was prepared by condensation polymerization of anthranilic acid (0.1 mol) and salicylic acid (0.1 mol) with formaldehyde (0.2 mol) in glacial acetic acid medium at 140 ± 2°C in an oil bath for 6 h. The resulting mixture was then cooled, poured into crushed ice with constant stirring and left overnight. The yellow coloured resin obtained was washed with warm water and ether and then filtered off to remove the unreacted monomers. Finally, the



Scheme I. Reaction sequence of the synthesis of ASF resin.

terpolymer resin was air dried. The dried resin was further purified by dissolving in 8% NaOH and regenerated in 1/1(v/v%) HCl/water solution [9,10]. This process was repeated twice to separate the pure polymer.

The resin was then filtered off and cured at 75°C for 24 h in an air oven. The yield of the terpolymer was found to be 78%. The dried resin sample finely ground and sieved to obtain uniform particles of 100 mesh size and stored in a polyethylene container. The sieved resin was used for further characterization. The reaction sequence of the synthesis of ASF terpolymer resin is shown in Scheme I.

Physicochemical and Elemental Analysis

The physicochemical parameters such as moisture content, solid percentage, void volume fraction, true density and sodium exchange capacity were calculated as per the reported procedure [17]. The percentage of elements such as C, H, and N present in the terpolymer resin were also determined using Elementar instrument (Model Vario EL III, Germany).

Spectral Analysis

The FTIR spectrum of the synthesized resin sample was scanned in KBr pellets on a Bruker (Model Tensor 27, USA) spectrophotometer to identify the linkages and functional groups. The proton NMR spectrum of the terpolymer resin was recorded in DMSO-d_6 solvent using Bruker 400 MHz, USA. ^{13}C NMR spectrum was also recorded using Bruker 100 MHz, USA.

Thermal Analysis

Thermal stability of the resin was analyzed using thermogravimetric analyzer (TA Instruments Model SDT Q600, USA) at a heating rate of 10°C/min in static nitrogen atmosphere. Based on the results obtained, the degradation pattern was proposed for the terpolymer. The activation energy (E_a) and the order of reaction for the terpolymer resin were also calculated by Freeman-Caroll method [18] using the following equation:

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = \frac{-E_a}{2.303R}\langle\frac{\Delta(1/T)}{\Delta \log W_r}\rangle + n$$

where, dw/dt is the rate of change of weight with time, $W_r = W_c - W$, in which W_c is the weight loss at the completion of reaction or at definite time and W is the total weight loss up to time t, n is the order of reaction and T and R are the temperature and the gas constant, respectively. Hence, a plot of $\Delta log(dw/dt)/\Delta logW_r$ versus $\Delta(1/T)/\Delta logW_r$ gives a slope of $-E_a/2.303R$ with an intercept equal to n on the y-axis where x = 0.

GPC and Viscometric Measurements

The average molecular weight of the ASF terpolymer was determined by gel permeation chromatography using a Shimadzu instrument (Japan) and the viscosity-average molecular weight was also determined using a Brookfield viscometer (Model DV-II$^+$, USA) in DMSO solvent. By selecting the appropriate spindle and adjusting the spindle speed, the viscosity-average molecular weight was calculated by multiplying the recorded value from viscometer and its spindle number.

SEM Studies

The surface morphology of the ASF terpolymer resin was examined by scanning electron microscope with Hitachi instrument (Model S-3000H, Japan) at 4400× and 10000× magnifications.

Electrical Properties

The electrical conductivity of the terpolymer was measured using a Gans instrument (Germany) with nickel sheet as a blank substrate and the polymer in DMSO solvent by four point method at a current rate of 5 A/s. The electrical property of the terpolymer resin was measured at various concentrations such as 0.05, 0.2, 0.4, and 0.6 mM and temperatures ranging from 50 to 120°C.

Ion-exchange Studies

The ion-exchange properties of ASF terpolymer was studied by batch equilibrium method [9,10]. The finely ground terpolymer was used to determine its metal ion uptake capacity for specific metal ions such as Pb^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+} and Ba^{2+} in the form of their nitrate salt aqueous solutions. Metal ion binding capacity for the terpolymer was studied as a function of various electrolytes in different concentrations, pH ranges, and time intervals.

Determination of Metal Ion Uptake in Various Electrolytes at Different Concentrations

The synthesized ASF terpolymer (25 mg) was taken in a pre-cleaned glass bottles with each of the electrolytes (25 mL) such as KCl, KNO_3, $KClO_4$ and K_2SO_4 in different concentrations viz. 0.01, 0.1 and 0.5 M. The pH of the suspensions was adjusted to the desired value by adding required amounts of either 0.1 M HCl or 0.1 M NaOH solutions. The suspensions were mechanically stirred for 24 h at 25°C for the swelling of the terpolymer. To each suspension, 0.1 M of specific metal ion solution (2 mL) was added and vigorously stirred for another 24 h at 25°C.

The mixture was then filtered off and washed with distilled water. The filtrate and the washings were collected and then the amount of metal ion was estimated by titrating against standard Na_2EDTA solution. A blank experiment was also performed following the same procedure without the polymer sample. The amount of metal ions taken up by the polymer in the presence of a given electrolyte can be calculated from the difference between the actual titration value and that of the blank. The chelating mechanism of the terpolymer resin is as follows:

$$(Res.A^{-})B^{+} + C^{+}(solution) \leftrightarrow (Res.A^{-})C^{+} + B^{+}(solution)$$

where, *Res.*, A^-, B^+, and C^+ represent the polymeric resin, the anion attached to the polymeric framework, the active or mobile cation, and the metal ion, respectively.

Distribution of Metal Ions at Different pH

The distribution of each one of the metal ions at various pH range between 3 to 5.5 of the polymer phase and the aqueous phase were determined in the presence of 1 M KNO_3 at 25°C. The distribution ratio K_D may be defined as:

$$K_D = \frac{Metal\ ions\ (mg)\ taken\ up\ by\ 1\ g\ of\ resin}{Metal\ ions\ (mg)\ present\ in\ 1\ mL\ of\ solution}$$

Rate of Metal Ion Uptake

To estimate the time required for attaining the state of equilibrium under the experimental conditions, a series of experiments were carried out to determine the amount of metal ion adsorbed by the terpolymer at specific time intervals. 25 mg of the polymer sample was mechanically stirred with 25 mL of 1 M KNO_3 to allow the polymer to swell. The pH of the suspension was adjusted to the required value by adding either 0.1 M HCl or 0.1 M NaOH. It is observed that under the given experimental conditions the state of equilibrium is established within 24 h at 25°C. The rate of metal ion uptake is expressed as the percentage of the metal ion uptake after a specific time related to that in the state of equilibrium. It is given as follows:

$$Metal\ ion\ uptake\ (\%) = \frac{Metal\ ion\ adsorbed\ (mg)}{Metal\ ion\ adsorbed\ at\ equilibrium\ (mg)} \times 100$$

RESULTS AND DISCUSSION

The terpolymer resin obtained by polycondensation of anthranilic acid and salicylic acid with formaldehyde (ASF) is soluble in solvents like *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulphoxide (DMSO), and aqueous sodium and potassium hydroxide solutions.

Physicochemical and Elemental Analysis

The physicochemical parameters such as moisture content, solid percentage, void volume fraction, true density and sodium exchange capacity of the ASF terpolymer resin are shown in Table 1. The results of the elemental analysis of the resin are presented in Table 2. Based on the analytical data, the empirical formula of the repeating unit is found to be $C_{15}H_{11}N_1O_5$ which is in good agreement with the calculated values of C, H, and N.

Table 1. Physicochemical parameters of ASF terpolymer resin.

Properties	Value (±SD)
Moisture (%)	6.4 ± 0.25
Solid (%)	93.6 ± 0.25
True density (dry resin) g/cm^3	1.542 ± 0.02
Void volume fraction	0.681 ± 0.013
Sodium exchange capacity (mmol/g dry resin)	7.56 ± 0.30

Table 2. Elemental analysis of ASF terpolymer resin.

Sample name	Analysis (%)		
	Calculated (found)		
	C	H	N
ASF resin	64.75 (64.61)	5.64 (5.55)	4.68 (4.50)

Spectral Studies

The recorded FTIR spectrum of the ASF terpolymer resin is shown in Figure 1 and the important IR bands along with their assignments have appeared in the spectrum is tabulated in Table 3. The spectrum shows a broad band at 3401 cm^{-1} due to the (O-H) stretching vibration of Ar-OH involved in the intramolecular hydrogen bonding with Ar-COOH. The strong band appeared at 1207 cm^{-1} is due to (C-N) stretching vibration of Ar-NH_2 [19]. The strong band at 1672 cm^{-1} may be assigned to (C=O) stretching vibration of the carboxyl group present in the resin molecule [20]. The band appeared at 3401 cm^{-1} is due to NH-stretching vibration of amino group [21]. This band seems to be merged with a broad band of -OH group of -COOH groups. The tetra-substitution in the benzene ring is established by the presence of the medium bands at 1100 and 803 cm^{-1} which are attributed to (C-H) bending vibration [21]. The weak band at 3018 cm^{-1} is due to the (C-H) stretching vibration of methylene group [19].

^1H NMR spectrum of ASF terpolymer resin is depicted in Figure 2 and the spectral data are presented in Table 4. The NMR spectrum reveals that the signals around 2.7-4.4 ppm are due to the methylene proton of the Ar-CH_2-Ar linkage [22]. The multiplet signals observed in the range of 6.6-7.4 ppm are indication of the presence of aromatic protons

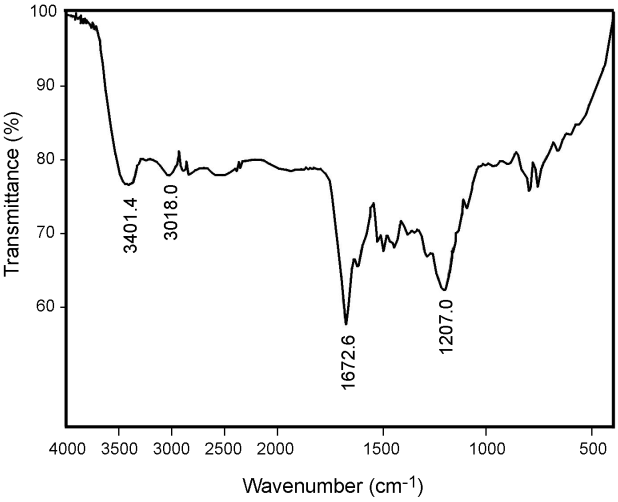


Figure 1. FTIR Spectrum of ASF resin.

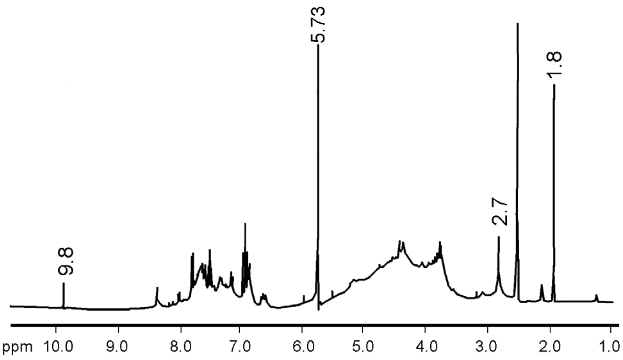


Figure 2. ^1H NMR Spectrum of ASF resin.

Table 3. FTIR spectral data of ASF terpolymer resin.

Vibrational mode	Frequency (cm^{-1})	
	Reported	Observed
-OH of Ar-OH group involved intramolecular hydrogen bonding with Ar-COOH	3500-3200	3401.45
Methylene(-CH_2) stretching	3000-2850	3018.01
>C=O Stretching (carboxylic ketone)	1690-1620	1672.66
1,2,3,5-Substituted benzene ring	1200-800	1100.34 & 803.15
(C-N) Stretching of Ar-NH_2	1200-1300	1207.07
Aromatic ring stretching (C-H)	2700-3000	2884.70

Table 4. ^1H NMR spectral data of ASF terpolymer resin.

Nature of the proton assigned in the spectrum	Expected chemical shift (δ) ppm	Observed chemical shift (δ) ppm of the ASF resin
Aromatic proton (Ar-H)	6.5-8.5	6.6-7.4
Ar-NH_2	5.5-6.0	5.73
Ar-COOH	8.0-12.0	8.35
-OH of Ar-OH group involved intramolecular hydrogen bonding with Ar-COOH	7.5-12.0	9.8
Ar-CH_2- moiety	1.5-2.5	1.8-2.2
Ar-CH_2-Ar moiety	2.5-4.5	2.7-4.4

[16]. The signal displayed at 8.35 ppm may be due to the carboxylic proton of Ar-COOH [23]. The signal in the region of 9.8 ppm is assigned to the -OH group of Ar-COOH involved in the intramolecular hydrogen bonding with proton of -OH in Ar-OH [24]. An intense signal appeared in the region of 5.7 ppm is assigned to the -NH_2 protons of Ar-NH_2 group in the terpolymer resin [25].

The ^{13}C NMR spectrum of ASF resin is shown in Figure 3 and the peaks are assigned with reference to literature values [22,25]. The ^{13}C NMR spectrum shows the corresponding peaks at 112.8, 149.1, 129.5, 136.0, 130.2 and 119.1 ppm with respect to C_1-C_6 of the aromatic ring of the anthranilic acid group. The intense signals appeared at 111.6, 161.0, 129.5, 135.6, 130.2 and 117.0 ppm may be attributed to C_1-C_6 of the aromatic ring of salicylic acid group. Peaks around 169.7 and 171.8 ppm are due to the -C=O group of carboxylic acid functions present in both the aromatic rings of the terpolymer. The peak appeared at 54.86 ppm may be assigned to the -CH_2 bridge between the two aromatic rings in the terpolymer resin. Based on the spectral data obtained from FTIR, ^1H NMR and ^{13}C NMR, the structure of the ASF terpolymer resin is proposed.

Thermogravimetric Analysis

The thermogravimetric analysis is an effective tool to assess the thermal stability of the terpolymer resin. The thermogram of the terpolymer resin is shown in Figure 4 and the thermogravimetric data are presented in Table 5. The ASF resin exhibits three stages of degradation pattern. The first degradation stage begins at 182°C and it extends to 262°C with the weight loss of 25% which corresponds to the loss of carboxylic group attached to the aromatic ring as CO_2 [16]. The second degradation takes place from 262°C and ends at 537°C with the weight loss of 50% which may be due to the elimination of side chain attached

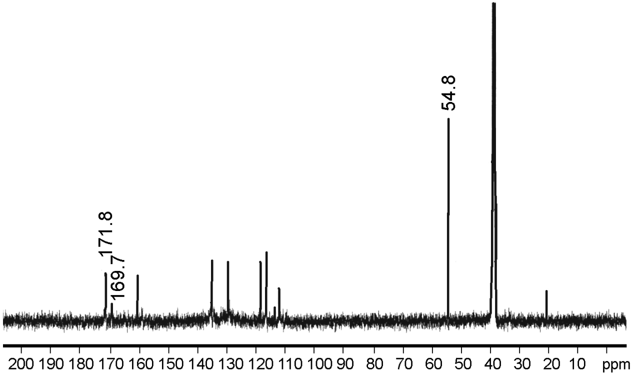


Figure 3. ^{13}C NMR Spectrum of ASF resin.

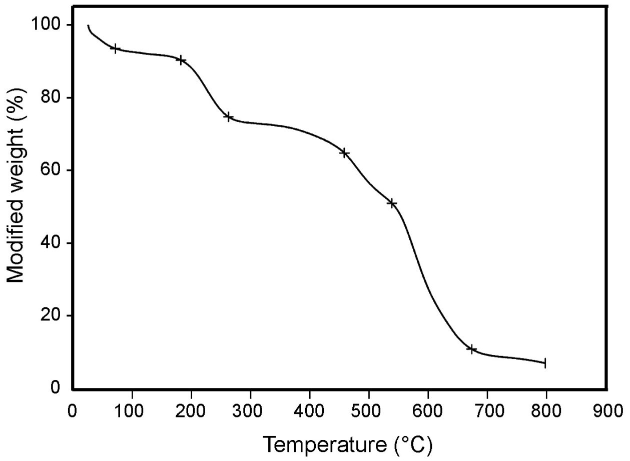


Figure 4. Thermogram of ASF resin.

Table 5. Thermal behaviour data of ASF terpolymer resin.

Sample	Temperature (°C)					Degradation temperature range (°C)	T_{max}[1] (°C)	T_{50}[2] (°C)
	250	350	450	550	650			
	Weight loss of resin (%)							
ASF resin	23.3	27.6	33.9	51.5	85.7	182.2-671.7	671.7	544.1

(1) Maximum decomposition temperature of ASF terpolymer resin. (2) Temperature of 50% weight loss of ASF terpolymer resin.

Table 6. Kinetic parameters of ASF terpolymer resin.

Sample	Degradation temperature (°C)	Activation energy (E_a) (kJ/mol)	Order of reaction (n)
ASF resin	262.28	23.01	0.901

to the aromatic ring. Finally the third degradation stage starts at 537°C and the complete degradation takes place at 671°C. The half degradation temperature of the terpolymer resin is also given in Table 5. On basis of the thermogravimetric data, the activation energy (E_a) and the order of reaction for the terpolymer resin are calculated by Freeman-Caroll method and presented in Table 6.

Molecular Weight Average Measurements

The average molecular weight of the ASF terpolymer is determined by gel permeation chromatography. The number and weight average molecular weights are 2018 and 2074, respectively. The polydispersity index is found to be 1.027. Further the viscosity-average molecular weight of the terpolymer is found to be 2050. The data obtained from molecular weight measurements are presented in Table 7.

Table 7. Molecular weights of ASF terpolymer resin.

Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_v$	Polydispersity ($\overline{M}_w/\overline{M}_n$)
ASF resin	2018	2074	2050	1.027

Morphological Studies

The scanning electron micrographs at magnifications ×4400 and ×10000 are shown in Figures 5 and 6, respectively. This clearly furnishes the surface

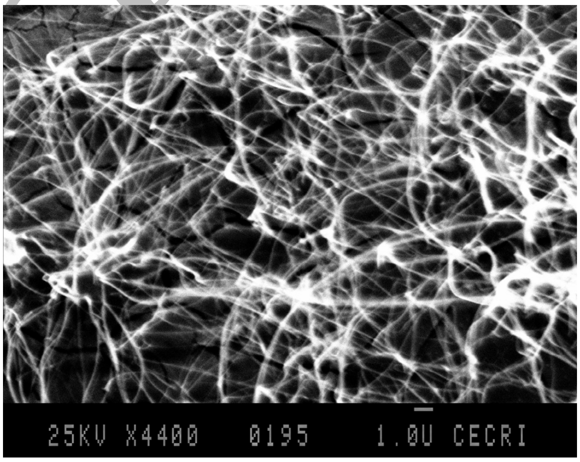


Figure 5. SEM Micrograph of ASF resin at magnification ×4400.

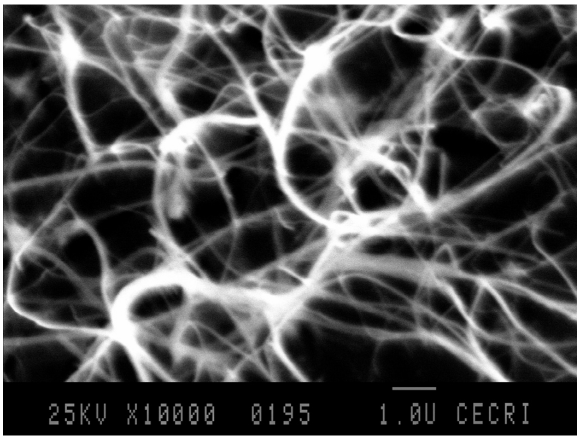


Figure 6. SEM Micrograph of ASF resin at magnification ×10000.

Table 8. Electrical conductivity of ASF resin at various concentrations.

Concentration (mM)	Conductivity (mho.m^{-1})
0.05	0.131
0.20	0.122
0.40	0.111
0.60	0.106

features of the ASF terpolymer resin. The SEM images show deeper pits and strong cracks on the surface. Furthermore, it is interesting to note that the less close packed and high porosity of the surface increase the metal ion binding property of the terpolymer resin [15].

Electrical Conductivity Measurements

The electrical conductivity of the ASF terpolymer resin is found to be 0.131 mho m^{-1} at 0.05 mM and it decreases as the concentration increases (Table 8). Furthermore, the conductivity of the terpolymer resin decreases on increasing the temperature (Table 9). This trend is very similar to the conductors. It is also suggested that the decrease in conductivity is due to the elimination of the adsorbed or absorbed gases or solvent traces present in the terpolymer [16]. The plots of concentration versus electrical conductivity and temperature versus electrical conductivity are presented in Figures 7 and 8, respectively.

Table 9. Electrical conductivity of ASF resin at various temperatures.

Temperature (°C)	Conductivity (mho.m^{-1})
50	0.135
60	0.135
70	0.131
80	0.079
90	0.078
100	0.075
110	0.072
120	0.070

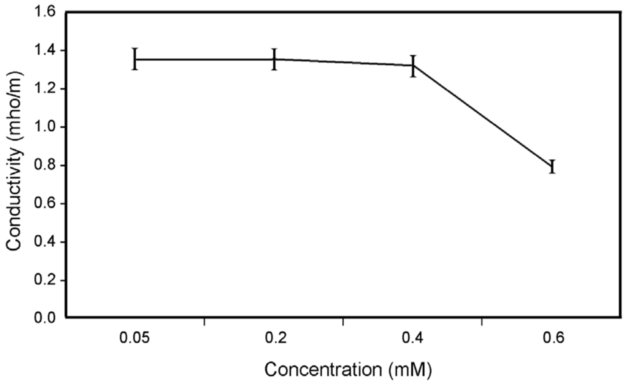


Figure 7. Electrical conductivity of the ASF resin at various concentrations.

Ion-Exchange Properties

Metal Ion Uptake in Various Electrolytes of Different Concentrations

The chelating ion-exchange property of the ASF terpolymer resin was measured by batch equilibrium method involving Pb^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+}, and Ba^{2+} ions in various electrolytes viz. KCl, KNO_3, $KClO_4$ and K_2SO_4 with different concentrations of 0.01, 0.1, and 0.5 M. The results are presented in Table 10. From the data it is observed that the amount of metal ion uptake for a given amount of terpolymer resin depends on the nature and concentrations of the electrolyte used for the chelation studies [26].

The increase in the metal ion uptake with the increase of concentration may be explained on the basis of the stability constants of the complexes. From the results, it is observed that the amount of uptake of metal ion by the terpolymer resin increases with the

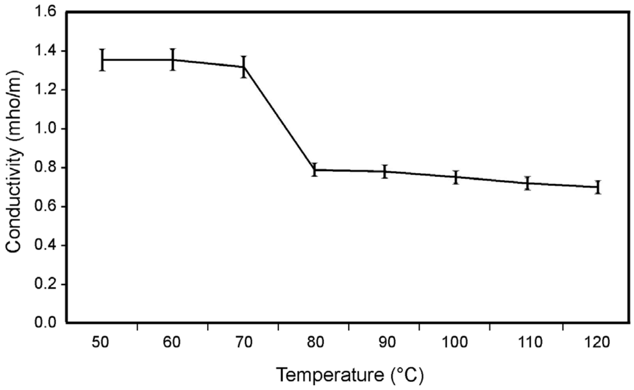


Figure 8. Electrical conductivity of the ASF resin at various temperatures.

Table 10. Quantitative evaluation of metal ion uptake by ASF terpolymer resin.

Metal ions	Concentration of electrolytes (mol.L^{-1})	Metal ion uptake in presence of electrolytes (mg)			
		KCl	KNO_3	$KClO_4$	K_2SO_4
Pb^{2+}	0.01	04.28	10.37	03.14	03.08
	0.10	08.49	14.49	04.21	02.15
	0.50	10.00	16.56	06.28	01.28
Zn^{2+}	0.01	02.65	05.87	01.90	01.94
	0.10	03.91	07.18	02.81	01.11
	0.50	04.57	11.70	03.08	00.91
Cu^{2+}	0.01	02.54	03.17	00.65	01.54
	0.10	03.81	05.71	01.95	00.95
	0.50	06.98	08.25	03.22	00.23
Mg^{2+}	0.01	01.21	02.18	00.72	01.01
	0.10	01.45	03.15	01.01	00.81
	0.50	02.91	03.71	01.45	00.24
Ba^{2+}	0.01	01.02	02.37	00.37	01.12
	0.10	01.34	03.74	01.05	00.92
	0.50	02.11	06.85	01.28	00.11

$M^{2+}(NO_3)_2$: 0.1 M; volume: 2 mL; volume of electrolyte: 25 mL; weight of resin: 25 mg; time: 24 h; temperature: 25°C.

increasing concentration of Cl^-, NO_3^-, and ClO_4^- and decreases with the increased SO_4^2 concentration. This may be due to the sulphate ion forming strong chelates with metal ions, while other anions form weak chelates. The influence of Cl^-, NO_3^-, and ClO_4^- ions is less than that of SO_4^{2-} ion on the position of the equilibrium of metal chelates.

The amount of uptake of Pb^{2+} and Zn^{2+} ions by the polymer is comparatively higher than that of the other metal ions such as Cu^{2+}, Ba^{2+} and Mg^{2+}. This may be due to the relative weak chelation of Pb^{2+} and Zn^{2+} ions with the anions of the electrolytes compared to that of the other metal ions.

Furthermore, the polymer has high porosity in its structure; hence it can easily accommodate metal ions of specific size into its cavities and acts as a better ion-exchanger which is evident from the SEM studies. The better ion-exchange property of the resin may also be due to the amino and hydroxyl groups present in the resin structure. The metal binding property of the ASF terpolymer resin is found to be higher than that of the other polymeric resins reported earlier [19,24].

Distribution of Metal Ions at Different pH

The distribution of each one of the metal ions, e.g., Pb^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+} and Ba^{2+} between polymer phase and the aqueous phase was determined at 25°C in the presence of 1 M KNO_3 at various pH range 3 to 5.5. The study was restricted up to maximum pH of 5.5, due to the hydrolysis of metal ions at higher pH.

The formation of metal hydroxide interferes with the ion-exchange process. The amount of the metal ion remaining in the aqueous phase can be estimated. By evaluation of the original metal ion concentration the metal ion adsorbed by the resin can be calculated. The effect of pH on the amount of metal ion distributed between the two phases is given in Table 11, and it reveals that the amount of uptake of metal ions by the terpolymer at equilibrium increases with increasing pH. It is assumed that the equilibrium state is attained at 25°C under the given conditions in 24 h. It

Table 11. Distribution ratios K_D as a function of pH for ASF terpolymer resin.

Metal ions	Distribution ratio (K_D) of the metal ions					
	pH of the medium					
	3	3.5	4	4.5	5	5.5
Pb^{2+}	120.36	201.25	312.11	422.21	514.78	607.32
Zn^{2+}	95.79	172.47	269.12	369.74	444.25	540.28
Cu^{2+}	87.64	158.94	245.86	337.50	440.86	491.35
Mg^{2+}	65.35	125.01	211.64	304.45	416.79	412.01
Ba^{2+}	61.24	125.12	205.33	310.77	391.98	410.28

$M^{2+}(NO_3)_2$: 0.1 M; volume: 2 mL; KNO_3: 1 M; volume: 25 mL; weight of resin: 25 mg; time: 24 h; temperature: 25°C.

is also observed that the terpolymer uptakes Pb^{2+} ions more effectively than the other tested ions at all pH values.

Among the other ions taken up for the study, the terpolymer showed selective uptakes of Zn^{2+} and Cu^{2+} compared to the other metal ions under moderate pH values. Further, Mg^{2+} and Ba^{2+} ions have lower distribution ratio over the pH range 3-5.5. This can be explained as the weak stabilization energy of the metal chelates formed by these ions. In the present investigation it is observed that the order of the distribution ratio of the metal ions is $Pb^{2+} > Zn^{2+} > Cu^{2+} > Mg^{2+} > Ba^{2+}$ for the pH range 3-5.5. The values of the distribution ratio and the order at different pH are dependent on the nature of the polymeric resin and its structure. The distribution of the metal ions at different pH in the ASF terpolymer resin is found to be higher than that of the other polymeric resins reported earlier [11,24].

Rate of Metal Ion Uptake

The rate refers to the change in the concentration of the metal ions in the aqueous solution, which is in contact with the terpolymer. Perusal of the Table 12 reveals that the time taken for the uptake of the different metal ions at a given stage depends on the nature of the metal ion under given condition. Among the five metal ions taken for study, Pb^{2+} ion requires about 5 h (shortest time), whereas Zn^{2+} requires about 6 h to reach equilibrium. Cu^{2+}, Mg^{2+}, and Ba^{2+} ions require 7 h to attain the state of equilibrium. Hence, for the ASF terpolymer the rate of metal ion uptake follows the order $Pb^{2+} > Zn^{2+} > Cu^{2+} > Mg^{2+} > Ba^{2+}$.

Reusability of the Resin

One of the most important advantages of this ASF chelating resin is its possible reusability after the exchange process. The resin, once used, can be recovered back to its original form by desorption of

Table 12. Rate of metal ion uptake by ASF terpolymer resin.

Metal ions	Equilibrium attainment (%)						
	Time (h)						
	1	2	3	4	5	6	7
Pb^{2+}	64	72	77	84	93	-	-
Zn^{2+}	49	57	71	83	90	96	-
Cu^{2+}	38	44	57	68	76	82	97
Mg^{2+}	21	34	48	59	71	87	92
Ba^{2+}	12	29	36	48	64	77	89

$M^{2+}(NO_3)_2$: 0.1 M; volume: 2 mL; KNO_3: 1 M; volume: 25 mL; weight of resin: 25 mg; temperature: 25°C.

the complexed metal ions using hydrochloric acid. The metal free resin can be reused after repeated washing with distilled water. Addition of several metal ion solutions into the purified resin results in the uptake of almost the same amounts of the respective metal ions as initially adsorbed by unused resin. The retention of the initial metal ion uptake capacity, even after few cycles of repeated exchanges, suggests that the resin can be used effectively.

CONCLUSION

ASF terpolymer resin was prepared from anthranilic acid and salicylic acid with formaldehyde in glacial acetic acid medium by polycondensation method. Thermogravimetric data reveal that the degradation of the terpolymer involves three stages and showing good thermal stability, as well. The terpolymer has good electrical conductivity at lower concentrations and temperatures. The GPC and viscometric determination show that the molecular weight of the terpolymer is around 2100. The semicrystalline nature of the ASF terpolymer resin which is confirmed by SEM studies reveals that the terpolymer can act as an effective ion-exchanger for various divalent metal ions. The order of the distribution ratio of metal ions are found to be $Pb^{2+} > Zn^{2+} > Cu^{2+} > Mg^{2+} > Ba^{2+}$.

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