



An Eco-friendly Synthesis of A Terpolymer Resin: Characterization and Chelation Ion-exchange Property

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A B S T R A C T

Anthranilic acid-thiourea-formaldehyde terpolymer resin was synthesized by an eco-friendly technique using dimethylformamide as a reaction medium. The resin was characterized by FTIR, ¹H NMR, ¹³C NMR, thermal analysis and viscosity-average molecular weight. The physicochemical parameters have been evaluated for the terpolymer resin. The kinetic parameters such as energy of activation and the order of the reaction have also been evaluated on the basis of the thermogravimetric data using Freeman-Carroll method. The surface morphology of the terpolymer resin was examined by scanning electron microscopy and the transition state between crystalline and amorphous nature was established. The colour of the terpolymer resin was confirmed by optical microscopy. The electrical property of the terpolymer resin showed an appreciable change in its conductivity at various concentrations and temperatures. One of the important applications of these types of polymers is their capability to act as chelating ion-exchangers. The chelation ion-exchange property of the terpolymer showed a powerful adsorption towards specific metal ions like Zn²⁺, Mn²⁺, Cu²⁺, Ba²⁺, and Mg²⁺. A batch equilibration method was adopted to study the selectivity of the metal ion uptake involving the measurement of the distribution of the given metal ion between the polymer sample and a solution containing the metal ion over a wide range of concentrations and pHs of different electrolytes.

Key Words:

terpolymers;
thermal analysis;
electrical properties;
ion-exchangers;
microwave irradiation.

INTRODUCTION

Terpolymers find very useful applications as adhesives, high temperature flame resistant fibres, coating materials, semiconductors, catalysts, and ion-exchange resins [1-5]. Ion-exchange resins have attracted much interest in the recent years due to their application in waste water treatment, metal recovery and for the identification of specific metal ions [6,7]. Chelating ion-exchange properties of the resin involving poly[(2,4-dihydroxybenzophenone)butylene]

and its polychelates with transition metals are reported [8]. A new chelating sorbent for metal ion extraction under saline conditions has also been studied [9]. Poly(2-hydroxy-4-acryloyloxybenzophenone) resin [10] and resin functionalized with dithioamide [11] are found to be chelation ion exchangers. Copolymers involving 2-hydroxyethylmethacrylate and 2-methacryloyl-amidocysteine [12], polyacrylonitrile beads and 2-amino-2-thiazoline [13] and

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4-hydroxy acetophenone-biuret-formaldehyde [14] are reported for their ion-exchange characteristics. The synthesis of o-nitrophenol-thiourea-paraformaldehyde terpolymer has been studied with its chelation ion exchange properties by a static batch equilibrium method [15]. Poly[(2-hydroxy-4-methoxybenzophenone)ethylene] resin has shown good binding capacity for the lanthanum (III) at various conditions [16]. The copolymer from 2,4-dichlorophenyl acrylate/8-quinolinyl methacrylate and acrylic copolymer derived from 8-quinolinyl methacrylate was found to be a good cation exchanger resin due to its pendant ester-bound quinolinyl group [17,18]. Recently, Shah et al. reported the chelating ability of the resin synthesized by a microwave irradiation technique involving salicylic acid, formaldehyde, and resorcinol [19].

The present work deals with the synthesis and characterization of anthranilic acid-thiourea-formaldehyde (ATF) terpolymer resin by microwave irradiation, an eco-friendly and short time process in dimethylformamide medium (DMF) for the first time. The synthesized terpolymer was characterized by FTIR, ^1H NMR, ^{13}C NMR, thermal analysis and viscosity-average molecular weight determination. The electrical measurement of the terpolymer was determined by changing the concentration and temperature to assess the effectiveness of the terpolymer as semiconducting materials under different conditions. One of the important applications of chelating and functional polymers is their capability to recover metal ions from waste solutions. Hence, the chelation ion-exchange property of the ATF terpolymer resin is also demonstrated for specific metal ions.

EXPERIMENTAL

Materials

Anthranilic acid and thiourea were used as received from SRL, Mumbai. Stock solutions of metal ions such as Zn^{2+} , Mn^{2+} , Cu^{2+} , Ba^{2+} , and Mg^{2+} were prepared by dissolving their nitrate salts in distilled water. The other chemicals and solvents procured from Qualigens were used as received without further purification. The indicators such as fast sulphon

black F for copper, methyl thymol blue for barium and solochrome black for zinc, manganese and magnesium were used for titrations.

Synthesis of Resin

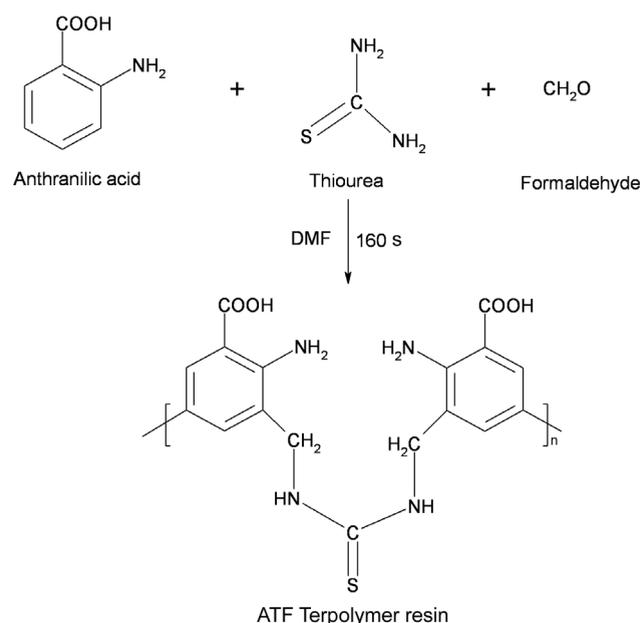
The terpolymer resin involving anthranilic acid (0.1 mol) and thiourea (0.1 mol) with formaldehyde (0.2 mol) was synthesized by microwave irradiation technique (2.46 GHz, 300 W) using dimethylformamide as the reaction medium at $80 \pm 2^\circ\text{C}$ for 160 s [19]. The reaction mixture was then cooled, poured into crushed ice with constant stirring and left overnight. The yellow coloured resin obtained was then washed with warm water and methanol. It was then filtered off to remove unreacted monomers. Finally, the terpolymer resin was air dried. The yield of the terpolymer was found to be 6.5 g. The reaction route is shown in Scheme I.

Regeneration of the Resin

The dried resin sample was then dissolved in 8% NaOH and regenerated using 1:1(v/v) HCl/water. It was then filtered off and cured in an air oven at 75°C for 24 h.

Viscometric Measurements

The viscosity-average molecular weight of the terpolymer was determined using a Brooke Field



Scheme I. Reaction route of the synthesis of ATF resin.

viscometer in DMSO solvent. By selecting the appropriate spindle and adjusting the spindle speed, the viscosity-average molecular weight of the terpolymer was calculated by multiplying the recorded value from viscometer and its spindle number. The experiment was repeated to determine the average molecular weight of the resin.

Thermal Analysis

Thermal stability of the terpolymer was determined using thermogravimetric analyzer (Model SDT Q 600) at a heating rate of 10°C/min in nitrogen atmosphere. On the basis of the results, the decomposition pattern was proposed for the terpolymer. The kinetic parameters of the terpolymer resin were calculated by Freeman-Carroll method [20]. In the Freeman-Carroll method, the following expression was used to evaluate various kinetic parameters of the terpolymer resin:

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

where, dw/dt is the rate of change of weight with time; $W_r = W_c - W$, where 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 gas constant, respectively.

Hence, a plot of $\Delta \log(dw/dt)/\Delta \log W_r$ versus $\Delta(1/T)/\Delta \log W_r$ gives a slope of $-E_a/2.303R$ with an intercept equals to n on the y -axis where $x = 0$.

Spectral Analysis

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

Electrical Properties

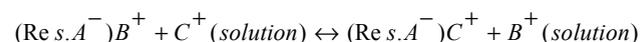
The electrical conductivity of the terpolymer was measured by doping carbon fibre with the polymer using DMSO solvent by four point method at a

current rate of 5 A/s. The electrical property of the terpolymer resin was measured at various concentrations such as 0.05, 0.2, 0.6 and 0.8 mM and temperatures ranging from 50° to 120°C with nickel sheet as a substrate using Gans instrument.

Ion-exchange Studies

Evaluation of Metal Ion Uptake at Different Electrolytes

A batch equilibrium method was adopted to determine the metal ion uptake of specific metal ions like Zn^{2+} , Mn^{2+} , Cu^{2+} , Ba^{2+} , and Mg^{2+} . The pH of the suspension was adjusted to the required value using either 0.1 M HCl or 0.1 M NaOH. The polymer samples (25 mg) were taken in a pre-cleaned glass bottles and 25 mL of each of the electrolytes, e.g., NaCl, KCl and KNO_3 at various concentrations viz. 0.01, 0.1 and 0.5 N are added. These solutions were mechanically stirred vigorously for 24 h to allow the polymer to swell. Exactly 2 mL of 0.1 mol of a specific metal ion solution was added to each glass bottle and stirred for 24 h. The polymer was then filtered off from each bottle and washed with distilled water. The filtrates and the washings were collected and then, the amount of metal ions was estimated by titrating against standard Na_2EDTA solution. A blank experiment was also performed following the same procedure without the addition of the polymer sample. The amount of metal ions taken by the polymer in the presence of a given electrolyte can be calculated from the difference between the actual titre value and that of the blank. The chelating mechanism of the terpolymer resin is as follows.



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

Evaluation of the Distribution of Metal Ions at Different pH

The distribution of each one of the metal ions at various pH ranging from 3 to 5.5 between polymer phase and aqueous phase was determined in the presence of 1 M KNO_3 at room temperature. The distribution ratio K_D , may be defined as follows:

$K_D = \text{Weight (mg) of metal ions taken up by 1 g of resin sample} / \text{Weight (mg) of metal ions in 1 mL of solution}$

Scanning Electron Microscopy

The surface morphology of the terpolymer resin was investigated by a Jeol scanning electron microscope at 5400× and 10000× magnifications. An optical photograph was also recorded to substantiate the morphological characteristics of the terpolymer using a Zeiss optical microscope at 20× magnification.

RESULTS AND DISCUSSION

The yellow coloured ATF terpolymer resin was soluble in solvents like *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulphoxide (DMSO) and aqueous sodium and potassium hydroxide solutions. The physicochemical parameters such as moisture content, solid percentage, void volume fraction, true density and sodium exchange capacity were also determined [21]. The results are shown in Table 1.

Spectral Studies of ATF Resin

The composition and the structure of the terpolymer were assigned on the basis of FTIR, ¹H NMR, and ¹³C NMR spectroscopy techniques.

FTIR Spectral Study

The spectrum of ATF resin is depicted in Figure 1 and the spectral data are presented in Table 2. A strong band at 1297.6 cm⁻¹ is due to C-N stretching of (Ar-NH₂) [22]. A broad band appeared in the region 3443.4 cm⁻¹ may be assigned to the hydroxyl group of -COOH [23]. The consistent appearance of band at 953.1 cm⁻¹ is attributed to -C=S [13]. A peak at 2829.5 cm⁻¹ may be assigned to aromatic ring

Table 1. Physicochemical parameters of ATF terpolymer resin.

Properties	Value (SD)
Moisture (%)	7.4 ± 0.5
Solid (%)	92.6 ± 0.5
True density (dry resin) (g/cm ³)	1.101 ± 0.015
Void volume fraction	0.512 ± 0.002
Sodium exchange capacity (mmol/g dry resin)	7.21 ± 0.40

stretching modes [23]. The peaks related to 1,2,3,5 tetra substitution of aromatic benzene ring by sharp, medium/weak absorption bands have appeared between 1200 cm⁻¹ and 800 cm⁻¹ [24]. The band at 1622.6 cm⁻¹ may be due to -C=O (carboxylic ketone) stretching vibrations [23]. The presence of -NH bridge in the spectrum is confirmed by the absorption band at 3443.4 cm⁻¹ [24]. This band seems to be merged with a broad band of -OH group of -COOH group. Finally a peak appeared at 2893.7 cm⁻¹ may be attributed to -CH₂ linkage present in the terpolymer resin [23].

¹H NMR Spectral Study

¹H NMR spectrum of ATF resin is shown in Figure 2 and the spectral data are presented in Table 3. The chemical shift (δ, ppm) observed is assigned on the basis of the data available in the literature [24]. The medium singlet at 2.78 ppm may be due to methylene proton of Ar-CH₂ bridge. A singlet observed in the region 3.61 ppm is due to methylene proton of Ar-CH₂-N moiety. A singlet observed in the region 5.03 ppm may be attributed to the protons in -NH linkage. The signal at 9.6 ppm is assigned to the -OH group of Ar-COOH and it indicates the intramolecular hydrogen bonding between -OH group of Ar-COOH and -NH₂ group of Ar-NH₂ in the terpolymer resin. The peaks in the region of 7.1-8.8 ppm may be assigned to the protons in the aromatic ring [23,24].

¹³C NMR Spectral Study

The ¹³C NMR spectrum of ATF resin is shown in

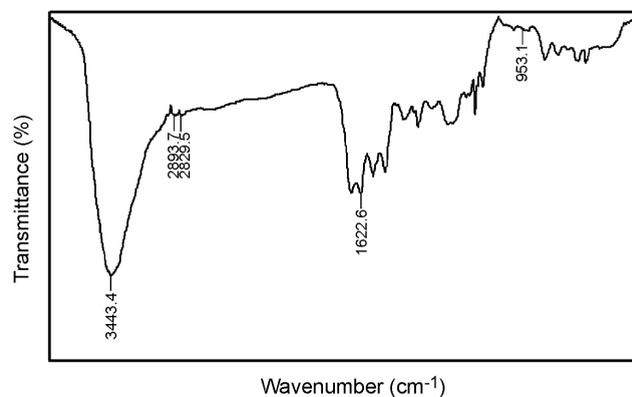


Figure 1. IR spectrum of ATF resin.

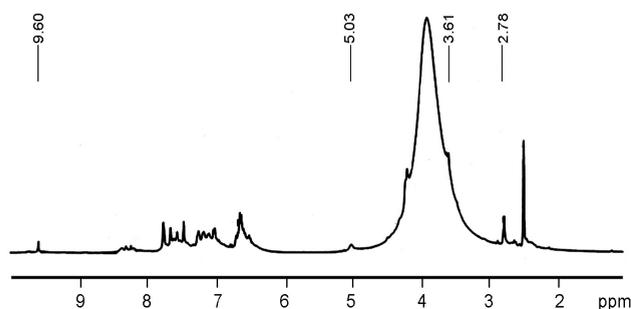
Table 2. FTIR spectral data of ATF terpolymer resin.

Vibrational mode	Frequency (cm ⁻¹)	
	Reported	Observed
-OH in -COOH group	3500-3200	3443.4
Aromatic ring stretching (C-H)	2700-3000	2829.5
Methylene(-CH ₂) stretching	3000-2850	2893.7
>C=O stretching (carboxylic ketone)	1690-1620	1622.6
1,2,3,5-Substituted benzene ring	1200- 800	1161.7 & 819.3
(C-N) stretching of Ar-NH ₂	1200-1300	1297.6
-NH bridge	3500-3200	3443.4
-C=S	-	953.1

Table 3. ¹H NMR spectral data of ATF terpolymer resin.

Nature of the proton assigned in the spectrum	Expected chemical shift (δ) ppm	Chemical shift (δ) ppm of the ATF terpolymer resin
Aromatic proton (Ar-H)	6.5-8.5	7.4
Proton of -OH in -COOH group involved in intramolecular hydrogen bonding with proton of -NH ₂ in Ar-NH ₂	8.00-12.00	9.6
Methylenic proton of Ar-CH ₂ -N moiety	3.00-3.7	3.61
Proton of -NH bridge	5.00-8.00	5.03
Ar-CH ₂ moiety	2.00-3.00	2.78

Figure 3 and the peak positions are assigned according to the literature [23]. The ¹³C NMR spectrum shows the corresponding peaks at 110.3, 150.1, 128.1, 131.6, 128.1, 131.6 ppm with respect to C₁ to C₆ of the aromatic ring. Peak at 170.16 ppm is due to the -C=O group of carboxylic acid present in the aromatic ring. The peak appeared at 190.3 ppm confirms the presence of -C=S group in the resin. The peak appeared at 46.1 ppm may be assigned to the

**Figure 2.** Proton NMR spectrum of ATF resin.

-CH₂ bridge in the terpolymer. The ¹³C NMR spectrum clearly establishes the linear structure of the terpolymer synthesized from anthranilic acid-thiourea-formaldehyde. Based on the spectral data obtained from FTIR and NMR, the structure of the synthesized ATF terpolymer resin is shown in Scheme I.

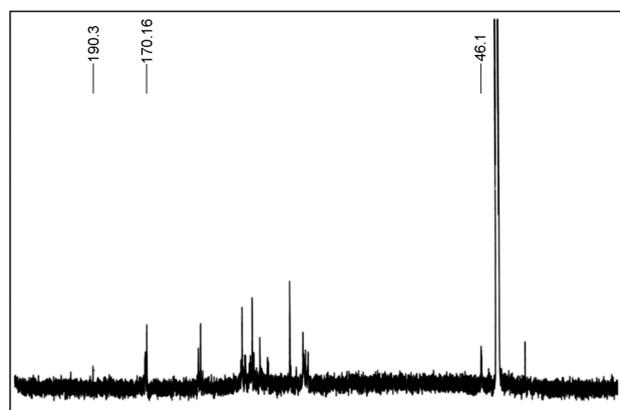
**Figure 3.** ¹³C NMR spectrum of ATF resin.

Table 4. Thermal behaviour data of ATF terpolymer resin.

Sample	Weight loss at various temperatures (%)					Decomposition temperature range (°C)	T _{max} ¹ (°C)	T ₅₀ ² (°C)
	350 (°C)	450 (°C)	550 (°C)	650 (°C)	750 (°C)			
ATF terpolymer resin	36.5	41.5	53.9	73.5	96.0	174.86-762.7	762.7	526.1

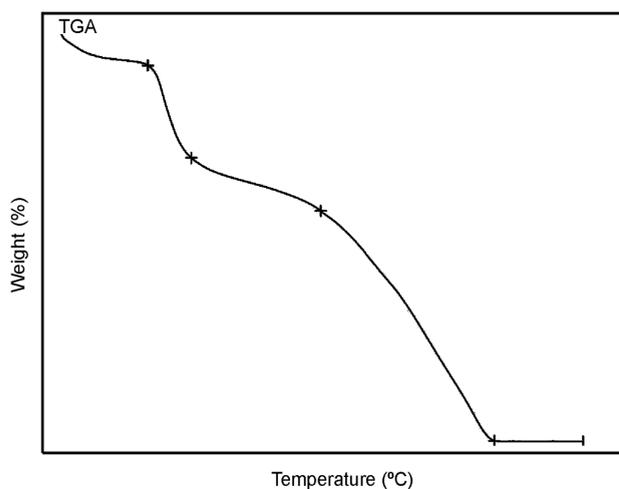
(1) Maximum decomposition temperature of ATF terpolymer resin; (2) Temperature of 50% weight loss of ATF terpolymer resin.

Table 5. Kinetic parameters of ATF terpolymer resin.

Sample	Decomposition temperature (°C)	Energy of activation (kJ/mol)	Order of reaction (n)
ATF terpolymer resin	248.48	20.22	0.891

Thermogravimetric Analysis

Thermogravimetric analysis is found to be a very useful method to assess the thermal stability of a polymeric resin. TGA data of the terpolymer is presented in Table 4 and the kinetic parameters of the terpolymer are presented in Table 5. The thermogram recorded is shown in Figure 4. The ATF resin exhibits a three stage decomposition process. The first stage decomposition starts at 174.86°C with a weight loss of 8% of the resin. The weight loss may be due to the removal of carboxylic group (-COOH) present in the terpolymer as CO₂. In the second stage, the decomposition starts at 248.48°C involving 70.46%

**Figure 4.** TGA thermogram of ATF resin.

of weight loss and end up at 468°C which corresponds to the weight loss of 57.73% due to the loss of side chain attached to the aromatic nucleus. Third stage of the decomposition starts at 468°C and the complete decomposition of the terpolymer takes place at 762.7°C involving 98% of weight loss of the sample. The half decomposition temperature of the terpolymer resin is also presented in Table 4.

Electrical Conductivity Measurements

The electrical conductivity of the ATF terpolymer resin was measured by four point method using Gans instrument at various concentrations, i.e., 0.05, 0.2, 0.6, and 0.8 mM and temperatures range 50-120°C with nickel sheet as a substrate. The electrical conductivity of the terpolymer resin is 1.51×10^{-1} mho.m⁻¹ at 0.05 mM and it decreases till the concentration reaches 0.6 mM (Table 6). Further, the increase in concentration increases the conductivity of the terpolymer. This is a quite an interesting result observed due to the amorphous nature of the synthesized terpolymer. However, the conductivity of the terpolymer resin decreases on increasing the temperature (Table 7). This trend is very similar to metallic 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 [25]. The plots of

Table 6. Electrical conductivity at various concentrations.

Concentration (mM)	ATF terpolymer resin (mho m ⁻¹) × 10 ⁻¹
0.05	1.51
0.20	1.36
0.60	1.31
0.80	1.35

concentration versus electrical conductivity (Figure 5) and temperature versus electrical conductivity (Figure 6) are also presented.

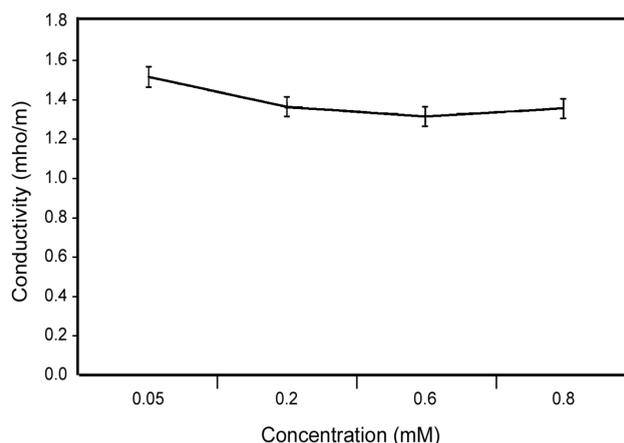
Ion-exchange Studies

Evaluation of Metal Ion Uptake in Different Electrolytes

The chelation ion-exchange property of the ATF terpolymer resin was carried out by batch equilibrium method involving Zn²⁺, Mn²⁺, Cu²⁺, Ba²⁺, and Mg²⁺ ions in various electrolyte media viz. NaCl, KCl and KNO₃ with different concentrations such as 0.05, 0.1 and 0.5 M. The results are presented in Table 8 and the bar graphs for the measurements are given in Figures 7, 8, and 9. 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 present in the solution. As the concentration of the electrolyte increases, the uptake of metal ion increases. Further, in presence of NaCl electrolyte the metal ion uptake is very high when compared to KNO₃. However, the metal ion uptake in the case of KCl lies between those for NaCl

Table 7. Electrical conductivity at various temperatures.

Temperature (°C)	ATF terpolymer resin (mho m ⁻¹) × 10 ⁻¹
50	1.31
60	1.28
70	1.21
80	0.078
90	0.078
100	0.074
110	0.073
120	0.073

**Figure 5.** Electrical conductivity of the ATF resin at various concentrations.

and KNO₃ electrolytes. The increase in the metal ion uptake with increased concentration may be explained on the basis of the stability constants of the terpolymer [26].

The amounts of uptake of Ba²⁺ and Zn²⁺ ions in NaCl and KCl electrolytes by the polymer are comparatively higher than that of the other metal ions such as Cu²⁺, Mg²⁺, and Mn²⁺, because of the formation of stronger complexes by the chloride anion in the electrolytes with Ba²⁺ and Zn²⁺ ions. The strong complexing ability of Ba²⁺ and Zn²⁺ ions may be the reason behind the higher uptake of metal ion by the terpolymer at higher concentration of the electrolytes. However, the amount of uptake of Cu²⁺ and Ba²⁺ in KNO₃ electrolyte is higher than Mg²⁺, Mn²⁺, and Zn²⁺ ions. This may be due to the stronger

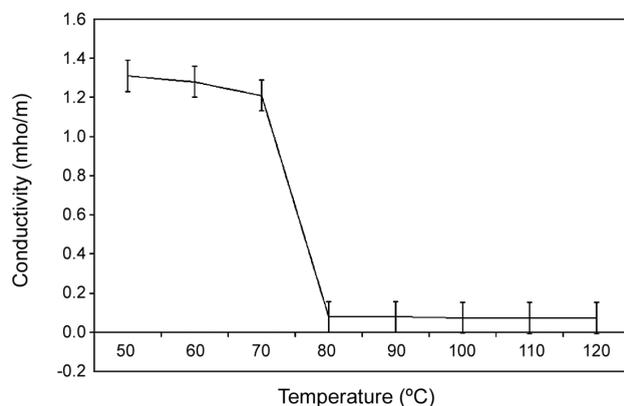
**Figure 6.** Electrical conductivity of the ATF resin at various temperatures.

Table 8. Evaluation of the effect of different electrolytes in the uptake of metal ions by ATF terpolymer resin.

Metal ions	Electrolyte (mol.L ⁻¹)	Weight of metal ion uptake in presence of electrolyte (mg)		
		NaCl	KCl	KNO ₃
Zn ²⁺	0.01	5.87	2.61	2.61
	0.10	6.53	3.91	3.26
	0.50	8.48	4.57	3.26
Mn ²⁺	0.01	3.29	2.19	1.09
	0.10	4.39	2.74	1.64
	0.50	5.49	3.84	3.29
Cu ²⁺	0.01	4.44	1.27	3.17
	0.10	5.71	1.91	3.81
	0.50	6.35	2.54	4.44
Ba ²⁺	0.01	6.85	4.11	2.74
	0.10	9.59	5.48	4.11
	0.50	10.96	6.85	4.51
Mg ²⁺	0.01	1.94	1.21	0.48
	0.10	2.18	1.45	0.72
	0.50	2.43	1.70	0.97

M²⁺(NO₃)₂ = 0.1 M; volume=2 mL; volume of electrolyte = 25 mL; weight of resin=25 mg; time=24 h; temperature=room temperature.

complexing ability of Cu²⁺ and Ba²⁺ ions in the presence of nitrate anions of the electrolyte. The amount of metal ion uptake by the ATF terpolymer resin is found to be higher when compared to the other polymeric resins [8,14].

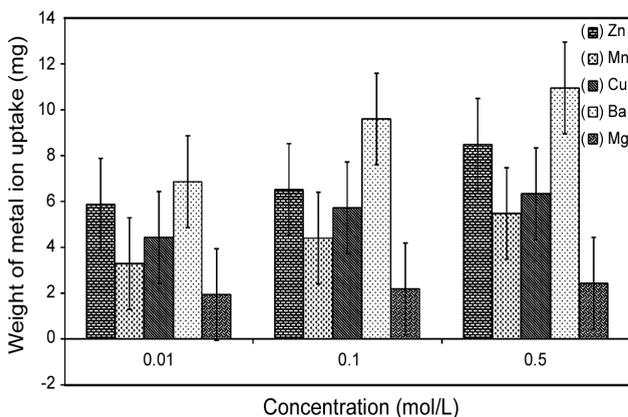


Figure 7. Effect of sodium chloride electrolyte on metal ion uptake by ATF resin.

Evaluation of Distribution of Metal Ions at Different pH

The distribution of each one of the metal ions such as Zn²⁺, Mn²⁺, Cu²⁺, Ba²⁺, and Mg²⁺ between polymer phase and the aqueous phase was determined at room temperature in the presence of 1 M KNO₃ at various

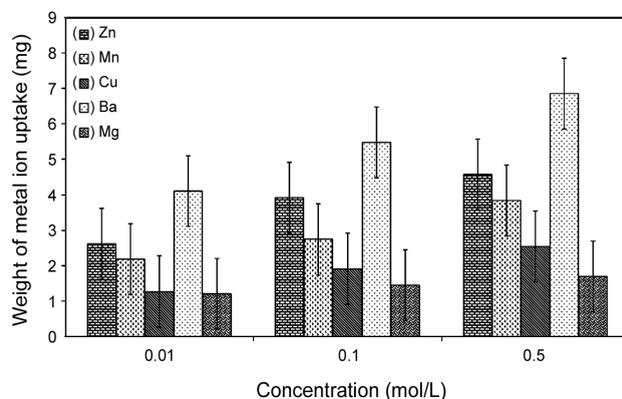


Figure 8. Effect of potassium chloride electrolyte on metal ion uptake by ATF resin.

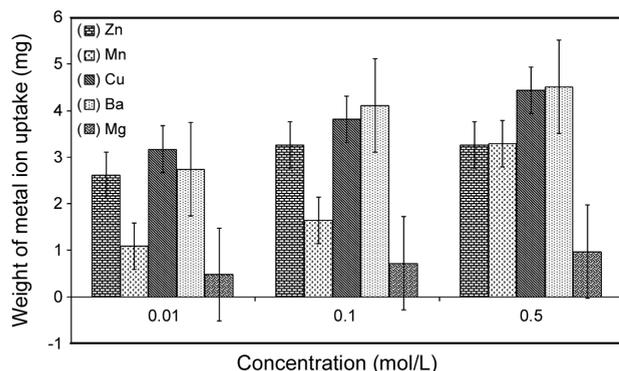
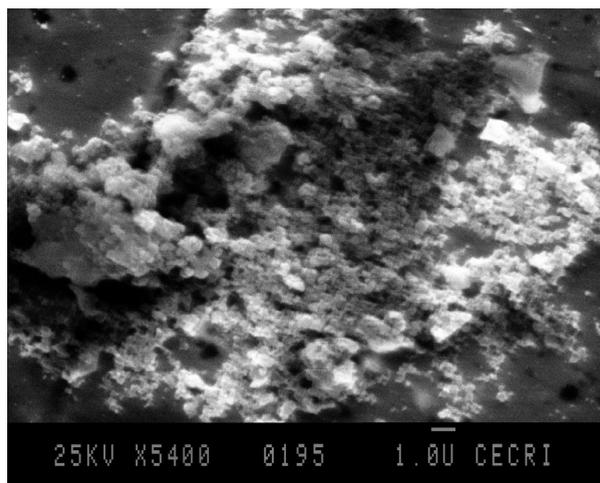


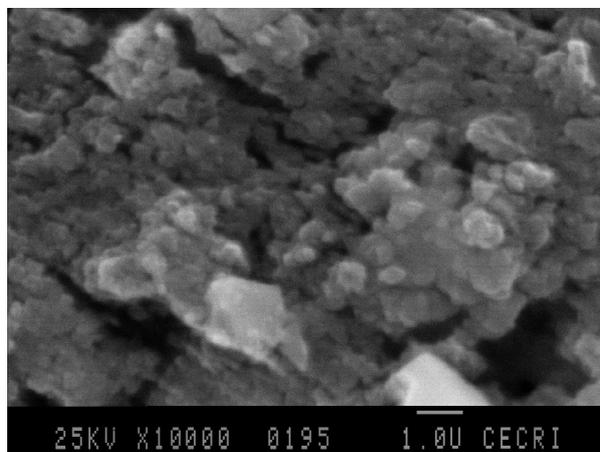
Figure 9. Effect of potassium nitrate electrolyte on metal ion uptake by ATF resin.

pH range from 3 to 5.5. The amount of the metal ion remaining in the aqueous phase was estimated as well. If the original metal ion concentration is known, the metal ion adsorbed by the resin can be determined. The effect of pH on the amount of metal ion distributed between the two phases is given in Table 9. Perusal of the Table 9 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 [8,26].

It is also observed that the terpolymer takes up Cu^{2+} ions more effectively than the other ions under study at all pH values. Among the other ions selected for the study, Zn^{2+} and Ba^{2+} show selectivity under moderate pH values. Furthermore, Mg^{2+} and Mn^{2+} ions have lower distribution ratios over the pH range



(a)



(b)

Figure 10. SEM micrographs of ATF resin at: (a) 5400x magnification and (b) 10000x magnification.

Table 9. Distribution ratios (K_D), of different metal ions as a function of pH.

Metal ions	Distribution ratio (K_D) of the metal ions					
	pH of the medium					
	3	3.5	4	4.5	5	5.5
Mg^{2+}	58.20	110.54	200.20	310.36	417.36	501.32
Mn^{2+}	54.69	115.36	199.34	289.97	376.49	489.59
Cu^{2+}	79.81	144.28	250.69	334.50	450.26	541.35
Zn^{2+}	69.35	125.01	222.65	325.25	426.79	512.01
Ba^{2+}	71.24	135.12	226.33	310.89	441.98	520.28

$\text{M}^{2+}(\text{NO}_3)_2 = 0.1 \text{ M}$; volume=2 mL; volume of electrolyte= 25 mL; weight of resin= 25 mg; time= 24 h; temperature= room temperature.

from 3 to 5.5. This can be explained by weaker stabilization energy of the metal complexes formed from these ions. In the present investigation it is observed that the order of distribution ratio of metal ions are found to be $\text{Cu}^{2+} > \text{Ba}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{Mn}^{2+}$ for the pH range from 3 to 5.5. The values of the distribution ratio and the order at different pH are dependent on the nature of the polymeric resin [8]. The distribution of the metal ions at different pH by the ATF terpolymer resin is found to be higher than that of the other polymeric resins [8,14].

Molecular Weight Measurement and Morphology

The viscosity-average molecular weight of the terpolymer was found to be 3600. The surface analyses of the synthesized terpolymer resin investigated by scanning electron microscope are shown in Figures 10a and 10b in which the white bar at the bottom of the micrographs represents the scale. The morphology of the resin shows a transition between amorphous and crystalline states. However, the ATF terpolymer resin shows a more amorphous structure rather than crystalline with deep pits and less closed package surface as seen from the scanning electron microscopy and optical photographs. Hence, the resin exhibits excellent chelation ion-exchange characteristics for selective metal ions. When compared to the other resins [19], the ATF terpolymer resin is more amorphous in nature, hence possesses higher metal ion-exchange capacity. The light

colour of the ATF terpolymer is further evident from the optical photograph as shown in Figure 11.

CONCLUSION

Terpolymer resin involving anthranilic acid-thiourea-formaldehyde in dimethylformamide reaction medium has been synthesized by an eco-friendly technique. The ATF resin shows good thermal stability and the kinetic parameters have also been evaluated. The terpolymer has good electrical conductivity at higher concentrations and lower temperatures. The ATF resin is an effective cation exchanger for Zn^{2+} , Mn^{2+} , Cu^{2+} , Ba^{2+} , and Mg^{2+} ions. However the effectiveness is very high for Ba^{2+} and Zn^{2+} ions in NaCl and KCl electrolytes. Furthermore, the ATF resin exhibits higher uptake for Cu^{2+} and Ba^{2+} ions in KNO_3 electrolyte. As the pH of the medium increases, there is an increasing trend in the distribution ratio for all the metal ions under study. The amorphous nature of the terpolymer resin has also been established.

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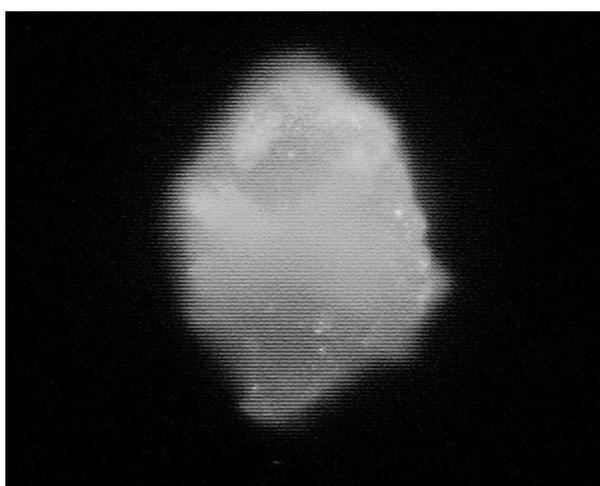


Figure 11. Optical photograph of ATF resin at 20x magnification.

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