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Sorption behavior of heavy metal ions using a terpolymeric resin and its composite: Synthesis, characterization and ion-exchange studies

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ABSTRACT

The ion-exchange technique has been involved for the removal of heavy metal from different aqueous solution. The terpolymer resin was synthesized by condensation polymerization of o-toludine and 8-hydroxyquinoline with formaldehyde resin using dimetylformamide (DMF) as a reaction medium in 1:1:2 ratio at 130°C for 6 Hrs. The composite was prepared by terpolymer and activated charcoal. The structure of the prepared Terpolymer resin and composite were established by the elemental analysis and other spectral studies such as FTIR and NMR(^{1}H&^{13}C). The surface morphology of the adsorbents have been determined by SEM. The prepared adsorbents were subjected to removal of selective metal ions like Cu^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+} in different electrolyte concentrations, different pH ranges and different rates by Batch equilibrium method. The results revolved that, the terpolymer and its composite have good adsorbents. The adsorbents were an effective metal ion removal for Zn^{2+} than other metal ions. The metal ion capacity of the adsorbents also compared with other commercial resin.

Keywords: Terpolymer resin, Composite, Ion-Exchange, Batch equilibrium

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INTRODUCTION

In recent years, universal environment affect by toxic heavy metals like lead, cadmium, cobalt, mercury. To increased the percentage of heavy metals can affect human health and ecosystems and causes some diseases and damage some body system like kidney, nerves system, liver and brain [1]. The main sources of heavy metals from chemical industries such as acid batteries manufacturing, paint industries etc. The main issue is to remove or prevent the toxic heavy metals from environment. Many researcher have been focused on the removal of toxic heavy metals using conventional methods. Many more conventional methods can be used for removal of heavy metals such as adsorption, flotation, ion-exchange process. Among these methods ion-exchange is one of the best methods [2]. This is may be due to the exchange of ions between terpolymer and metal ion. For the ion-exchange process many researcher used a Varity of synthetic polymer, because it has more hydroxyl and amino containing aromatic functional groups, these functional groups can act as good ion-exchanger. Number of researchers have been synthesized and removal of some toxic heavy metals given follows.

ASF terpolymer resin was prepared from anthranilic acid and salicylic acid with formaldehyde in glacial acetic acid medium by polycondensation method [3]. *o*-Nitrophenol and thiourea with paraformaldehyde terpolymer was identified as an excellent cation-exchanger for Zn^{2+} and Co^{2+} ions [4]. 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 [5]. The synthesized 2-amino-6-nitrobenzothiazole and ethylenediamine with formaldehyde in the presence of acid medium, terpolymer resin employing removal of various metal ions with different electrolytes, wide pH and rate [6]. A chelating resin have been synthesized by reacting 2,2-dihydroxybiphenyl with urea and formaldehyde in presence of 2M HCl as reaction medium to involve removal of selective metal ions by using ion- exchange method [7]. 4-hydroxyacetophenone, oxamide and formaldehyde copolymer prepared by condensation of 4-hydroxyactophenone and oxamide with formaldehyde in the presence of an acid catalyst proved to be a selective chelation ion-exchange for certain metals reported by W.B. Gurunule and Co-workers [8]. To synthesized a novel terpolymer resin by 2-amino-6-nitro-benzothiazole and semicarbazide with formaldehyde (BSF) by solution condensation technique. This resin was good ion-exchange behavior for removal of selected metal ion like Fe^{2+}, Cu^{2+}, Ni^{2+}, $Co^{2+,}$ Zn^{2+}, Cd^{2+} and Pb^{2+} using batch equilibrium technique with different electrolyte concentrations, pH ranges and time intervals [9]. 8-hydroxyquinoline 5-sulfonic acid, oxamide and formaldehyde has been synthesized from polycondensation technique. The synthesized resin has been involved removal of heavy metals by batch equilibrium method. The polymeric resin adsorbed for higher selectivity for Fe^{3+}, Cu^{2+}, and Ni^{2+} ions than for Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions [10]. A comparative account was carried out between the commercial activated carbon, chitosan and chitosan/activated carbon composite for the enhanced of cadmium ions from aqueous solution. pH solution is very important factor for the removal of heavy metal ions [11]. A novel comparative study was done between a synthesized terpolymer and its composite for the removal of heavy metals. The order of removal of heavy metal ions by the terpolymer and composite is $Zn^{2+} > Cu^{2+} > Co^{2+} > Pb^{2+} > Cd^{2+}$ and $Pb^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+}$ respectively[12].

It is clear from the literature, the *o*-toludine and 8-hydroxyquinoline with formaldehyde resin type of terpolymer have not been synthesized for its chelation ion exchange properties. Hence it is planned to synthesize the *o*-toludine and 8-hydroxyquinoline with formaldehyde resin terpolymer by condensation polymerization technique. The novel composite was prepared by activated charcoal and terpolymer. The prepared adsorbents were characterized by elemental analysis, spectral studies to identify the functional groups present in it and to establish the structure of the resin and also study with morphology of the adsorbents. The ion-exchange properties of the terpolymer and its composite for the removal of specific metal ions were carried out by batch equilibrium method. The results were compared with the earlier literatures and commercially available resins.

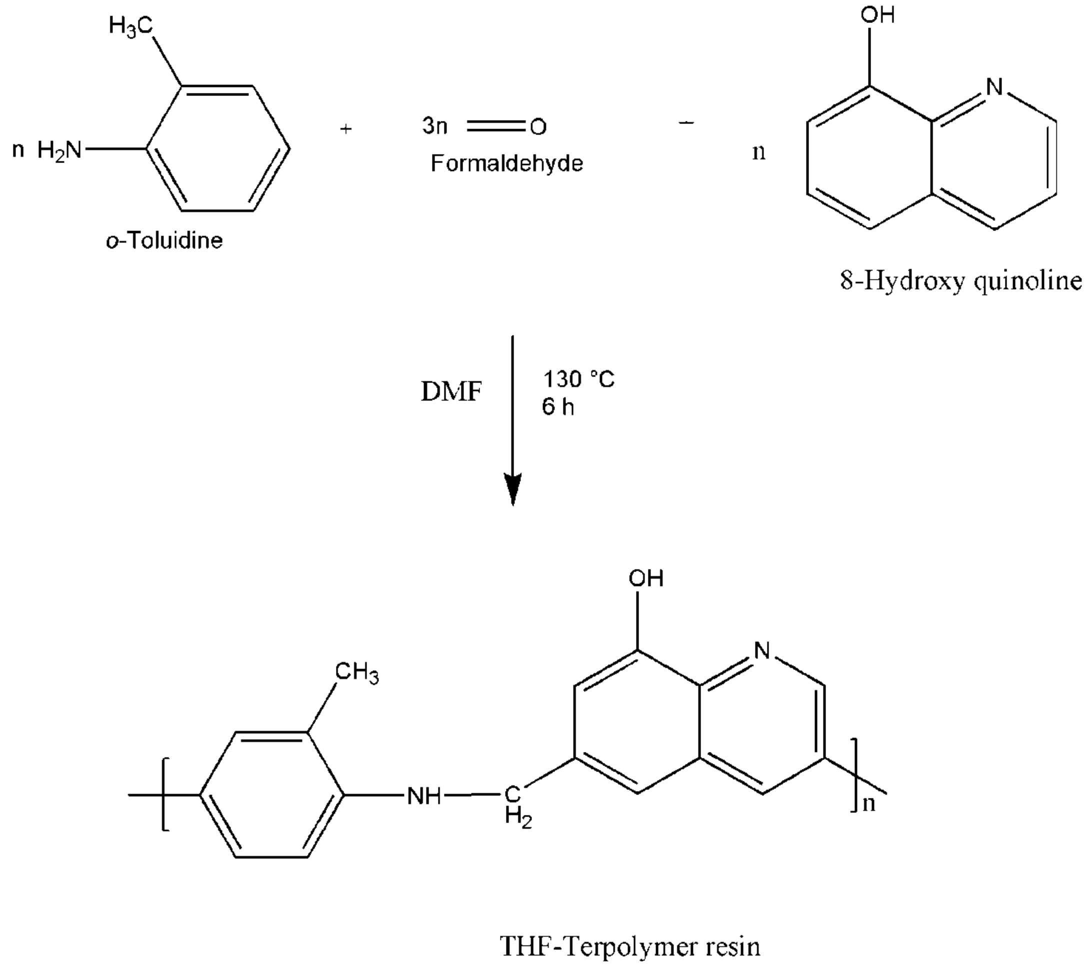
EXPERIMENTAL SECTION

Materials

o-toludine and 8-hydroxyquinoline with formaldehyde were used as purchased from Merck, India. Heavy metal ion solutions such as Cu^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+} were prepared by its nitrate salts from Sigma Aldrich. The other chemicals and solvents procured from Merck were used as received without further purification.

Synthesis of terpolymer

A mixture of *o*-toludine (1M) and 8-hydroxyquinoline (1M) with formaldehyde (2 M) was taken in a round bottom flask, the content of the flask were periodically shaken well to ensure homogeneous mixing. They were refluxed in an oil bath at 130 ^{0}C for 6 hours in presence of dimethylformamide. After the stipulated reaction time, the content of the flask were poured into a beaker containing ice crystals with vigorous shaking and left over night. The separated resin was washed with Methanol, acetone, ether and then warm water to remove unreacted monomers. The resin was filtered and air dried at 70^{0}C for 6 hours in an air oven. The dried resin sample was finely grounded and sieved to obtained uniform particle size. The yield of the terpolymer was found to be 83%. The synthesized resin was found to be soluble in some mineral acids and bases. The mechanism of the synthesis of terpolymer is shown in Scheme 1. The novel terpolymer/activated charcoal composite was prepared by THF terpolymer and activated charcoal in 1:2 ratio. The terpolymer was dissolved in 25 mL of DMSO and the activated charcoal was added into it and the mixture was subjected to ultrasonication for 3 h with constant stirring for 24 h at room temperature. After the specific time, the obtained composite was separated, filtered and dried at 70°C for 24 h.



Scheme 1. Synthetic route of THF terpolymer

Elemental, spectral and SEM analyses

The proportion of elements likes that C, H and N was analyzed using an Elementar instrument (Model Vario EL III, Germany). The functional groups of the adsorbents have been established by FTIR spectra scanned in KBr pellets on a Bruker (Model Tensor27, MA, USA) spectrophotometer and the (^{1}H & ^{13}C) NMR spectra were recorded using Bruker 400 MHz, MA, USA in DMSO-d_6 as a solvent for the nature of the hydrogen and carbon present in the resin. The surface morphology of the synthesized compound was determined by Jeol scanning electron microscope (Hitachi Model S-3000H, Tokyo, Japan) at different magnification.

Ion-exchange studies

Analysis of metal ion uptake at different electrolytes

A batch equilibrium method was adopted to determine the metal ion uptake of specific metal ions like Cu^{2+}, Zn^{2+}, Pb^{2+} and Co^{2+} 25mg of the polymer sample was taken in a pre cleaned glass bottles and 25ml of electrolytes like NaCl, $NaNO_3$ and $NaClO_4$ at various concentrations viz 0.1, 0.5, and 1.0 M are added in to it. This solution was mechanically stirred vigorously for 24 h to allow the terpolymer for swelling. Exactly 2ml of 0.1 M of specific metal ion was added and again stirred for 24 h. The filtrate 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 addition of the resin sample. The amount of metal ions taken up by the adsorbents in the presence of a given electrolyte can be calculated from as follows,

$$Q = \frac{V(C_0 - C_e)}{M}$$

Where, Q is the ion-exchange capacity, V is the volume of the metal ion, C_0 is the initial concentration, C_e is the final concentration, M is the weight of the polymer/composite

Analysis of metal ions at different pH
The metal uptake was used at various pH range between 1.5 to 5.0 of the adsorbent and the aqueous solution were determined in the presence of 0.1 M NaCl at 25°C.

$$Q = \frac{V(C_0 - C_e)}{M}$$

Where, Q is the ion-exchange capacity, V is the volume of the metal ion, C_0 is the initial concentration, $C_e$is the final concentration, M is the weight of the polymer/composite

Analysis of rate of metal ion uptake
To estimate the time required to reach the state of equilibrium under the experimental conditions, a series of experiments were made to estimate the amount of metal ion uptake by the terpolymer at require time intervals, 25 mg of the adsorbents samples was mechanically stirred with 25 mL of 1 M NaCl and titrated against Na_2EDTA. The rate of metal ion uptake is showed as the percentage of the amount of metal ion uptake after a specific time related to that in the state of equilibrium. The Percentage of metal ion was calculated by,

$$Removal\ efficiency\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100$$

RESULTS AND DISCUSSION

Elemental analysis
From the elemental data, the empirical formula of the terpolymer found to be $C_{19}H_{18}N_2O$.

The percentage of the elements present in the terpolymer was concluded by the calculated and experimental values found for carbon is 78.59, hydrogen is 6.25, nitrogen is 9.65, and oxygen is 5.51. which are in good agreement with each other. The values of elemental analysis confirm the proposed structure of the terpolymer presented in scheme 1.

Spectral studies
FTIR spectral analysis
The structure of synthesized resin was analyzed by FTIR spectrum of THF is depicted in Fig.1. A broad peak appeared in the region of 3423.21 cm^{-1} is assigned to the amine group of Ar-NH and -OH merged in the terpolymer. A peak appeared at 2855 $cm^{-1}$is attributed to aromatic ring stretching modes. A peak appeared in the region at 2925 cm^{-1} is attributed to $>CH_2$ linkage present in the terpolymer. The FTIR spectrum of composite is showed in Figure 2. From the figure, the composite slightly changes from terpolymer. The specific adsorption band at 3358.21 was caused by –NH bridge from terpolymer . The adsorption of band around 2858.97 can be attributed to aromatic ring stretching (C-H) present in the terpolymer. A band at 2928 indicates $-CH_2$ stretching involved in the terpolymer. Based on the above data, it is confirmed that the terpolymer has got adsorbed on the charcoal to form a composite. [13].

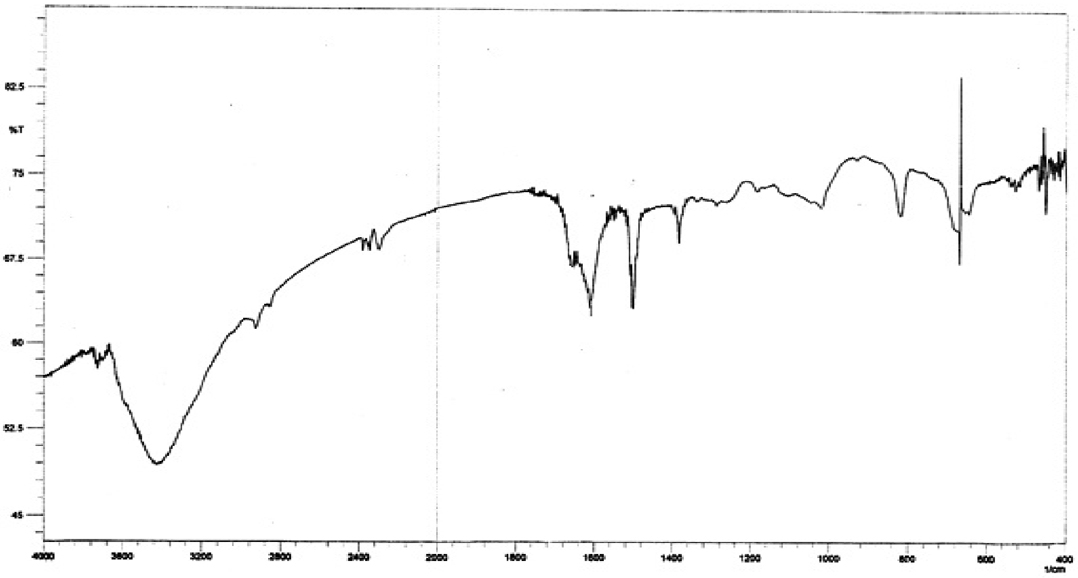


Fig.1 FTIR spectra of THF terpolymer

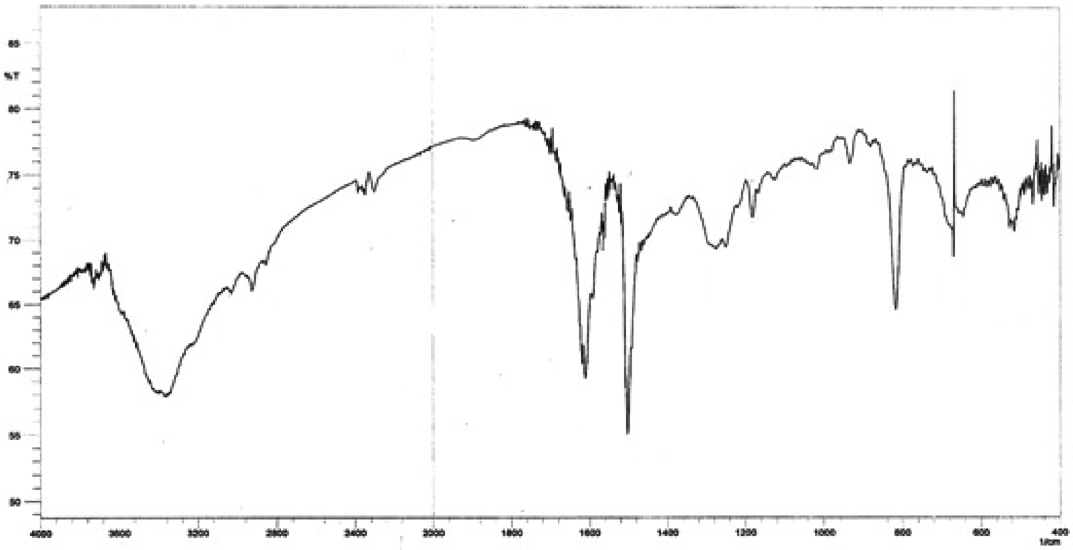


Fig.2 FTIR spectra of THF composite

NMR spectral analysis

The ^{1}H NMR spectrum of the THF terpolymer resin are depicted in Figure.3. The resonance signal at 9.5 ppm is assigned to the -OH of quinoline ring. The signals appeared in the region of 7.0–7.6 ppm are attributed to all the protons of the aromatic ring. The methylene proton of -CH_2 bridge was assigned at 5.03 [14].

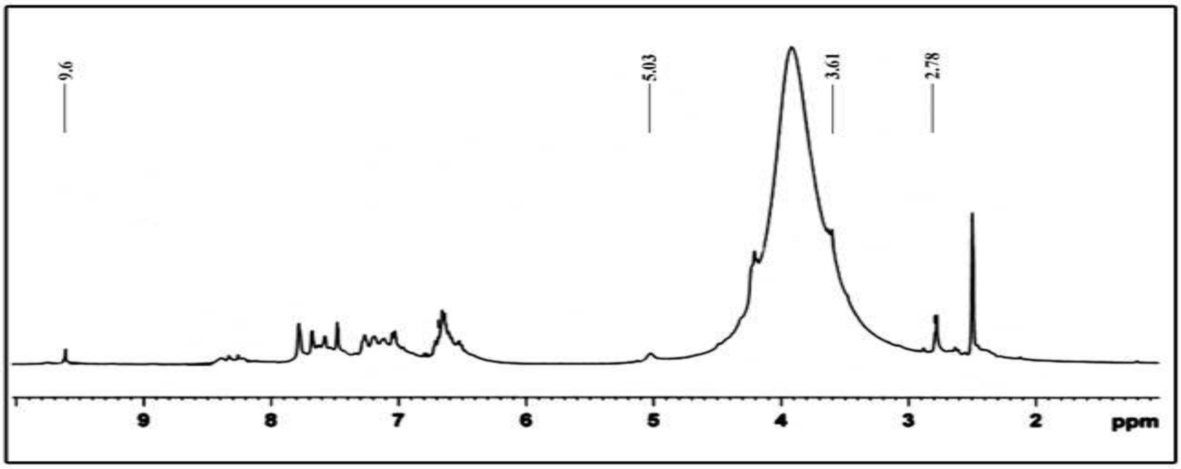


Fig.3 ^{1}H NMR spectra of THF terpolymer

The ^{13}C NMR spectrum of the terpolymer is shown in Figure. 4. The spectrum of THF resin shows the corresponding peaks at 112.84, 117.03, 119.15, 129.54, 130.21, 135.6 ppm with respect to C1 to C6 of the aromatic ring. The peak observed at 54.86 ppm to indicates the–CH_2 bridge in the terpolymer.

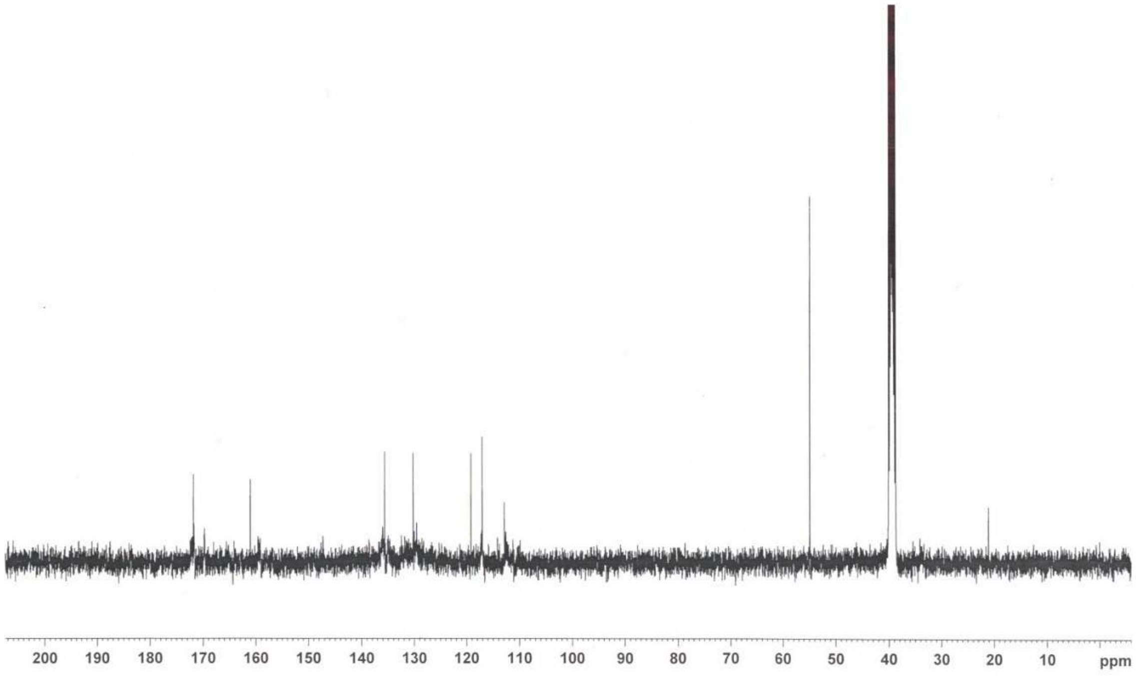


Fig.4 ^{1}C NMR spectra of THF terpolymer

Surface analysis

The surface morphology of the terpolymer and composite have been investigated by SEM analysis. The SEM images are depicted in the Figure. 5. The surface morphology of the terpolymer was found to be fracture based surface shown in Fig. 5 (a). The figure Fig. 5 (a) shows that, the terpolymer surface having closed packed arrangement surface more active sites. The SEM photograph of the composite is shown in Fig. 5 (b), from the figure the surface morphology of the composite different from terpolymer. Which is evidence for formation of composite. The surface morphology of the composite having more active sites and different pores size present on the surface compared to terpolymer. This is implies that increasing the surface area, increasing the larger number of cavities for composite. from this images, the terpolymer and composite have better metal ion removal capacity [12].

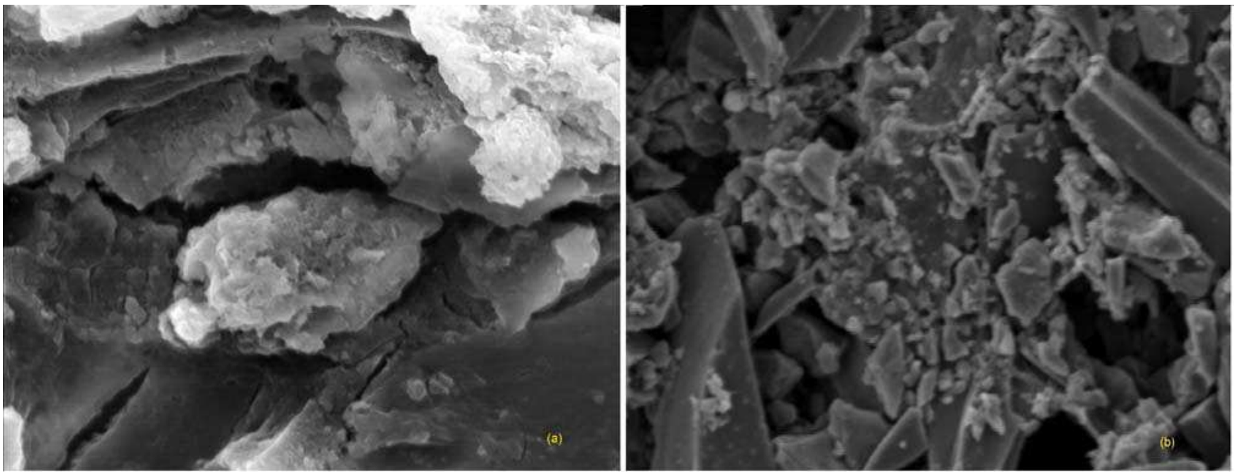


Fig.5 SEM photographs of (a) TCF terpolymer, (b) composite

Table 1. Effect of metal ion uptake by THF terpolymer & its composite

Metal ions	Concentration of electrolytes (mol L^{-1})	Metal ion uptake in the presence of electrolytes (m.mol/g)					
		NaCl		$NaNO_3$		$NaClO_4$	
		THF	Composite	THF	Composite	THF	Composite
Pb^{2+}	0.1	0.748	0.932	1.208	1.315	0.756	0.812
	0.5	0.831	1.08	1.328	1.486	0.832	1.08
	1	1.504	1.732	1.631	1.845	0.916	1.256
Cu^{2+}	0.1	0.856	1.232	1.142	1.384	1.108	1.235
	0.5	2.574	2.645	1.231	1.745	1.642	1.853
	1	2.731	2.832	1.8	2.08	1.9	2.132
Co^{2+}	0.1	0.758	0.965	0.654	1.345	0.635	0.875
	0.5	0.972	1.08	1.708	1.516	1.514	1.6
	1	1.608	1.831	2.425	1.915	1.636	1.723
Zn^{2+}	0.1	1.504	1.874	1.346	1.543	1.718	1.854
	0.5	2.672	2.756	1.822	2.08	1.915	2.08
	1	2.736	2.987	2.331	2.532	2	2.416

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

Ion-exchange studies

Effect of metal ion uptake in different electrolytes with variation in concentrations

The chelating ion-exchange property of the terpolymer and composite were measured by batch equilibrium method involving Co^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} ions in various electrolytes viz. NaCl, $NaNO_3$ and $NaClO_4$ with different concentration of 0.1, 0.5 and 1.0 M. The results are presented in Table-1. 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 [15]. The increase in the metal ion uptake with the increase of concentration may be explained on the basis of the stability constant of the complexes and due to the ions forming strong chelates with metal ions [16]. From the results the terpolymer and its composite were found to be higher amount metal ion uptake for Zn^{2+} than other metal ions. This is may be due to small size of the metal ion easily enter on the surface cavities [12]. The amount of Pb^{2+}, Cu^{2+} and Co^{2+} ions by the both adsorbents are less than that of the

Zn^{2+}. This may be due to the relative weak chelation of metal ions with the electrolytes. Furthermore, the large size of the metal ions was slowly through in to the terpolymer surface. Hence Zn^{2+}can easily removed by the terpolymer and its composite. the terpolymer and composite can acts as a better ion-exchanger. The comparative account study was involved terpolymer and its composite, from the results the composite has higher metal ion uptake compared to terpolymer. Which is may be due to the large surface area and more active sites on the surface. Hence, the order of the selective metal ion uptake were found to be $Zn^{2+} > Cu^{2+} > Co^{2+} > Pb^{2+}$.

Analysis of metal ions removal at different pH

The effect of pH is very important role of the ion- exchange process. The ion-exchange behaviour of the terpolymer and composite have been investigated by the influence of the different pH range at 1.5 to 5. The purpose of the using pH, to avoid the precipitation of the meal ion [17]. The effect of pH, the amount of metal ion uptake between the two phase are given in Table 2&3. At low pH, increases the concentration of the H^+ ion compete with metal ion on the surface. The amount of metal ion uptake by the adsorbents increases with increasing pH [18]. At low pH, the metal ion cannot easily enter in to the active sites due to higher concentration of H^+ ions. From the observed results the terpolymer and composite takes up Zn^{2+} ions more effectively than the other metal ions. This is may be due to the low concentration of H^+ ions and stability constant of the adsorbents and metal ion complexes [12]. Further Pb^{2+} ions have lower metal ion uptake by the terpolymer and composite. This can be explained as the weak stabilization energy of the metal complex formed from these ions. In this investigation it is observed that the order of metal ion were found to be $Zn^{2+} > Cu^{2+} > Co^{2+} > Pb^{2+}$ by terpolymer and composite.

Table 2. Metal ion uptake at different pH by THF terpolymer

Metal ions	Metal ion uptake (m.mol/g)					
	pH of the medium					
	1.5	2	3	4	5	6
Pb^{2+}	0.325	0.564	0.652	0.937	1.118	1.342
Cu^{2+}	0.623	0.914	1.23	1.324	1.625	1.73
Co^{2+}	0.425	0.615	1.08	1.238	1.52	1.653
Zn^{2+}	0.64	0.78	0.915	1.08	1.923	2.312

$M^{2+}(NO_3)_2$ = 0.1 M; volume = 2 mL; NaCl = 1 M; volume = 25 mL; weight of resin = 25 mg; time = 24 h; room temperature

Table 3. Metal ion uptake at different pH by composite

Metal ions	Metal ion uptake (m.mol/g)					
	pH of the medium					
	1.5	2	3	4	5	6
Pb^{2+}	0.415	0.545	0.712	0.925	1.08	1.735
Cu^{2+}	0.523	0.634	0.915	1.12	1.512	1.954
Co^{2+}	0.4	0.512	0.632	0.815	1.23	1.832
Zn^{2+}	0.654	0.831	1.08	1.214	1.832	2.454

$M^{2+}(NO_3)_2$ = 0.1 M; volume = 2 mL; NaCl = 1 M; volume = 25 mL; weight of resin = 25 mg; time = 24 h; room temperature

Analysis of metal ions removal at different rate

The effect of rate is significant parameter for ion-exchange study. The comparative account of the terpolymer and composite is subjected to the different rate. The effect of rate for selective metal ions Cu^{2+}, Zn^{2+}, Co^{2+} and Pb^{2+}. The observed results are given in Table 4 & 5. The rate of metal ion adsorption was estimate to which the metal ion uptake has the shortest period of time to attain the close to equilibrium condition during the ion-exchange process [19]. From the observed results, the terpolymer and composite were found Zn^{2+} ion is the shortest period of time to attain equilibrium at 4 h[20]. Which may be due to the more available active sits and large surface area [12]. In other hand, small size of the metal ion is easily penetrate to the surface active sites. Slow metal ion uptake for Pb^{2+} may be due to higher ionic radius and large size of the metal ion [21]. From the above results, the order of rate of metal ion uptake by the terpolymer and composite were found $Zn^{2+} > Cu^{2+} > Co^{2+} > Pb^{2+} >$. However, the metal ion uptake capacity of the composite is higher than terpolymer. Due to higher pores nature and large surface area. Finally, the resin and its composite are better ion-exchangers for selective metal ions than some commercial ion-exchangers.

Table 4. Rate of metal ion uptake by THF terpolymer

Metal ions	Equilibrium attainment (%)						
	Time (h)						
	1	2	3	4	5	6	7
Pb^{2+}	13	35.3	47.8	56.7	67.4	75	83
Cu^{2+}	15.5	25	48.7	56.4	68.7	80.2	88.6
Co^{2+}	13.8	38.4	46.7	59.8	68.4	76.8	84.1
Zn^{2+}	34	52	95	95	-	-	-

$M^{2+}(NO_3)_2$ = 0.1 M; volume = 2 mL; NaCl = 1 M; volume = 25 mL; weight of resin = 25 mg; time = 24 h; room temperature

Table 5. Rate of metal ion uptake by composite

Metal ions	Equilibrium attainment (%)						
	Time (h)						
	1	2	3	4	5	6	7
Pb^{2+}	15	30	46.4	60.5	71.2	77.4	82.8
Cu^{2+}	25.6	48.6	65.4	78.5	85.3	93.2	-
Co^{2+}	23.4	40.5	51.3	70.2	77.8	86.7	-
Zn^{2+}	45.8	62.3	78.4	98.2	98.2	-	-

$M^{2+}(NO_3)_2$ = 0.1 M; volume = 2 mL; NaCl = 1 M; volume = 25 mL; weight of resin = 25 mg; time = 24 h; room temperature

CONCLUSION

A new terpolymer and composite were successfully carried out by polycondensation technique. The synthesized adsorbents were characterized by various spectral analysis. Using FTIR and surface morphology data were confirmed formation composite. The prepared adsorbents to involved removal of selective toxic heavy metal (Co^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}) ions by batch studies. Sorption capacity of the adsorbents varied by the influence of nature and pH. The terpolymer and its composite have higher metal ion uptake. Which may be due to different pores size, large surface area. The results evolved that the terpolymer and its composite were found to be higher metal ion uptake for Zn^{2+} ion than other metal ion. This is indicates strong stability constant of the adsorbents with metal ion. Moreover, the comparative account was found, the composite has higher metal ion uptake than terpolymer. Hence, the terpolymer and composite can act as better ion-exchanger for metal ion removal.

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