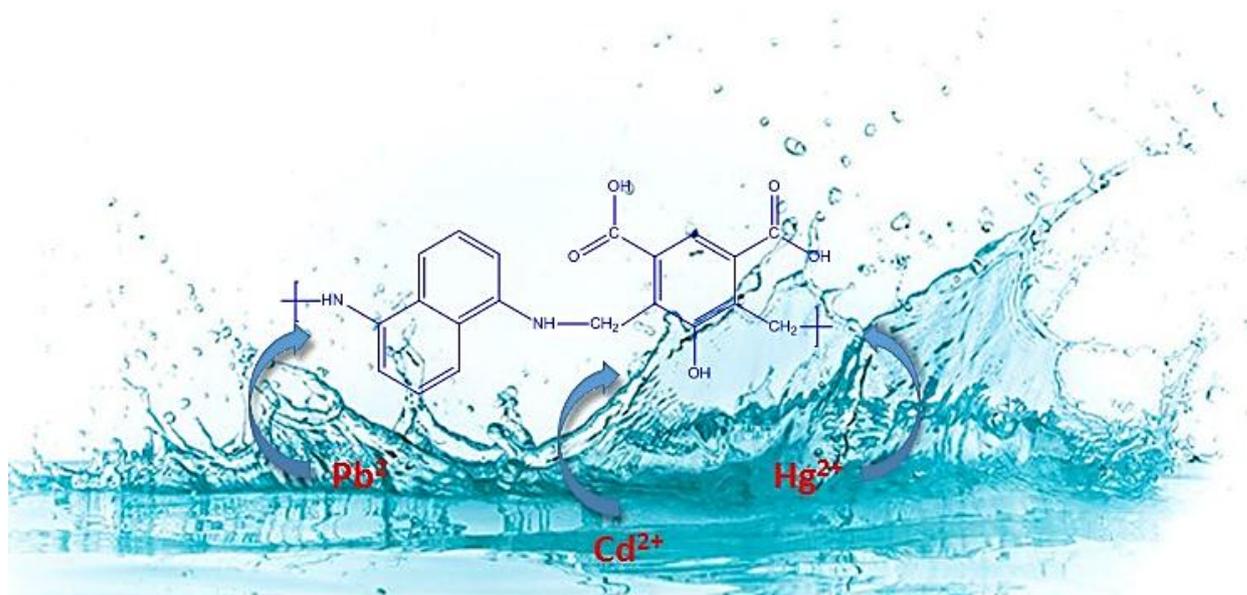


Chapter 5

Environmental Impact of New DHF Terpolymer: Synthesis, Characterization and Its Toxic Metal Ions Removal Properties

Highlights

- ❖ A newer DHF terpolymer via condensation reaction was synthesized.
- ❖ The synthesized terpolymer showed excellent ability to remove Pb^{2+} , Cd^{2+} and Hg^{2+} ions from waste water.
- ❖ The terpolymer containing alcoholic and amino group is responsible for the removal of heavy metal ions form solution.
- ❖ The resins show potential application for wastewater treatment.



5.0 Abstract

The use of terpolymer for environmental clean-up is an emerging technology. In this chapter, adsorption of significant metal ions on terpolymer was investigated. 1,5-diaminonaphthalene, 5-hydroxyisophthalic acid and formaldehyde (DHF) terpolymer was synthesized via condensation polymerization techniques using 2 M DMF as a catalyst. The characterization of the synthesized DRF terpolymer was conducted by various techniques such as elemental analysis, GPC, FTIR, TGA, XRD, SEM and EDAX measurements. The obtained terpolymer was further utilized for the removal of toxic metal ions such as Pb^{2+} , Cd^{2+} and Hg^{2+} from aqueous environments. The results demonstrate that the terpolymer with adsorption properties can effectively be utilized in the removal of pollutants and a promising network provide advantageous over conventional techniques.

5.1 Introduction

Terpolymers, very unique classes of polymers, are well-known for their multipurpose uses and are originated to be amorphous, crystalline or resinous in nature. The synthesis of new terpolymers attracts the attention of researchers because of their versatile utility in our day-to-day life¹. The synthesis of functional terpolymer has collected a lot of interest in recent years owing to their usages in energy materials, ion exchangers, semiconductors, bonding agent/additives, molding material, high temperature flame resistant fibers, hardners, anticorrosive, tissue engineering, biosensors and controlled release devices for pharmaceuticals²⁻⁹.

The removal of toxic and polluting metal ions from industrial effluents, water supplies as well as mine waters is an important challenge to avoid the major causes of water and soil pollution. Various methods have been proposed to remove heavy metal ions from sea water and waste waters using ion exchange resins¹⁰, some of which includes adsorption, electrolytic or liquid extraction, electron dialysis, chemical precipitation, membrane filtration and biosorption^{11,12} however, adsorption is one of the most popular method for treating the industrial effluents. Many researchers have studied the adsorption, separation or removal of heavy metal ions using chelating terpolymer resins with different functional groups including N, O and S atoms¹³. Terpolymer involving o-nitrophenol–thiourea–paraformaldehyde and anthranilic acid–thiourea–paraformaldehyde resins were synthesized and reported for their ion-exchange capacity due to the presence of nitrogen atom present in the resin and reported as excellent chelating ion-exchangers for the separation of metal ions from the waste solutions^{14,15}. An eco-friendly application of p-cresol–melamine–formaldehyde and 4-hydroxyacetophenone-biuret-formaldehyde copolymers have been reported and found to be used as ion-exchangers^{16,17}. The terpolymer resins of 2,2'-dihydroxybiphenyl - urea - formaldehyde and their ion-exchange properties were studied for Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions and the studies was carried out over a wide pH range and in media of various ionic strengths¹⁸. 8-hydroxyquinolin and salicylic acid with formaldehyde terpolymer resin was synthesized and batch separation technique was adapted for the elimination of particular divalent metal ions such as Pb^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Ba^{2+} , Co^{2+} and Mn^{2+} in several electrolyte concentrations, extensive pH ranges and different time intervals¹⁹. The terpolymer resin salicylic acid-diaminonaphthalein-formaldehyde was synthesized by the

condensation process and the chelation ion exchange properties have also been studied for Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions employing a batch equilibrium method. It was employed to study the selectivity of metal ion uptake involving the measurements of distribution of a given metal ion between the polymer sample and a solution containing the metal ions²⁰. A novel cross-linked maleic anhydride–allyl propionate–styrene terpolymer was synthesized and reported its outstanding adsorption capacity towards uranyl ion from the waste solutions²¹. Removal of cations using ion-binding terpolymer involving 2-amino-6-nitro-benzothiazole and thiosemicarbazide with formaldehyde resin is found to be an excellent cation exchanger because of the availability of ion-exchange group in the terpolymer²².

However, the literature studies have revealed that no terpolymer has been synthesized using the monomers, 1,5-diaminonaphthalene, 5-hydroxyisophthalic acid and formaldehyde. Therefore, in this article, we describe the synthesis of terpolymer derived from 1,5-diaminonaphthalene, 5-hydroxyisophthalic acid and formaldehyde. The synthesized terpolymer resin has been characterized by elemental analysis, GPC, FTIR and XRD measurement. Thermal properties of the terpolymer was analysed by TGA. The surface feature of the terpolymer resin was established by SEM. The metal ion uptake capacity of the terpolymer resin by batch equilibrium method for Pb^{2+} , Cd^{2+} and Hg^{2+} ions in different electrolytes and pH ranges has been also studied and reported for the first time.

5.2 Experimental

5.2.1 Chemicals and reagents

1,5-diaminonaphthalene and 5-hydroxyisophthalic acid were purchased from Sigma-Aldrich. Formaldehyde (37 %) was procured from Merck, India. Metal nitrate of chosen metals were purchased from AR grade merck, India. Multi-elemental standard solution for ICP-OES was obtained from PerkinElmer (USA). The 200 ppm of Pb^{2+} , Cd^{2+} and Hg^{2+} ions contaminated waste water was prepared artificially by spiking of ultrapure water, which is environmentally relevant concentrations and used for all the adsorption parameters. All working metal ions and standard solutions were prepared immediately before use, by stepwise dilutions of 1000 mg L^{-1} . All other chemicals and solvents were of AR grade and used as received. Milli-Q water was used for all the experiments.

5.2.2 Terpolymerization

The DHF terpolymer resin was synthesized by the solution condensation polymerization of 1,5-diaminonaphthalene (0.1 M), 5-hydroxyisophthalic acid (0.1 M) and formaldehyde (0.2 M) using 2 M DMF as a catalyst and refluxing this mixture with occasional shaking at 140 ± 2 °C in an oil bath for 6 h. After the reaction time was over, the resultant product was cooled, poured into crushed ice with constant stirring and left overnight. The obtained product was separated, washed with warm water, ethanol and ether to remove starting materials and unreacted monomers^{23,24}. The yield of the terpolymer was found to be 85%. The terpolymer was finely grounded and sieved to obtain uniform particles of 100 mesh size and sample was dried in air and kept in vacuum desiccator over silica gel. The sieved terpolymer was used for further characterization. The synthesis route of the BSF terpolymer resin is shown in **Figure 5.1**.

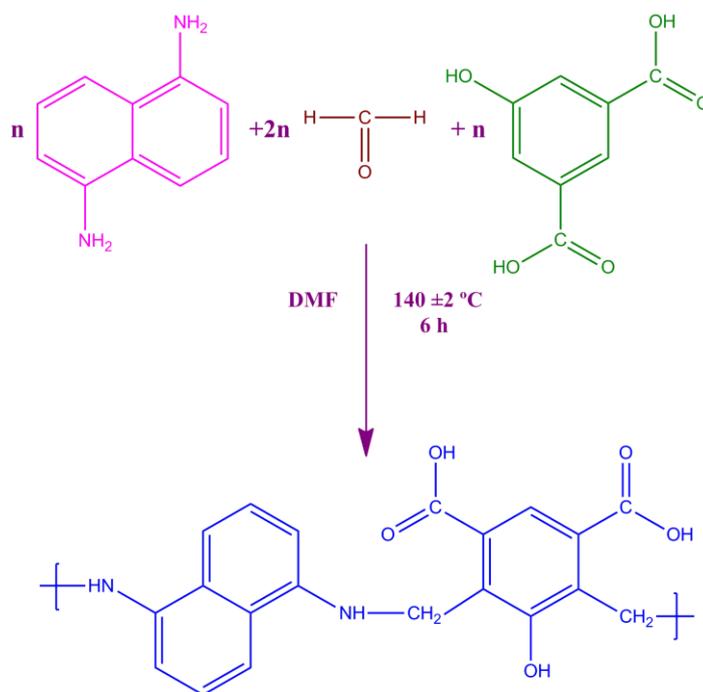


Figure 5.1. Synthesis route of the DHF terpolymer

5.2.3 Characterization of DHF terpolymer

The percentage of elements such as C, H and N present in the DHF terpolymer were determined using elemental instrument (Model vario EL III, Germany). The number-average (M_n), weight-average molecular weights (M_w) and polydispersion index ($PDI = M_w/M_n$, M_w/M_z) of the terpolymer were determined by gel permeation chromatographic (GPC) system equipped with Waters 2690D separations module. Waters millennium module software was used to calculate molecular weight, on the basis of a

universal calibration curve generated by polystyrene standard. IR spectra of DHF terpolymer resins were recorded on a Bruker Tensor 27 Spectrophotometer in the wavenumber region of 4000–400 cm^{-1} by using the KBr pellets technique to identify the linkages and functional groups. The thermal degradation of the terpolymer was analyzed using thermogravimetric analyzer (TA Instruments Model SDT Q600) at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in static nitrogen atmosphere in the range of 30–800 $^{\circ}\text{C}$. X-Ray Diffraction analysis (Rigaku Rotoflux) was performed to investigate phase structure of the terpolymer. The surface analysis of the DHF terpolymer resin was examined by scanning electron microscope using Zeiss instrument (Zeiss 18 Evaluation) and the chemical composition were characterized by energy dispersive X-ray spectroscopy (EDAX Oxford X-Act).

5.2.4 ICP-OES measurement

Determination of all metal ions was performed with inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima™ 7000 DV dual view series sequential spectrometer (Shelton, CT, USA) equipped with WinLab™ 32 for ICP Version 4.0 software. In order to avoid any carry-over effect, the ultrasonic nebulizer was washed out with 1% (v/v) HNO_3 for 60 s between each sample run. Argon gas (99.99%) was used as the ICP torch gas and nitrogen gas was used as the optical purge gas. The CCD-array detector was used to collect both the analyte spectra and the nearby background spectra, which provide improved precision and analytical speed. The instrumental operating conditions and parameters are given in **Table 5.1**. The following spectral lines (wavelength in nm) were monitored for various analyte quantification: Pb-220.353, Cd-228.802 and Hg-253.652. All emission lines monitored are ionic (II). These results were obtained by high sensitive detection of ultra-trace and trace analysis^{25,26}.

Table 5.1. ICP OES: Operational conditions and instrumental parameters.

RF power	1450 Watts
Plasma gas flow rate	15 L/min
Auxiliary gas flow rate	0.2 L/min
Nebulizer carrier gas flow rate	0.75 (pneumatic) & 0.70 (ultrasonic)
Sample pump rate	1.5 mL/min
Plasma view mode	axial and radial
Resolution	high
Background correction	2 points <i>per</i> peak
Integration time (min-max)	2.5-5.0 Sec
Signal processing	peak area (3-7 points per peak)

5.2.5 Adsorption experiment

Adsorption experiments were performed as a function of various electrolytes in different concentrations and pH in different ranges by batch equilibrium mode. 50 mg of synthesized DHF terpolymer was suspended in 30 mL of electrolyte solutions such as NaCl, Na₂SO₄ and NaNO₃ in different concentrations *viz.* 0.1, 0.5, 1.0, 1.5 and 2.0 M. To each suspension, 300 ppm (10 mL) mixture of Pb²⁺, Cd²⁺ and Hg²⁺ metal ions was added. Then, the mixture was shaken homogeneously with shaker rotating at a speed of 200 rpm for 10 h to facilitate adsorption of the metal ions into the DHF terpolymer. After the specified time, the DHF terpolymer was separated from the solution by filtration through the filtered using a Whatman #40 filter paper. The filtrate was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) PerkinElmer Optima™ series. The blank was analyzed to ensure that no metal ions were carried over from the previous sample. Highly pure deionized water was chosen as the blank solution. The blank values were subtracted from the values determined for the different metal ions to give the exact adsorbed metal ions concentration^{27,28}.

The effect of pH was studied in the pH range of 2–7 at an initial concentration of 300 ppm for cations and contact time of 10 h. Before mixing the metal ions, the pH of the suspension was adjusted to required value by adding minimum amount of (0.5 M) HCl and/or NaOH. The amount of metal ions uptake by the DHF terpolymer during the series of batch investigations were determined using the following equation:

$$\text{Removal (\%)} = [(C_o - C_f) / C_o] \times 100$$

where: C_o and C_f are the initial and equilibrium concentration (ppm) of metal ions in solution, respectively.

5.3 Results and discussion

5.3.1 Analytical and elemental data

The results of the elemental analysis of the DHF terpolymer resin are presented in Table 2. Based on the analytical data, the empirical formula of the repeating unit was proposed. The yield of the DHF terpolymer is 85 %. The empirical formula and the empirical weight of the single repeating unit of the terpolymer are found to be C₁₉H₁₆N₂O₅ and 366.37 respectively, the observed results are in good agreement with the calculated values of carbon (%C), hydrogen (%H) and nitrogen (%N).

The gel permeation chromatography (GPC) analysis revealed an The weight average (M_w) and number average (M_n) molecular weight of the terpolymer are found to be 3984 and 3911 respectively. The polydispersity index (M_w/M_n) is found to be 1.0186. It should be pointed out that the polydispersity of the molecular weight of the macro-branched terpolymer is fairly narrow and which can only be considered as indicative for the terpolymer.

Table 5.2. Elemental and GPC data of the DHF terpolymer.

Terpolymer	Formula of the repeating unit	Mass of the repeating unit	(M_n) (g/mol)	(M_w) (g/mol)	(M_w/M_n)	Elemental Analysis(%) Found (Calc.)		
						% C	%H	% N
DHF	$C_{20}H_{16}N_2O_5$	366.37	3911	3984	1.0186	62.84	6.24	6.41

5.3.2 FT-IR spectral analysis

FT-IR spectroscopy is a useful tool for the identification of presence/ absence of functional groups in a terpolymer. The FTIR spectra of the DHF terpolymer before and after metal ions sorption are presented in (Figure 5.2a-b). In the spectrum, a broad band appear at 3405 cm^{-1} is assigned to the hydroxyl group of Ar-COOH present in the aromatic ring which is due to intramolecular hydrogen bonding. The band appearing at 3222 cm^{-1} is assigned for NH stretching vibrations of Ar-NH₂ group and it is further confirmed by the Ar-NH bending vibrations appearing at 1514 cm^{-1} . The bands appear in the region of $2990\text{--}2793\text{ cm}^{-1}$ are attributed to $-\text{CH}_2$ asymmetric and symmetric vibrations present in the terpolymer resin. The band at 1662 cm^{-1} is due to $-\text{C}=\text{O}$ (carboxylic ketone) stretching vibrations of the $-\text{COOH}$ group. The substitution of the aromatic benzene ring, recognized by sharp, medium/weak absorption bands, appear at $800\text{--}1200\text{ cm}^{-1}$. The band obtained at 1382 cm^{-1} suggests the presence of a methylene ($-\text{CH}_2$) bridge in the terpolymer resin^{28,29}. The FTIR spectrum of metal ions treated terpolymer was presented in Figure 5.2b. The band at 3405 cm^{-1} is shifted to the higher wavenumbers after adsorption and other peaks are shifted slightly to the lower wave numbers and some peaks are disappeared. After adsorption, new peak is found at around 1655 cm^{-1} is can be due to sorption of metal ions with the functional groups of terpolymer and the spectra of DHF and metal ion treated terpolymer have a considerable difference between them which indicate the efficient adsorption of metal ion on the on the terpolymer.

Figure 5.3 represents the powder XRD patterns of the synthesized terpolymer before and after metal ions treatment. The synthesized terpolymer shows diffraction patterns of broad peaks between 2θ of 19 and 23 angles and broadened peaks suggest the formation of amorphous nature of the terpolymer as shown in **Figure 5.3(a)**. The same characteristic peaks are observed for metal ions treated terpolymer as shown in **Figure 5.3(b)**. However after treatment, the intensity of the amorphous characteristic peaks slightly increases and some new peaks are appeared in the 2θ range of 30.96 and 36.43 which are due to the conversion of amorphous to semicrystalline state³⁰.

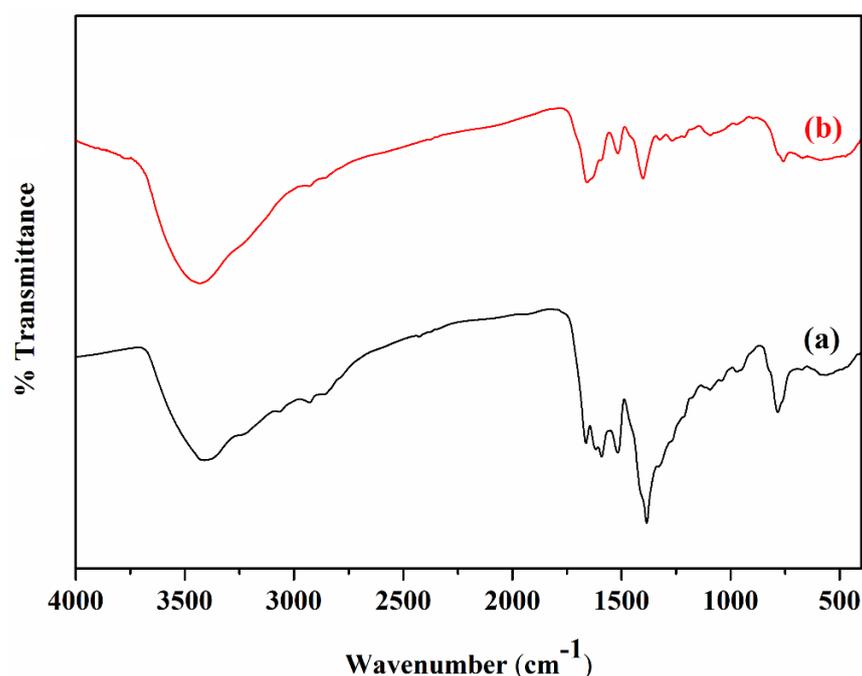


Figure 5.2. (a) FT-IR spectra of before and (b) after metal-loaded DHF terpolymer.

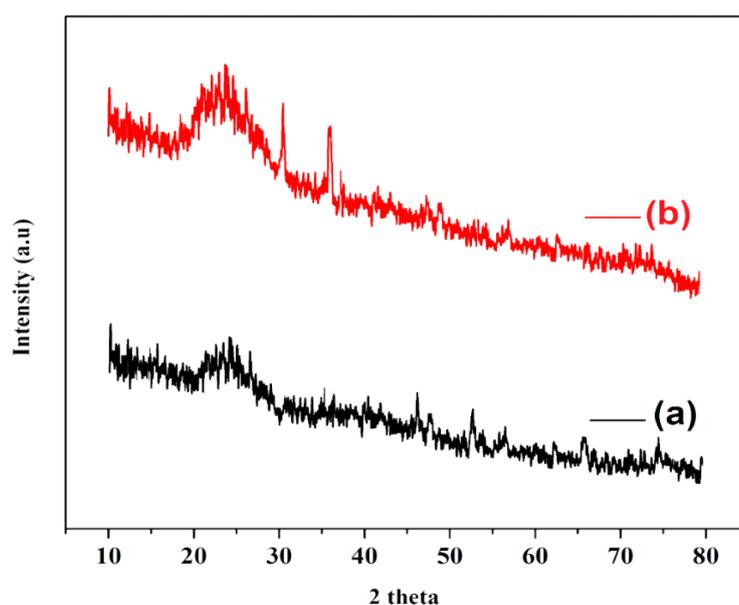


Figure 5.3. XRD patterns of DHF (a) before and (b) after metal ions removal.

5.3.3 Thermal behaviour of the terpolymer

Thermogravimetric technique is found to be a valuable method to evaluate the thermal decomposition characteristics of the terpolymer. TGA curve of the terpolymer is shown in **Figure 5.4**, and the data are presented in **Table 5.3**. The obtained terpolymer involves four stage decomposition. The initial weight loss of 5.96 % take place from room temperature to 168.88 °C which may be due to the removal of physically/chemically absorbed water and solvents present in the terpolymer. The second stage decomposition begins at 168.88 °C with a weight loss of 31.1% of the resin and ends at 379.66 °C which is assigned to the loss of the -COOH group as CO₂ and the hydroxyl group present in the terpolymer. In the third stage, the decomposition starts at 379.66 °C with 48.86 % weight loss and ends at 522.26 °C, this loss may be due to the elimination of -NH₂, carboxylic group and CH₂ present in the terpolymer. Finally the fourth degradation stage takes place between 522.56 and 616.05 °C involving 50.99 % mass loss is due to the strong intramolecular hydrogen bonding established in the aromatic ring in the terpolymer

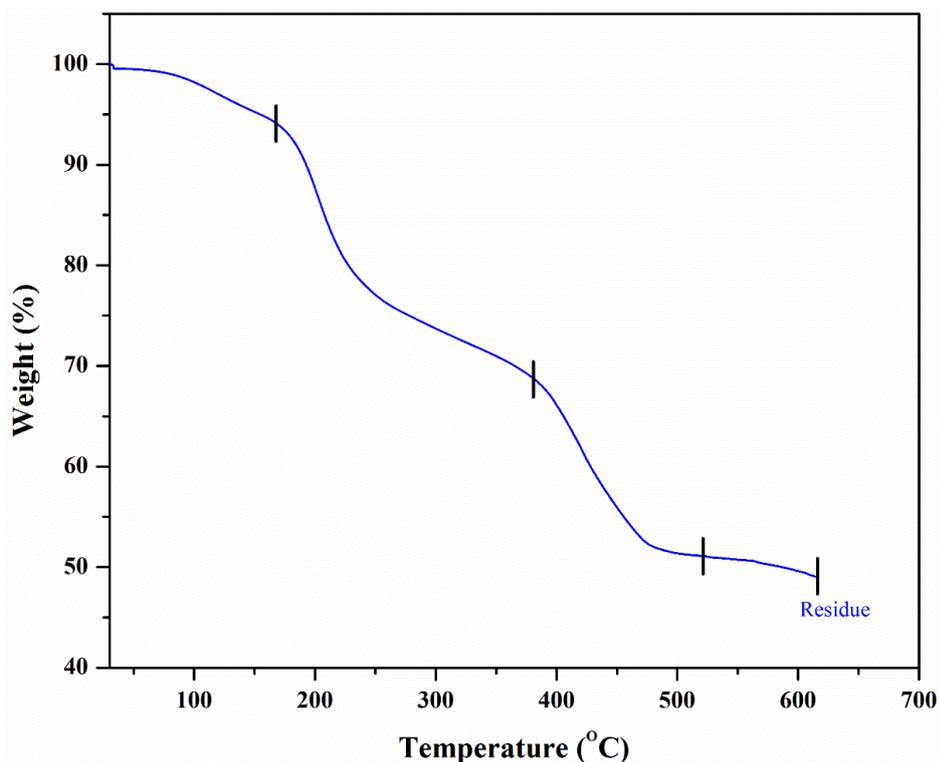


Figure 5.4. TGA thermogram of DHF terpolymer.

Table 5.3. TGA data of the DHF terpolymer.

Sample	Temperature (°C)					Degradation Temperature Range (°C)	T _{max} ^a (°C)	T ₅₀ ^b (°C)
	150	250	350	450	550			
	Weight loss of terpolymer (%)							
DHF	4.8	22.9	29.13	44.01	49.21	31.14 to 616.05	616.05	581.95

^aMaximum decomposition temperature. ^bTemperature at 50% weight loss

5.3.4 Sorption capacity of DHF terpolymer with the metal ions

5.3.4.1 Effect of electrolytes and pH

The effect of electrolyte and its ionic strength on metal uptake by the DHF terpolymer was estimated by batch equilibrium study. Briefly, 50 mg of DHF terpolymer and mixture of 300 ppm of Pb²⁺, Cd²⁺ and Hg²⁺ metal ions in various electrolytes such as NaCl, Na₂SO₄ and NaNO₃ with different concentrations *viz.* 0.1, 0.5, 1.0, 1.5 and 2.0 M at room temperature for 10 h and the results presented in **Figures 5.5 (a-c)** respectively, From the data it is observed that the amount of metal ion uptake for a given amount of DHF terpolymer depends on the nature and concentrations of the electrolyte used for the chelation studies. The amount of uptake of Pb²⁺, Cd²⁺ and Hg²⁺ ions by the polymer is comparatively higher in presence of NaNO₃ its may be due to the Pb²⁺, Cd²⁺ and Hg²⁺ ions forming weak chelates with the anions of the electrolytes. Generally, As the concentration of the electrolyte increases, the ionization decreases, hence the movement of the anions is restricted in the electrolyte medium. Therefore, more metal ions are available for the adsorption with the terpolymer³¹⁻³³.

The stability of the complexes depends on the charge of metal ions and nature of ligands. Among all above three electrolytes SO₄²⁻ is a strong ligand, as it has more number of electrons for donation to the metal ion during complex formation, forms strong and stable complex with all the three metal ions under study. Therefore, overall metal ions uptake is less in sodium sulfate electrolyte because less number of ions are available for uptake of polymer.

To ascertain the pH dependence on the uptake of Pb²⁺, Cd²⁺ and Hg²⁺ ions, experiments were carried out in the pH range of 2-7 by adding minimum amount of (0.5 M) HCl and/or NaOH. The optimum pH for the uptake of selected metal ions is found to be 6-7. The pH has a very strong effect on the adsorption capacities for Cd²⁺ as evident in **Figure 5.5 (d)**, the adsorption for Pb²⁺, Cd²⁺ and Hg²⁺ at pH 2.8 is very low but it increases

with rise in pH and maximum adsorption is reached at pH 7 Pb^{2+} (78), Cd^{2+} (84) and Hg^{2+} (81). The pH values higher than 7 was not employed to avoid the formation of insoluble metal hydroxides, which might have led to erroneous data on the adsorption by the terpolymer, with increasing pH values owing to a decrease in the H^+ concentration. Increased negative charge density on the polymer backbone would impart a stronger electrostatic force, which encourages ion exchange as well as complexation via formation of coordination bonds with the metal ions³⁴. There is also the possibility that, at higher metal loads, the adsorption capacities may be improved.

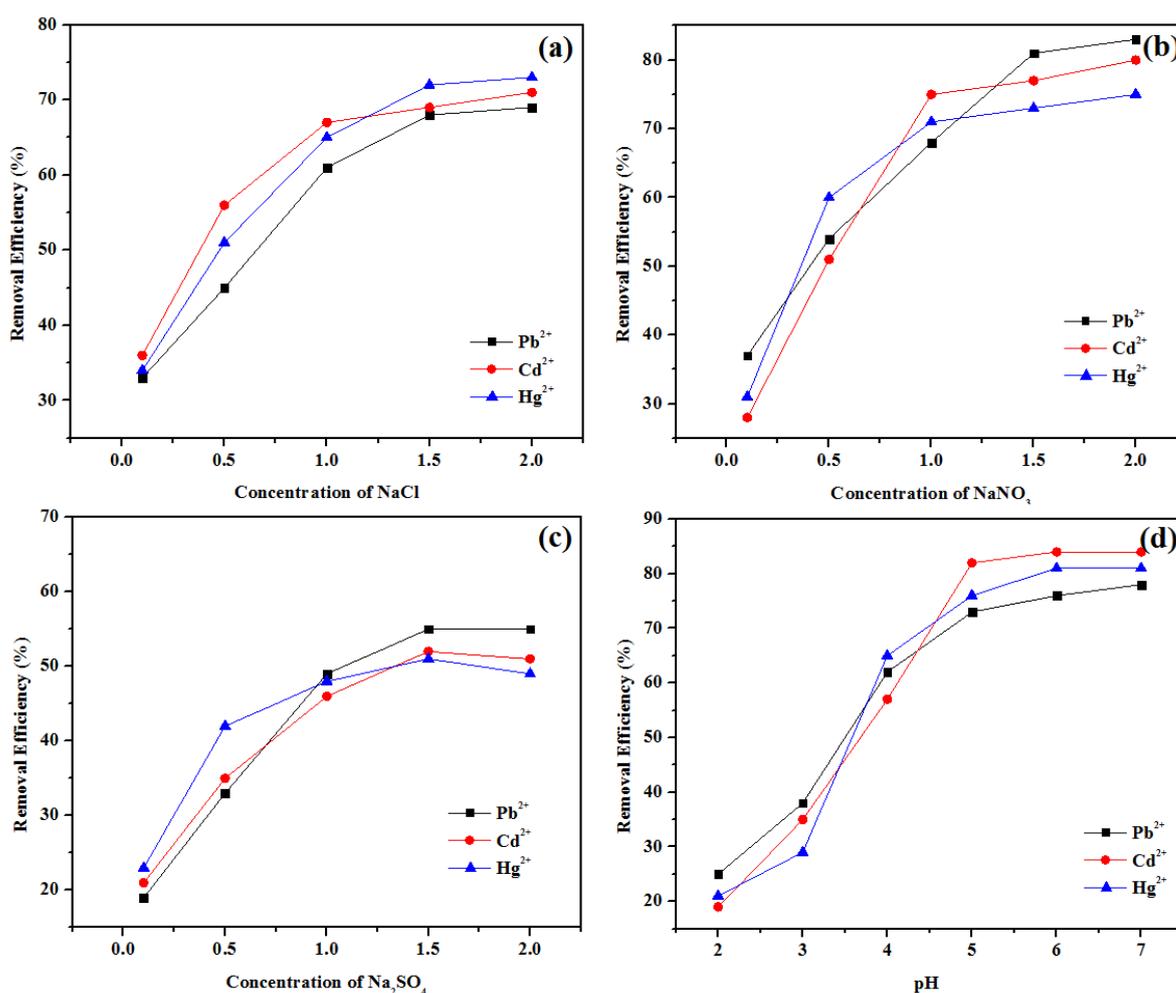


Figure 5.5. The removal percentage of Pb^{2+} , Cd^{2+} and Hg^{2+} metal ions on DHF terpolymer under various conditions. (a) Effect of NaCl (b) Na_2SO_4 (c) NaNO_3 and (d) pH.

5.3.5 Scanning electron microscopy and EDAX analysis

Surface morphologies of the DHF terpolymer was investigated by scanning electron microscopy. The terpolymer dried sample were sputter-coated with gold for 6 min, and then they were subjected to scanning and SEM micrographs of DHF are depicted in **Figure 5.6**, It can be observed that the DHF terpolymer exhibits a smooth and dense

surface without cracks surface that allows greater area for adsorption. The degree of dispersion of monomers in the terpolymer is more important for an smooth surface. The chemical composition of DHF terpolymer was characterized by energy dispersive X-ray spectroscopy (EDAX) and the spectrum is shown in **Figure 5.7**. The spectrum indicates the presence of the expected elements, such as C, N, S and O. The percentage of elements are approximately 66.21% of C, 8.49% of N and 14.21% of O.

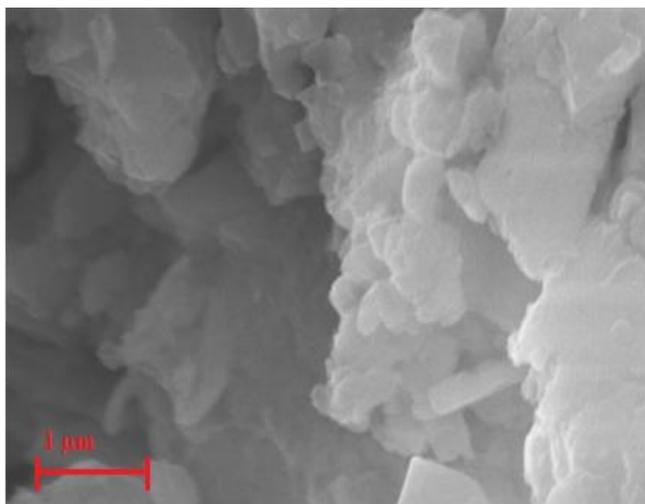


Figure 5.6. SEM image of the DHF terpolymer

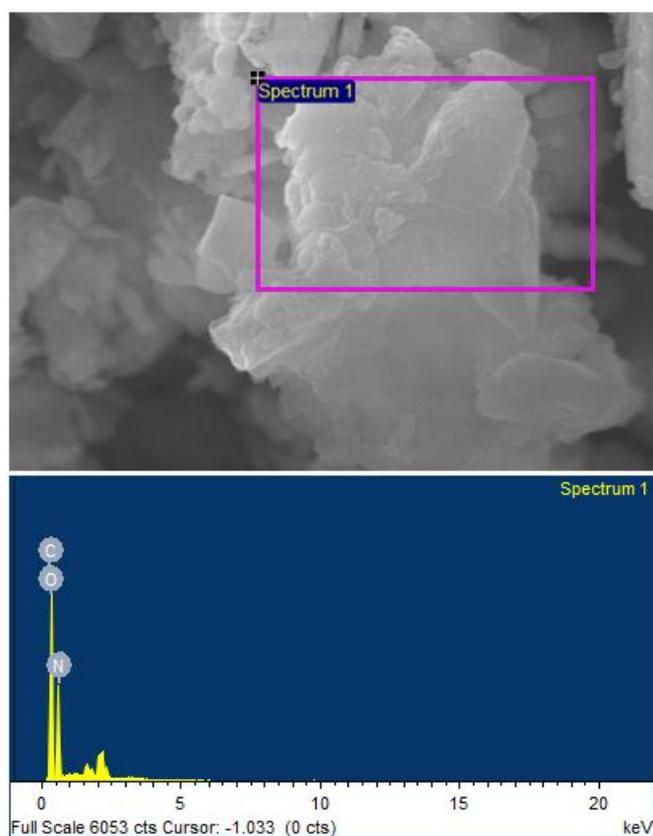


Figure 5.7. EDX analysis and the spectral analysis of the DHF terpolymer.

5.4 Conclusion

DHF terpolymer resin was prepared from 1,5-diaminonaphthalene, 5-hydroxyisophthalic acid with formaldehyde by condensation technique. On the basis of elemental analysis and Fourier transform infrared spectral studies, the proposed structure of the DHF terpolymer was confirmed. Thermal analysis data reveals that the terpolymer has good thermal stability. The phase structure of the DHF terpolymer was confirmed by the SEM and XRD studies. The batch equilibrium studies reveal that the terpolymer has effective heavy metal ions removal properties for various divalent metal ions such as Pb^{2+} , Cd^{2+} and Hg^{2+} ions. Since DHF terpolymer contains alcoholic and amino groups, it plays a key role in the sorption phenomenon. Thus DHF terpolymer has immense applications in separation of metal ions from waste water.

Reference

- 1 J. D. J. M.M.Patel, M.A.Kapadia, G.P.Patel, *React. Funct. Polym.*, 2007, **67**, 746–757.
- 2 P.K. Rahangdale, W.B. Gurnule, L.J. Paliwal, R.B. Kharat, *Synth. React. Inorganic, Met. Nano-Metal Chem.*, 2003, **33**, 1205–1212.
- 3 F. Xia, Z. Cheng, H. Xu, H. Li, Q. Zhang, G. J. Kavarnos, R. Y. Ting, G. Abdul-Sedat and K. D. Belfield, *Adv. Mater.*, 2002, **14**, 1574–1577.
- 4 S. B. Kim, H. A. Um, H. J. Kim, M. J. Cho and D. H. Choi, *Org. Electron. physics, Mater. Appl.*, 2016, **31**, 198–206.
- 5 R. K. Jian, L. Chen, B. Zhao, Y. W. Yan, X. F. Li and Y. Z. Wang, *Ind. Eng. Chem. Res.*, 2014, **53**, 2299–2307.
- 6 T. Farajpour, Y. Bayat, M. Abdollahi and M. H. Keshavarz, *Polym. Sci. Ser. a*, 2016, **58**, 186–195.
- 7 F. Fang, W. Yang and W. Yang, *J. Appl. Phys.*, , DOI:10.1063/1.3182809.
- 8 M. S. C. Kumar and M. Alagar, *Eur. Polym. J.*, 2002, **38**, 2023–2031.
- 9 N. Tanveer and M. Mobin, *Prog. Org. Coatings*, 2012, **75**, 231–240.
- 10 T. Sata, *Ion exchange membranes: preparation, characterization, modification and application*, Royal Society of Chemistry, 2004.
- 11 G. Borbély and E. Nagy, *Desalination*, 2009, **240**, 218–226.
- 12 N. Feng, X. Guo, S. Liang, Y. Zhu and J. Liu, *J. Hazard. Mater.*, 2011, **185**, 49–54.
- 13 M. Tuzen, K. O. Saygi and M. Soylak, *J. Hazard. Mater.*, 2008, **152**, 632–639.
- 14 A. B. M. Karunakaran, *Orient. J. Chem.*, 2001, **18**, 65–68.
- 15 A. B. M. Karunakaran, *Orient. J. Chem.*, 2003, **19**, 225–228.
- 16 R. N. Singru, W. B. Gurnule, V. A. Khati, A. B. Zade and J. R. Dontulwar, *Desalination*, 2010, **263**, 200–210.
- 17 W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal and R. B. Kharat, *React. Funct. Polym.*, 2003, **55**, 255–265.
- 18 M. M. Jadhao, L. J. Paliwal and N. S. Bhave, *Desalination*, 2009, **247**, 456–465.

- 19 R. S. Azarudeen, M. A. R. Ahamed and A. R. Burkanudeen, *Desalination*, 2011, **268**, 90–96.
- 20 K. P. K. Dhanraj T. Masram, Narayan S. Bhawe, *J. Appl. Polym. Sci.*, 2010, **117**, 315–321.
- 21 O. A. EO Akperov, AM Maharramov, *Hydrometallurgy*, 2009, **100**, 76–81.
- 22 A. R. B. Mohamed A. RiswanAhamed, DuraisamyJeyakumar, *J. Hazard. Mater.*, 2013, **248–249**, 59–68.
- 23 V. Vasanthakumar, A. Saranya, A. Raja, S. Prakash, V. Anbarasu, P. Priya and V. Raj, *RSC Adv.*, 2016, **6**, 54904–54917.
- 24 M. A. Riswan Ahamed, R. S. Azarudeen, R. Subha and A. R. Burkanudeen, *Polym. Bull.*, 2014, **71**, 3209–3235.
- 25 C. B. Boss and K. J. Fredeen, *Concept, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry*, Perkin-Elmer, Norwalk, CT, 2nd ed., 1997.
- 26 *U.S. EPA Method 200.7, Determination of metals and trace elements in water and wastes by Inductively Coupled Plasma Optical Emission Spectrometry*, Cincinnati, Ohio, U.S., 1994.
- 27 Q. He, Z. Hu, Y. Jiang, X. Chang, Z. Tu and L. Zhang, *J. Hazard. Mater.*, 2010, **175**, 710–714.
- 28 J. R. Gao, Z. Hu, X. Chang, Q. He, L. Zhang, Z. Tu and J. Shi, *J. Hazard. Mater.*, 2009, **172**, 324–329.
- 29 E. Pretsch, P. Buhlmann and M. Badertscher, *Structure Determination of Organic Compounds*, 2010, vol. 43.
- 30 S. Nanjundan, C. S. J. Selvamalar and R. Jayakumar, *Eur. Polym. J.*, 2004, **40**, 2313–2321.
- 31 S. Dutta and A. K. Das, *J. Appl. Polym. Sci.*, 2007, **103**, 2281–2285.
- 32 R. N. Singru and W. B. Gurnule, *J. Appl. Polym. Sci.*, 2010, **116**, 3356–3366.
- 33 M. M. Jadhao, L. J. Paliwal and N. S. Bhawe, *J. Appl. Polym. Sci.*, 2008, **109**, 508–514.
- 34 M. G. Zahra Sekhavat Pour, *RSC Adv.*, 2015, **5**, 64106–64118.