IJARSCT

ISSN (Online) 2581-9429

International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

Impact Factor: 5.731

Volume 12, Issue 4, December 2021

# An Eco-Friendly Terpolymer Resin: Synthesis, Characterization and Ion - Exchange Properties

**Renuka P. Chopde[1] and M. B. Thakre[2]**
Department of Chemistry, S. Chandra Mahila Mahavidyalaya, Sakoli, Bhandara[1]
Department of Chemistry, D. R. B. Sindhu Mahavidyalaya, Nagpur[2]
renukapchopde82@gmail.com

**Abstract:** *2, 2'- Biphenol-Hexamethylenediamine-formaldehyde Terpolymers (BPHDF) were synthesized by the condensation of 2, 2'- Biphenol, Hexamethylenediamine, and formaldehyde in the presence of acid catalyst with varying molar ratios of reacting monomers. Terpolymer composition has been determined on the basis of their elemental analysis and the number–average molecular weight of these resins was determined by conductometric titration in nonaqueous medium. The viscosity measurements were carried out in N, N-dimethyl formamide which indicate normal behaviour. IR spectra were studied to elucidate the structure. The terpolymer resin has been further characterized by UV–visible and $^{1}$H-NMR spectra. The surface morphology of the terpolymer resin was examined by scanning electron microscopy. One of the important applications of these terpolymers is their capability to act as chelating ion-exchangers. The newly synthesized terpolymers proved to be selective for chelating ion-exchange properties and showed a powerful adsorption towards specific metal ions like $Co^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Pb^{2+}$. 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. The terpolymers showed a higher selectivity for $Co^{2+} > Hg^{2+} > Cd^{2+} > Pb^{2+}$.It is also observed that the amount of metal ions absorption by the BPHDF terpolymer resins increases in the order: BPHDF-3 > BPHDF-2 > BPHDF-1 due to introduction of more and more phenolic groups in terpolymer resins from BPHDF-1 to BPHDF-3.*

**Keywords:** 2,2'-Biphenol-Hexamethylenediamine-formaldehyde Terpolymersresins, BPHDF, Chelating properties, Batch equilibrium, Distribution ratio, Metal ion uptake

## I. Introduction

Over the past few decades, significant research work has been done on enhancing the properties of new synthesized ion-exchange terpolymers for the treatment of waste water and pollution control. Ion-exchange may be defined as the reversible exchange of ions between the substrate and surrounding medium. The removal of heavy metal ions from industrial wastewater has been given much attention in the last decade, as the heavy metals released into the environment pose potential threat, because of their tendency to accumulate in living organisms. The necessity to reduce the amount of heavy metal ions pollution in wastewater streams has led to an increasing interest in ion-exchange terpolymers [1-5]. Therefore, attempt has been made to synthesize terpolymer and to evaluate the ion-exchange properties. Copolymers of 8-hydroxyquinoline with formaldehyde have been studied extensively[6].Synthesis, chacterization, and thermal Study of terpolymeric resin derived from m-cresol, hexamine and formaldehyde have been reported[7]. Masram D. T. and Karia K. P. have been reported the terpolymer resins of hydroxy compounds with various diamines with formaldehyde and their properties such as electrical conductivity[8], thermal stability[9], and ion exchange properties[10] have also been studied. Synthesis, characterisation and thermal degradation studies of 8-hydroxyquinoline-ethylene diamine-formaldehyde have been studied by Trivedi and co-workers[11]. Extensive research work has been carried out on synthesis, characterisation, thermal degradation and ion exchange properties of terpolymers derived from 2,2'-dihydroxy biphenyl, substituted carbamide and formaldehyde [12-16].The chelating

IJARSCT
ISSN (Online) 2581-9429
International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)
Volume 12, Issue 4, December 2021
Impact Factor: 5.731

behaviour of the synthesized resin was studied using metal ions Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) and the sorption capacities of the resin follows the order Pb(II)<Zn(II)<Cd(II)<Cu(II). However, the literature studies have revealed that no terpolymer has been synthesized using the monomer2, 2'-biphenol, hexamethylene diamine and formaldehyde. Therefore, in the present communication we report the synthesis, structural characterization and ion exchange properties of BPHDF terpolymer resins.

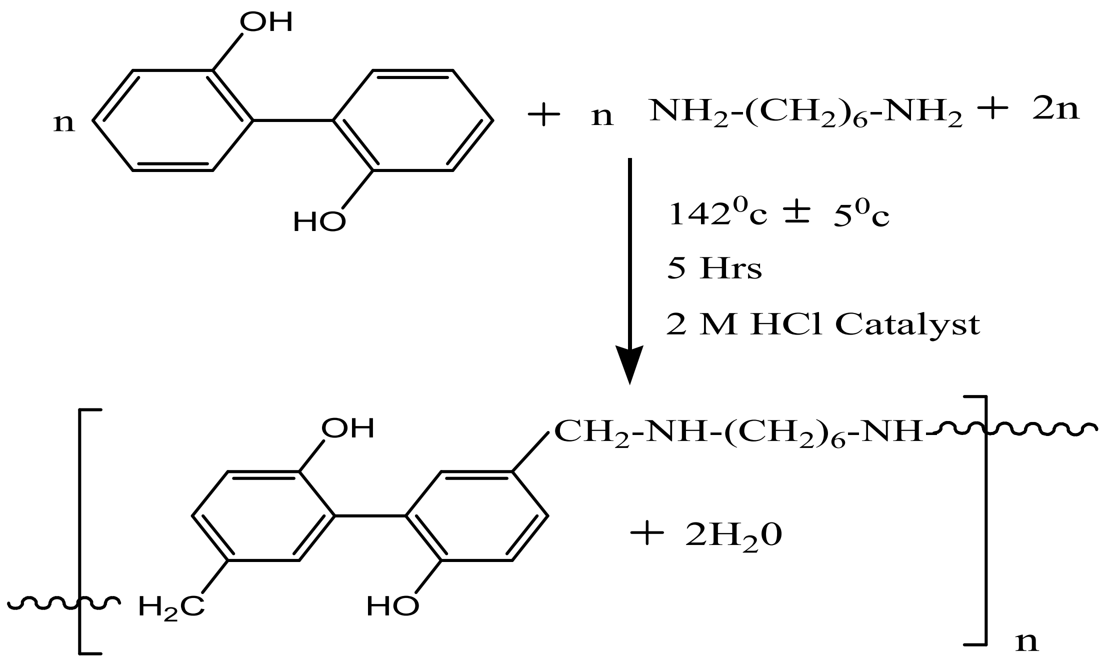
## II. Experimental

### 2.1 Chemicals and Reagents

2,2'-biphenol (Aldrich Chem.), and hexamethylene diamine (Merck, India) were purified by rectified spirit. Formaldehyde (37%), metal nitrates of chosen metals (AR grade, Merck) was used as received. All the other chemicals, solvents (N, N'-dimethyl formamide, dimethylsulphoxide) and the indicators were of analytical grade procured from Merck, India. Standardized $Na_2EDTA$ was used as a titrant for all the complex metric titrations. Double distilled water was used for all the experiments.

### 2.2 Terpolymerization

The terpolymer resin was synthesized by the condensation reaction of 2, 2'-biphenol (0.1 mol), ethylene diamine (0.1 mol), and formaldehyde (0.2 mol) in presence of 2M HCl as the reaction medium and refluxed with occasional shaking at $142^0c \pm 5^0c$ for 5 hr [8-13]. The tangy orange separated resinous product was washed with hot water to remove unreacted monomers. It is then thoroughly washed with methanol to remove copolymers which might be present along with terpolymer resin. The terpolymer resin was purified by dissolving in 8m NaOH and reprecipitated by dropwise addition of 1:1 (v/v) HCl with constant stirring. The regenerated product was washed repeatedly with hot water, powdered with the help of an agated mortar and pestle and dried in a vacuum desiccator over anhydrous calcium chloride. The yield of this terpolymer resin was found to be 53-70%. The reaction taking place in the synthesis of BPHDF terpolymer resin -I is as shown in Scheme-1.




**Scheme 1:** Reaction route of BPHDF terpolymer resin.

Different resin samples of BPHDF namely, BPHDF-II (2:1:3) and BPHDF-III (3:1:4) were prepared using different molar ratios of reactants.

**2.3 Physicochemical Analysis, Elemental Analysis, molecular weight determination**

The average molecular weight of the BPHDF terpolymers was determined by Number Average Molecular Weight by Non-aqueous Conductometric Titration. Viscometric measurements were carried out in DMF at 30°C by using Tuan-Fuoss viscometer at different concentrations, using Huggins and Kraemers equation. The elemental analysis of the terpolymer resin was carried out for C, H, and N by using a Thermo Finnigan CHNSO Analyser, Italy, FLASHEA 1112 series SAIF, IIT, Powai.

**2.4 Spectral Analysis**

The FTIR spectrum of the synthesized terpolymer had been scanned in the region of 600-4000 $cm^{-1}$ on Nicolet Instruments corporations, USA, Model MAGNA 550, SAIF, IIT, Powai, Mumbai to identify the linkages and the functional groups. The UV-Visible studies were carried out on a spectrophotometer in the range of 200-1200 nm at RTM Nagpur university, Nagpur. The proton NMR spectrum of the terpolymer was recorded in DMSO-d6 solvent using BRUKER AVANCE II 400 NMR spectrometer, SAIF Punjab University Chandigarh.

**2.5 Surface Analysis**

The surface analysis of the BPHDF terpolymers was examined by scanning electron microscope at 150 x to 3500x magnification by JEOL JSM-6380A analytical scanning electron microscope at Visvesvaraya National Institute of Technology (VNIT), Nagpur.

**2.6 Ion-Exchange Characteristics**

The cation-exchange properties of BPHDF terpolymers were studied by batch equilibrium method. The finely ground terpolymer was used to determine the metal ion uptake capacity of the metal ions like $Co^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Pb^{2+}$ in the form of their aqueous metal nitrate solutions. Metal ion binding capacity for the terpolymer was studied in various electrolytes with different concentrations, pH ranges and time intervals.

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

The prepared BPHDF terpolymer (25 mg) was taken in a pre-cleaned glass bottles and each of the electrolytes ($^{25}$ mL) such as NaCl, $NaNO_3$, $NaClO_4$, and $Na_2SO_4$ in different concentrations viz. 0.1, 0.5 and 1.0 M. The pH of the suspension was adjusted to the required value either by adding 0.1 M HCl or 0.1 M NaOH. This suspension was mechanically stirred for 24 h at 25 °C for the swelling of the terpolymer. To this suspension 2 ml of 0.1 M of specific metal ion solution was added and vigorously stirred for 24 h at 25 °C. It 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 titre value and that of from the blank. The chelating mechanism of the terpolymer resin is as follows.

$$(Res.A^-)B^+ + C^+ \text{ (solution)} \leftrightarrow (Res.A^-)C^+ + B^+ \text{ (solution)} \quad (1)$$

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

**2.8 Effect of the distribution of metal ions at various pH**

The distribution of each one of the metal ions at various pH ranging from 3 to 5.5 between the polymer phase and the aqueous phase were determined in the presence of 1 M $NaNO_3$ at 25 ºC. The distribution ratio $K_D$, may be defined as

$$KD\,\frac{Weight\ (in\ mg)of\ metal\ ions\ taken\ up\ by\ 1\ g\ of\ the\ resin\ sample}{Weight\ (in\ mg)of\ metal\ ions\ present\ in\ 1\ ml\ of\ the\ solution} ------(2)$$

**2.9 Effect of rate of metal ion uptake**

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 $NaNO_3$ 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 assumed 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 of the state of equilibrium. It is given as,

$$\begin{array}{c}\text{\% of amount of metal ions} \\ \text{taken up at different time}\end{array} = \frac{\text{Amount of metal ion absorbed} \times 100}{\text{Amount of metal ion absorbed at equilibrium}} \quad (3)$$

## III. Result and Discussion

### 3.1 Physicochemical, Elemental Analysis and Molecular Weight Measurements

The polymers were found to be tangy orange in colour, insoluble in commonly used organic solvents but were partly soluble in DMF and DMSO. These synthetic polymers do not show a sharp melting point but undergo decomposition above 300°C (Table 1). These terpolymers were analysed for carbon, hydrogen, and nitrogen content. Experimental details and Elemental analysis data are shown in table 1and table 2 respectively.

**Table 1**: Experimental details regarding to synthesis of terpolymers.

| Terpolymers | Molar ratio | Monomers | | | Catalyst 2m HCL (ml) | Reflux temp (±5K) | Reflux time (hr) | yield % | colour |
|---|---|---|---|---|---|---|---|---|---|
| | | 2,2'-biphenol BP (mol) | Hexa-Methylene dimine HD (mol) | HCHO (mol) | | | | | |
| BPHDF-I | 1:1:2 | 0.2 | 0.2 | 0.4 | 100 | 415 | 5 | 57 | Tangy orange |
| BPHDF-II | 2:1:3 | 0.4 | 0.2 | 0.6 | 100 | 410 | 5 | 64 | Tangy orange |
| BPHDF-III | 3:1:4 | 0.3 | 0.1 | 0.4 | 100 | 411 | 5 | 70 | Tangy orange |

**Table 2**: Elemental (C, H and N) analysis data for terpolymers.

| Terpolymers | % C (obs.) | % C (cal.) | % H (obs.) | % H (cal.) | % N (obs.) | % N (cal.) |
|---|---|---|---|---|---|---|
| BPHDF-I | 66.12 | 66.29 | 8.23 | 8.28 | 7.68 | 7.73 |
| BPHDF-II | 68.37 | 68.51 | 7.24 | 7.26 | 4.76 | 4.84 |
| BPHDF-III | 69.49 | 69.52 | 6.79 | 6.80 | 3.48 | 3.52 |

### 3.2 Conductometric Titration and Viscometric Method

The average molecular weight of the BPHDF terpolymer is determined by Number Average Molecular Weight by Non-aqueous Conductometric Titration. The number average molecular weight (Mn) and weight average molecular weights (Mw) for all these terpolymer resins are lying in the range 2000 to 15000. The polydispersity index (Mw/ Mn) is found to be 1.032. The average molecular weight ( Mz) of the terpolymer is 5763. The polydisperstiy (Mz/ Mn) is 1.063. The data obtained from molecular weight measurements are presented in Table 3.

The molecular weight (Mn) of the terpolymer was determined by non-aqueous conductometric titration in DMF against KOH in alcohol using 100 mg of resin sample. A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 mg of terpolymer was made. Inspection of such a plot revealed that there are many breaks in the plot. From this plot the first and the last break were noted. The calculation of (Mn) by this method is based on the following considerations[17,18].

1. The first break corresponds to neutralization of the more acidic phenolic hydroxy group of all of the repeating units; and
2. The break in the plot beyond which a continuous increase in conductance is observed represents the stage at which the phenolic hydroxy group of all repeating units is neutralized.

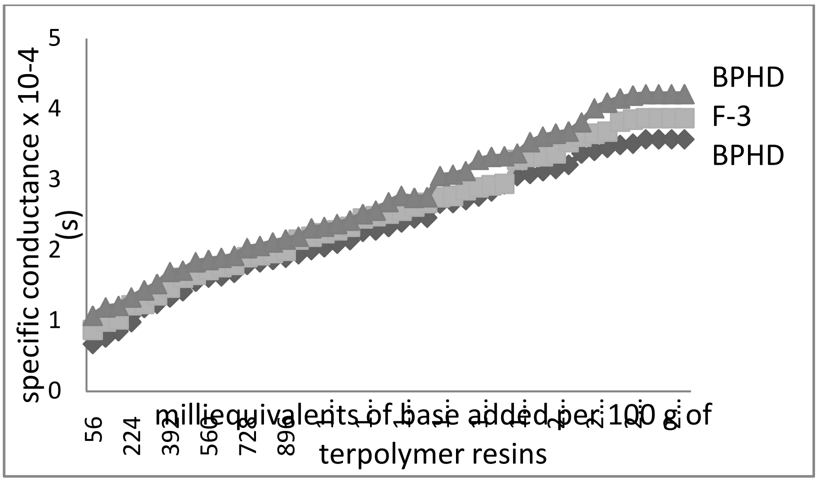



**Figure 1**: Conductometric titration curve of BPHDF terpolymers.

The average degree of polymerization ($\overline{Dp}$) is given by relation.

$$\overline{Dp} = \frac{total\ milliequivalents\ of\ base\ required\ for\ complete\ neutralisation\ i.e.last\ break}{milliequivalents\ of\ base\ required\ for\ smallest\ interval\ i.e.first\ break}$$

The number average molecular weight (Mn) could be obtained by multiplying the Dp by the formula weight of the repeating unit[19]. The results are shown in Table 3. Viscometric measurements were carried out in DMF at 30°C. All terpolymers showed normal behaviour. The intrinsic viscosity was determined by the Huggins[20] equation and the Kraemers[21] equation.

$$\eta_{sp}/ C = [\eta] + k_1 [\eta]^2 C \quad (1)$$

$$\ln\eta rel / C = [\eta] - k_2 [\eta]^2 C \quad (2)$$

From the Huggins and Kraemers equation, ηsp / C and ηrel / C against C were plotted and found to be linear, giving slopes $k_1$ and $k_2$ respectively. The intercept on the axis of viscosity function gave the value of [η] in both the plots. The calculated values of constants $k_1$ and $k_2$ (Table II) in most cases satisfy the relation k1 + k2 = 0.5 favorably[22]. The values of [η] obtained from Eqs. (1) and (2) were in close agreement with each other. The intrinsic viscosity increases with an increase in molecular weight of the terpolymer.

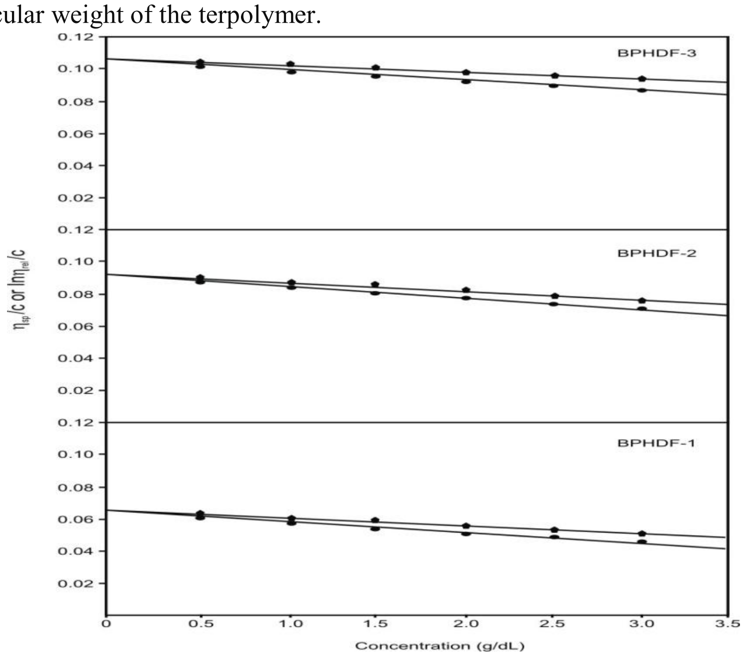



**Figure 2**: Viscometric Plot of BPHDF Terpolymer Resins

**Table 3**: Molecular weight determination and viscometric data of terpolymers

| Terpolymer resin | Empirical formula of repeating unit | Empirical formula weight | Dp | $\overline{M}_n$ | Intrinsic viscosity [η] dl $g^{-1}$ | Huggins constant ($k_1$) | Kraemer Constant ($k_2$) | $K_1+k_2$ |
|---|---|---|---|---|---|---|---|---|
| BPHDF-I | $C_{20}H_{26}O_2N_2.2H_2O$ | 362 | 8 | 2896 | 0.0660 | -1.16 | 1.66 | 0.5 |
| BPHDF-II | $C_{33}H_{36}O_4N_2.3H_2O$ | 578 | 11 | 6358 | 0.0974 | -0.754 | 1.232 | 0.478 |
| BPHDF-III | $C_{46}H_{46}O_6N_2.4H_2O$ | 794 | 20 | 15880 | 0.1077 | -0.6563 | 1.147 | 0.491 |

### 3.3 Spectral studies

The electronic spectra of these terpolymers are depicted in figure 3. The spectra show three absorption maxima in the region 270 - 420 nm. The intense band at 250 - 295 nm is due to phenolic – OH groups in repeated units of the terpolymer and is assigned to (n→σ*) transition[12-16,18]. The intense band at 310-350 nm is due to (π→π*) allowed transition of biphenyl moiety, which readily attain coplanarity[12-16,18], while the later intense band at 370-410 may be attributed to n→π*transitions for the presence of the phenolic hydroxyl group (auxochrome)[12-16,18]. This observation is in good agreement with the proposed probable structure for the BPHDF terpolymers.

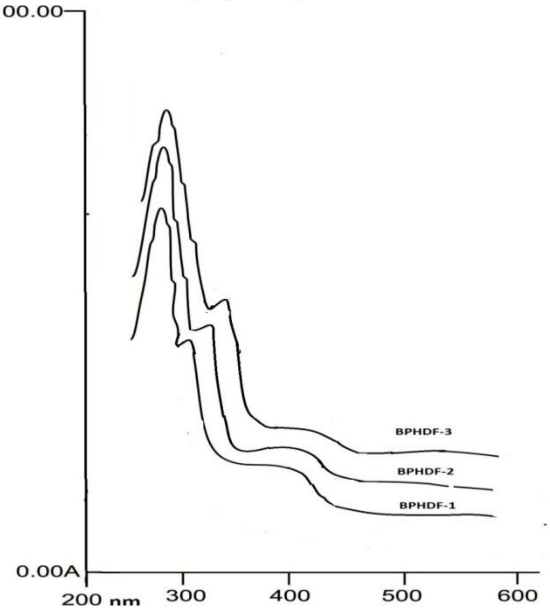



**Figure 3**: Electronic spectra of terpolymers

The IR spectras of these terpolymers are shown in figure-4 and the spectral data are shown in table-4. From the IR spectra, it revealed that all of these polymers give rise to a nearly similar pattern of spectra. A broad band appearing in the region 3550-3300 $cm^{-1}$ may be assigned to a stretching vibration of phenolic –OH groups[12-18]. The band at 2920 - 2925 $cm^{-1}$**,** 1496 cm-1, and 630 – 668 cm-1are assignable to –NH- stretching, bending and deformation out of plane respectively[12-18]. The band at 1570 -1600 $cm^{-1}$ may be ascribed to an aromatic skeletal ring[34]. The presence of methylene bridges (-CH2-) in the polymeric chain may be assigned to the presence of a band at 1440-1467, 1200-1220 and 751-754 $cm^{-1}$ [-CH2- bending, wagging and rocking] [12-18]. The band at 1222 – 1228 $cm^{-1}$ may be due to >C-O stretch of the polymeric phenol [12-18]. The bands obtained in the range 937 – 939 $cm^{-1}$, 1067 - 10075 $cm^{-1}$and 1123 – 1130 $cm^{-1}$ confirms the 1,2,3,5 substituted aromatic ring [12-18]. The 1,2,3,5 – substitution of the benzene ring is also confirmed by the presence of a band at 887-892cm-1and 830 cm-1for a tetrasubstituted benzene ring [13-18].

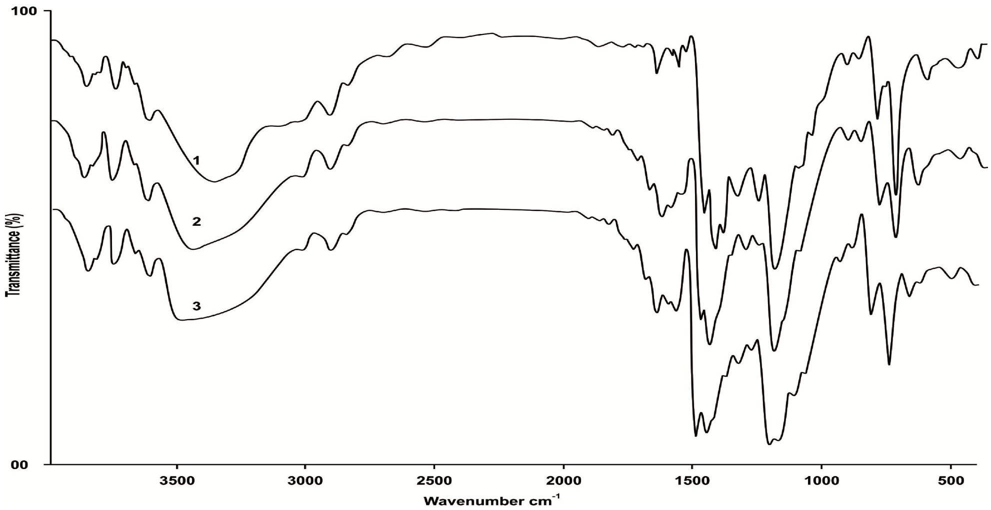



**Figure 4**: Infrared spectra of BPHDF terpolymers

**Table 4:** Infra-Red spectral data of BPHDF terpolymers

| Assignment | Observed band frequency $cm^{-1}$ | | | Expected band frequency |
|---|---|---|---|---|
| | BPHDF-I | BPHDF-II | BPHDF-III | |
| Phenolic -OH intermolecular hydrogen bonding | 3348.80(b, st) | 3419.36(b, st) | 3402.39(b, st) | 3200-3750 |
| >NH stretching | | | | |
| >NH bending | 2926.03(sh.st) | 2918.49(sh,st) | 2915.53(sh, st) | 2800-3500 |
| >NH deformation out of plane | 1496.76(m) | 1496.53(m) | 1496.82(m) | 1490-1570 |
| Aromatic ring vibration | 629.42(w) | 667.68(w) | 668.37(w) | 600-900 |
| Methylenic bridge (-CH2) mode | | | | |
| -CH2- bending | 1596.10(sh, b) | 1581.26(sh, b) | 1575.85(sh, b) | 1500-1600 |
| -CH2- wagging | | | | |
| -CH2- rocking | | | | |
| >C-O stretch in phenol | 1442.41(m) | 1458.64(m) | 1452.18(m) | 1460 |
| 1, 2, 3, 5 - substituted benzene ring | 1360.10(sh, b) | 1326.65(sh, b) | 1330.34(sh, b) | 1280-1370 |
| | 753.55(m) | 752.60(m) | 749.38(m) | 710-800 |
| | 1228.24(sh, b) | 1227.69(sh, b) | 1222.45(sh, b) | 1230 |
| Tetrasubstituted benzene ring | 937.98(w) | 937.13(w) | 939.19(w) | 950 |
| | 1075.84(w) | 1067.86(w) | 1073.16(w) | 1058 |
| | 1125.68(m) | 1123(m) | 1130(m) | 1125 |
| | 820.86(sh) | 824.67(sh) | 824.27(sh) | 830 |

$^{1}$H NMR spectra of terpolymers are presented in figure 5 and NMR spectral data is shown in table 5. These spectra show a multiple signal (asymmetrical pattern) in the region 6.6 to 7.4 (∂) ppm, which are due to aromatic protons[12-16,18]. A doublet signal appearing in the region 8.8-9.0 (∂) ppm can be assigned to the proton of the phenolic –OH group involved in hydrogen bonding[12-16,18]. A broad signal at 9.2-9.4 (∂) ppm shows intermolecular hydrogen bonding of the –$NHCH_2$- group or intermediate proton exchange reaction of both phenolic –OH groups[12-16]. A weak signal at 7.8-8.0 (∂) ppm may be due to protons of the –NH- bridges[12-16,18]. A signal at 3.2-3.6 (∂) ppm may be assigned to ethylenic protons of an Ar-$CH_2$-NH-$CH_2$ moiety[12-16]. A medium signal in the range of 3.7-4.0 (∂) ppm is attributed to the presence of –NH- bridging[16,18].

**Table 5**: Nuclear Magnetic Resonance ($^1$HNMR) Spectral Data of BPHDF Terpolymers.

| Nature of proton assigned in the NMR spectrum | Chemical shift (δ) of the terpolymer resin (ppm) | | | Expected chemical shift (δ, ppm) |
|---|---|---|---|---|
| | BPHDF-I | BPHDF-II | BPHDF-III | |
| Phenolic (Ar-OH) i.e. Proton of phenolic –OH involved in hydrogen bonding. | 8.8-9.2 | 8.9-9.3 | 8.8-9.3 | 7.5-12.0 |
| Aromatic proton (Ar-H) | 6.6-7.5 | 6.7-7.4 | 6.7-7.5 | 7.3-8.8 |
| Proton of –NH- bridge | 7.6-8.0 | 7.7-8.2 | 7.6-8.3 | 5.0-8.5 |
| Methylenic proton of Ar-CH2-NH- | 3.3-4.3 | 3.3-4.1 | 3.2-4.2 | 3.0-5.0 |
| Intermediate proton exchange of phenolic –OH group | 10.1 | 10.2 | 9.8-10.3 | 8.0-12.0 |

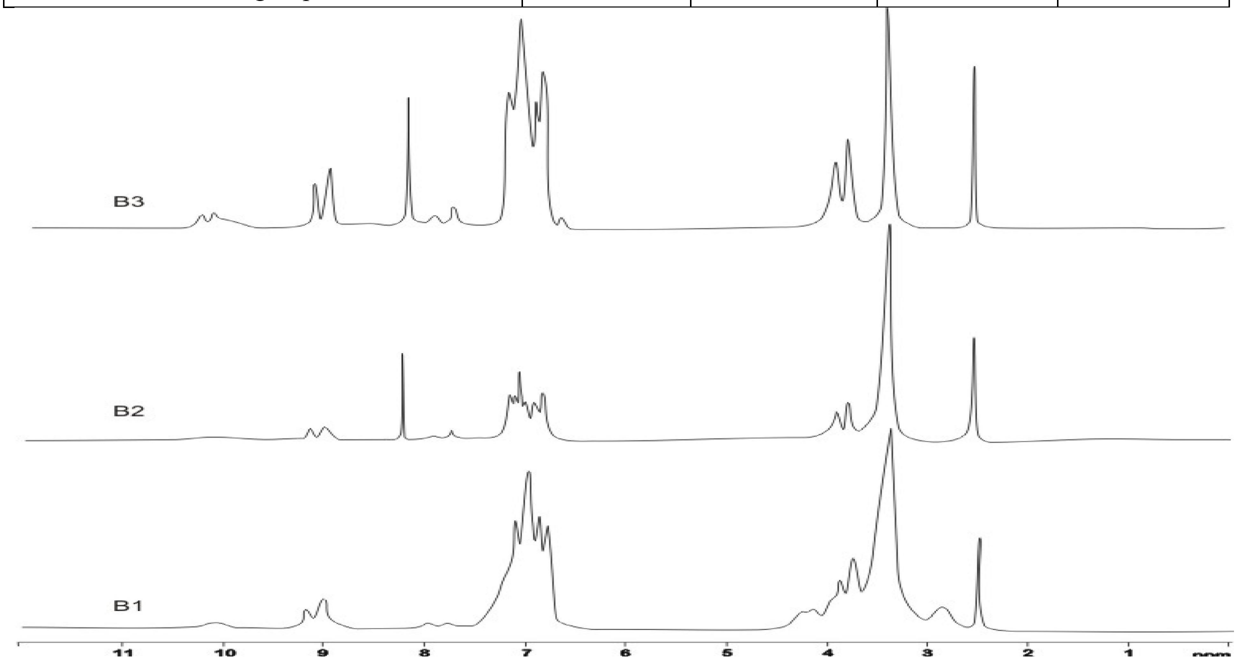


**Figure 5**: Nuclear Magnetic Resonance Spectra of BPHDF Terpolymers.

### 3.4 Surface Morphological Studies

The typical microphotograph at 3000× magnification from SEM of BPHDF is shown in Figure-6.SEM enables imaging to surface feature of 10-105 times magnification and resolution of features down to 3-100 nm depending upon the sample. Surface analysis has been found to be of great use in understanding the surface features of the materials. A brief account of surface morphology of the synthesized and purified terpolymer resins under investigation has been studied. But for reason of economy of space the surface morphology of only one representative case BPHDF-1 has been given here. morphology of the terpolymer resin shows fringed, scattered, miscellaneous model of the crystalline amorphous structure. The fringe and scattered structure represent transition material between the crystalline and amorphous phases. This tends to draw attention away from the details of the fine structure and gives little insight into the structure of large entities such as spherulites. The SEM photographs exhibits such spherulites which are the aggregate of crystalline present along with amorphous regions. The amorphous region shows secondary structural feature such as corrugations and having shallow pits.

Therefore, it is interesting to note that the high porosity and deep shallow pits provide enough space for the metal ions of specific size to be accommodated in the pores. Hence, these kinds of polymers can act as effective ion

IJARSCT

ISSN (Online) 2581-9429

International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

Impact Factor: 5.731

Volume 12, Issue 4, December 2021

exchangers. Hence the BPHDF terpolymer resin can be used as ion exchanger in the purification purpose.

The analysis of SEM micrographs has been carried out using literature[23].

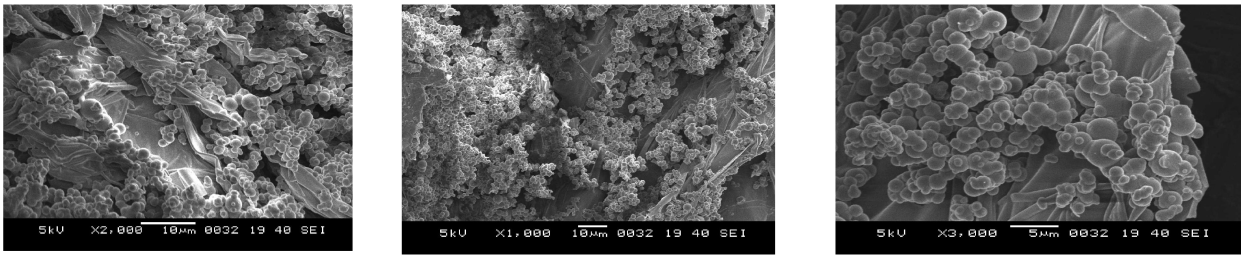



**Figure 6:** SEM photograph of BPHDF – I terpolymer

### 3.5 Effect of Metal Ion Uptake in Different Electrolytes with Variation in Concentrations

The chelation ion-exchange property of the BPHDF terpolymer was measured by batch equilibrium method involving $Co^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Pb^{2+}$metal ions in various electrolytes viz. NaCl, $NaNO_3$, $NaClO_4$, and $Na_2SO_4$ in different concentrations such as 0.01, 0.05, 0.1, 0.5, and 1.0 M. The results are presented in Table 6.

**Table 6:** Effect of metal ion uptake by BPHDF Terpolymer resin

| Metal ions | Electrolyte Conc. | Weight of the metal uptake (mili mol.$g^{-1}$) in the presence of [b] electrolyte | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | NaClNNaCl | | | $NaNO_3$ | | | $NaClO_4$ | | | $Na_2SO_4$ | | |
| | | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| $Co^{2+}$ | 0.01 | 3.11 | 3.22 | 3.28 | 2.65 | 2.65 | 2.68 | 1.26 | 1.37 | 1.43 | 2.89 | 2.92 | 3.12 |
| | 0.05 | 2.48 | 2.62 | 2.65 | 2.42 | 2.48 | 2.53 | 1.15 | 1.20 | 1.32 | 2.58 | 2.72 | 2.78 |
| | 0.10 | 2.33 | 2.36 | 2.34 | 2.13 | 2.22 | 2.31 | 1.04 | 1.09 | 1.26 | 1.92 | 2.15 | 2.44 |
| | 0.50 | 2.19 | 2.11 | 1.99 | 1.16 | 1.22 | 1.28 | 0.91 | 1.05 | 1.14 | 1.58 | 1.87 | 1.87 |
| | 1.00 | 0.85 | 0.82 | 0.93 | 0.93 | 0.96 | 0.99 | 0.79 | 0.90 | 1.03 | 0.72 | 0.75 | 0.58 |
| $Hg^{2+}$ | 0.01 | 3.51 | 3.63 | 3.70 | 1.99 | 1.48 | 2.18 | 1.66 | 1.73 | 1.79 | 1.53 | 1.60 | 1.69 |
| | 0.05 | 2.74 | 2.87 | 3.00 | 1.80 | 2.18 | 2.24 | 1.38 | 1.47 | 1.53 | 1.25 | 1.28 | 1.34 |
| | 0.10 | 1.13 | 1.19 | 1.22 | 1.48 | 1.67 | 1.70 | 1.10 | 1.15 | 1.21 | 1.09 | 1.18 | 1.31 |
| | 0.50 | 0.97 | 0.88 | 0.78 | 1.16 | 1.22 | 1.26 | 0.81 | 0.87 | 0.94 | 1.12 | 0.96 | 1.18 |
| | 1.00 | 0.59 | 0.65 | 0.69 | 0.81 | 0.78 | 0.84 | 0.55 | 0.63 | 0.68 | 0.90 | 0.93 | 0.80 |
| $Cd^{2+}$ | 0.01 | 1.87 | 1.98 | 2.09 | 1.76 | 1.82 | 1.93 | 1.59 | 1.71 | 1.82 | 2.11 | 2.14 | 2.16 |
| | 0.05 | 1.71 | 1.71 | 1.76 | 1.60 | 1.65 | 1.71 | 1.26 | 1.37 | 1.48 | 1.67 | 1.70 | 1.72 |
| | 0.10 | 1.44 | 1.44 | 1.49 | 1.55 | 1.55 | 1.66 | 0.92 | 1.03 | 1.14 | 1.23 | 1.45 | 1.56 |
| | 0.50 | 1.00 | 1.06 | 1.17 | 1.14 | 1.17 | 2.02 | 0.58 | 0.69 | 0.77 | 0.74 | 0.79 | 0.91 |
| | 1.00 | 0.73 | 0.89 | 0.91 | 0.78 | 0.73 | 0.89 | 0.36 | 0.47 | 0.58 | 0.58 | 0.63 | 0.69 |
| $Pb^{2+}$ | 0.01 | 1.82 | 1.92 | 1.95 | 2.02 | 2.13 | 2.13 | 1.25 | 1.33 | 1.65 | - | - | - |
| | 0.05 | 1.74 | 1.84 | 1.83 | 1.93 | 1.95 | 2.11 | 1.65 | 1.21 | 1.50 | - | - | - |
| | 0.10 | 1.53 | 1.62 | 1.62 | 1.83 | 1.82 | 1.93 | 0.84 | 0.98 | 1.19 | - | - | - |
| | 0.50 | 1.23 | 1.27 | 1.33 | 1.43 | 1.41 | 1.43 | 0.63 | 0.76 | 0.96 | - | - | - |
| | 1.00 | 0.92 | 1.02 | 1.13 | 1.01 | 1.02 | 1.13 | 0.42 | 0.53 | 0.74 | - | - | - |

[a]$[M(NO_3)_2]$ = 0.1 mol/l; Volume = 2 ml; Volume of electrolyte solution : 25 ml, Weight of resin = 25 mg; time: 24 h: Room temperature.

From the data it is observed that the amount of metal ion taken up by the terpolymer depends on the nature and concentrations of the electrolytes. The increase in the metal ion uptake with the increase in concentration may be explained on the basis of the stability constants of the complexes. From the results, it is observed that the amount of metal ion $Co^{2+}$, $Hg^{2+}$, $Cd^{2+}$ and $Pb^{2+}$taken up by the terpolymer decreases with the increasing concentration of $Cl^-$, $No_3^-$, $ClO_4^-$ and $SO_4^{2-}$ ions. This may be explained in terms of the stability constants of the complexes of $Co^{2+}$, $Hg^{2+}$, $Pb^{2+}$ and

$Cd^{2+}$ metal ions form with these anions. The sulphate, chloride, perchlorate and nitrate form strong complexes with $Co^{2+}$, $Hg^{2+}$, $Pb^{2+}$ and $Cd^{2+}$ and therefore, it is expected to influence the position of $Co^{2+}$, $Hg^{2+}$, $Pb^{2+}$ and $Cd^{2+}$ complex equilibrium. Further, the polymer is amorphous in nature and has porosity in its structure; hence they can accommodate metal ions of specific size, easily into its cavities. The metal binding property of the BPHDF terpolymers is found to be good than that of the other polymeric resins reported earlier [24-28].

It is also observed that the amount of metal ions taken up by the BPHDF terpolymer resins increases in the order:

BPHDF-3 > BPHDF-2 > BPHDF-1

This observed order may be due to introduction of more and more phenolic groups in terpolymer resins from BPHDF-1 to BPHDF-3. The maximum metal uptake in case of BPHDF-3 terpolymer resin may be due to introduction of more phenolic hydroxy group in repeating unit of terpolymer chain.

### 3.6 Effect of distribution of metal ions at various pH

The results of the effect of pH on the amount of metal ion distributed between two phases are summarized in table-7. The distribution of each one of the metal ions such $Co^{2+}$, $Hg^{2+}$, $Cd^{2+}$and $Pb^{2+}$ between polymer phase and the aqueous phase was determined at 25 °C in the presence of 1 M NaNO3 at various pH ranging from 3 to 6.5. The amount of the metal ion which remained in the aqueous phase was estimated. If the original metal ion concentration is known, the metal ion adsorbed by the resin can be calculated. The effect of pH on the amount of metal ions reveals that the uptake of metal ions by the terpolymer at equilibrium increases with increasing pH (Table-7). It is perceived that the equilibrium state is attained in 24 h at 25 ºC under the given conditions.

Studies on the effect of pH on the amount of metal ions distributed between two phases indicate that the relative amount of metal ion taken up by the BPHDF terpolymer resins increases with the increasing of pH of the medium[24-28]. The magnitude of increase, however, is different for different metal ions. The values of the distribution ratio and the order at different pH depend on the nature of the polymeric resin and its structure.

The study was restricted up to maximum pH of 6.5 in order to prevent hydrolysis of the and the precipitation of metal ions at higher pH. The formations of metal hydroxide interfere with the ionexchange process. All the four metal ions $Co^{2+}$, $Hg^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ have low distribution ratio (D) over the pH range 3 to 6.5. This could be attributed to low stability constants i.e. the weak ligand stabilization energy of the metal complexes [24-28]

The order of distribution ratio of divalent ions measured in the range of pH from 3 to 6.5 in the present work was found to be $Hg^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$.

Results given in table-7 are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different metal ions.

**Table 7:** Effect of distribution ratios ($K_D$), as a function of pH by BPHDF Terpolymer

| Metal ions | Resins | Distribution ratios of different metal ions at different pH | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1.5 | 1.75 | 2 | 2.5 | 3 | 4 | 5 | 6 |
| $Co^{2+}$ | BPHDF-1 | - | - | - | - | 50.60 | 134.93 | 195.99 | 234.64 |
| | BPHDF-2 | - | - | - | - | 54.00 | 138.85 | 224.00 | 246.06 |
| | BPHDF-3 | - | - | - | - | 59.17 | 147.15 | 249.05 | 255.18 |
| $Hg^{2+}$ | BPHDF-1 | - | - | - | - | 40.35 | 56.19 | 128.67 | 290.66 |
| | BPHDF-2 | - | - | - | - | 42.32 | 62.44 | 138.46 | 318.42 |
| | BPHDF-3 | - | - | - | - | 46.05 | 69.29 | 142.38 | 331.63 |
| $Cd^{2+}$ | BPHDF-1 | - | - | - | - | 32.17 | 53.65 | 124.71 | 209.71 |
| | BPHDF-2 | - | - | - | - | 36.06 | 56.37 | 132.51 | 217.43 |
| | BPHDF-3 | - | - | - | - | 40.22 | 59.21 | 136.63 | 225.57 |
| $Pb^{2+}$ | BPHDF-1 | - | - | - | - | 40.05 | 55.81 | 102.13 | 142.53 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | BPHDF-2 | - | - | - | - | 44.57 | 59.83 | 106.23 | 153.51 |
| | BPHDF-3 | - | - | - | - | 48.94 | 67.29 | 108.35 | 162.05 |

[a]D = weight (in mg) of metal ions taken up by 1g of copolymer/weight (in mg) of metal ionspresent in 1ml of solution.
[b][$M(NO_3)_2$]= 0.1 mol/l; volume : 2ml; $NaNO_3$ = 1.0 mol/l; volume: 25ml, time 24h (equilibrium state)at Room temperature.

### 3.7 Effect of rate of metal ion uptake

The rate of metal adsorption was determined to evaluate the shortest period of time for which equilibrium could be carried out while operating as close to equilibrium conditions as possible. The rate refers to the change in the concentration of the metal ions in aqueous solution, which is in contact with the given polymer. The result in Table-8 shows that the time taken for the uptake of different metal ions at a given stage depends on the nature of the metal ionand its ionic size.It is found that $Co^{2+}$ and $Hg^{2+}$ require about 5 h for equilibrium. $Cd^{2+}$, $Pb^{2+}$ required higher time i.e. 6 h to attain equilibrium. The rate of metal ion uptake follows the order: $Hg^{2+} \approx Co^{2+} > Cd^{2+} > Pb^{2+}$.

This observed order indicates that the rate of metal ion uptake depends on the nature of metal ion i.e. as the size of the metal ion increases the time taken for the uptake metal ions increases. Comparison of the rate up take of given metal ion by terpolymers is made on the basis of data presented in Table-8. It reveals that the rate of metal uptake by the terpolymer follows the order: BPHDF-3 > BPHDF-2 > BPHDF-1.

**Table 8:** Effect of rate of metal ion uptake by BPHDF Terpolymers

| Metal ions | Resins | Percentage of the amount of metal ion[a] taken up[b] at different time (hrs) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| $Co^{2+}$ | BPHDF-1 | 44.02 | 56.02 | 64.92 | 82.32 | 94.52 | - |
| | BPHDF-2 | 45.72 | 57.42 | 67.04 | 85.12 | 94.72 | - |
| | BPHDF-3 | 47.42 | 58.92 | 68.02 | 85.52 | 94.32 | - |
| $Hg^{2+}$ | BPHDF-1 | 44.32 | 56.22 | 64.22 | 83.02 | 96.32 | - |
| | BPHDF-2 | 45.42 | 58.42 | 67.12 | 83.52 | 96.12 | - |
| | BPHDF-3 | 46.42 | 58.52 | 69.62 | 85.42 | 96.32 | - |
| $Cd^{2+}$ | BPHDF-1 | - | 24.02 | 28.41 | 30.32 | 33.02 | 36.02 |
| | BPHDF-2 | - | 26.02 | 32.22 | 38.02 | 36.62 | 38.42 |
| | BPHDF-3 | - | 44.02 | 50.62 | 56.32 | 56.32 | 57.52 |
| $Pb^{2+}$ | BPHDF-1 | - | - | 22.22 | 26.72 | 28.92 | 31.12 |
| | BPHDF-2 | - | - | 28.12 | 30.12 | 32.32 | 36.22 |
| | BPHDF-3 | - | - | 36.22 | 38.02 | 41.62 | 45.32 |

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

## IV. Conclusion

A terpolymer resins (BPHDF) were prepared from 2, 2'- Biphenol, Hexamethylenediamine, and formaldehyde in the presence of acid catalyst with varying molar ratios of reacting monomersby condensation polymerization technique. From the elemental analysis, FTIR, and NMR spectral studies the proposed structure of the terpolymer was confirmed. The amorphous nature of the BPHDF terpolymers confirmed by SEM studies proves that the terpolmer can act as an effective ion-exchanger. The exchange capacity of the chosen metal ions is comparable to the commercial resins.

In the ion-exchange studies, the resin was highly selective for $Hg^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$ions and the amount of metal ions absorption by the BPHDF terpolymer resins increases in the order: BPHDF-3 > BPHDF-2 > BPHDF-1 due to introduction of more and more phenolic groups in terpolymer resins from BPHDF-1 to BPHDF-3 and by the presence of N atoms in diamine group which helps in chelation[24-28].

## ACKNOWLEDGMENT

Authors are grateful to the Principal, Hislop College, Nagpur for providing laboratory facilities and all necessary instrumental facilities. Authors are also grateful to the Head of Department of Chemistry RTM Nagpur university, Nagpur for providing facilities and rendering their valuable guidance. The authors also like to thanks SAIF, Punjab University, Chandigarh for providing facilities for NMR spectral study and also to RSIC, IIT, Powai, Mumbai for providing facilities for Infrared spectral study, elemental and thermal analysis.

## REFERENCES

**[1].** A.A. Elassar, O.A. Al-Fulaij, and A.E.M. El-Sayed, "Novel synthesis of poly (N1',N3'-diacryloylmalonohydrazide): characterization, complexation, ion selectivity, thermogravimetry, swelling, morphology and biological activity," J. Polym. Res. vol. 17, pp. 447–458, 2010.

**[2].** S.D. Alexandratos , C.A. Shelley, E.P. Horwitz, and R. Chiarizia, "A mechanism for enhancing ionic accessibility into selective ion exchange resins," Solv. Extr. Ion Exch., vol. 16(4), pp. 951–966, 1998.

**[3].** A. Singh, and S.K. Saraf, "Synthesis, characterization and ionexchanging properties of a novel ion-exchange resin, part II," Int. J. Polym. Mater., vol. 58(10), pp. 499–508, 2009.

**[4].** E.P. Michael Pratik, J.M. Barbe, H.D. Juneja, and L.J. Paliwal, "Synthesis, characterization and thermal degradation of 8- hydroxyquinoline–guanidine–formaldehyde terpolymer," Eur. Polym. J., vol. 43, pp. 4995–5000, 2007.

**[5].** O. Szabadka, E. Varga, and L. Nagy, "Determination of protonation and metal complex stability constants for a chelating monomer and its immobilized in polymer resin," Talanta., vol. 59, pp. 1081–1088, 2003.

**[6].** R.C. Degeiso, L.G. Donaruma, E.A. Tomic, Preparation and chelating properties of 8-hydroxy-quinoline-formaldehyde polymers. J. of Appl. Polym. Sci. (1965), Vol 9, Issue 2:411–419.

**[7].** K.M. Khedkar, V.V. Hiwase, A.B. Kalambe, S.D. Deosarkar, Synthesis, chacterization, and thermal Study of terpolymeric resin derived from m-cresol, Hexamine and Formaldehyde. E-Journal of Chem. (2012), Vol 9, (4):1911-1918.

**[8].** D.T. Masram, K.P. Karia, N.S. Bhave, Electrical Conductivity Study of Resin Synthesized From Salicylic Acid, Butylenediamine and Formaldehyde. Archives of Appl. Sci. Research. (2010),2 (2):153-161.

**[9].** D.T. Masram, K.P. Karia, N.S. Bhave, Kinetics Study of Thermal Degradation of Resin Derived from Salicylaldehyde, Ethylenediamine and Formaldehyde. E-Journal of Chemistry. (2010), 7(2):564-568.

**[10].** D.T. Masram, K.P. Karia, N.S. Bhave, Physicochemical and ion exchange studies of resin derived from p-hydroxybenzoic acid and ethylenediamine with formaldehyde. Der PharmaChemica. (2011), 3(3): 124-134.

**[11].** Y.S. Trivedi, K.P. Karia, P.K. Pandey, L.J. Paliwal, N.S. Bhave, Synthesis, Characterisation and Thermal Degradation Studies of 8-Hydroxyquinoline-Ethylenediamine-Formaldehyde Terpolymer Resin. International Conference on Polymers for Advanced Technologies. Macro, (2004).

**[12].** M.M. Jadhao, L.J. Paliwal, N.S. Bhave, Resin. III. Synthesis, characterization, and ion-exchange properties of a 2,2prime-dihydroxybiphenyl-formaldehyde copolymer resin. J. Appl. Polym. Sci. (2008), Vol. 109:508-514.

**[13].** M.M. Jadhao, L.J. Paliwal, N.S. Bhave, ResinI: Synthesis and characterization of 2, 2prime-dihydroxybiphenyl-urea-formaldehyde terpolymers. J. Appl. Polym. Sci. (2005), Vol. 96:1605-1610.

**[14].** M.M. Jadhao, L.J. Paliwal, N.S. Bhave, Thermal degradation studies of terpolymer resins derived from 2,2prime-dihydroxybiphenyl, urea, and formaldehyde. J. Appl. Polym. Sci. (2006), Vol. 101:227-232.

**[15].** Resins IV: Preparation and characterization of terpolymer resins prepared from biphenol, thiourea and formaldehyde. J. of Appl. Polym. Sci. (2010), Vol 118:1245-1251.

**[16].** M.M. Jadhao, Sandeep Kumar, L.J. Paliwal, N.S. Bhave, SarfarazAlam. Resin-V: Synthesis and physicochemical studies of a biphenol–guanidine–formaldehyde terpolymer resin. J. of Appl. Polym. Sci. (2010), Vol 118:1969-1978.

**[17].** K. Nakanishi, Infrared Absorption Spectroscopy, 2nd ed., Nankodo Co. Ltd: Japan, 1964.

**[18].** R.M. Silverstein, and F.X. Webster, Spectrometric Identification of Organic Compounds, 6th ed., John Wiley: New York, 1998.

**[19].** A. Vogel, Text Book of Quantitative Chemical Analysis, 5th ed., Longman group: UK, 1989.

**[20].** R.G.Charles, Metal chelate polymers derived from tetraacetylethane. J. of Polym. Sci. Part A: General Papers, (1963), Vol.1, Issue 1:267–276,

**[21].** M.N. Patel, S.H. Patil, Studies on polyazomethine chelate polymers. J. Makromol Sci. Chem. Part-A. (1982), Vol.17: 675-687.

**[22].** P.W.M. Jacobs, F.C. Tompkin, Chemistry of Solid State; WI Graver, London, (1955), P 188.

**[23].** J.A. Raj, C. Vedhi, A. Burkanudeen, P. Arumugam, and P. Manisankar, "Synthesis and characterization of novel nano-size polyreactive yellow 107," Ionics., vol. 16, pp. 171–175, 2010. b) M.K. Gaidhane, A.M. Ghatole, K.R. Lanjewar, "Synthesis of Chromone Functionalized Chitosan Polymer: Application/Screening of Its Physical Parameters," Polymer Science, Series B, 62(3), pp. 1–12, 2020.

**[24].** P.M. Shah, A.V. Shah, and B.A. Shah, "Metal ions uptake by chelating resin derived from o-substituted benzoic acid and its synthesis, characterization and properties," Macromol. Symp. vol. 274, pp. 81–90, 2008.

**[25].** V.V. Hiwase, A.B. Kalambe, K.M. Khedkar, and S.D. Deosarkar, "Ion exchange properties of resins derived from phydroxybenzaldehyde, resorcinol and formaldehyde," E. J. Chem., vol. 7(1), pp. 287–294, 2010.

**[26].** R.N. Singru, and W.B. Gurnule, "Chelating ion-exchange properties of copolymer resins derived from p-cresol, oxamide and formaldehyde," Iran. Polym. J., vol. 9(3), pp. 169–183, 2010.

**[27].** R.S. Azarudeen, M.A. RiswanAhamed, D. Jeyakumar, and A.R. Burkanudeen, "An eco-friendly synthesis of a terpolymer resin: characterization and chelation ion-exchange property," Iran. Polym. J., vol. 18(10), pp. 821–832, 2009.

**[28].** M.A. RiswanAhamed, R.S. Azarudeen, M. Karunakaran, and A.R. Burkanudeen, "Metal ion binding properties of a terpolymer resin: synthesis, characterization and its applications," Iran. Polym. J., in press.