

Synthesis, Characterization and Ion-Exchange Properties of Terpolymer Resin-II Derived from *p*-Hydroxybenzaldehyde, Thiourea and Ethylene Glycol

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Abstract: Ion-exchange resin (HBTE-II) was synthesized by polycondensation in the presence of polyphosphoric acid as a catalyst using monomers *p*-hydroxybenzaldehyde (0.2 M), thiourea (0.1 M) and ethylene glycol (0.4 M) at 120 °C. The terpolymer resin was characterized by elemental analysis, the number average molecular weight, UV-Visible, IR and ¹H NMR spectrum. Chelating ion-exchange properties of this copolymer were studied for Bi³⁺, Sb³⁺, Zn²⁺ and Mg²⁺ ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurements of the distribution of a given metal ion between the polymer sample and a solution containing the metal ion. The study was carried out over a wide pH range and in media of various ionic strengths. The metal ions were estimated spectrophotometrically. The HBTE-II terpolymer resin was found to be selective chelating ion-exchange resin for Sb³⁺, Bi³⁺ and Zn²⁺.

Keywords: Polycondensation, Ion-exchange, Distribution ratio, Rate of metal ion uptake, Batch-equilibrium method

Introduction

Ion-exchangers are used in great application for selective removal of waste material in nuclear plants, analytical chemistry, hydrometallurgy, separation of radioisotopes, metal pollution control and water treatment¹⁻². Quality of water obtained by an ion - exchange process is like as the de-ionized water and is the best for all industrial purposes, especially boilers, heat exchangers, pharmaceutical industries. Ion-exchangers remove not only heavy metal ions from water but also all positive and negative ions too depending on functional groups on the matrix of exchangers. Synthetic resins derived from hydroxyl and amino compounds have attention of research coworkers because of their versatile use as ion-exchangers, photographic binders and thermal stabilizers³.

Rahangdale *et al.*⁴ synthesized 2,4-dihydroxyacetophenone-dithiooxamide-formaldehyde terpolymer and chelating ion-exchange properties have also been studied employing the batch equilibrium method and reported the overall rate of metal uptake follows the order: Fe³⁺ > Cu²⁺ > Ni²⁺ > Co²⁺ = Zn²⁺.

Azarudeen *et al.*⁵ synthesized phthalic acid-urea-formaldehyde terpolymer resin and proved to be a selective chelation ion-exchange terpolymer for metals. A batch equilibrium method was employed to study the selectivity and sorption capacity of the resin towards certain divalent metal ions such as Pb^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Ba^{2+} , Co^{2+} and Mn^{2+} in various electrolyte concentrations, wide pH ranges and different time intervals. Hence the resin used to recover certain metal ions from waste solutions and for the purpose of purification of wastewater and removal of iron from boiler water.

Pancholi *et al.* synthesized polymer by condensation of 2-hydroxy-4-methoxyacetophenone-thiourea-trioxane⁶. They studied ion-exchange properties of terpolymers for Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+} , Fe^{2+} and UO_2^{2+} ions over the pH range 3.5-5.5 in media of various ionic strengths. They reported that the polymer showed a higher selectivity for Cu^{2+} , Fe^{2+} and UO_2^{2+} ions over any other ion.

The present communication deals with synthesis, characterization and ion-exchange properties of HBTE-II terpolymer resin derived from *p*-hydroxybenzaldehyde, thiourea and ethylene glycol.

Experimental

All chemicals were AR grade or chemically pure grade, *p*-hydroxybenzaldehyde, thiourea, ethylene glycol and polyphosphoric acid were procured from s.d. fine chemicals, India.

Synthesis of HBTE-II terpolymer

A terpolymer resin abbreviated as HBTE-II was synthesized by polycondensation of monomers *p*-hydroxybenzaldehyde, thiourea and ethylene glycol in the presence of polyphosphoric acid. To a well-stirred and ice-cooled mixture of *p*-hydroxybenzaldehyde (0.2 M), thiourea (0.1 M) and ethylene glycol (0.4 M), polyphosphoric acid (PPA) was added slowly with continuous stirring as a catalyst. The reaction mixture was left at room temperature for 30 minutes then heated on oil bath at $120 \pm 2^\circ\text{C}$ for 5.30 h. The reaction mixture was cooled, poured on crushed ice and left over night⁷⁻⁸. The reddish brown solid was separated. The crude product was squeezed with ether so as to remove thiourea-glycol copolymer which might be formed along with HBTE-II. The terpolymer was further purified by dissolving in 0.1 N NaOH solution and reprecipitated by drop wise addition of 1:1 HCl with constant stirring. The product was washed several times with hot water and cold water. The product was air dried and kept in vacuum over silica gel. Yield was found to be 80 %. The scheme of synthesis of HBTE-II is shown in Figure 1.

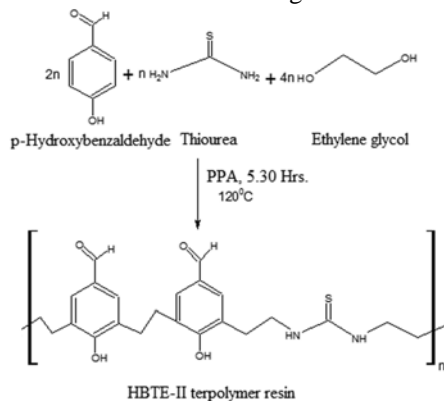


Figure 1. Scheme of synthesis of HBTE-II terpolymer resin

Ion exchange experimental procedures

The ion-exchange property of the HBTE-II terpolymer resin was determined by the batch equilibrium method. Estimation of metal carried out using a spectrophotometer.

Procedure for determination of the effect of electrolyte on metal uptake

The resin sample (25 mg) was suspended in an electrolyte solution of required concentration (25 mL) for 24 h. The pH of the solution was to 6.0 using 0.1 M HNO₃ or 0.1 M NaOH. To this solution 5 mL of 0.1 M metal nitrate solution added at room temperature and pH was adjusted to the required value. The mixture was stirred again at room temperature for 24 hours and filtered. Solids were washed and washings were quantitatively combined with the filtrate. The metal content was determined by a spectrophotometer. The amount of metal exchanged was determined from the difference between reading in blank and actual experiments⁹⁻¹¹. The amounts of metal ion in mg per g of resin were calculated in the presence of NaCl, NaNO₃, NaClO₄ and Na₂SO₄ electrolyte for metal ions Sb³⁺, Bi³⁺, Zn²⁺ and Mg²⁺.

Procedure for evaluation of rate of metal ion uptake

In order to determine optimum time required to reach the equilibrium the experiments were performed as above but here metal ion uptake was estimated as a function of time in hrs in the presence of 1.5 M NaNO₃ solution (25 mL). It was assumed that the equilibrium state was established within 24 h. The rate of metal uptake was expressed in terms of percent metal uptake related to a state of equilibrium¹²⁻¹⁴ by the formula (1).

$$\% \text{ metal uptake} = \frac{\text{mg of metal sorbed in given time}}{\text{mg of metal sorbed in 24 h}} \times 100 \quad (1)$$

Procedure to study the effect of pH on metal uptake

The resin sample 25 mg was allowed to swell for 24 hours in 1.5 M NaNO₃ solution. The pH was adjusted to the required value as above. 5 mL of 0.1 M metal nitrate solution was added. The pH was maintained again and stirred for 24 h. Metal was estimated by a spectrophotometer to determine the distribution ratio (D) between polymer phase and solution phase¹⁵⁻¹⁷. The distribution ratio was calculated by the formula (2),

$$D = \frac{\text{weight (mg) of metal ions taken up by 1 g of polymer}}{\text{weight (mg) of metal ions present in 1 ml of solution}} \quad (2)$$

Results and Discussion

HBTE-II terpolymer resin was reddish brown in color and soluble in DMSO and NaOH solution where as insoluble in acids and common organic solvents.

Elemental analysis and molecular weight determination (\overline{M}_n)

Elemental analysis has been carried out in CIMFR unit, Nagpur, by analytical functional testing Vario MICRO CHN elemental analyzer (Germany). The elemental analysis data of HBTE-II terpolymer are tabulated in Table 1.

Table 1. Elemental analysis data of HBTE-II terpolymer resin

% C		% H		% N		% S		Mol. Formula repeat unit
Calc	Found	Calc	Found	Calc	Found	Calc	Found	
64.77	64.72	6.14	6.10	6.57	6.53	7.52	7.50	(C ₂₃ H ₂₆ N ₂ O ₄ S) _n

The number average molecular weight (\overline{Mn}) was determined by non-aqueous conductometric titration in DMSO using 0.1 M KOH in absolute alcohol as titrant¹⁸. The degree of polymerization (\overline{Dp}) and the number average molecular weight (\overline{Mn}) have been calculated using following equations (3) and (4),

$$\overline{Dp} = \frac{\text{Total Meq of base required for last break}}{\text{Meq of base requires for first break}} \quad (3)$$

$$\overline{Mn} = \overline{Dp} \times \text{Repeat unit weight} \quad (4)$$

The repeating unit weight was obtained from elemental analysis. The molecular weight determination data of HBTE-II terpolymer are tabulated in Table 2.

Table 2. Molecular weight determination data of HBTE-II terpolymer resin

Meq. of KOH/100 g of resin for first break	Meq. of KOH/100 g of resin for last break	\overline{Dp}	Molecular weight of repeat unit	Molecular weight (\overline{Mn})
380	5280	13.90~14	426	5964

IR spectra

IR spectrum of HBTE-II terpolymer was recorded at department of pharmacy, RTM Nagpur University, Nagpur, using FT-IR spectrophotometer, Shimadzu, model No-8101A. FT-IR spectrum of synthesized terpolymer is shown in Figure 2.

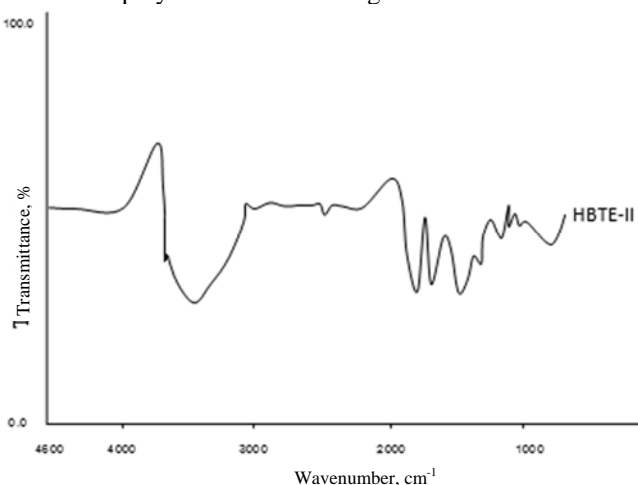


Figure 2. IR-spectra of HBTE-II terpolymer resin

A medium peak at 3575 cm^{-1} was clearly due to N-H stretching of secondary amide group. A broad absorption band appeared in the region 3434 cm^{-1} was assigned to the stretching vibrations of phenolic hydroxyl (-OH) group exhibiting intermolecular hydrogen bonding. The presence of peaks at 2745, 2916 cm^{-1} was due to the -C-H- stretch in the aldehyde (doublet due to Fermi resonance). The peaks at 1686 cm^{-1} and 1655 cm^{-1} assigned due to the C=O band (an aldehyde). The presence of peak at 1601 cm^{-1} was due to aromatic ring. The N-H bends and C-N were stretching band at 1560 cm^{-1} also be observed. A sharp medium peak at 1509 cm^{-1} was ascribed to N-H bending of secondary amide group. A peak appeared at 1458 cm^{-1} was due to methylene bridge coupled with aromatic ring. A peak

appeared at 1383 cm^{-1} was assigned to in plane bending vibration of phenolic $-\text{OH}$. 1345 cm^{-1} appeared due to aldehyde C-H bend. 1, 2, 3, 5- tetra substitution of aromatic ring was assigned due to the peaks at 1220 , 1080 and 963 cm^{-1} . The bands appeared at 1297 cm^{-1} and 1285 cm^{-1} were attributed to C-N stretching in secondary amide. A strong peak appeared at 1200 cm^{-1} was due to C=S stretching vibration. The presence¹⁹⁻²⁰ of peak at 831 cm^{-1} was due to the $-\text{CH}_2-$ (wagging). IR spectrum data of HBTE-II terpolymer is tabulated in Table 3.

Table 3. IR spectrum data of HBTE-II terpolymer resins

Observed frequency, cm^{-1}	Assignment
3575 (m)	NH-stretching– secondary amide
3434 (b)	Phenolic $-\text{OH}$ group with intermolecular polymeric association
2745 (w), 2916 (m)	C-H stretches in aldehyde (doublet due to Fermi resonance)
1686 (m), 1655 (s)	C=O band (aldehyde)
1601 (w)	Aromatic-ring
1560 (w)	N-H bending
1509 (s)	Secondary amide
1458 (m)	CH_2 bending
1383 (m)	Phenolic $-\text{OH}$ in plane bending
1345 (m)	Aldehydic C-H bending
1297(w), 1285 (m)	C-N stretching band $-\text{CSNH-}$
1220 (m), 1080 (m), 963 (w)	1,2,3,5 tetra substituted aromatic ring
1200 (s)	C=S stretching vibration
831 (w)	$-\text{CH}_2-$ wagging

(b) = Broad, (s) = Sharp, (w) = Weak, (m) = medium

^1H NMR spectrum

^1H NMR spectrum of HBTE-II terpolymer using DMSO-d_6 solvent was scanned on NMR spectrophotometer SAIFNM100820A, at Sophisticated Test and Instrumentation Center (STIC), Cochin University, Kerala, India. The ^1H NMR spectrum of HBTE-II terpolymer is shown in Figure 3.

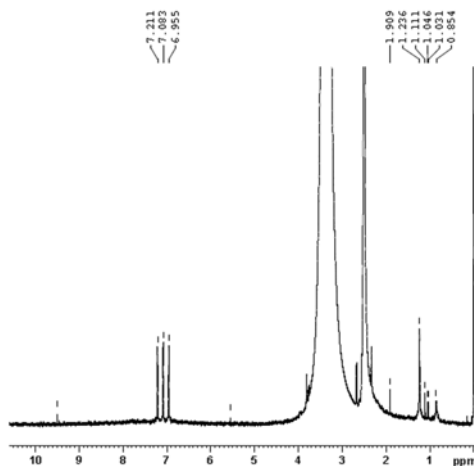


Figure 3. ^1H NMR spectra of HBTE-II terpolymer resin

A signal at 2.5 δ ppm was due to DMSO solvent. The medium singlet at 2.6 δ ppm due to the methylene proton of the Ar-CH₂ bridge. A singlet observed in the region 3.8 δ ppm was due to the methylene proton of an Ar-CH₂-NH moiety. A singlet observed in the region 5.5 δ ppm attributed to the protons in -NH linkage. The peaks in the region of 7.1 δ ppm assigned to the protons in the aromatic ring. The signal at 9.5 δ ppm was assigned to the -OH group of Ar-OH and it indicates the intramolecular hydrogen bonding between -OH group of Ar-OH and -NH group of the terpolymer resin²¹⁻²³.

UV-Visible spectrum

UV-Visible spectrum of HBTE-II terpolymer in DMSO solvent recorded by UV-Visible double beam spectrophotometer, Shimadzu, model-1800 at the department of nanotechnology, Shivaji Science College, Nagpur. The electronic spectrum of the HBTE-II terpolymer is shown in Figure 4 and UV-Visible spectrum data is presented in Table 4.

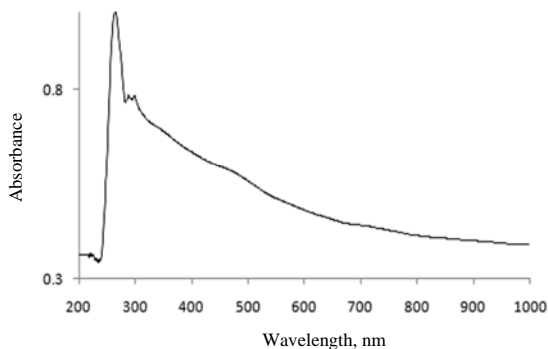


Figure 4. UV-Visible spectra of HBTE-II terpolymer resin

A peak at 220.5 nm was assigned to $n-\sigma^*$ transition was due to C-NH- moiety and peak at 264.5 nm was assigned to $\pi-\pi^*$ due to the aromatic ring. $n-\pi^*$ transitions at 288.0 nm and 298.0 nm, these were due to $>C=S$ in amide linkage and -CHO moiety²⁴.

Table 4. UV-Visible spectrum data of HBTE-II terpolymer

Transition	Wavelength, nm	Group / moiety assigned
$n-\sigma^*$	220.5	C-NH- moiety
$\pi-\pi^*$	264.5	Aromatic ring
$n-\pi^*$	288.0	$>C=S$ in amide linkage
$n-\pi^*$	298.0	-CHO group

Ion-exchange properties

To ascertain the selectivity of HBTE-II, The ion-exchange properties of resin were studied with reference to the influence of various electrolytes, the rate of metal uptake and distribution of metal ions between the resin and solution. The results of the batch equilibrium study carried out with the HBTE-II terpolymer resin is presented in Table 5-6 and in graph Figure 5. Estimation of metal carried out using a spectrophotometer.

Effect of electrolytes on the metal uptake

Effect of electrolyte on metal uptake is summarized in Table 5. The inspection of the data reveals that the amount of metal ions taken up in the presence of NaNO₃ is larger than NaCl, Na₂SO₄ and NaClO₄. For the metal ions Sb³⁺, Bi³⁺, Mg²⁺ and Zn²⁺, the exchange capacity

increases with increases in the concentration of NO_3^- , ClO_4^- and Cl^- , whereas it decreases with increases in concentration of SO_4^{2-} . This is due to the fact that metal ions under study form kinetically more inert compound with respect to SO_4^{2-} as compared to metal-resin interaction. On a contrary increase in the metal exchange capacity of metal resin in the presence of NO_3^- , ClO_4^- and Cl^- attributed to high kinetically inert metal-resin interaction as compared to metal-electrolyte interactions²⁵⁻²⁷.

Table 5. Effect of different electrolytes on the uptake of several metal ions on HBTE-II resin

Metal ion	Electrolyte Conc. Mol/L	Wt. of metal ion (mg) exchanged per of gram resin in the presence of different electrolytes			
		NaCl	Na_2SO_4	NaClO_4	NaNO_3
Sb^{3+}	0.25	19.65	22.96	16.10	18.74
	0.50	20.46	20.34	16.96	20.09
	0.75	21.70	19.71	19.32	22.52
	1.00	21.95	18.68	19.63	23.71
	1.25	23.30	17.19	20.80	25.24
	1.50	24.28	15.44	22.07	25.51
Bi^{3+}	0.25	9.60	12.66	7.50	7.08
	0.50	10.95	11.66	9.16	8.68
	0.75	12.49	10.66	11.29	10.53
	1.00	13.45	9.20	12.43	12.41
	1.25	15.24	8.34	14.63	14.85
	1.50	16.55	7.87	16.09	17.08
Mg^{2+}	0.25	4.02	8.78	3.46	4.48
	0.50	4.76	8.17	3.87	5.24
	0.75	5.50	7.62	4.31	6.17
	1.00	6.54	6.90	5.17	7.14
	1.25	7.38	6.47	5.81	8.27
	1.50	8.18	5.93	6.66	9.38
Zn^{2+}	0.25	7.74	9.67	7.11	8.68
	0.50	8.44	9.51	8.05	9.79
	0.75	9.25	8.40	8.55	10.20
	1.00	9.93	7.04	9.44	10.60
	1.25	10.46	6.65	10.25	11.20
	1.50	10.96	6.42	10.51	11.30

Metal nitrate solution = 0.1 Mol/L, 5 mL; Electrolyte= 25 mL; Equilibrium state= 24 h; Wt. of resin=25 mg; Temperature = Room temperature; Metal ions were estimated spectrophotometrically, Error= $\pm 1.5\%$

Rate of metal uptake

From the graph present in Figure 5, initially the rate of metal uptake was steeply increased, become gradual and finally remain constant as the time passes for all metal ions. For Sb^{3+} and Mg^{2+} the equilibrium was reached within 7 h whereas for Bi^{3+} and Zn^{2+} , the time required to reach equilibrium was 6 h. The rates of metal uptake for trivalent metal ions (Bi^{3+} and Sb^{3+} ions) were higher than divalent metal ions (Mg^{2+} and Zn^{2+} ions)²⁸⁻³⁰. The rate of metal ion uptake decreases in order $\text{Bi}^{3+} > \text{Sb}^{3+} > \text{Zn}^{2+} > \text{Mg}^{2+}$.

Distribution ratio of metal ions at different pH

The effect of pH on a distribution ratio of metal ions between resin and solution phase can be explained by Table 6. The study was carried out in the limit of higher pH in order to

prevent hydrolysis of metal ions³¹. Distribution ratios for Mg^{2+} and Zn^{2+} ions were found to increase with increases in pH values. However reverse effect of pH was observed on distribution ratios for Sb^{3+} and Bi^{3+} ions.

At pH 4, the order of distribution ratio in HBTE-II resin was decreasing as $Bi^{3+} > Sb^{3+} > Zn^{2+} > Mg^{2+}$. At pH 5 and 6, the order of distribution ratio was same as follows $Zn^{2+} > Mg^{2+} > Sb^{3+} > Bi^{3+}$. At pH 7, the order of distribution ratio was $Zn^{2+} > Mg^{2+} > Bi^{3+} > Sb^{3+}$.

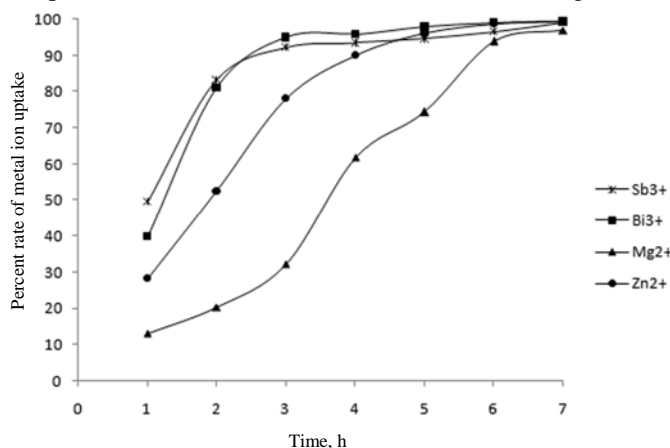


Figure 5. Metal ion uptake of HBTE-II terpolymer resin

Table 6. Distribution ratio (D) of different metal ions as a function of the pH

pH	Distribution ratio of the metal ion			
	Sb^{3+}	Bi^{3+}	Mg^{2+}	Zn^{2+}
4	129	450.7	96	117
5	155	114.8	157	209
6	95	91.7	215	464
7	39	44.5	302	559

Metal nitrate solution = 0.1 Mol/L, 5 mL; Electrolyte = $NaNO_3$, 1.5 M, 25 mL; Equilibrium state = 24 h; Wt. of resin = 25 mg; Temperature = Room Temperature; Error = $\pm 1.5\%$, Metal ions were estimated spectrophotometrically

Conclusion

The data of elemental analysis, FT-IR spectra, ¹H NMR spectra and UV-Visible spectra supports the structure of HBTE-II terpolymeric resin. Among the electrolytes such as $NaNO_3$, $NaCl$, $NaClO_4$ and Na_2SO_4 , the $NaNO_3$ are found to be more suitable electrolyte supporting to the ion exchange of metal ion under study by HBTE-II resin. Trivalent metal ion shows comparatively higher rates of metal uptake than divalent. This may be due to electrostatic assistance to ion exchange process. HBTE-II terpolymer resin is a selective chelating ion exchange resin for metals as Bi^{3+} ions at pH 4 and Zn^{2+} ions at pH 5 to 7 in the mixture of Sb^{3+} , Bi^{3+} , Mg^{2+} and Zn^{2+} metal ions. The HBTE-II resin may be used to separate Zn^{2+} and Bi^{3+} metal ions. Similarly it may be used to preconcentrate Sb^{3+} from the solution containing Sb^{3+} and Bi^{3+} .

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