

SYNTHESIS, CHARACTERIZATION AND ION-EXCHANGE PROPERTIES OF TERPOLYMER RESIN-I DERIVED FROM p-HYDROXYBENZALDEHYDE, THIOUREA AND ETHYLENE GLYCOL

AMIT N. GUPTA^a, VINAY V. HIWASE^b, N. T. KHATY^c, ASHOK B. KALAMBE^d

^aDepartment of Chemistry, J.D. College of Engineering & Management, Nagpur, India

^bDepartment of Chemistry, Arts, Commerce and Science College, Arvi, Wardha, India

^cRashtrasant Tukadoji Maharaj Nagpur University, Nagpur, India

^dDepartment of Chemistry, Institute of Science, R. T. Road, Nagpur, India

angupta2020@gmail.com

Abstract: Ion-exchange resin abbreviated as HBTE-I was synthesized by polycondensation in the presence of polyphosphoric acid as a catalyst using monomers p-hydroxybenzaldehyde (0.1M), thiourea (0.1M) and ethylene glycol (0.3M) 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 Bi(III), Sb(III), Zn(II) and Mg(II) 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-I terpolymer resin was found to be selective chelating ion-exchange resin for Sb(III), Bi(III) and Zn(II).

Key words: Terpolymer, Ion-exchange, Distribution ratio, Rate of metal ion uptake, Batch-equilibrium method.

INTRODUCTION:

Ion-exchange technique can be used to remove traces of ionic impurities from water/process liquors and gives out a product of ultra pure quality in a simple efficient and technoeconomically viable manner. Diversified processes and methods are being applied for the production of polymer which are shown extremely dependable characteristics which open up new challenges in modern society today (Rahangdale *et al.*, 2012). 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 treatment (Kapse *et al.*, 2013).

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

MATERIALS AND METHODS :

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-I terpolymer: A terpolymer resin abbreviated as HBTE-I 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 (0.1M), thiourea (0.1M) and ethylene glycol (0.3M), 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°C ± 2°C for 5.30 hrs. The product was washed

several times with hot water and cold water (Gupta *et al.*, 2012,a). The product was air dried and kept in vacuum over silica gel. Yield was found to be 77 %. The scheme of synthesis of HBTE-I is shown in figure 1.

Figure 1: Scheme of synthesis of HBTE-I terpolymer resin

Ion exchange experimental procedures
The ion-exchange property of the HBTE-I 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 hrs. 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 experiments. The amounts of metal ion in mg per gm of resin were calculated in the presence of NaCl, NaNO₃, NaClO₄ and Na₂SO₄ electrolyte for metal ions Sb(III), Bi(III), Zn(II) and Mg(II).

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 hrs. The rate of metal uptake was expressed in terms of percent metal uptake related to a state of equilibrium by the formula (1).

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

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 hrs. Metal was estimated by a spectrophotometer to determine the distribution ratio (D) between polymer phase and solution phase. The distribution ratio was calculated by the formula (2),

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

RESULTS AND DISCUSSION :

Elemental analysis and molecular weight determination (M_n): The elemental analysis and molecular weight determination data of HBTE-I terpolymer are tabulated in table 1.

Table 1: Elemental analysis and molecular weight determination data of HBTE-I terpolymer resin.

UV-Visible spectra of HBTE terpolymer resins : In figure 2, HBTE-I, A peak at 220.5 nm was assigned to n-σ* transition was due to C-NH- moiety and peak at 263.0 nm was assigned to π-π* due to aromatic ring. n-π* transitions at 287.5 nm and 299.0 nm, these were due to >C=S and -CHO moiety (Gupta *et al.*, 2012,b).

Figure 2: UV-Visible spectra of HBTE-I terpolymer resin
IR spectra of HBTE-I terpolymer resins: In figure 3, HBTE-I, A medium peak at 3578 cm⁻¹ was clearly due to N-H stretching of secondary amide group. A broad absorption band appeared in the region 3435 cm⁻¹ was assigned to the stretching vibrations of phenolic (-OH) group exhibiting intermolecular hydrogen bonding. (Gupta *et al.*, 2013,a) The peaks at 1682 cm⁻¹ and 1655 cm⁻¹ were due to C=O band (aldehyde). The N-H bending at 1560 cm⁻¹ was observed (Gupta *et al.*, 2014,a). A peak appeared at 1462 cm⁻¹ was due to methylene bridge coupled with aromatic ring. The bands appeared at 1295 cm⁻¹ and 1284 cm⁻¹ were attributed to C-N stretching in CSNH-. 1, 2, 3, 5- tetra substitution of aromatic ring were assigned due to the peaks at 1220, 1095 and 973 cm⁻¹. A strong peak appeared at 1200 cm⁻¹ was due to C=S stretching vibration. The presence of peak at 831 cm⁻¹ was due to the -CH₂- (wagging) (Gupta *et al.*, 2014,b).

Figure 3: IR spectra of HBTE-I terpolymer resin

¹H NMR spectra of HBTE terpolymer resins: In figure 4, the medium singlet at 2.8 δ ppm due to the methylene proton of the Ar-CH₂ bridge (Gupta *et al.*, 2014,c). A singlet observed in the region 3.9 δ ppm was due to the methylene proton of an Ar-CH₂-NH moiety (Gupta *et al.*, 2015,a). A singlet observed in the region 5.6 δ ppm attributed to the protons in -NH linkage. The peaks in the region of 6.9 δ ppm assigned to the protons in the aromatic ring. The signal at 9.3 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 resin (Gupta *et al.*, 2016).

Figure 4: ¹H NMR spectra of HBTE-I terpolymer resin
Ion-exchange properties: To ascertain the selectivity of HBTE-I, 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. Estimation of metal carried out using a spectrophotometer (Gupta *et al.*, 2013,b).

Effect of electrolytes on the metal Uptake: Effect of electrolyte on metal uptake is summarized in Table 2. 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 Sb(III), Bi(III), Mg(II), Zn(II), the exchange capacity increases with increases in the concentration of NO₃⁻, ClO₄⁻ and Cl⁻, whereas it decreases with increases in concentration of SO₄²⁻. This is due to the fact that metal ions under study form kinetically more inert compound with respect to SO₄²⁻ as compared to metal-resin interaction. On a contrary increase in the metal exchange capacity of metal resin in the presence of NO₃⁻, ClO₄⁻ and Cl⁻ attributed to high kinetically inert metal-resin interaction as compared to metal-electrolyte interactions (Gupta *et al.*, 2014,d).

Table 2: Effect of different electrolytes on the uptake of several metal ions on HBTE-I resin.

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(III) and Mg(II) the equilibrium was reached within 7 hours whereas for Bi(III) and Zn(II), the time required to reach equilibrium was 6 hrs. The rates of metal uptake for trivalent metal ions [Bi(III) and Sb(III) ions] were higher than divalent metal ions [Mg(II) and Zn(II) ions] (Gupta *et al.*, 2015,b). The rate of metal ion uptake decreases in order Bi(III) > Sb(III) > Zn(II) > Mg(II).

Figure 5: Rate of metal ion uptake of HBTE-I terpolymer resin

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 figure 6. The study was carried out in the limit of higher pH in order to prevent hydrolysis of metal ions (Rahangdale *et al.*, 2013). Distribution ratios for Mg(II) and Zn(II) ions were found to increase with increases in pH values. However reverse effect of pH was observed on distribution ratios for Sb(III) and Bi(III) ions.

At pH 4, the order of distribution ratio in HBTE-II resin was decreasing as Bi(III) > Sb(III) > Zn(II) > Mg(II). At pH 5 and 6, the order of distribution ratio was same as follows Zn(II) > Mg(II) > Sb(III) > Bi(III). At pH 7, the order of distribution ratio was Zn(II) > Mg(II) > Bi(III) > Sb(III).

Figure 6: Distribution ratio (D) of different metal ions as a function of the pH

Table 1: Elemental analysis and molecular weight determination data of HBTE-I terpolymer resin.

%C		%H		%N		%S		Mol. Formula repeat unit	\overline{Dp}	Molecular Weight of Repeat Unit	Molecular Weight (\overline{Mn})
Calc	Found	Calc	Found	Calc	Found	Calc	Found				
60.43	60.43	6.47	6.07	10.07	10.15	11.51	11.73	$(C_{14}H_{17}O_2N_2S)_n$	11.2~11	277	3047

Table 2: Effect of different electrolytes on the uptake of several metal ions on HBTE-I resin.

Metal ion	Electrolyte Conc. (Mol/l)	Wt. of metal ion (mg) exchanged per of gram resin in the presence of different electrolytes				Metal ion	Electrolyte Conc. (Mol/l)	Wt. of metal ion (mg) exchanged per of gram resin in the presence of different electrolytes			
		NaCl	Na ₂ SO ₄	NaClO ₄	NaNO ₃			NaCl	Na ₂ SO ₄	NaClO ₄	NaNO ₃
Sb(III)	0.25	18.97	22.46	15.13	18.22	Mg(II)	0.25	3.82	8.17	3.25	4.24
	0.50	19.49	19.99	16.28	19.21		0.50	4.46	7.88	3.56	5.07
	0.75	21.25	18.81	18.61	21.92		0.75	5.24	7.38	4.07	6.23
	1.00	21.73	18.10	19.20	22.72		1.00	5.79	6.72	4.81	6.90
	1.25	22.60	16.93	20.01	24.60		1.25	6.56	6.25	5.65	7.53
	1.50	23.60	14.92	21.75	25.38		1.50	7.38	5.74	6.41	8.50
Bi(III)	0.25	6.08	12.51	7.32	6.90	Zn(II)	0.25	7.55	9.10	6.81	8.15
	0.50	8.09	11.50	8.99	8.50		0.50	8.22	8.52	7.63	8.50
	0.75	9.71	9.88	10.85	10.33		0.75	9.12	7.50	8.39	9.31
	1.00	10.77	8.94	12.28	12.22		1.00	9.75	6.85	9.29	9.87
	1.25	11.66	8.08	14.45	14.74		1.25	10.31	6.48	10.07	10.49
	1.50	13.47	7.69	15.73	16.86		1.50	10.79	6.25	10.31	11.10

Metal nitrate solution = 0.1 Mol/l, 5ml; Electrolyte= 25 ml; Equilibrium state= 24hrs; Wt. of resin=25 mg; Temperature = Room Temperature; Metal ions were estimated spectrophotometrically, Error= ± 1.5 %

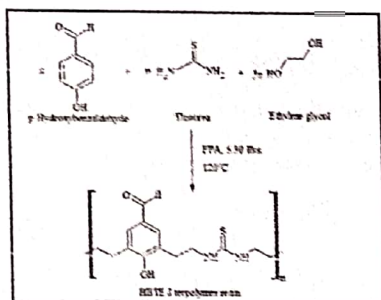


Figure 1: Scheme of synthesis of HBTE-I

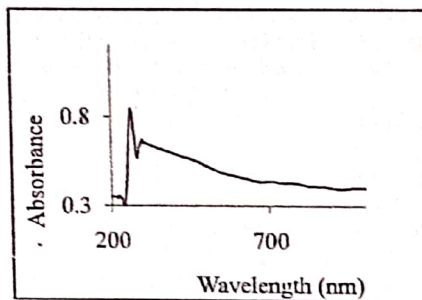


Figure 2: UV-Visible spectra of HBTE-I

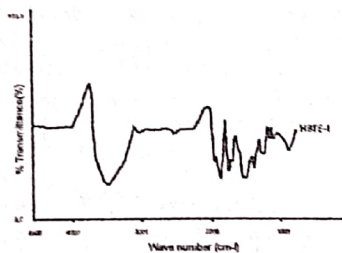


Figure 3: IR spectra of HBTE-I

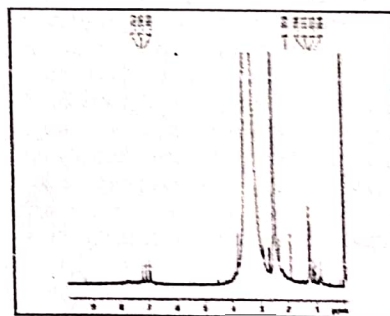


Figure 4: ¹H NMR spectra of HBTE-I

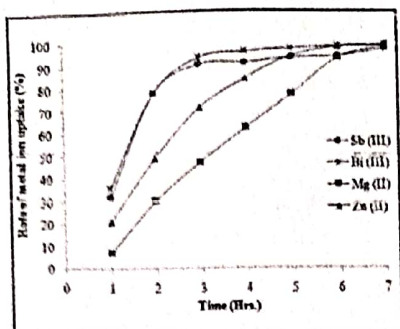


Figure 5: Rate of metal ion uptake of HBTE-I

CONCLUSION :

The data of elemental analysis, FT-IR spectra, ¹H NMR spectra and UV-Visible spectra supports the structure of HBTE-I terpolymeric resin. Among the electrolytes such as NaNO₃, NaCl, NaClO₄, and Na₂SO₄, the NaNO₃ are found to be more suitable electrolyte supporting to the ion exchange of metal ion under study by HBTE-I 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-I terpolymer resin is a selective chelating ion exchange resin for metals as Bi(III) ions at pH 4 and Zn(II) ions at pH 5 to 7 in the mixture of Sb(III), Bi(III), Mg(II) and Zn(II) metal ions. The HBTE-I resin may be used to separate Zn(II) and Bi(III) metal ions. Similarly it may be used to preconcentrate Sb(III) from the solution containing Sb(III) and Bi(III).

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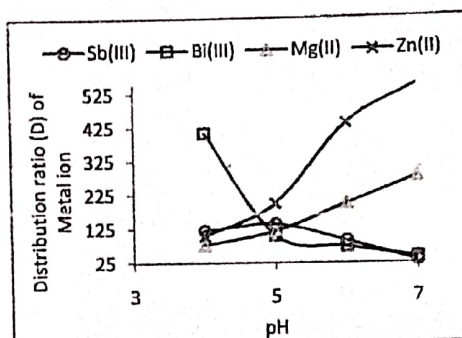


Figure 6: Distribution ratio (D) of different metal ions as a function of the pH

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