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Surface morphological study and kinetics of removal of As^{+3} metal ion on terpolymer resin by Batch equilibrium Method.

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ABSTRACT

Terpolymer resin (BPEDF-2) has been synthesized by the condensation of 2, 2'-biphenol and ethylenediamine with formaldehyde in 2:1:3 proportion in the presence of 2M HCl as a catalyst. The number average molecular weight of terpolymer resins has been determined by conductometric titration in nonaqueous medium. Viscometric measurement in dimethyl formamide has been carried out with a view to ascertain the characteristic functions and constants. Terpolymer resin composition has been determined on the basis of their elemental analysis. The structure of terpolymer resin has been elucidated on the basis of IR, NMR, UV-Visible spectral studies. The surface morphological feature of the BPEDF terpolymer resin was established by scanning electron microscopy (SEM). The concentration of different toxic metals has increased beyond environmentally and ecologically permissible lends due to increase in industrial activity. Many of the waste streams contain As (III) which can be removed by ion exchange method. 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 terpolymer sample and the solution containing the metal ion. The study was carried out over a wide pH range and in media of various ionic strengths.

Keywords: Synthesis; BPEDF-2; Terpolymer Resin; Characterisation; Spectral Study; SEM Study; batch equilibrium method.

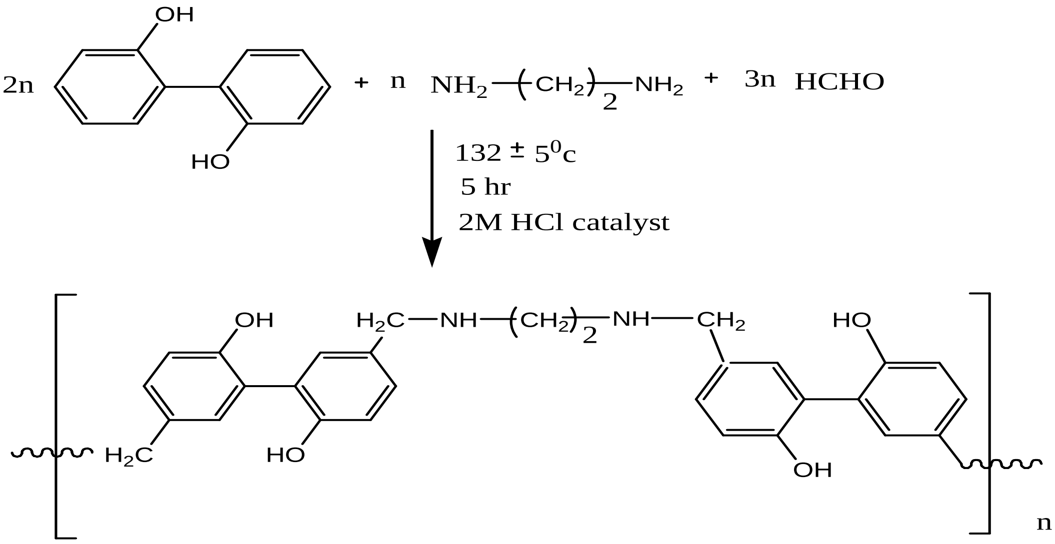
INTRODUCTION

Arsenic is widely distributed in nature in air, water and soil. Acute and chronic arsenic exposure via drinking water has been reported in many countries, especially Argentina, Bangladesh, India, Mexico, Mongolia, Thailand and Taiwan, where a large proportion of ground water is contaminated with arsenic. Batch equilibrium method is one of the process for the removal of various harmful poisonous ions by using ion exchange technique[1- 3]. The use of terpolymers in all spheres of life has been abundantly increased in recent years because of its novelty and versatile practical application as Ion exchangers[1- 3, 10,11,15,16]. Ion exchangers play an important role in pollution control, in antibiotic purification, analytical chemistry, hydrometallurgy, separation of radioisotopes and in large scale water treatment[4]. Ion exchange technique can remove traces of ionic impurities from water / process liquors and gives out a product of ultra pure quality in a simple efficient and techno-economically visible manner[3, 5]. Ion exchangers are widely used in water treatment and pollution control[5, 6]. Terpolymer resins are found to be amorphous crystalline or resinous in nature[7]. Ion-exchange resins refer to synthetic organic substances of high molecular weight. They replace certain negative or positive ions that they encounter in solutions[8]. Deepti b. Patle and coworkers have been studied the synthesis, characterisation, ion exchange properties and surface study of terpolymer derived from 4-hydroxybenzophenone, biuret and formaldehyde, from the surface study of this terpolymer it reveals that the resin shows more amorphous nature and thus it has higher exchange capacity for metal ions[9]. Ion exchange study of salicylic acid - naphthalene diamine – formaldehyde resin has been reported by Dhanraj t. Masram and coworkers[10]. M. M. Jadhao and coworkers synthesized a polymer resins by the condensation of 2, 2'-dihydroxybiphenyl with substituted carbamide and formaldehyde[11-17] in presence of acid catalyst. The chelating ion exchange properties of these polymers have been studied for various metal ions by batch equilibrium method[11, 15-17]. In which, metal uptake in the presence of various electrolytes, rate of metal uptake, distribution of metal ions at different pH has been studied. In this present communication we report synthesis, characterization, surface morphological study, and kinetics of removal of As^{+3} by 2, 2'-biphenol-etylenediamine-formaldehyde (BPEDF-II) terpolymer resin.

MATERIALS AND METHODS

All the chemicals used were of analytical grade or pure grade. 2, 2'-dihydroxybiphenyl (Aldrich chem.) ethylene diamine, formaldehyde, dimethyl formamide, dimethylsulphoxide (all from Merk) were used.

A mixture of 2, 2'-biphenol, ethylene diamine, and formaldehyde in 2:1:3 molar proportion in the presence of 2M HCl was refluxed in an oil bath at $132^0c \pm 5^0c$ for 5 hr with occasional shaking. The 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 with hot water, dried in a vacuum desicator over anhydrous calcium chloride and ground to a powder with the help of an agated mortar and pestle. The yield of this terpolymer resin was found to be 67%. The reaction taking place in the synthesis of BPEDF-2 terpolymer resin is as shown in scheme 1:



Scheme 1: Synthesis of BPEDF-2 terpolymer resin.

1. Characterisation of the Terpolymer Resin

The number average molecular weights (Mn) were determined by conductometric titration in DMF using KOH in alcohol as a titrant. The viscosity measurement studies were done by using a Tuan-Fuoss viscometer at six different concentrations (3.0% to 0.5%) in DMF at 30^0c. The terpolymer resin was subjected to elemental analysis for C, H, and N by using a ThermoFinnigan CHNSO Analyser (Italy), FLASHEA 1112 series. Infrared spectrum was recorded in the region of 600-4000 cm^{-1} on Nicolet Instruments corporations (USA), Model MAGNA 550. The electronic absorption spectrum was recorded on a Shimadzu double beam spectrophotometer in the range of 200-1200 nm. NMR studies in dimethylsulphoxide as a solvent, was carried out on BRUKER AVANCE II 400 NMR spectrophotometer. The surface morphology of the gold coated pellets of terpolymer resin was examined at different magnification using scanning electron microscope at JNARDDC, Wadi, Nagpur. The removal of arsenic by BPEDF-2 (2:1:3) terpolymer resin was determined by the batch equilibrium method.

1.1. Adsorption of As^{+3} by batch equilibrium method

The resin sample (25 mg) was suspended in an electrolyte solution (25 ml) of known concentration. The pH of the suspension was adjusted to the required value by using either 0.1M HNO_3 or 0.1 M NaOH. The suspension was stirred for 24 hr at 25^0c. To this suspension, 2 ml of 0.1 M As^{+3} ion solution was added and the pH was adjusted. The mixture was again stirred at 25^0c for 24 hr and filtered. The solid was washed and the filtrate and washing was combined. It is then titrated against standard EDTA. The amount of As^{+3} ion uptake of the BPEDF-2 terpolymer resin was calculated from the difference between a blank experiment without resin and the reading in the actual experiment the experiment was repeated in the presence of several electrolytes[10,11,15-17].

After the influence of different electrolytes on the uptake of As^{+3} metal ion on BPEDF-2 terpolymer resin at 25^0c, the rate of As^{+3} ion uptake on the BPEDF terpolymer resin was determined. The metal ion uptake by the chelating resin was determined at time interval of 1 hr at 25^0c in the presence of 25 ml 1M $NaNO_3$ solution. It was assumed that under the given conditions, the state of equilibrium was established within 24 hr. The rate of As^{+3} metal ion uptake is expressed as the percentage of the amount of the metal ion taken up after a certain time related to that at the state of equilibrium.

The rate of As^{+3} ion uptake on the BPEDF terpolymer resin is determined by the following formula[16]:

$$\text{Metal ion uptake} = \frac{\text{amount of metal ion absorbed X 100}}{\text{amount of metal ion at equilibrium}}$$

The distribution of As^{+3} metal ion between the polymer phase and the aqueous phase was determined at 25^0c in the presence of 1M NaNO3 at different pH values. The distribution ratio (D) is defined by the following relationship[10, 11, 15-17]:

$$D = \frac{\text{Weight of As} + 3 \text{ metal ion taken up by 1g of BPEDF} - 2 \text{ terpolymer resin}}{\text{Weight of As} + 3 \text{ metal ion present in 1ml of solution}}$$

RESULTS AND DISCUSSION

The resin sample was light pink in colour. It is Insoluble in commonly used organic solvents but partly soluble in DMF and DMSO. The terpolymer resin does not show a sharp melting point but undergo decomposition above 320^0c. The synthesized terpolymer resin was analysed for carbon, hydrogen and nitrogen content. The composition of the synthesized terpolymer resin obtained on the basis of the elemental analysis for carbon, hydrogen and nitrogen content was found to be in good correlation to that of the calculated value.

Calculated value for BPEDF-2 resin: -	C: 62.74%; H: 7.19%; N: 9.15%
Observed value for BPEDF-2 resin: -	C: 62.43%; H: 7.13%; N: 9.08%

1.2. Molecular weight determination by conductometric titration.

The molecular weight (Mn) of the terpolymer resin was determined by nonaqueous 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. The conductometric titration curve is depicted in Figure1:

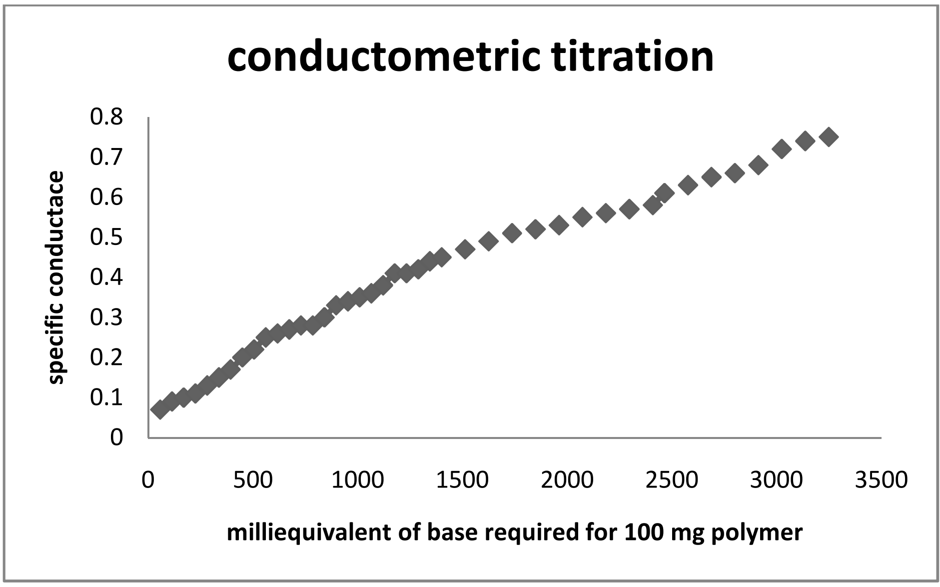


Figure 1: Conductometric Titration Curve of BPEDF-2 Terpolymer Resin.

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[10, 12, 13,30,31].

(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.

The average degree of polymerization (Dp) is given by relation.

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

The number average molecular weight (Mn) could be obtained by multiplying the Dp by the formula weight of the repeating unit[18]. The first and the last break were noted at 112 and 2464. The average degree of polymerization is found to be 22. The number average molecular weight (Mn) is 11,484.

4.2. Viscometric titration

Viscometric measurement was carried out in DMF at 30°C. BPEDF-II resin showed normal behaviour. The intrinsic viscosity was determined by the Huggins[19] equation and the Kraemers[20] equation.

$\eta_{sp} / C = [\eta] + k_1 [\eta]^2 C$ (1)
$\ln \eta rel / C = [\eta] - k_2 [\eta]^2 C$ (2)

From the Huggins and Kraemers equation, ηsp / C and ηrel / C against C were plotted as shown in figure 2, which is 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 is found to be satisfy the relation k1 + k2 = 0.5 favorably[12]. The intrinsic viscosity is found to be 0.073. The values of [η] obtained from Eqs. (1) and (2) were in close agreement with each other.

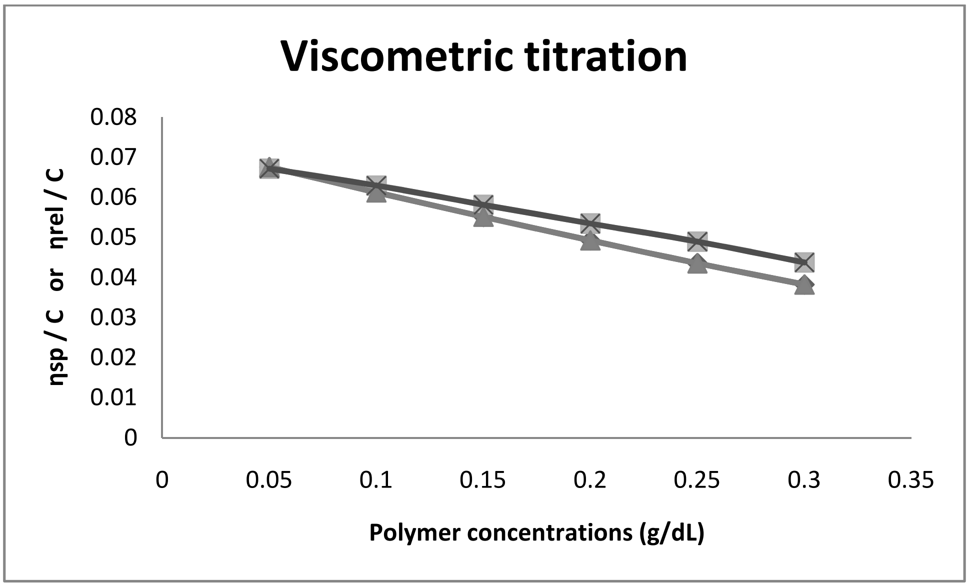


Figure 2: Viscometric Plot of BPEDF-2 Terpolymer Resin

4.3. Spectral studies

The electronic spectrum of this terpolymer resin is depicted in figure 3. The spectrum shows three absorption maxima in the region 230-420 nm. The intense band at 230-250 nm is due to the C-O of the phenolic – OH groups in terpolymer resin and was assigned to ($n \rightarrow \sigma^*$) transition[21]. The intense band at 270-300 may be due to the ($\pi \rightarrow \pi^*$) allowed transition of biphenyl moiety[21-25]. The intense band at 350-420 nm may be due to ($n \rightarrow \pi^*$) transition for the presence of the phenolic hydroxyl group (auxochrome)[22-25].

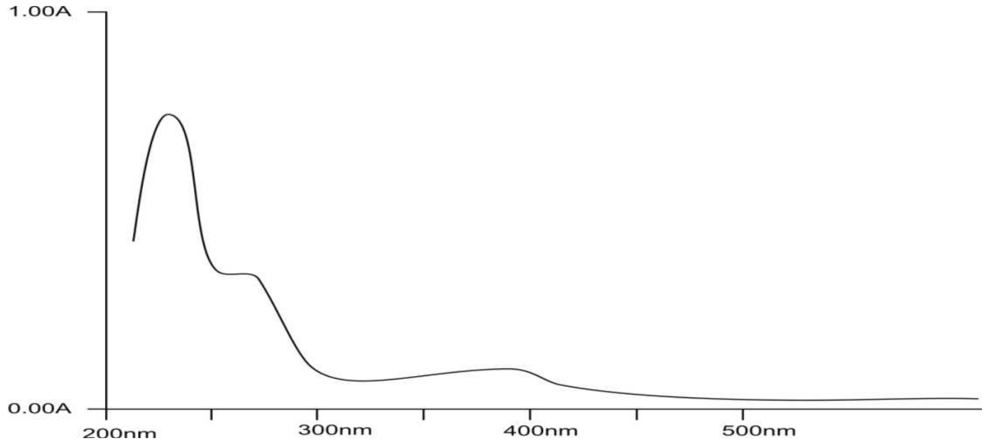


Figure 3: Electronic Spectra of BPEDF-2 Terpolymer Resin

The IR spectrum of this terpolymer resin is shown in figure 3, and the spectral data is shown in table 3. A broad band appearing in the region 3455.13 cm^{-1} may be assigned to a stretching vibrations of phenolic –OH groups[21, 22, 25]. The band at 2923.51cm^{-1} may be due to –NH- stretching[21, 22]. The band at 1600.7 cm^{-1} may be ascribed to an aromatic skeletal ring[23]. The presence of methylene bridges (-CH2-) in the polymeric chain may be assigned to the presence of a band at 1447.12 cm^{-1}, 1324.72 cm^{-1} and 751.56 cm^{-1} [-CH2- bending, wagging and rocking] [21-27]. The bands obtained at 935 cm^{-1}, 1025.18 cm^{-1}, and 1112.96 cm^{-1} suggest that the aromatic rings are 1, 2, 3, 5 [21-25] substituted. The 1, 2, 3, 5 substitution of the benzene ring is also confirmed by the presence of band at 900cm^{-1} and 827.19 cm^{-1} [21-25].

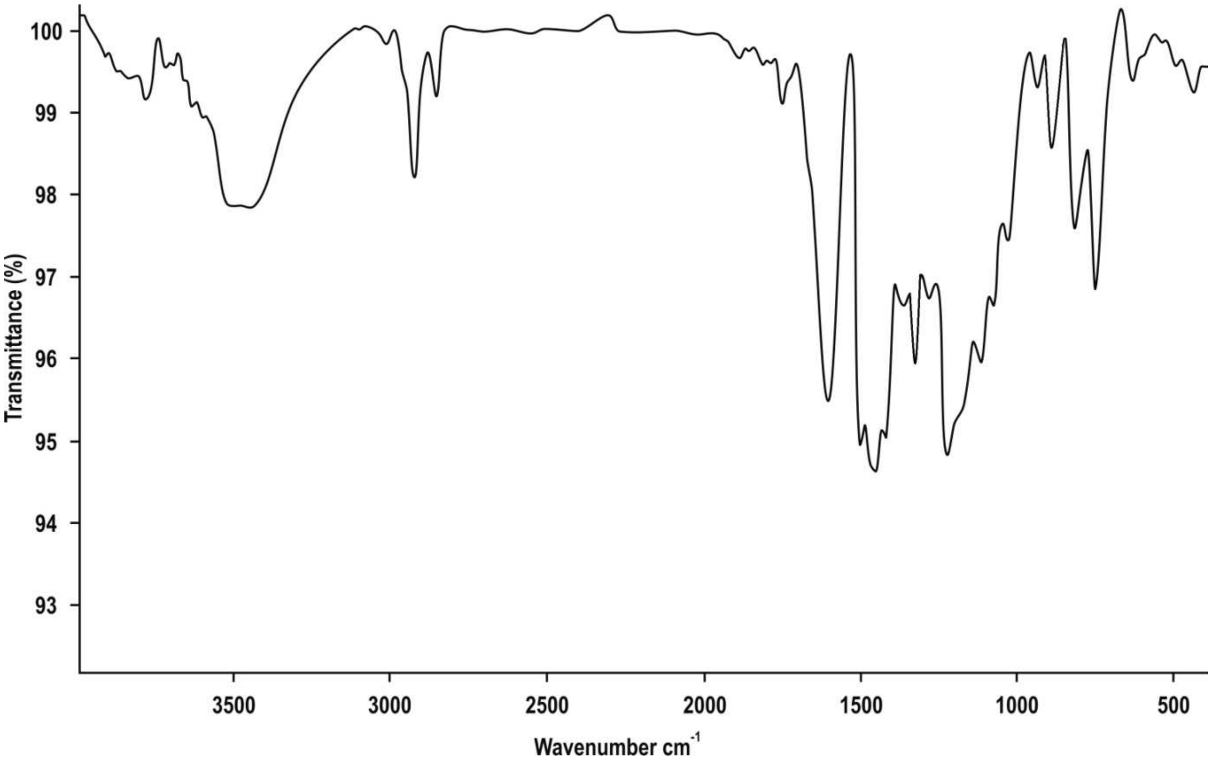


Figure 4: Infrared Spectra of BPEDF-2 Terpolymer Resin

^{1}H NMR spectrum of terpolymer resin is presented in figure4 and MMR spectrum data is shown in table 4. This spectrum shows a multiple signal (asymmetrical pattern) in the region 6.6-7.4 (∂) ppm, which is due to aromatic protons[24, 25]. 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[22, 24, 28]. A broad signal at 9.2-9.4 (∂) ppm shows intermolecular hydrogen bonding of the –NHCH2- group or intermediate proton exchange reaction of both phenolic –OH groups[24, 28]. A weak signal at 7.8-8.0 (∂) ppm may be due to protons of the –NH- bridges. A signal at 3.2-3.6 (∂) ppm may be assigned to ethylenic protons of an Ar-CH2-NH-CH2 moiety[21-26]. A medium signal in the range of 3.7-4.0 (∂) ppm is attributed to the presence of –NH- bridging [30].

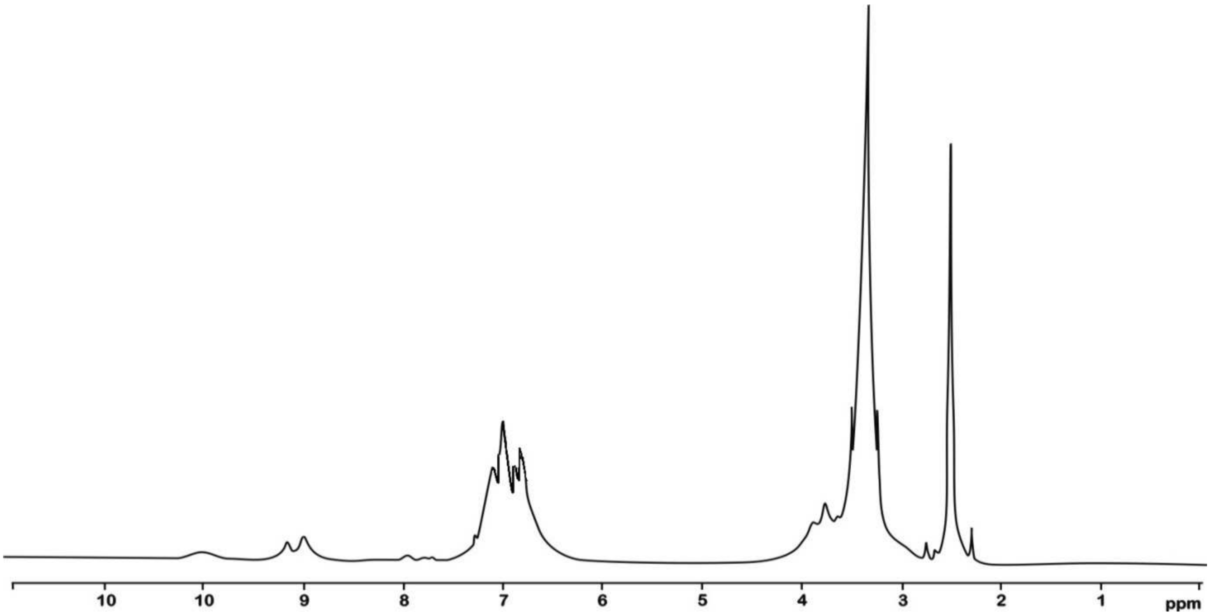


Figure 5: Nuclear Magnetic Resonance Spectra of BPEDF-2 Terpolymer Resin.

4.4. Scanning Electron Micrograph

Surface study has found to be in great use for understanding the surface feature of the materials. The scanning electron micrographs of the terpolymer resin BPEDF-II has been recorded at different magnification (20 KV 400 X; 20KV 1,100 X; 15KV 30,000 X; 20KV 30,000 X) which is shown in figure. The SEM images clearly show the porous morphology in resin and the porosity may be due to spherulites with deep corrugation. The spherulites are typical crystalline in nature and they grows in size in contact with a high viscous and concentrated solutions. The spherulites morphology of resin exhibit crystalline structure with deep corrugation which is clearly visible in SEM photographs of resin. From the SEM photographs it indicates that resin is nanoporous in nature and showing higher exchange capacity for metal ions[9].

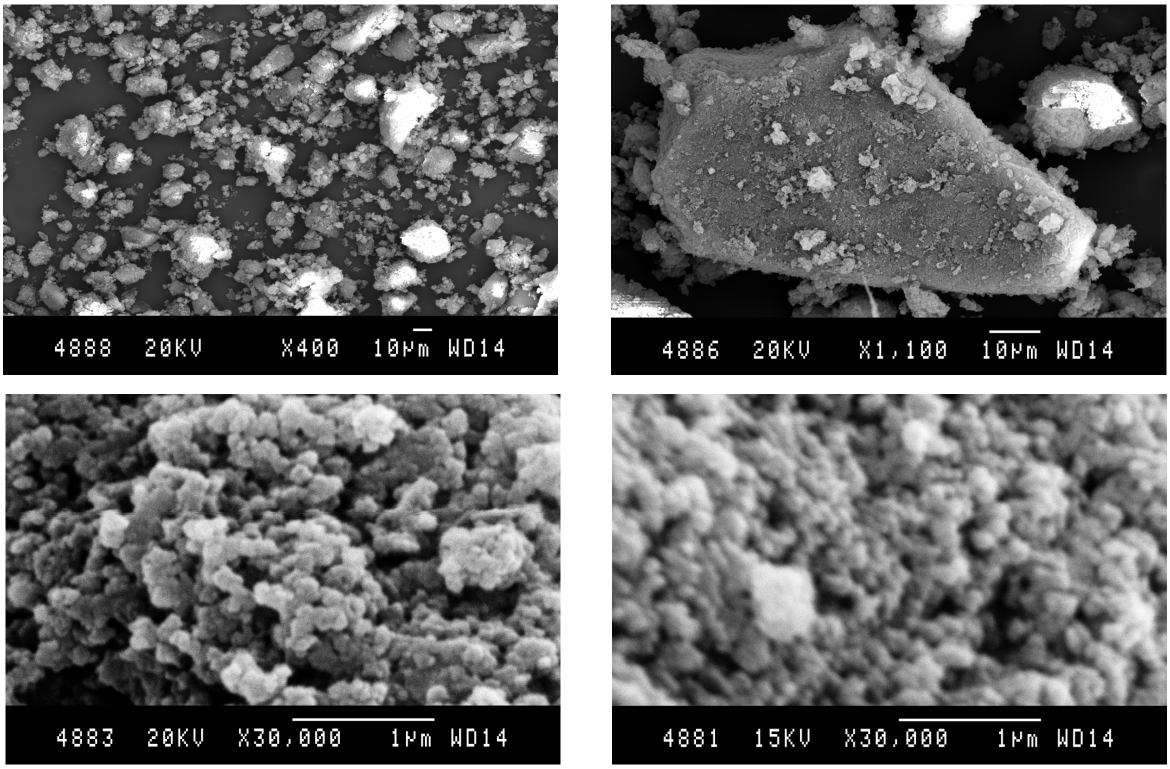


Figure 6: SEM Photographs of Bpedf-2 Terpolymer Resin.

4.5. Removal of As^{+3}metal ion

The influence of electrolytes was examined by varying concentrations of N03, Cl , and SO4 on the equilibrium of metal resin interaction. The amount of metal ion taken up by the given amount of resin depends on the nature and concentration of the electrolyte present in the solution shown in table 1.

Table 1: Influence of different electrolytes on the uptake of As^{+3} metal ion on BPEDF-2 resin at room temperature.

Metal ion	Electrolyte conc. (mol L^{-1})	As^{+3} ion uptake (mg)in presence of		
		NaCl	NaNO3	Na2SO4
As^{+3}	0.01	5.00	8.05	7.08
	0.05	5.08	8.40	6.69
	0.1	5.50	8.55	6.87
	0.5	5,65	8.60	5.85
	1.0	5.89	8.87	4.57

The rate of metal adsorption was determined to find the shortest time period for attaining the equilibrium and the rate of metal ion uptake refers to the change in concentration of the metal ion in the aqueous solution which is in contact with the polymer. From the distribution ratio of the As^{+3} metal ion at different pH, it is concluded that the relative amount of As^{+3} metal ion taken up by the BPEDF-2 terpolymer resin increases with increasing pH of the medium.

Table-2: The rate of As^{+3} metal ion uptake of BPEDF-2 terpolymer resin at room temperature and distribution ratio (D) of As^{+3} metal ion as a function of the pH of BPEDF-2 terpolymer resin at room temperature.

Metal ion	Time in hours	% of the amount of As^{+3} taken up at different time	pH	Distribution ratio (D) of As+3 ionat different pH
As^{+3}	1	50	4-0	86
	2	53	4.5	198
	3	67	5.0	397
	4	80	6.0	648
	5	87	6.5	935
	6	89	7.0	1147

CONCLUSION

The terpolymer resin DBPEDF is light pink in colour and partly soluble in DMF, DMSO and is insoluble in commonly used organic solvents and concentrated acids. On the basis of nature and reactive positions of the monomers, molecular weight, elemental analysis, electronic, IR, and NMR spectra, the most probable structure has been proposed for BPEDF-2 resin as shown in scheme 1. BPEDF-2 terpolymer resin is found to be nanoporus in nature. BPEDF resin is a selective chelating ion-exchange copolymer for As^{+3} metal ion. It can be concluded that the BPEDF resin has a capacity to absorb the As^{+3} metal ions. So by the help of the resin, the toxic As^{+3} metal ion can be separated from waste streams.

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