



## **METAL – ION BINDING PROPERTIES OF A TERPOLYMER RESIN I: SYNTHESIS, CHARACTERIZATION AND ITS APPLICATION AS AN ION- EXCHANGER**

**M. B. Thakre**

Department of Chemistry, Laxminarayan Institute of Technology,

E-mail: mbthakre@yahoo.com

### **ABSTRACT**

Copolymer (4-HBAF) was synthesized by the condensation of 4-hydroxybenzoic acid [4-HB] and adipamide [A] with formaldehyde [F] in the presence of acid catalyst at 127 °C was proved to be a selective chelating ion-exchange copolymer for certain metals. A copolymer composition has been determined on the basis of their elemental analysis and the number average molecular weight of this copolymer was determined by conductometric titration in non-aqueous medium. The viscosity measurements in dimethyl sulphoxide (DMSO) has been carried out with a view to ascertain the characteristic functions and constants. The newly synthesized copolymer resin was characterized by UV-visible spectra, IR spectra, and <sup>1</sup>H NMR spectra. The copolymer has been further characterized by absorption spectra in non-aqueous medium to elucidate the structure. Ion-exchange properties of this resin was studied by batch equilibrium method for Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> ions over the pH range, 1.5 to 6.5 and in media of various ionic strengths. The resin shows a higher selectivity for Fe<sup>3+</sup> ion over any other ions. Study of distribution ratio as a function of pH indicates that the amount of metal ion taken by resin is increases with the increasing pH of medium. The surface morphology of the copolymer resin was examined by scanning electron microscopy and it establishes the transition state between crystalline and amorphous nature.

**Keywords:** Copolymer; Degree of polymerization; Polycondensation; Ion-exchanger; Synthesis.

### **INTRODUCTION**

Much research is being directed towards the preparation of polymeric chain, which is propagated by the formation of metallic chelates. Some success has been achieved in formation of polychelates derived from copolymer ligand. An efficient method for synthesizing such type of polymers by introducing phenols and diamides. The literature survey reveals that copolymers based on 4-hydroxybenzoic acid and its derivatives have received attention due to their application in various areas such as in waste water treatment, for metal recovery, in protective coating and in biological activity [1-3]. Ion-exchangers are widely used for the treatment of radioactive wastes from nuclear power stations[4,5]. The chelation ion-exchange behavior of poly (2-hydroxy, 4-acryloyloxy benzophenone) resin towards the divalent metal ions were studied by batch equilibrium method as a function of time and pH [6]. A cross linked





styrene/meleic acid chelating matrix has been reported for its higher ability to removes the metal ions such as  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  [7]. Acidic polymers such as poly (methacrylic acid) and poly (acrylic acid) have the tendency of removes the metal ions like  $\text{Ag}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$  at different pH and polymer-metal ion ratios [8]. Salicylic acid melamine with formaldehyde terpolymer found to have higher selectivity for  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions then for  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions [9]. Resin synthesized by the condensation of a mixture of phenol or hydroxybenzoic acid with formaldehyde and various amines have also been reported [10]. The metal ion uptake increases with increasing mole proportions of the terpolymer synthesized from substituted benzoic acid [11]. o-nitrophenol and thiourea with p-formaldehyde terpolymer was identified as an excellent ion-exchanger for  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  ions [12]. Salicylic acid – formaldehyde – resorcinol resin has been synthesized and explored its use for the removal and separation of heavy metal ions from their binary mixture [13]. 8-hydroxyquinoline formaldehyde – catechol copolymer found to have lower moisture content indicating the high degree of cross linking in the resin [14].

However no work seems to have been carried out on synthesis and chelation ion-exchange studies of the terpolymer resins synthesized from 4-hydroxybenzoic acid, adipamide and formaldehyde. The purpose of present study, is to explore the adsorption behavior of eight metal ions  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  on the newly synthesized copolymer resins 4-HBAF at different pH values, different concentrations of different electrolytes and at different shaking time intervals. The adsorption behavior of these metal ions are based on the affinity differences towards the chelating resins as functions of pH, electrolyte concentrations and shaking time. One of the important applications of chelating and functional polymers is their capability to recover metal ions from waste solution. Hence the chelating ion exchange property of the 4-HBAF terpolymer resin was also reported for specific metal ions. Pollution by toxic heavy metals due to their toxicities in relatively low concentration and tendency to bioaccumulation in the ecosystem, agriculture and human body has received wide spread attention in recent years. Various approaches such as ion-exchange, reverse osmosis, electro dialysis, precipitation and adsorption techniques have been developed for the removal and recovery of the metal ions from sewage and industrial wastewater. Among these techniques, many research works have focused on





metal ions removal by adsorption on chelating polymers, because they are reusable, easily separable, and with higher adsorption capacity and selectivity having physical and chemical stabilities [15-16]. Some commercially available ion-exchange resins are given in Table 1.

**Table 1. Commercially available ion-exchange resins**

Trade name	Fuctional group	Polymer matrix	Ion-exchange Capacity (mmol.g <sup>-1</sup> )
Amberlite IR-120	-C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H	Polystyrene	5.0-5.2
Duolite C-3	-CH <sub>2</sub> SO <sub>3</sub> H	Phenolic	2.8-3.0
Amberlite IRC-50	-COOH	Methacrylic	9.5
Duolite ES-63	-OP(O) (OH) <sub>2</sub>	Polystyrene	6.6
Zeocarb-226	-COOH	Acrylic	10.00
Dowex-1	-N(CH <sub>3</sub> ) <sub>3</sub> Cl	Polystyrene	3.5
Amberlite IRA-45	-NR <sub>2</sub> , -NHR, -NH <sub>2</sub>	Polystyrene	5.6
Dowex-3	-NR <sub>3</sub> , -NHR, -NH <sub>2</sub>	Polystyrene	5.8
Allassion A WB-3	-NR <sub>2</sub> , -N <sup>+</sup> R <sub>3</sub>	Epoxy-amine	8.2

## EXPERIMENTAL

### Starting Materials

The important chemicals (starting materials) like 4-hydroxybenzoic acid, adipamide and formaldehyde used in the preparation of new 4-HBAF copolymer resin were procured from the market and were of chemically pure grade, and wherever necessary the purity was tested and confirmed by thin layer chromatography.

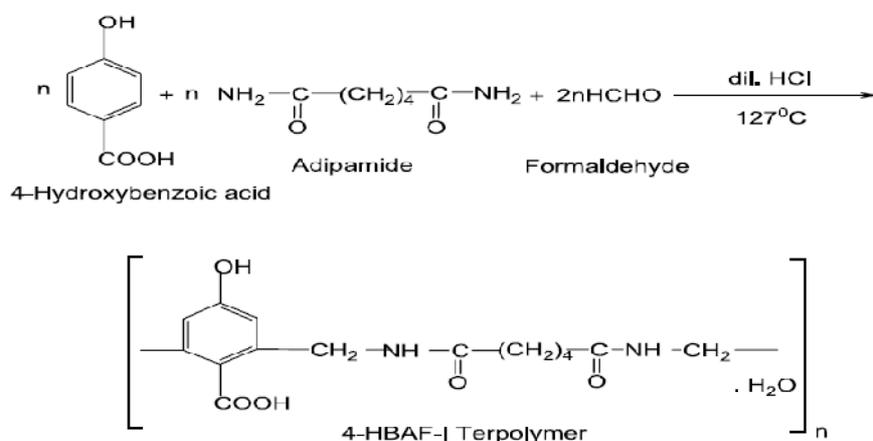
### Synthesis of 4-HBPBF copolymer resin

The 4-HBAF copolymer resin was prepared by the condensation polymerization of 4-hydroxybenzoic acid (0.1 mol) and adipamide (0.1 mol) with formaldehyde (0.2 mol) in hydrochloric acid medium at 127 ± 2 °C in an oil bath for 5 hrs. The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water, dried and powdered. The powder was repeatedly





washed with hot water to remove excess of 4-hydroxybenzoic acid - formaldehyde copolymer, which might be present along with the 4-HBAF copolymer. The purified copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in a vacuum over silica gel. The yields of these copolymer resins found to be 87% and the melting point is between 420-425°K. The sieved resin was used for further characterization. The reaction sequence of the synthesis of 4-HBAF copolymer resin is shown in fig. 1.



**Figure 1. Synthesis and suggested structure of 4-HBAF copolymer resin**

### Characterization of copolymer resin

The copolymer resin was subject to micro analysis for C, H and N on an Elementar Vario EL III Carlo Erba 1108 elemental analyzer. The number average molecular weight  $\bar{M}_n$  was determined by conductometric titration in DMSO medium using ethanolic KOH as the titrant by using 25 mg of sample. A plot of the specific conductance against the milliequivalants of potassium hydroxide required for neutralization of 100 gm of copolymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot the first break and the last break were noted. The calculation of  $\bar{M}_n$  by this method is based on the following consideration [17] : (1) the first break corresponds to the stage at which the first acidic phenolic hydroxyl group is neutralized, and (2) the last break observed beyond the first break represents the stage at which phenolic hydroxyl group of all the repeating units





are neutralized. On the basis of the average degree of polymerization, ( $\overline{DP}$ ) the average molecular weight has to be determined by following eq. (1)...

$$\overline{DP} = \frac{\text{(Total milliequivalents of base required for complete neutralization)}}{\text{(Milliequivalents of base required for smallest interval)}} \dots\dots\dots(1)$$

$$\overline{Mn} = \overline{DP} \times \text{molecular weight of the repeating unit}$$

The intrinsic viscosity was determined using a Tuan-Fuoss viscometer [18] at six different concentrations ranging from 0.3 wt % to 0.05 wt % of resin in DMSO at 30°C. Intrinsic viscosity ( $\eta$ ) was calculated by the Huggin's eq.(2) [19] and Kraemer's eq.(3) [20].

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2 C \dots\dots\dots(2)$$

$$\ln \eta_{rel}/C = [\eta] + K_2[\eta]^2 C \dots\dots\dots(3)$$

Electronic (UV-visible) absorption spectra of the copolymer in DMSO was recorded with a double beam spectrophotometer fitted with an automatic pen chart recorder on thermosensitive paper in the range of 200 – 850 nm at L.I.T. RTM , Nagpur University Nagpur. Infrared spectra of 4-HBAF copolymer resin was recorded in najol mull with Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pallets in the range of 4000 – 500  $\text{cm}^{-1}$  at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Proton NMR spectra and Carbon NMR spectra were recorded with Bruker Adanve – II 400 NMR spectrophotometer using DMSO- $\text{d}_6$  as a solvent, at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. The surface analysis was performed using scanning electron microscope at different magnifications. SEM has been scanned by JEOL JSM-6380A Analytical Scanning Electron Microscope at VNIT, Nagpur.

### Ion-exchange properties

The ion-exchange properties of the 4-HBAF copolymer resin was determined by the batch equilibrium method. We studied the influence of various electrolytes, the





rate of metal uptake and distribution of metal ions between the copolymer and solutions.

### **Determination of metal uptake in the presence of electrolytes of different concentrations**

The copolymer 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 0.1 N HCl or 0.1 N NaOH. The suspension was stirred for a period of 24 hrs at 25°C. To this suspension was added 2 ml of a 0.1 M solution of metal ion and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24 hrs and filtered [21, 22]. The solid was washed and the filtrate and washings were combined and the metal ion content was determined by titration against standard EDTA. The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments [23]. The experiment was repeated in the presence of other three electrolyte such as NaCl, NaClO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>.

### **Evaluation of the rate of metal uptake**

In order to estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type describe above were carried out, in which the metal ion taken up by the chelating resin was determined from time to time at 25°C (in the presence of 25 ml of 1 M NaNO<sub>3</sub> solution). It was assumed that under the given conditions, the state of equilibrium was established within 24 hrs. the rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain related to that at the state of equilibrium.

The percent amount of metal ions taken up at different time is defined as.

$$\text{Percentage of amount of metal ion taken up at different time} = \frac{\text{Amount of metal ion adsorbed}}{\text{Amount of metal ion adsorbed at equilibrium}} \times 100$$

### **Evaluation of the Distribution of Metal Ions at Different pH**

The distribution of each one of the eight metal ions i.e. Fe<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> between the polymer phase and the aqueous phase was determined at 25°C and in the presence of a 1M NaNO<sub>3</sub> solution.





The experiments were carried out from 1.5 to 6 pH for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . In case of  $\text{Fe}^{3+}$  the study was carried out from 1.5 to 3.0 pH. After 24 hrs the mixture was filtered, the filtrates and washing were collected. Amount of the metal ion which remained in the aqueous phase was estimated by back titration with standard EDTA solution using appropriate indicator. Similarly blank experiment was carried out without adding polymer sample. The amount of metal adsorbed by the polymer was calculated from the difference between sample and blank reading. The original metal ion concentration is known and the metal ion adsorbed by the polymers was estimated. The distribution ratio 'D' is calculated from the following equation-

$$D = \frac{\text{Amount of metal ion on resin}}{\text{Amount of metal ion in solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of resin (g)}}$$

If we consider

'Z' is the difference between actual experiment reading and blank reading,

'C' gm is the amount of metal ion in 2ml 0.1M metal nitrate solution,

'Y' gm of metal ion in 2ml of metal nitrate solution after uptake.

$$\text{Metal ion adsorbed [uptake] by the resin} = \frac{ZX}{Y} \frac{2}{0.025} = \left( \frac{ZX}{Y} \right) 133.33$$

## RESULTS AND DISCUSSION

The resin sample was light pink in color, insoluble in commonly used organic solvents, but was soluble in dimethyl formamide, dimethyl sulphoxide, tetrahydrofuran, pyridine and concentrated  $\text{H}_2\text{SO}_4$ . The resin synthesized do not show sharp melting point but undergo decomposition 420-425°K. Based on the analytical data, the empirical formula of the copolymer resin is found to be  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_5$ , which is in good agreement with the calculated values of C, H, N and O. The resin was analyzed for carbon, hydrogen, and nitrogen content. C =58.82% (Cal) and 58.60% (F), H=5.88% (Cal) and 5.72% (F), N =9.15%(Cal) and 9.02% (F). The number average molecular weight ( $\bar{M}_n$ ) could be obtained by multiplying the  $\bar{DP}$  by the formula weight of the repeating unit [24, 25]. The calculated molecular weight for 4-HBAF resin is 3519. Viscometric measurement was carried out in DMSO at 30°C. 4-HBAF resin showed normal behavior. The intrinsic viscosity was determined by the Huggin's eq. (2) and Kraemer's, eq. (3) which is 0.28 and 0.26 respectively. In accordance with the

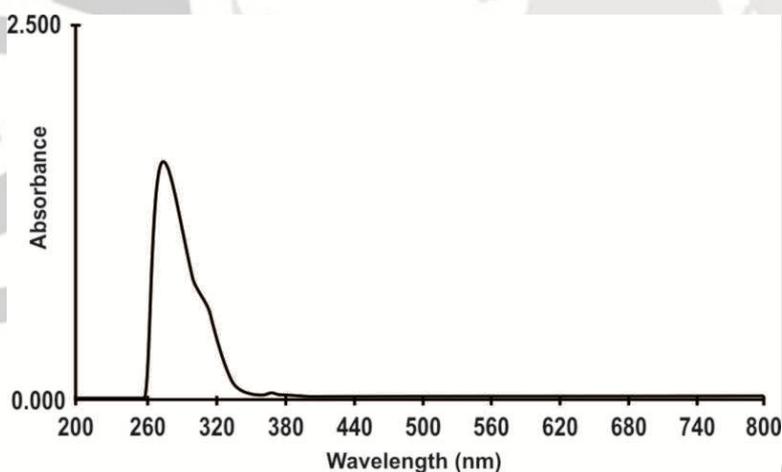




above relations, the plot of  $\eta_{sp}/c$  and  $\eta_{rel}/c$  against  $C$  was linear giving as slopes  $K_1$  and  $K_2$  (0.542) respectively. The intercept on the axis of viscosity function gave the ( $\eta$ ) value in both the plots [26, 27]. The values of ( $\eta$ ) obtained from both relations were in good agreement with each other.

### Spectral Analysis

The UV-visible spectram of 4-HBAF terpolymer resin shown in Fig.2. UV-visible spectra of 4-HBAF resin has been recorded in pure DMSO in the region of 200 – 800 nm at a scanning rate of 100 nm min<sup>-1</sup> and at a chart speed of 5 cm min<sup>-1</sup>. The spectra of these copolymers exhibit two absorption maxima in the region 280 nm and 320 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) processing double bond, which is in conjugation with the aromatic nucleus [28, 29]. The appearance of former band (more intense) can be accounted for  $\pi \rightarrow \pi^*$  transition while the later band (less intense) may be due to  $n \rightarrow \pi^*$  electronic transition. The shift from the basic value (viz. 260 nm and 310 nm respectively) may be due to conjugation effect, and presence of phenolic hydroxyl group (auxochromes) is responsible for hyperchromic effect i.e.  $\epsilon_{max}$  higher values.



**Figure 2. Electronic spectra of 4-HBAF copolymer resin**





The IR spectrum of 4-HBAF copolymer resin is presented in Fig. 3 and IR data are specified in Table 2. [30-31]. A broad absorption band appeared in the region 3506-3507  $\text{cm}^{-1}$  may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding. The peak, at 3397-3399  $\text{cm}^{-1}$  and at 1556-1557  $\text{cm}^{-1}$  and indicate the presence of >NH stretching (amide/imides). The peak at 3080-3081  $\text{cm}^{-1}$  (-CH stretching), 2566-2567  $\text{cm}^{-1}$  (-CH stretching of -CH<sub>2</sub> group), 1312-1313  $\text{cm}^{-1}$  (-CH<sub>2</sub> banding wagging and twisting), 1302-1303  $\text{cm}^{-1}$  (-CH<sub>2</sub> plane banding), indicate the presence of methylene (-CH<sub>2</sub>) group and methylene bridge in terpolymer chain. The bands appeared at 3102-3104  $\text{cm}^{-1}$  (Aryl C-H stretching) and 1550-1552  $\text{cm}^{-1}$  (substituted aromatic ring) may be ascribed to aromatic Skeletal ring. The band appeared at 1412-1413  $\text{cm}^{-1}$  indicates the presence of -SO<sub>3</sub>H group. The band at 856-857  $\text{cm}^{-1}$  indicates the presence of tetra substituted aromatic ring. 1,2,3,5 substitution in aromatic ring was confirmed by the bands appeared at 956-958  $\text{cm}^{-1}$ , 1070-1072  $\text{cm}^{-1}$ , 1140-1142  $\text{cm}^{-1}$ . The band of -NH stretching (3397-3399  $\text{cm}^{-1}$ ) seems to be merged with very broad band of phenolic hydroxyl group.

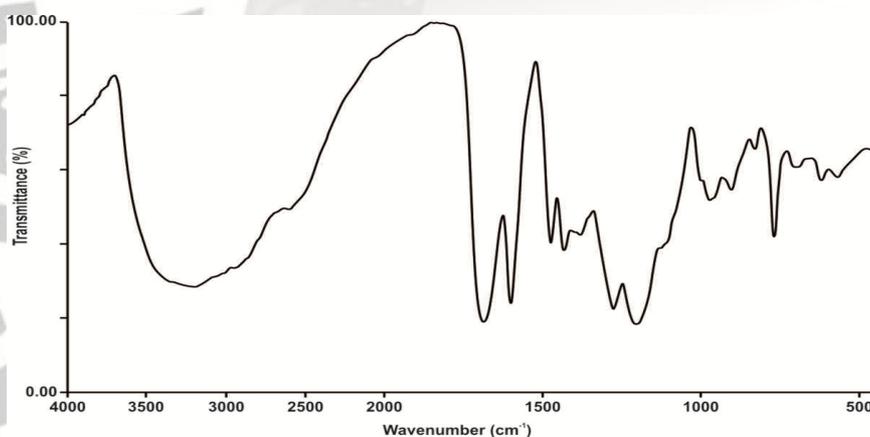


Figure 3. Infrared spectrum of 4-HBAF copolymer resin

Table 2. FT-IR Frequencies of 4-HBAF Copolymer Resin

Observed band frequencies ( $\text{cm}^{-1}$ )	Assignment	Expected band frequencies ( $\text{cm}^{-1}$ )
4-HBAF -I		





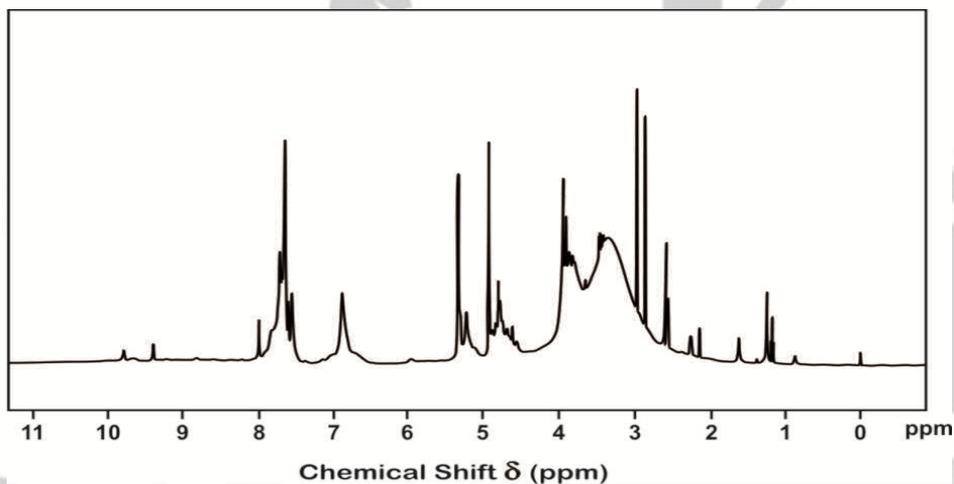
---

3196.6(b,st)	-OH phenolic intermolecular hydrogen bonding	3750-3200
2910.0(b,st)	>NH stretching (amide/imide)	3400-3100
2505(m)	-C-H stretching of CH <sub>2</sub> group	2800-2500
1684.0(sh,st)	>C=O stretch	1750-1600
1603(sh)	Aromatic ring vibration	1600-1500
1478.6 (st)	Phenolic C=O stretch	1600-1400
1435.3(sh,st)	-C=C- stretching	1600-1500
1279.6(m)	-CH <sub>2</sub> - plane bending	1300-1250
772.4(sh)	Tetrasubstituted aromatic ring	830
910.1(m)		914-908
977.9(m)	3,4,5 substitution in aromatic ring	979-977
1205.1(m)		1215-1210

---

<sup>1</sup>H NMR spectrum of 4-HBAF copolymer is shown in Fig. 4 and Proton NMR data are specified in Table 3 [32, 33, 34]. The chemical shift ( $\delta$ ) ppm observed is assigned on the basis of data available in the literature. The singlet obtained in the region of 4.67-4.65 ( $\delta$ ) ppm may be due to the methylene proton of Ar-CH-N moiety. The signal in the region 7.45-7.43 ( $\delta$ ) ppm are attributed to protons of -NH bridge. The weak multiplet signal (unsymmetrical pattern) in the region of 8.98-8.96 ( $\delta$ ) ppm may be attributed to aromatic proton (Ar-H). The signal appeared at 9.05 to 9.03 ( $\delta$ ) ppm may be due to phenolic hydroxyl group protons. The much downfield chemical shift for phenolic -OH indicates clearly the intramolecular hydrogen bonding of -OH group. The signal appeared at 10.02 – 10.01 ( $\delta$ ) ppm are attributed to proton of -SO<sub>3</sub>H group.





**Figure 4. Proton NMR spectrum of 4-HBAF copolymer resin**

**Table 3.  $^1\text{H}$  NMR Spectral Data of 4-HBAF copolymer resin in  $\text{DMSO-d}_6$**

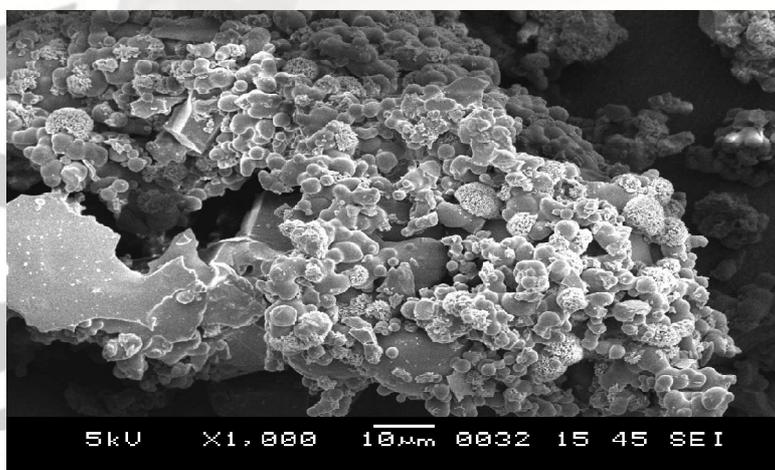
Observed Chemical Shift (□) ppm	Nature of proton assigned	Expected chemical shift (□) ppm
4-HBAF -I		
2.6	Methyl proton Ar- $\text{CH}_3$ group	2.00 to 3.00
2.90	Methylenic proton of Ar- $\text{CH}_2$ moiety	2.00 to 3.00
3.35	Methylenic proton of Ar- $\text{CH}_2$ -N moiety	3.00 to 3.5
4.94	Phenolic proton	5.00
5.30	Proton of -NH bridge	5.00 to 8.00
6.84	Aromatic proton (Ar-H)	6.2 to 8.5
7.76	Proton of phenolic - OH involved intramolecular hydrogen bonding	8.00 to 10.00

### Scanning electron micrographs





The SEM micrographs of 4-HBAF terpolymer resin are shown in Fig.5 (a). The white bars at the bottom of micrographs represent the scale. The micrographs were represented at two different magnifications. The SEM micrographs of 4-HBAF-I terpolymer resin sample exhibits spherulites with deep corrugation. The spherulites are typical crystalline formation and they grow in high viscous and concentrated solution. In the present case, the spherulites are complex polycrystalline formation composed of simplest structural formula having smoothest surface free from defects of growth. The crystals are smaller in surface area with less closely packed structure. Thus the spherulites morphology of resin exhibit crystalline structure of resin with deep corrugation which is clearly visible in SEM photographs of resin. These evidences indicate that more or less the resin shows amorphous character with less close packed surface having deep pits. The resin thus possesses amorphous nature and showing higher exchange capacity for metal ions[35, 36]. Thus SEM study shows that the 4-HBAF terpolymer resin has crystalline and some amorphous characters. Thus it has the transition structure between crystalline and amorphous.



(A)

**Fig. 5:** SEM Micrographs of 4-HBAF -I Terpolymer Resin.

### **Ion-exchange properties**





With a view to ascertain the selectivity of the studied the influence of various electrolytes on the selectivity of metal ions, the rate of metal uptake and the distribution ratio of metal ions between the copolymer and solution containing the metal ions, by using batch equilibrium method [37, 38]. Data of experimental procedure for direct EDTA titration is presented in Table 4.

**Table 4. Data of experimental procedure for direct EDTA titration**

Metal ion	Buffer used	Indicator used	Colour change
Fe(III)	Dil.HNO <sub>3</sub> /dil.NaOH	Variamineblue	Blue-Yellow
Cu(II)	Dil.HNO <sub>3</sub> /dil.NaOH	Fast sulphon black	Purple-Green
Ni(II)	Aq.NH <sub>3</sub> /NH <sub>4</sub> Cl	Murexite	Yellow-Violet
Zn(II)	Aq.NH <sub>3</sub> /NH <sub>4</sub> Cl	Salochrom	Wine Red-Blue
Cd(II)	Hexamine	Xylenol orange	Red-Yellow
Co(II)	Hexamine	Xylenol orange	Red-Yellow
Pb(II)	Hexamine	Xylenol orange	Red-Yellow

The 4-HBAF copolymer (Fig.1) shows that the group -OH and -NH contain lone pair of electrons, which can be donated to the metal ion during complex formation. Hence it shows chelating behavior. When polymer is suspended in metal ion solution, the chelating tendency of copolymer forms the cyclic complex with the metal ion, which absorbs the metal ion from solution to surface of polymer. This mechanism of adsorption of metal ion by polymer ligands is known as metal uptake of polymer. Due to metal uptake concentration of metal ion in solution decreases, this can be determined by titration with standard EDTA solution. The metal uptake capacity of polymer is different for different metal ion, is also known as selectivity of polymer towards the uptake of metal ion. The metal uptake of copolymer depends on three variables, concentration of electrolyte solution, shaking time and pH of the solution. The chelating behavior of 4-HBAF copolymer was studied with these three variables by keeping two variable constant at each time.





Polymer + metal ion solution + shaking → polymer – metal ion chelate  
(Metal uptake capacity of polymer depends on stability of polymer – metal ion chelate)

Batch equilibrium technique developed by Gregor et al. and DeGeiso et al. was used to study of ion exchange property of 4-HBAF copolymer resin. The result of the batch equilibrium study carried out with the copolymer resin 4-HBAF is presented in Fig. 7-12. eight metal ions  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Pb}^{2+}$  in the form of aqueous metal nitrate solution were used. The ion exchange study was carried out using three experimental variables: (a) electrolyte and its ionic strength (b) shaking time and (c) pH of the aqueous medium. Among three variables, two were kept constant and only one was varied at a time to evaluable its effect on metal uptake capacity of the polymer [20, 22, 36].

#### **Effect of electrolytes and their concentration on the metal ion uptake capacity**

We examined the effect of  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{ClO}_4^-$  at various concentrations on the equilibrium of metal resin interaction of constant pH. Different metal ions have different pH in solution, has been mentioned in [Fig.7-10], which shows that the amount of metal ion taken up by a given amount of terpolymers depends on the nature and concentration of the electrolyte present in the solution. In the presence of perchlorate, chloride and nitrate ions the uptake of Fe(III), Cu(II) and Ni(II) ions increase with increasing concentration of the electrolytes, whereas in the presence of sulphate ions the amount of the above mentioned ions taken up by the terpolymer decrease with increasing concentration of the electrolyte. Moreover, the uptake of Co (II), Zn (II), Cd (II) and Pb (II) ions decrease with increasing concentration of the chloride, nitrate, perchlorate and sulphate ions[39]. This may be explained on the basis of the stability constants of the complexes with those metal ions.  $\text{SO}_4^{2-}$  may form strong complexes with  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  ions while  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{ClO}_4^-$  may form weak complexes therefore increases uptake by increasing concentration.



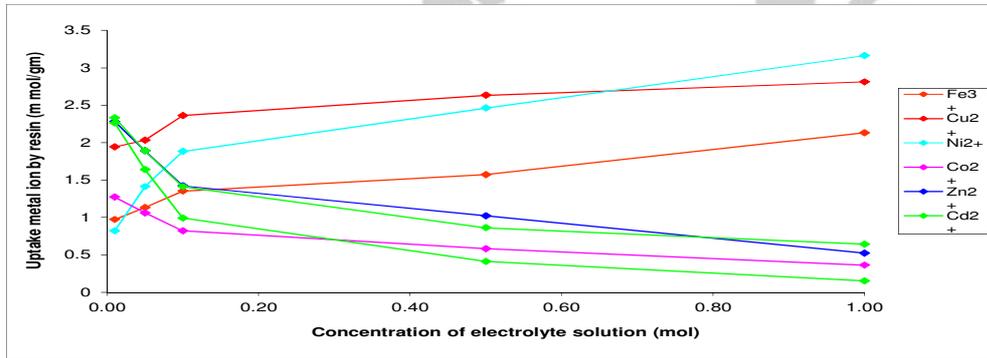


FIGURE. 7. Uptake of several metal ions by 4-HBAF copolymer resin at five different concentration of electrolyte solution  $\text{NaNO}_3$

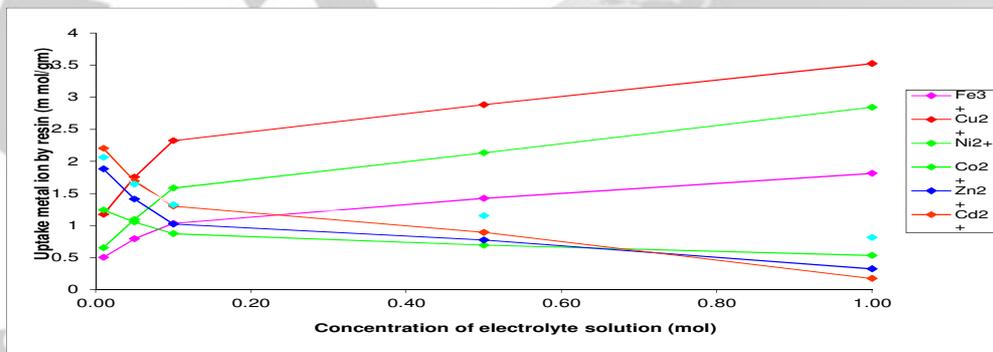


FIGURE. 8. Uptake of several metal ions by 4-HBAF copolymer resin at five different concentration of electrolyte solution  $\text{NaCl}$

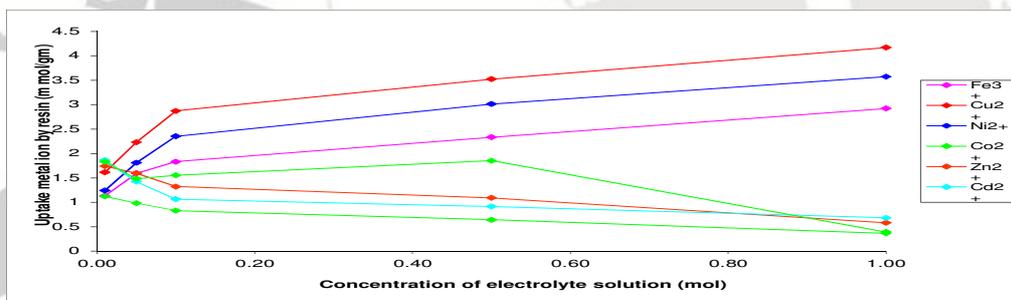
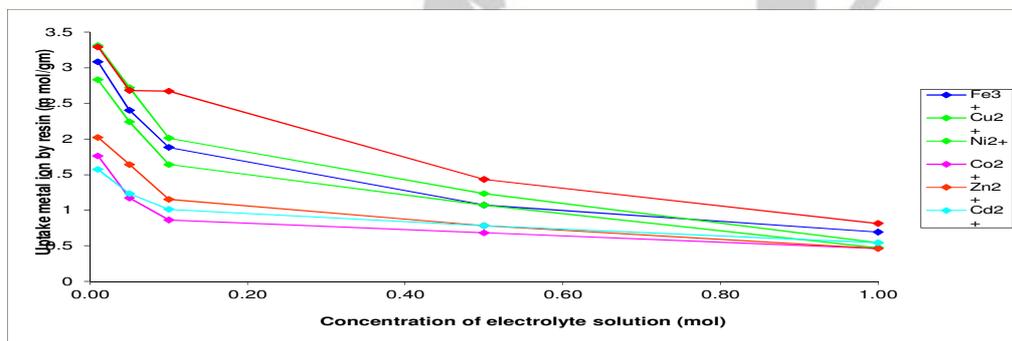


FIGURE. 9. Uptake of several metal ions by 4-HBAF copolymer resin at five different concentration of electrolyte solution  $\text{NaClO}_4$

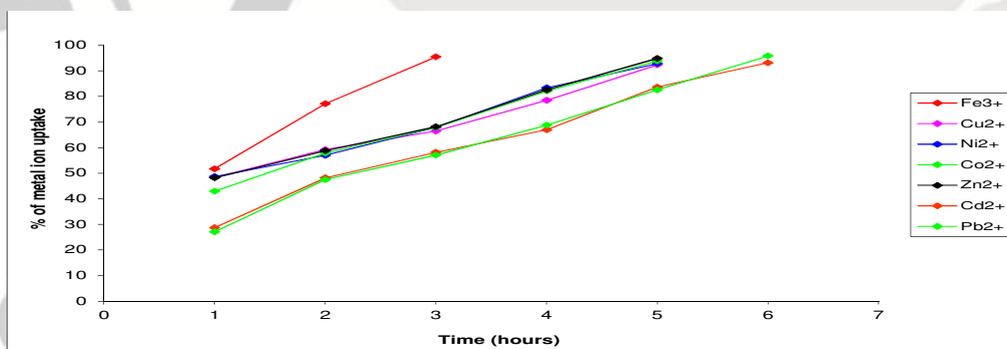




**FIGURE. 10. Uptake of several metal ions by 4-HBAF copolymer resin at five different concentration of electrolyte solution  $\text{Na}_2\text{SO}_4$**

### Rate of metal ion uptake as a function of time

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried out while operating as close to equilibrium condition as possible. During rate of metal ion determination, the concentration of metal ion and electrolyte solution and pH of the solution remain constant and pH of each metal ion is different, which is given in Fig 11. As shaking time increases the polymer gets more time for adsorption, hence uptake of metal ions increases. Fig.11 shows the results of rate of uptake of metal ion on 4-HBAF copolymer resin. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given copolymer. The figure shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of metal ions under given conditions. It is found that Fe (II) ions require about 3 hrs for the establishment of the equilibrium, where as Cu (II), Ni (II), Co (II) and Zn (II) requires 5 hrs and Cd(II) and Pb(II) require 6 hrs for the establishment of the equilibrium. Thus the rate of metal ions uptake follows the order  $\text{Fe(III)} > \text{Cu(II)} \approx \text{Ni(II)} > \text{CO(II)} \approx \text{Zn(II)} > \text{Cd(II)} \approx \text{Pb(II)}$  for all four 4-HBAF terpolymer resins [40 - 46].



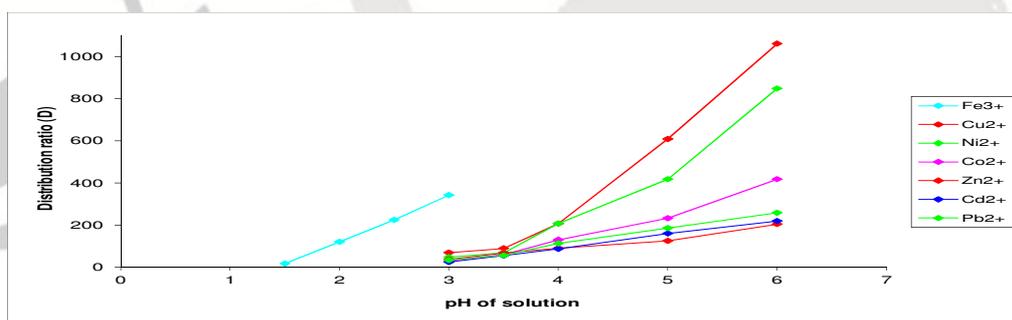


**FIGURE. 11. Comparison of the rate of metal ion uptake by 4-HBAF copolymer resin**

**Distribution ratios of metal ions at different pH**

The distribution of metal ion depends upon pH of the solution. By increasing pH, the H<sup>+</sup> ion concentration in the solution decrease and only metal ion in the solution available for adsorption which increase uptake of metal ions.

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results given in [Fig.12]. The data on the distribution ratio as a function of pH indicates that the relative amount of metal ion taken up by the 4-HBAF terpolymer increases with increasing pH of the medium. The magnitude of increase however, is different for different metal cations. The 4-HBAF terpolymer resin take up Fe (III) ion more selectively at lower pH of 1.5 to 3, than any other metal ions under study. The order of distribution ratio of metal ions measured in pH range 1.5 to 3 is found, to be highest and in pH range of 3 to 6 the order is found to be Cu(II) > Ni(II) > Co(II) ≈ Zn(II) > Cd(II) > Pb(II). Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions. For example the result suggests the optimum pH 6.0 for separation of Co(II) and Ni(II) with distribution ratio 'D' are 417.3 and 847.7 respectively using 4-HBAF terpolymer resin as ion-exchangers. For the separation of Cu (II) and Fe (II) the optimum pH is 3, at which the distribution ratio 'D' for Cu (II) is 68.4 and for Fe (III) is 342.3.



**Figure 12. Distribution ration (D) of various metal ions as function of different pH by by 4-HBAF Copolymer resin**

**CONCLUSIONS**





4-HBAF copolymer resin was prepared from 4-hydroxybenzoic acid and adipamide with formaldehyde in hydrochloric acid medium by condensation technique. The amorphous nature of the 4-HBAF copolymer resins were confirmed by the SEM studies and reveals that the copolymer can act as an effective ion exchanger for trivalent and divalent metal ions such as  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Pb}^{2+}$  ions. This study of ion-exchange reveals that 4-HBAF copolymer resin is proved to be an eco-friendly cation exchange resin and can be used for the removal of hazardous metal ions from the environmental area, for the purification of industrial waste solution and for the purpose of purification and desalination of water.

#### ACKNOWLEDGMENT

Authors are thankful to the Director, Laxminarayan Institute of Technology, Nagpur, India, for providing the necessary laboratory facilities and also thankful to SAIF, Punjab University, Chandigarh for carrying out spectral analysis.

#### REFERENCES

- Angelova N.; Manolova N, Rashkov I, 1995, Eur polym J, 31 (8), 741.  
B. A. Shah; A. V. Shah; B. N. Bhandari; Asian J Chem, 13, 1305-1308.  
Beauvais R. A.; Alexandratos S D.; 2001, React Funct Polym, 36, 1998, 113-123.  
Burkanudeen A.; Karunakaran M.; 2002, Orient J Chem, 18, 65-68.  
D Gruyter Walter; 1991, Ion Exchangers (K. Dorfner, ed.), Berlin.  
Denizli, A.; Garipean B.; Karabakan A.; Emir, S.; Patir S.; 2003, Sep Pur Tech, 30, 3-10.  
Dutta, S.; Das A. K.; 2007, J Appl Polym Sci, 103, 2281-2287.  
Feng D.; Aldrich C.; Tan H.; 2000, Miner Eng, 13, 623-642.  
Gupta R. H.; Gurnule W. B.; Zade. A. B.; 2008, Journal of Applied Polymer Science, 109(5), 3315-3320.  
Gurnule W. B.; Rahangdale P. K.; Paliwal L. J.; R. B. Kharat; 2003, J of Appl Polym Sc. 89, 787-790.  
Gurnule W. B.; Rahangdale P. K.; Paliwal L. J.; R. B. Kharat; 2003, Synth React Inorg MetOrg Chem, 33, 1187-1205.  
Gurnule, W. B.; Juneja H. D.; Paliwal L. J.; 2003, Reactive and Functional Polymers, 55, 255-265.





- Gurnule, W. B.; Juneja H. D.; Paliwal L. J.; 2002, *React Funct Polym*, 50, 95-100.
- Helferich F.; 1962, *Ion Exchange*. McGraw Hill, New York.
- Jadhao M. M; Paliwal L.J.; Bhave N. S.; 2005, *Ind J of Chem*, 44, 656.
- Joshi J. D.; Patel N. B.; Patel S. D.; 2006, *Iran Polym J*, 15, 219-226.
- Karunakaran M.; Burkanudeen A.; 2003, *Orient J Chem*, 19, 225-228.
- Karunakaran M.; Burkanudeen A.; 2002, *Orient. J. Chem.* 18 65-68.
- Kaur H.; 2009, *Instrumental methods of chemical analysis*, Arihant Electric Press: Meerut.
- Liu X.; Zhu D. and Chang D., 2000, *Huazhong Nongye Daxue Xuebao*, 19 2009 15-17 *Chem. Abstr* 133, 34740w.
- M. Bankova; N. Manolova; I. Rashkov; 1999, *Eur polym J*, 34(2), 247.
- Mane V. D.; Gurnule W. B; Zade. A. B; *Journal of Applied Polymer Science*, 111, 3039-3049.
- Manolova N.; Ignalova M; Rashkov I; 1998, *Eur polym J*, 34(8), 1133.
- Patel S. A.; Shah B.S.; Patel R. M.; Patel P. M.; 2004, *Iran Polym J*, 13, 445-453.
- Patle Deepti B.; Gurnule W. B.; 2010, *Archives of Applied Science Research*, 2(1) 261-276.
- Patle Deepti B.; Gurnule W. B.; 2010, *Polymer Bulletin*, 1-18.
- Porter M ; *Handbook of Industrial Membrane Technology*, Noyes, Pork Ridge, New York, 1990.
- Preuss A.; Kunin R., *Proc. Inter. Conf. Peaceful Uses Atom. Energy-Geneva*, 8.
- Rahangdale S. S.; Gurnule W. B.; Zade. A. B; 2009, *Indian J Chem.* 48A, 531- 535.
- Rahangdale S. S.; Gurnule W. B.; Zade A. B; 2009, *E-Journal of Chemistry*, 6(3), 835-843.
- Rahangdale S. S.; Gurnule W. B; Zade. A. B.; 2008, *Journal of Applied Polymer Science*, 108, 747-756.
- Rimawi F. A.; Ahmad A.; Khalili F.I.; Mubarak M.; 2004 *Solvent Extr. Ion Exch.* 22, 721-735.
- Rivas B. L.; Pereira E. D.; Gallegos P.; Geckeler K. E.; 2002, *Polym Adv Technol*, 13, 1000-1005.
- Roy P. K.; Rawat A. S.; Rai P. K.; 2004, *J Appl Polym Sci*, 94 1771-1779.
- Shah B. A.; Shah A. V.; Bhandari B. N.; 2008, *J Iran Chem Soc*, 5, 25-22.





- Shah B. A.; Shah A. V.; Shah P. M, 2004, Iran Polym J, 13, 445-454. Katkamwar S. S.; Gurnule W. B; Zade. A. B.; 2009, J Appl Polym Sci, 113, 3330-3335.
- Shah B. A.; Shah A. V.; Shah P. M., 2006, Iran Polym J, 16, 173-184.
- Shah B. A.; Shah A. V.; Shah P. M.; 2006, Iran Polym J, 15, 809-819.
- Silverstein R. M.; Webster F. X.; Spectrometric identification of organic compounds John Wiley and Sons, New York, 1998.
- Singru R. N.; Gurnule W. B.; Zade. A. B.; J Appl Polym Sci, 109, 2008, 859-868.
- Singru R. N.; Gurnule W. B.; Zade. A. B.; 2010, Iranian Polymer Journal. 19 (3), 169
- Tarase, M. V.; Gurnule W. B; Zade. A. B; Journal of Applied Polymer Science, 116, 619-627.
- Tayllor R.; Pragnel R. J.; McLaren J. V.; 1982, Talanta, 29 (6), 489-494.
- Zalloum R. M.; Mubarak S. M.; 2008, J Appl Polym Sci, 109, 3180-3184.
- Zalloum, R. M.; Mubarak S. M.; J, 2008 Appl Polym Sci, 109 3180-3184.

