



## Ion exchange study of some new biphenol–thiourea–formaldehyde terpolymer resins

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### ABSTRACT

Terpolymer resins, synthesized by reacting 2,2'-dihydroxybiphenyl with thiourea and formaldehyde in presence of HCl as catalyst, proved to be selective chelating ion-exchange resins for certain metal ions. Chelating ion-exchange properties of these terpolymer were studied for Fe<sup>3+</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> ions. A batch equilibrium method has been 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 terpolymer showed higher selectivity for Fe<sup>3+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> ions than for Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> ions.

*Keywords:* Terpolymer; Ion exchange resin; Chelating properties; Metal ion uptake

### 1. Introduction

Majority of industrial effluents and wastewaters of chemical manufacturing, painting and coating, mining, extractive metallurgy, nuclear and other industries contains heavy metals such as zinc, lead, iron etc. are hazardous to the environment, aquatic ecosystem, human health [1]. Exposure to these toxic metals even at trace level is still a risk to human beings, thus, more stringent environmental legislations have been established to restrict the maximum contaminant level (MCL) of heavy metals in waters [2]. Several known methods and processes are commonly used for removal of toxic metals from their real matrices. These are often performed by evaporation, liquid–liquid extraction, ion exchange, electrochemical treatment, redox reaction, reverse osmosis and others [3]. Considerable research has been

carried out in developing cost-effective processes for the removal of heavy metal ions from aqueous solutions [4]. Ion exchange resin containing suitable chelating electron donor sites in the framework can be an ideal material due to their exceptionally high surface to bind a metal ion through chelation [5].

Various terpolymers with high thermal stability and metal binding chelation properties have been reported in literature. Terpolymers derived from phenol derivatives exhibits good chelating ion-exchange properties [6–8]. Rimawi et al. reported the chelation behaviour of the phenolic-formaldehyde polymers, poly(2,4-dihydroxybenzoic acid-3,5-dimethylene), poly(2-hydroxybenzoic acid-3,5-dimethylene) and poly(3-hydroxybenzoic acid-4,6-dimethylene) towards the trivalent lanthanide metal ions [9]. Das has derived copolymer from thiosemicarbazone derivatives of phenolic compound [10]. Among these, polymers possessing sulphur and nitrogen donor atoms exhibits good thermal stability, chelating property

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and can be used as an ion exchanger [11–15]. New chelating resin containing sulphur and nitrogen donor atoms has been synthesized by Chen et al. [15]. They have obtained this resin by incorporating 2-aminoethylthio methyl groups into styrene divinylbenzene copolymer. The resin exhibits exceptionally high affinity for soft metal ion, even in highly acidic aqueous media and concluded that metal ion coordinations occurs primarily at the nitrogen and sulphur donor atoms, but the polymeric backbone also makes significant contribution to metal binding. Salicylic acid/*p*-hydroxy benzoic acid and thiourea–trioxane terpolymer have been synthesized by Patel et al. [16,17]. Bavanker et al. [18] have also prepared terpolymer from salicylaldehyde–biuret with trioxane and studied its physicochemical properties. Dabrowski et al. have efficiently removed trace impurities and toxic metals from industrial waste water by various ion exchangers [19]. Karunakaran et al. have synthesized terpolymer from *o*-nitrophenol–thiourea–formaldehyde and  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{UO}_2^{2+}$  were used for chelation [20]. Hence in present context, we are reporting the ion exchange study of 2,2'-dihydroxybiphenyl–thiourea–formaldehyde terpolymer resin for various metal ions.

## 2. Experimental

### 2.1. Materials

The chemicals used were all of AR or chemically pure grade. DMF and DMSO were used as HPLC grade. 2,2'-dihydroxybiphenyl (Lancaster, purity-99%); formaldehyde solution (Merck, 35%) and Guanidine (Merck, 99%).

## 3. Synthesis of terpolymer resins

### 3.1. Preparation of BPhThF terpolymer resin [BPhThF-1]

A mixture of 2,2'-dihydroxybiphenyl [0.05 mol], thiourea [0.05 mol] and formaldehyde [0.1 mol] in the presence of 2 M HCl was heated in an oil bath at  $143 \pm 2^\circ\text{C}$  for 5 h with occasional shaking. The separated resinous product [BPhThF-1] was washed with hot water followed by methanol to remove unreacted monomers. Then it is extracted with ether in order to remove copolymer which may exist with terpolymer. The product so obtained was further purified by reprecipitation technique. For this terpolymer was dissolved in 8% NaOH and reprecipitated by drop wise addition of 1:1 (v/v) HCl, with constant stirring. The precipitated resin product was filtered off; washed with hot water until it was free from chloride ions and dried and powdered. The purified polymer sample was dried in vacuum at room temperature finely ground resin was pass through a 300 mesh size sieve and kept over silica gel. The yield of this terpolymer resin was found to be 83%. Similarly; other terpolymer resins viz. BPhThF-2; BPhThF-3 and

BPhThF-4 were synthesized by varying the molar proportion of the starting materials, that is 2,2'-dihydroxybiphenyl, thiourea and formaldehyde in ratio 1:2:4; 1:3:5 and 1:4:6. The details of mole ratio of reactants, reflux temperature, time of reflux and percent yield of product have been reported in our previous communication [21]. Purity of all terpolymers is checked by TLC. The terpolymer resins used in the present study have been characterized on the basis of elemental analysis, viscosity measurements, molecular weight determinations, UV-visible, infrared and NMR spectral studies as described elsewhere [21].

The purified terpolymers are used in all experiments to carry out the ion-exchange study were finely ground well to pass through a 300-mesh size sieve.

## 4. Ion exchange properties

Ion exchange properties of all newly synthesized BPhThF terpolymer resins were determined by the batch equilibrium method [6].

### 4.1. Determination of metal uptake in the presence of electrolytes of different concentrations

The terpolymers 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 using either 0.1 N  $\text{HNO}_3$  or 0.1 N NaOH. The suspension was stirred for a period of 24 h at  $25^\circ\text{C}$ . To this suspension 2 ml of 0.1 M solution of the metal ion was added and the pH was adjusted to required value. The mixture was again stirred at  $25^\circ\text{C}$  for 24 h and filtered [6,23]. The polymers was washed and filtered. The filtrate and the washings were combined and estimated for the metal ion content by titration against standard ethylenediaminetetracetic acid using appropriate buffer and suitable indicator [22]. The blank was also estimated for the metal ion content. The amount of metal ions taken up by polymer in the presence of the given electrolyte of known concentration was calculated from the difference of metal ion concentration between blank solution and the metal ion solutions in the actual experiment [6,23].

The experiment was repeated in presence of several electrolyte of known concentration with seven different metal ions viz.  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . The same procedure was applied to all molar ratios of the terpolymer resins.

### 4.2. 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 described

above were carried out, in which the metal ion taken up by the chelating resin was estimated from time to time at 25°C in presence of 25 ml of 1 M NaNO<sub>3</sub> solution. It is assumed that under the given conditions, the state of equilibrium is established within 24 h. The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to that in the state of equilibrium.

#### 4.3. Evaluation of the distribution of metal ions at different pH

The distribution of each one of seven metal ions Fe<sup>3+</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 polymer phase and aqueous phase was estimated at 25°C and in presence of 1 M NaNO<sub>3</sub> solution. The experiments were carried out as described earlier at pH range 1.5–6.5. The distribution ratio *D* is defined by following relationship:

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

#### 4.4. Results and discussion

In order to ascertain the selectivity of the BPhThF terpolymers for the selected metal ions, we have studied the influence of various electrolytes on the selectivity of metal ion, the rate of metal uptake, and the distribution ratio of metal ions between the polymer and the solution containing the metal ions. The results of the batch equilibrium study carried out with polymer samples of BPhThF terpolymers are incorporated in Figs. 1–3. From this study carried out with seven metal ions under limited variation

of experimental conditions, certain generalizations may be made about the behavior of the for polymer samples selected for ion exchange study.

### 5. Influence of electrolyte on metal uptake

Fig. 1 reveals that the amount of metal ions taken up from a given amount of terpolymer depends on the nature and concentration of the electrolyte present in the solution. In presence of chloride and nitrate ions, the uptake of Fe<sup>3+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> ions increases with increasing concentration of the electrolytes, whereas in presence of sulphate ions the amount of above mentioned ions taken up by the terpolymers decreases with increasing concentration of electrolytes. Moreover, the amount of Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> decreases with increasing concentration of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions [5,23,24]. This may be explained in terms of the stability constants of the complexes which Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> metal ions formed with these anions [25]. SO<sub>4</sub><sup>2-</sup> might form rather strong complexes with Fe<sup>3+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> while NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> might form weak complexes and therefore, might not be expected to influence the position of the [Fe<sup>3+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup>] chelate equilibrium as much as SO<sub>4</sub><sup>2-</sup>. The sulphate, chloride and nitrate might form rather strong complexes with Co<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> and therefore, might be expected to influence the position of Co<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> complex equilibrium.

It is also observed that the amount of metal ions taken up by the BPhThF terpolymer resins increases in the order: BPhThF-1 < BPhThF-2 < BPhThF-3 < BPhThF-4. This observed order may be due to introduction of more and more  $\text{-NH-C(=S)-NH-}$  group in terpolymer resins.

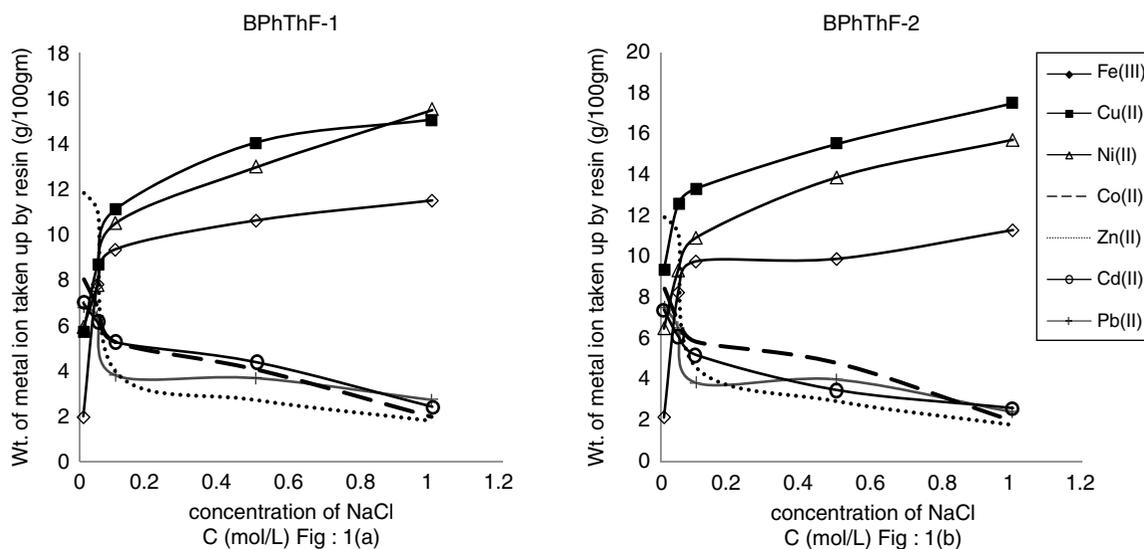


Fig. 1. (continued)

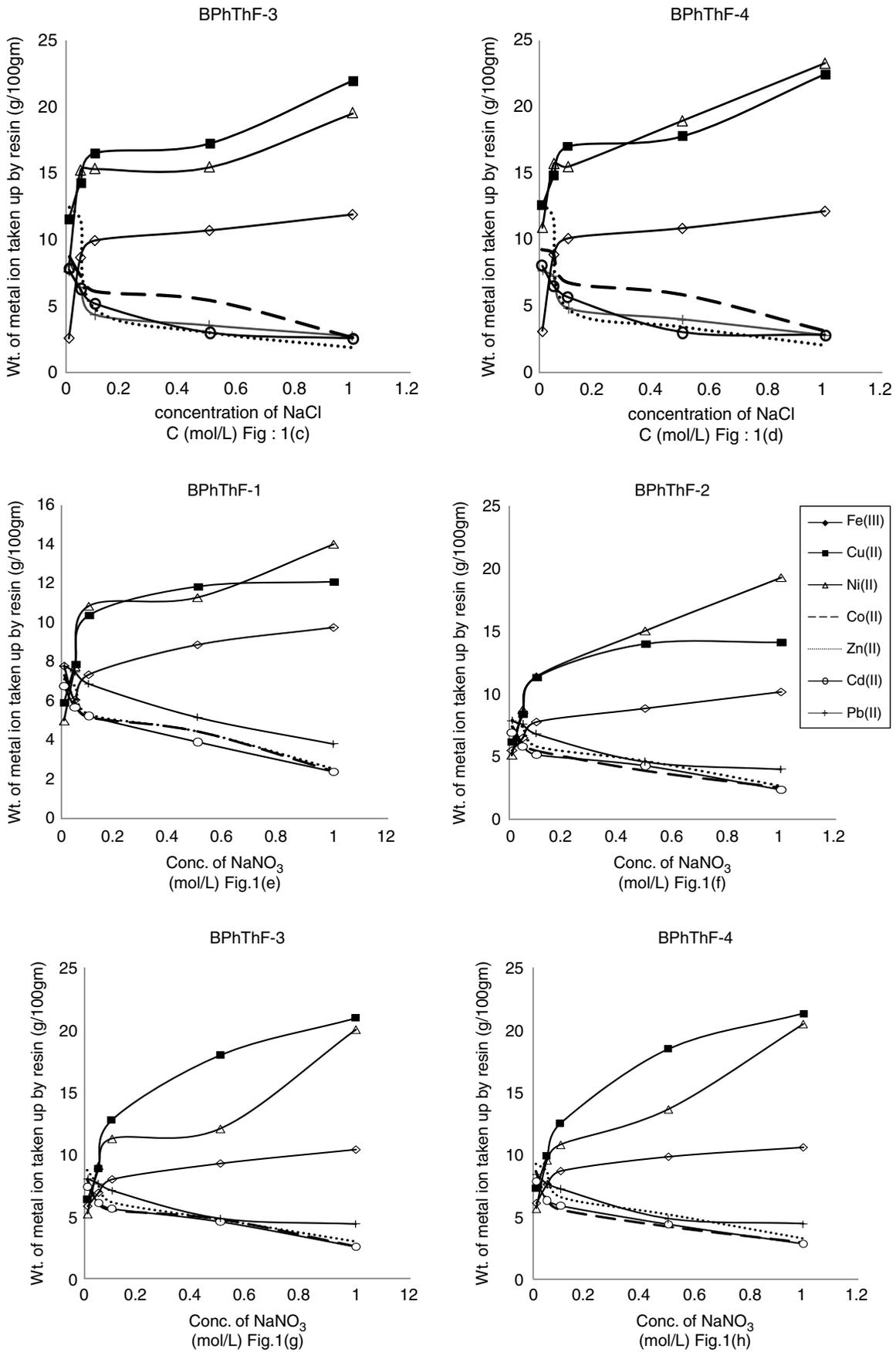


Fig. 1. (continued)

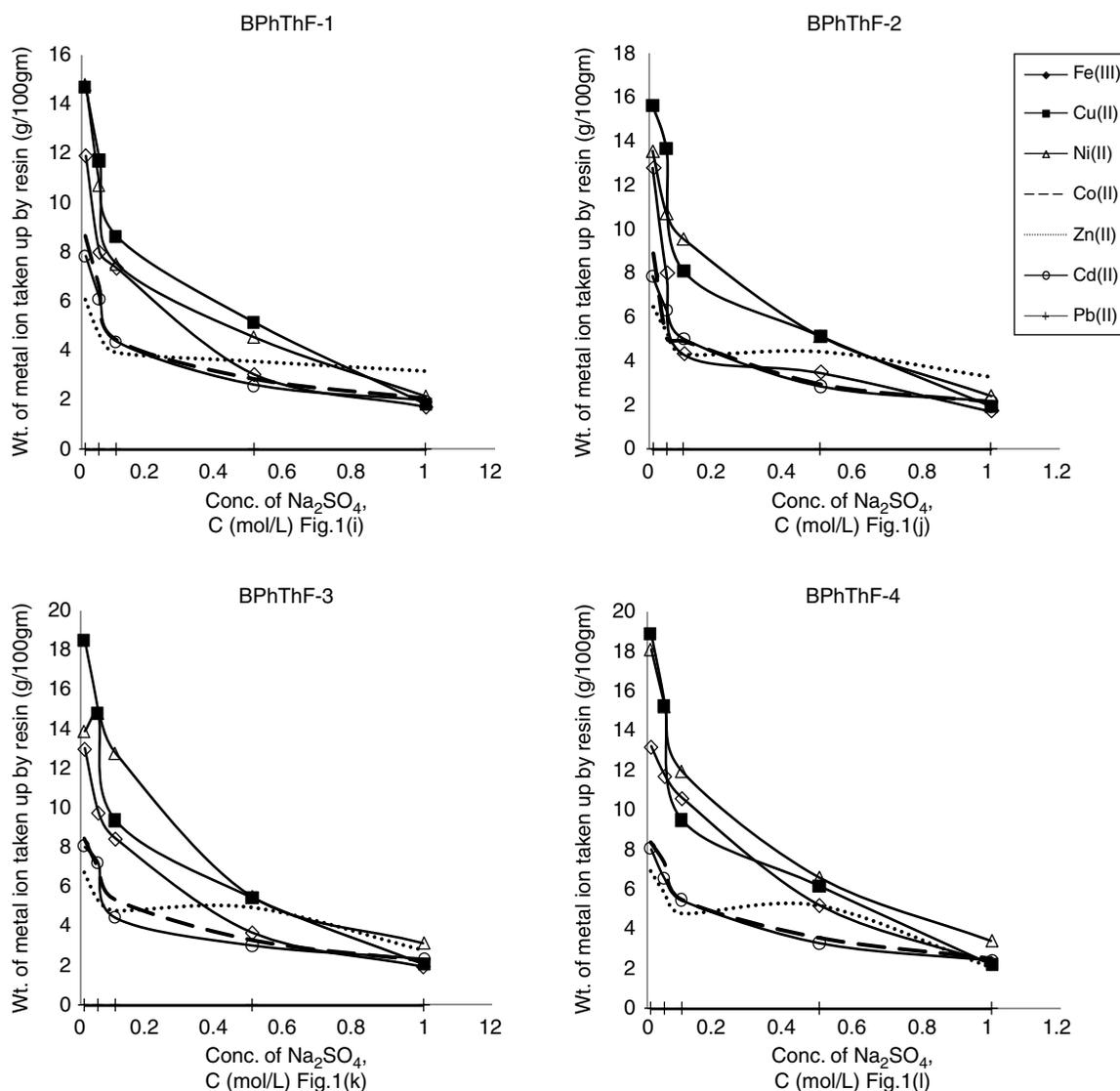


Fig. 1. Evaluation of the influence of different electrolytes<sup>1</sup> on the uptake of several metal ions<sup>2</sup> of BPhThF terpolymer resins. <sup>1</sup>(a)–(d) for NaCl; (e)–(h) for NaNO<sub>3</sub>; (i)–(l) for Na<sub>2</sub>SO<sub>4</sub>. <sup>2</sup>[Mt(NO<sub>3</sub>)<sub>2</sub>] = 0.1 mol l<sup>-1</sup>; volume of electrolyte solution = 25 ml; volume of metal ion solution = 2 ml; weight of resin = 25 mg; time = 24 h; room temperature.

## 6. Evaluation of the rate of metal uptake

The rate of metal adsorption by BPhThF terpolymer resins was determined to evaluate the shortest period of time for which equilibrium could be carried out while operating as close to equilibrium conditions as possible. The rate refers to the change in the concentration of the metal ions in aqueous solution, which is in contact with the given polymer. Fig. 2 shows the dependence of the rate of metal ion uptake on the nature of metal. These results indicate that the time taken for the uptake of different metal ions at a given stage depends on the

nature of the metal ion under given conditions. Examination of data shows that Fe<sup>3+</sup> ions require about 4 h for the establishment of equilibrium whereas Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> requires about 5 h for equilibrium Cd<sup>2+</sup>, Pb<sup>2+</sup> required highest time, that is 7 h to attain equilibrium. The rate of metal ion uptake follows the order. Fe<sup>3+</sup> > Cu<sup>2+</sup> > Ni<sup>2+</sup> ≈ Co<sup>2+</sup> ≈ Zn<sup>2+</sup> > Cd<sup>2+</sup> > Pb<sup>2+</sup> for all of the terpolymers [5,23,24]. This observed order indicates that the rate of metal ion uptake depends on the nature of metal ion, that is as the size of the metal ion increases the time taken for the uptake metal ions increases.

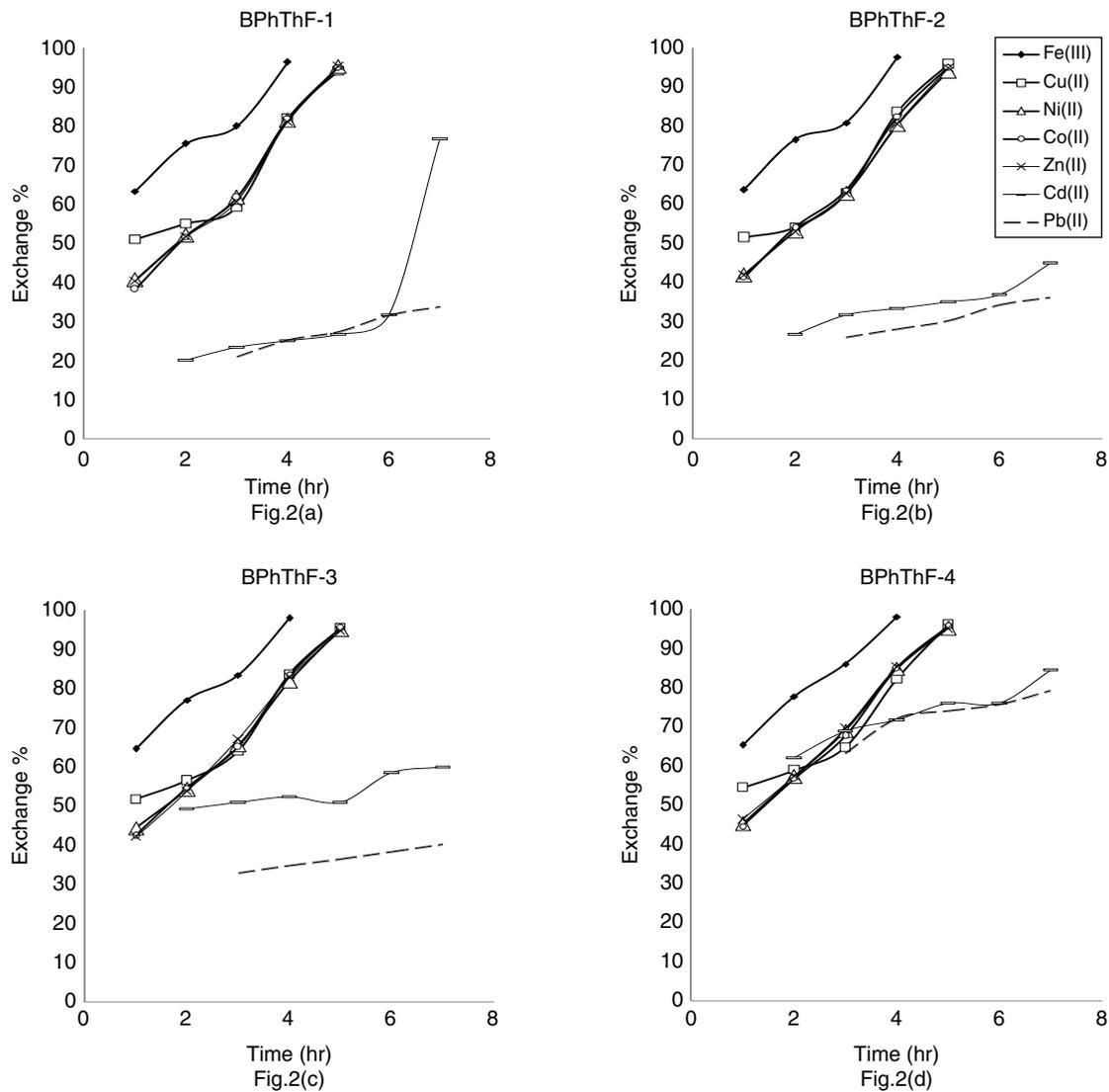


Fig. 2 (a)–(d) Comparison of the rate of metal ion  $[Mt]^{1}$  uptake of BPhThF terpolymer resins.  $[Mt(NO_3)_2] = 0.1 \text{ mol l}^{-1}$ ; volume of metal ion = 2 ml,  $NaNO_3 = 1.0 \text{ mol l}^{-1}$ ; volume of  $NaNO_3 = 25 \text{ ml}$ ; room temperature

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

### 7. Distribution ratio of metal ions at different pH

The results of the effect of pH on the amount of metal ion distributed between two phases are as shown in Fig. 3. The results indicate that the relative amount of metal ion taken up by the BPhThF terpolymer resin at equilibrium increases with the increase of pH of the medium [5,23,24]. The magnitude of increase, however, is different for different metal cations. The BPhThF terpolymer resin take-up  $Fe^{3+}$  ion more selectively than any other metal ions

under study. The observed order of distribution ratio of divalent ions measured in the range of pH from 2.5 to 6.5 was found to be  $Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$  [26,27]. Thus, the results of this study are helpful in selecting the optimum pH for a selective uptake of a metal ion from a mixture of different ions. For instance, the results suggest the optimum pH 3 for the separation of  $Cd^{2+}$  and  $Cu^{2+}$  using BPhThF-1 terpolymer resins with their distribution ratios 92.19 and 26.11 respectively.

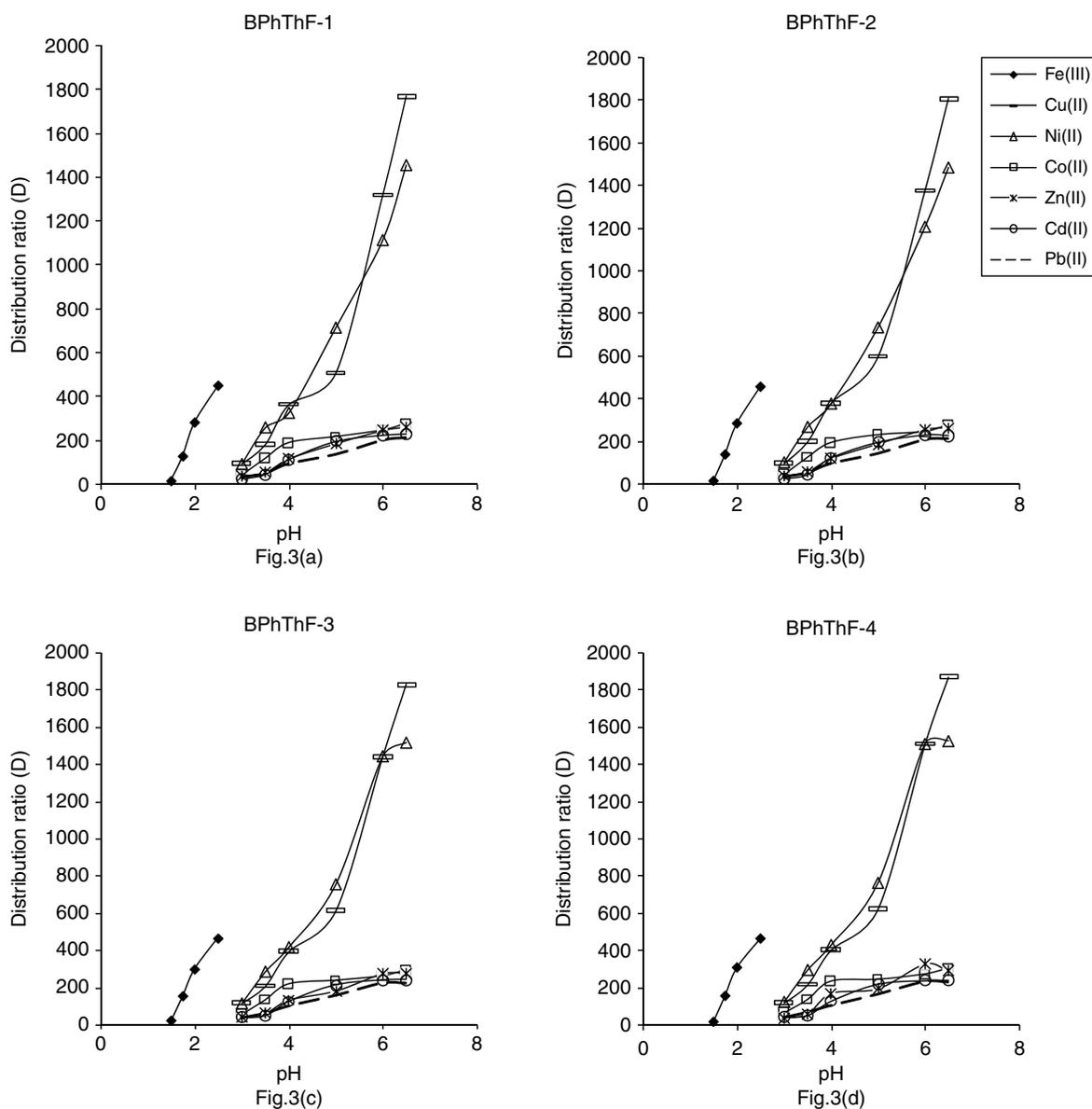


Fig. 3. Distribution ratio ( $D$ )<sup>1</sup> of different metal ions as function of the pH<sup>2</sup> of BPhThF terpolymer resins.

$${}^1D = \frac{\text{Amount of metal ion on resin}}{\text{Amount of metal ion in solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of resin (g)}}$$

<sup>2</sup>[ $\text{Mt}(\text{NO}_3)_2$ ] = 0.1 mol l<sup>-1</sup>; volume = 2 ml;  $\text{NaNO}_3$  = 1.0 mol l<sup>-1</sup>; volume of electrolyte  $\text{NaNO}_3$  = 25 ml; room temperature.

## 8. Conclusions

1. It is selective chelating ion-exchange resin for  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  metal ions.
2. These resins showed a higher selectivity for  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  ions as compared to  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions.
3. These polymers showed higher selectivity for  $\text{Fe}^{3+}$  at pH 2.5 as compared to other metal ions.
4. The amount of metal ions taken up by the BPhThF terpolymer resins increases in the order: BPhThF-1 <

BPhThF-2 < BPhThF-3 < BPhThF-4. It may be due to introduction of more and more ligand groups (thio-urea monomers) in the repeating unit of the terpolymer resins.

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## Symbols

A.R.	—	analytical grade
BPhThF	—	2,2'-dihydroxybiphenyl thiourea formaldehyde terpolymer
D	—	distribution ratio
DMF	—	dimethyl formamide
DMSO	—	dimethyl sulphoxide
h	—	hour
HNO <sub>3</sub>	—	nitric acid
NaNO <sub>3</sub>	—	sodium nitrate
NaOH	—	sodium hydroxide

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