

# Sorption Investigation of Metal Ions by Copolymers with Respect to pH, Time and in Media of Different Ionic Strength

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**Abstract:** A series of acid catalysed condensation copolymers has been synthesized by using *p*-nitrophenol, 4,4'-methylenedianiline and formaldehyde with different molar proportions of reacting monomers. Newly synthesized copolymers were proved to be selective chelating ion-exchangers for metal ions like  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  ions. A batch equilibrium method has been employed in the study of selectivity of metal ion uptake involving the distribution of given metal ions between the copolymer and a solution containing metal ion. The study was carried out over a wide pH range, shaking time, temperature and in media of various ionic strengths of different electrolytes. Distribution ratios of metal ions were found to be increased by increasing pH of solutions; hence the resins can be used to recover certain metal ions from waste solution. Sorption data obtained at optimized conditions were analyzed by Langmuir and Freundlich adsorption isotherm models. The adsorption process follows first order kinetics and specific rate constant ( $K_p$ ) was obtained by the application of Langargren equation. Thermodynamic parameters viz.  $\Delta G$ ,  $\Delta S$  and  $\Delta H$  have also been calculated for the metal-resin system.

**Keywords:** Ion-exchange; Batch equilibrium; Metal ion uptake; Distribution ratio; Isotherm; Thermodynamics.

## I. INTRODUCTION

Traces of organic and inorganic contaminants possessing strong ligand characteristics are widely occurred in aquatic systems. Pollution by hazardous and heavy metals due to their toxicities in relatively high concentration and tendency of bioaccumulation in the ecosystem, agriculture and human body has received wide spread attention in recent years. Sorption processes such as reverse osmosis, electro dialysis, reprecipitation and adsorption techniques have been frequently employed to achieve required degree of removal [1, 2]. However, the use of complexing agents in solution as ion exchangers is well established in order to enhance the efficiency of selective removal and separation of hazardous metals.

Copolymers as ligand exchangers are a class of promising sorbents that sorbs chemicals based on their ligand characteristics. It was observed that the chelating resins with nitrogen, sulphur and oxygen donor atoms can serve as excellent metal hosting capacity. Accordingly, the selectivity scale of different chelating exchangers towards metal reflects the stability of the corresponding metal-ligand complexes in liquid phase. Therefore, researchers have focused on metal ions removal by adsorption on chelating polymers because of its reusability, ease of separation, high adsorption capacity and selectivity [3].

Recently, much research work has been carried out to study the ion exchange properties of anchoring functional chelating groups on the polymeric network. But, as compared to anchored resins, the synthesized resins are more advantageous because it can provide good stability and flexibility in working conditions. An extensive literature survey has been carried out in the present investigation in order to interpret the experimental results in the light of practical applications of copolymers to explore its utility as ion exchangers.

Although, researches for metal ion-selective polymeric complexing agents started in early part of this century, there is still a need for the development of ion-exchange resins due to their wide application in waste water treatment and pollution control, hydrometallurgy, antibiotic purification and separation of radioisotopes, identification of specific metal ion and metal recovery [4, 5]. Batch equilibrium method has gained a rapid attention of researchers because of its acute degree of selectivity, variety of sorbent phases and enhanced hydrophilicity [6].

An eco-friendly synthesis of a copolymer resin, its characterization and chelation ion exchange properties has been reported by S. S. Butoliya [7]. Copolymer resins derived from 8-hydroxyquinoline-guanidine-formaldehyde [8], anthranilic acid-resorcinol-formaldehyde [9], 4-hydroxyacetophenone-biuret-formaldehyde [10], salicylic acid and formaldehyde with resorcinol [11], 2-hydroxyacetophenone-oxamide-formaldehyde [12] have been proved to be good ion exchangers. A detailed study on preparation and characterization of a new class of polymeric ligand exchangers for selective removal of trace contaminants from water has been reported by Henry and coworkers [13].

In an earlier communication [14-16], number of such copolymers has been reported. However, no work has been carried out on ion-exchange properties of copolymers derived from p-nitrophenol, 4,4'-methylenedianiline and formaldehyde. The purpose of present study is to explore the adsorption behavior of newly synthesized copolymer resins for the desalination of waste water which is high in metal ions like  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  to meet effluent discharge specifications.

## II. METHODOLOGY

### 2.1 Materials

All the chemicals used were of analytical grade purity. p-nitrophenol and formaldehyde (37%) were purchased from S. D. Fine Chemicals, India while 4,4'-methylenedianiline was procured from Acros Chemicals, Belgium. All the metal nitrates, electrolytes and indicators were purchased from Merck.

### 2.2 Synthesis

A mixture of p-nitrophenol (2.78 gm, 0.2 mol) and 4,4'-methylenedianiline (1.98 gm, 0.1 mol) was condensed with formaldehyde (11.25 ml, 0.3mol) having molar ratio of 2:1:3 in the presence of 200 ml, 2 M hydrochloric acid as a catalyst. The reaction mixture was taken in round bottom flask fitted with water condenser and heated in an oil bath at 130 °C for 3 hr with occasional shaking. The temperature of electrically heated oil bath was controlled with the help of dimmerstat. The dark reddish brown colored solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was repeatedly washed with hot water to remove unreacted monomers. The air dried copolymer resins were extracted with ether to remove excess of p-nitrophenol-formaldehyde copolymer, which might be present along with p-NP-4,4'-MDA-F-I copolymer resin. It was further purified by dissolving in 8 % sodium hydroxide solution and filtered. The process was repeated twice. The resulting polymer sample was washed with boiling water and dried in vacuum at room temperature. The purified copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yield of this copolymer resin was found to be 82.25%. Similarly, other copolymer resins, viz. p-NP-4,4'-MDA-F-II, p-NP-4,4'-MDA-F-III were synthesized by varying the molar proportions of starting materials in a ratio of 3:1:4, 4:1:5 respectively. The purity of newly synthesized polymer resins has been tested and confirmed by thin layer chromatography. The resin sample showing any sign of impurity was again purified by known standard methods like extraction, reprecipitation etc. and used for further studies only after the confirmation of 100 % purity of sample.

The details of mole ratio of reactants, reflux temperature, time of reflux and percentage yield of product, elemental analysis, spectral characterization and thermal properties have been reported in our previous publications [17, 18].

### 2.3 Physicochemical studies

Physicochemical studies such as moisture content, percentage solids, void volume fraction, true density and total exchange capacity were evaluated in accordance with reported procedures [19].

### 2.4 Moisture content

The purified 1g of copolymer was taken in a previously weight petri dish. The petri dish with copolymer sample was then dried in a vacuum oven at 105-110 °C for 8 h and reweighed after cooling in a desiccator. From the weight of the petri dish, moisture content (%) was calculated:

$$\text{Moisture content} = \frac{(\text{Weight of the petri dish with copolymer sample after drying}) - (\text{Weight of the petri dish})}{(\text{Weight of the petri dish with copolymer sample before drying}) - (\text{Weight of the petri dish})} \times 100 \text{ ----- (1)}$$

True density, apparent density and void volume fraction were also calculated by using expressions:

$$\text{True density } (d_{pol}) = \frac{W_p - W}{(W_w - W_{pw}) + (W_p - W)} \text{ ----- (2)}$$

Where, W = weight of the specific gravity bottle, W<sub>p</sub> = weight of the specific gravity bottle containing copolymer, W<sub>w</sub> = weight of the specific gravity bottle containing water and W<sub>pw</sub> = weight of the specific gravity bottle containing both copolymer and water.

$$\text{Apparent density}(d_{col}) = \frac{\text{Weight of copolymer}}{\text{Volume of copolymer}} \text{-----(3)}$$

$$\text{Void volume fraction} = 1 - \frac{d_{col}}{d_{pol}} \text{-----(4)}$$

### 2.5 Total exchange capacity

Total exchange capacity of the copolymer is the total number of exchanging sites available per unit volume of swollen copolymer. Dry copolymer (1.0 g, accurately weighed; H<sup>+</sup> form) of uniform particle size (30–60 mesh) was placed in a 250-mL Erlenmeyer flask. To this 200 ml standard solution of 0.1 M NaOH in 1 M NaCl was added. The mixture was equilibrated for 24 h with intermittent shaking. After 24 h, 50 ml of the mixture was withdrawn and titrated against standard 0.1 M HCl solution. The total cation exchange capacity (CEC) was calculated from:

$$\text{CEC} = \frac{(200 \times \text{Molarity of NaOH})}{\text{Weight of sample} \times [\frac{\text{Solid}(\%)}{100}]} - \frac{(4 \times \text{Volume of HCl} \times \text{Molarity of HCl})}{\text{Weight of sample} \times [\frac{\text{Solid}(\%)}{100}]} \text{-----(5)}$$

Where, CEC is the cation-exchange capacity of the copolymer.

### 2.6 Ion exchange studies

Ion-exchange studies of *p*-NP-4,4'-MDA-F copolymer resins were determined by the batch equilibrium method [20] and have been experimentally performed as follows.

#### 2.6.1. Determination of metal ion 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 suspension was adjusted to the required value by using either 0.1M HNO<sub>3</sub> or 0.1M NaOH. The suspension was stirred for 24 hrs at 30 °C. To this suspension 2 ml of 0.1M solution of the metal ion was added and the pH was adjusted to required value. The mixture was again stirred at 30 °C for 24 hrs and filtered [21]. The solid was washed; the filtrate and washing were combined and estimated for metal ion content by titration against standard ethylenediaminetetraacetic acid (EDTA) using appropriate buffer and suitable indicator as reported in Table 1[22]. The amount of metal ion uptake by the polymer was calculated from the difference between a blank reading and experimental reading [23]. The experiment was repeated in presence of several electrolytes of known concentration with eight different metal ions viz. Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup>. The same procedure was applied to all molar ratios of copolymer resins and results with eight different metal ions are incorporated in Figure 2 (a-l).

The metal ion uptake can be determined as,

$$\text{Metal ion adsorbed (uptake) by resin} = (X - Y)Z \text{ mmol/g.-----(6)}$$

Where,

X = Amount of metal ion in 2ml 0.1M metal nitrate solution before uptake.

Y = Amount of metal ion in 2ml 0.1M metal nitrate solution after uptake.

Z = Difference between actual experimental reading and blank reading.

Table 1. Summarised procedure for EDTA titrations of cation understudy

Metal Ions	Type of titration	pH range	Buffer Used	Indicator Used	Color Change
Fe <sup>+3</sup>	Direct	2 – 3	-	Variamine Blue-B	Blue-Violet to Yellow
Cu <sup>+2</sup>	Direct	10	dil. HNO <sub>3</sub> /dil NaOH	Fast Sulphone Black-F	Purple – Green
Hg <sup>+2</sup>	Direct	10	Conc. Ammonia	Eriochrome Black-T	Wine red – Blue
Cd <sup>+2</sup>	Direct	5	Hexamine	Xylenol Orange	Deep Red to Yellow
Co <sup>+2</sup>	Direct	5	Hexamine	Xylenol Orange	Deep Red to Yellow
Zn <sup>+2</sup>	Direct	10	Conc. Ammonia	Eriochrom Black-T	Wine red – Blue
Ni <sup>+2</sup>	Direct	7-10	Conc. Ammonia	Muroxide	Yellow – Bluish Violet
Pb <sup>+2</sup>	Direct	5	Hexamine	Xylenol Orange	Deep Red to Yellow

#### 2.6.2. Evaluation of the rate of metal ion 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 resins was determined from time to time at 30°C (in the presence of 25 ml of 1M 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 amount of metal ions taken up after a certain time related to that at the state of equilibrium using following relationship. The results have been graphically shown in Figure 3 (a-c).

$$\text{Metal ion uptake} = \frac{\text{Amount of metal ion adsorbed}}{\text{Amount of metal ion at equilibrium}} \times 100 \text{ -----(7)}$$

### 2.6.3. Distribution of metal ion at different pH

The distribution of each one of the eight metal ions i.e. Fe<sup>3+</sup>, Cu<sup>2+</sup>, Hg<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 the aqueous phase was determined at 30 °C and in the presence of 1M NaNO<sub>3</sub> solution. The experiments were carried out as described above at different pH values and the results are presented in Figure 4 (a-c). The distribution ratio, D, is defined by the following relationship.

$$D = \frac{\text{Amount of metal ion on resin}}{\text{Amount of metal ion in solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of resin (g)}} \text{ -----(8)}$$

### III. Result and discussion

The *p*-NP-4,4'-MDA-F resins were soluble in DMF, THF and DMSO. The results of physicochemical parameters such as moisture content, solid percentage, void volume fraction, true density and total exchange capacity of the resins are shown in Table 2.

Table 2. Physico-chemical properties of copolymers resins

Sr. No.	Properties	<i>p</i> -NP-4,4'-MDA-F-I	<i>p</i> -NP-4,4'-MDA-F-II	<i>p</i> -NP-4,4'-MDA-F-III
1.	Moisture (%)	3.1 ± 0.25	4.2 ± 0.25	4.9 ± 0.25
2.	Solids (%)	92.8 ± 0.25	93.4 ± 0.25	96.8 ± 0.25
3.	True density (dry resin) g/cm <sup>3</sup>	2.105 ± 0.05	2.118 ± 0.05	2.21 ± 0.05
4.	Void volume fraction	0.430 ± 0.025	0.510 ± 0.025	0.640 ± 0.025
5.	Sodium exchange capacity (mmol g <sup>-1</sup> dry resin)	4.84 ± 0.10	1.44 0.10	5.91 ± 0.10

### 3.1 Ion Exchange Properties

With a view to ascertain the selectivity of *p*-NP-4,4'-MDA-F copolymers for selected metal ions, we have 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 copolymer and solution containing the metal ions by using batch equilibrium technique developed by Gregor et al and De Geiso [24, 25]. Certain generalizations are made about the behavior of copolymers as ion exchangers.

#### 3.1.1 Effect of Electrolytes and their concentrations on metal ion uptake capacity

Graphical examination of Figure 2 (a-l) reveals that the amount of metal ions taken up by copolymer depends on nature and concentration of electrolyte present in solution. Generally, as the concentration of electrolyte increases, ionization decreases and number of ligand decreases in the solution which forms the complexes with less metal ions and more ions are available for adsorption. The variable nature of metal ion uptake capacity of copolymer resins may be due to strong and weak complex formation between electrolyte ligand and metal ions.

In presence of ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions, the uptake of Fe<sup>+3</sup>, Cu<sup>+2</sup>, Hg<sup>+2</sup>, Zn<sup>+2</sup>, Cd<sup>+2</sup>, Co<sup>+2</sup>, Ni<sup>+2</sup> and Pb<sup>+2</sup> metal ions by copolymer increases with rise in concentration of an electrolytes whereas in presence of SO<sub>4</sub><sup>-2</sup> ions, amount of above mentioned metal ions taken up by copolymers decreases with increasing concentration of electrolytes. Moreover, there is more increase in uptake of Fe<sup>+3</sup>, Hg<sup>+2</sup>, Cd<sup>+2</sup> and Pb<sup>+2</sup> ions with increasing concentration of ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions as observed from the results as compared to Cu<sup>+2</sup>, Zn<sup>+2</sup>, Co<sup>+2</sup> and Ni<sup>+2</sup> ions. But it decreases in presence of SO<sub>4</sub><sup>-2</sup> ions. Anions like ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> form weak association with above mentioned metal ions while SO<sub>4</sub><sup>-2</sup> ions form stronger complexes. This association is affecting equilibrium which may be explained on the basis of stability constants of complexes with these metal ions [26, 27, 28]. The stability of the complexes depends on the charge of metal ions and nature of ligands. Among all of the above four ligands, SO<sub>4</sub><sup>-2</sup> is a strong ligand having more number of electrons for donation during formation of complex. This association has been found to be affecting equilibrium which may be explained on the basis of stability constants of complexes with these metal ions as reported in literature [29]. This type of trend has also been observed by other investigators in this field as evident from the literature [30, 31]. It is observed that the amount of metal ions taken up by copolymer increases in the order *p*-NP-4,4'-MDA-F-I < *p*-NP-4,4'-MDA-F-II < *p*-NP-4,4'-MDA-F-III.

As oxygen and nitrogen present in the copolymer are responsible for the complexation, these observed trend may be due to introduction of more *p*-nitrophenol and 4,4'-methylenedianiline groups in the repeating unit of copolymers from *p*-NP-4,4'-MDA-F-I to III. As the molar ratio increases, the mobility of electrons of same group present on the copolymers also increases in same order. Therefore, resin containing higher concentration of *p*-nitrophenol and 4,4'-methylenedianiline groups show more chelating ability towards the metal ions under study. The most probable structure of metal-ligand (copolymer) interaction has been shown in Figure 1.

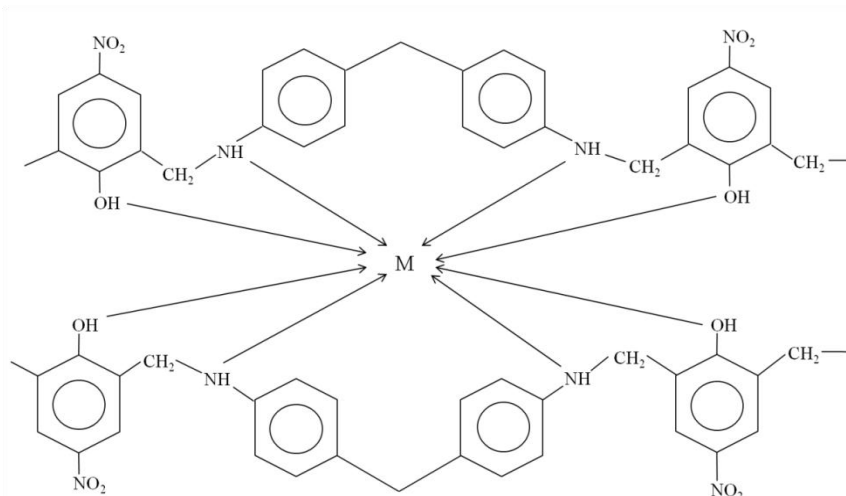


FIG. 1. Chelate structure of the *p*-NP-4,4'-MDA-F copolymer resin.

After adsorption when the solution is filtered and the polymer is shaking with dilute HCl, there is an exchange of metal ion and  $H^+$  ions, metal ions enter in the acid solution as  $H^+$  ions adsorbed on the polymer, this phenomena is known as desorption or regeneration of polymers. The regenerated polymers can again be used for readsorption by shaking it with metal ion solution. It is estimated that the amount of metal ion taken up by recycled polymer is no way inferior to the freshly prepared resin. Adsorption and readsorption depends on concentration of metal ions but desorption does not.

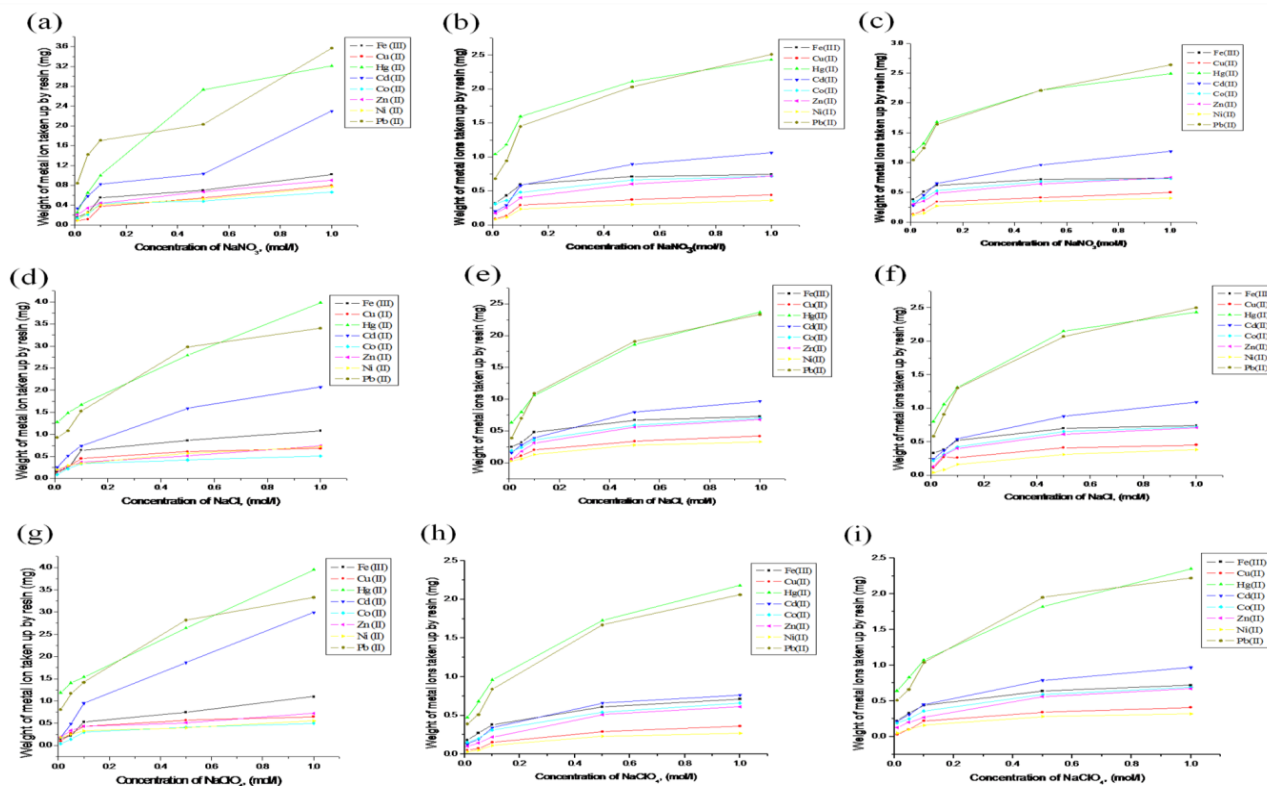


FIG. 2. (a-l) Evaluation of the influence of different electrolytes<sup>a</sup> on the uptake of several metal ions<sup>b</sup> of *p*-NP-4,4'-MDA-F copolymer resins.

<sup>a</sup>[Fig. 1 (a-c) for NaNO<sub>3</sub>; Fig. 1 (d-f) for NaCl; Fig. 1 (g-i) for NaClO<sub>4</sub>, Fig. 1 (j-l) for Na<sub>2</sub>SO<sub>4</sub>]

<sup>b</sup>[ $[Mt(NO_3)_2] = 0.1 \text{ mol/l}$ ; volume of electrolyte solution = 25 ml; volume of metal ion solution = 2 ml; weight of resin = 25 mg; time = 24 h; room temperature.

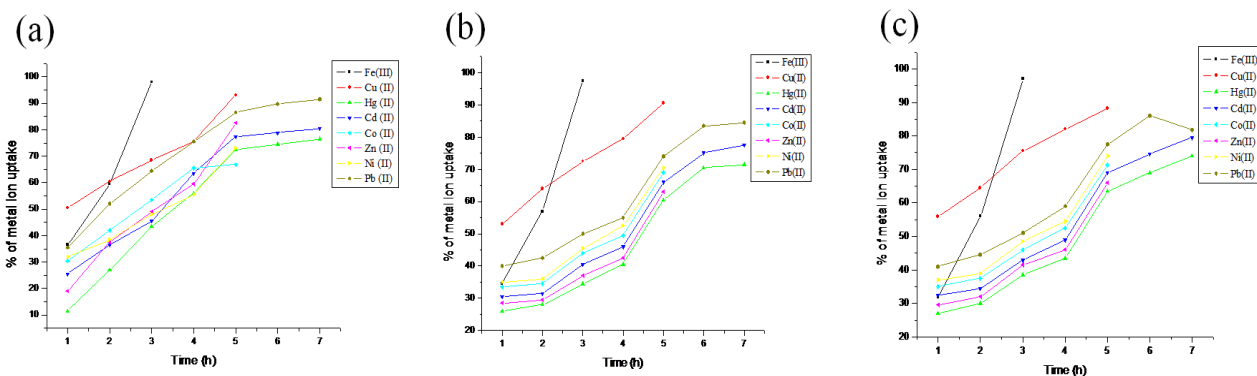
### 3.1.2 Rate of uptake for metal ions as a function of time

Rate of metal ion adsorption by copolymers were determined to find out the shortest period of time required for attaining the equilibrium which is operating as close to equilibrium conditions as possible as graphically shown in Figure 3 (a-c). As shaking time increases the polymer gets more time for adsorption, hence uptake increases. Rate refers to change in concentration of metal ions in aqueous solution which is in contact with given copolymer.

The result shows that time taken for the uptake of different metal ions at a given stage depends on the nature of metal ion and their ionic size under given conditions. Graphical interpretation reveals that  $\text{Fe}^{3+}$  has more charge and small size, therefore equilibrium is attained within 3 h, whereas other transition metal ions  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Co}^{+2}$  and  $\text{Zn}^{+2}$  have nearly equal cationic size, having same charges, therefore requires 5 hr and  $\text{Hg}^{+2}$ ,  $\text{Cd}^{+2}$  and  $\text{Pb}^{+2}$  have large atomic size, therefore requires about 7 hr. for the attainment of equilibrium. Rate of metal ion uptake follows the order as given below:

Metal ion (Ionic size):  $\text{Fe}^{3+}$  (0:55) >  $\text{Cu}^{2+}$  (0:57)  $\approx$   $\text{Ni}^{2+}$  (0:69) >  $\text{Co}^{2+}$  (0:90)  $\approx$   $\text{Hg}^{2+}$  (0:90)  $\approx$   $\text{Zn}^{2+}$  (0:90) >  $\text{Cd}^{2+}$  (1:10)  $\approx$   $\text{Pb}^{2+}$  (1:19)

This observed order indicates that the rate of metal ion uptake depends on the size of metal ion, as the size increases, the time taken for uptake of metal ions also increases in order to attend the equilibrium [32, 33, 34]. Comparison of the rate uptake of given metal ions reveals that the rate of metal ions uptake by the copolymer follows the order as:  $p\text{-NP-4,4'-MDA-F-III}$  >  $p\text{-NP-4,4'-MDA-F-II}$  >  $p\text{-NP-4,4'-MDA-F-I}$ . This shows that the rate of uptake capacity depends on molar ratio. As the molar ratio increases the metal uptake capacity also found to be increased, which may be due to introduction of more and more ligand groups in the repeating unit structure of polymer chain. Due to difference in the uptake rate of metal ion and shortest time required for adsorption of  $\text{Fe}^{3+}$ , it may be possible to use these polymers to separate  $\text{Fe}^{3+}$  ion from their admixture with  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Hg}^{+2}$  and  $\text{Pb}^{+2}$  ions.



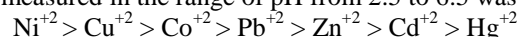
**FIG. 3.** (a–c) Comparison of the rate of metal ion  $[\text{Mt}]^a$  uptake of  $p\text{-NP-4,4'-MDA-F}$  copolymer resins.  $^a[\text{Mt}(\text{NO}_3)_2] = 0.1 \text{ mol/l}$ ; volume of metal ion = 2 ml,  $\text{NaNO}_3 = 1.0 \text{ mol/l}$ , volume of  $\text{NaNO}_3 = 25 \text{ ml}$ .

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

### 3.1.3 Distribution ratios of metal ion at different pH

Effect of pH on the amount of metal ions distributed between two phases can be explained by the results graphically shown in Figure 3 (a-c). Data of distribution ratio 'D' as a function of pH indicates that the relative amount of metal ion taken up by copolymer increases with rise in pH of medium [35, 36]. The increase in magnitude is different for different metal ions. The study was carried out in acidic medium from pH 1.5 to 6.5 to prevent the hydrolysis and precipitation at higher pH. In case of  $\text{Fe}^{+3}$ , the best results are obtained at pH 2.5 and indicate that  $\text{Fe}^{+3}$  ions taken up by the copolymer resins more selectively as compared to other metal ions under study.

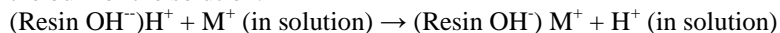
$\text{Fe}^{+3}$  ions are more selective among above mentioned metal ions within the pH range from 1.5 to 2.5.  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$  and  $\text{Co}^{+2}$  ions are taken up by copolymers more selectively as compared to other four metal ions i.e.  $\text{Pb}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$  and  $\text{Hg}^{+2}$  and having low distribution ratio (D) over the pH range 2.5 to 6.5. This could be attributed to low stability constants because of the weak metal-ligand stabilization energy of the metal complexes [37]. In present study the observed order of distribution ratios of transition metal ions measured in the range of pH from 2.5 to 6.5 was found to be



Similar trend have been reported by earlier investigators which are helpful in selecting optimum pH for a selective uptake of a particular cation from an admixture. Result suggests that at optimum pH 6.5, for the separation of  $Zn^{+2}$  and  $Hg^{+2}$  with distribution ratio 'D' having 1385.4 and 921.4 respectively using copolymer resins as an ion-exchanger is necessary. Similarly, separation of  $Pb^{+2}$  and  $Fe^{+3}$  carried out at optimum pH 2.5 having distribution ratio 'D' 7.51 and 1258.9 respectively. Higher distribution of  $Fe^{+3}$  shows the efficient separation from other metals. Distribution ratios 'D' of above mentioned metal ions at pH 2.5 in the mixture were found to be 7.51, 2.90, 4.35, 7.53, 11.85, 15.33 and 15.02 respectively i.e. very much lower than  $Fe^{+3}$  which found to be 1258.9. Lowering in distribution ratios of other metal ions with respect to  $Fe^{+3}$  has shown that the efficient separation could be achieved at lower pH.

Similarly, the binary mixtures such as  $Fe^{+3}$ - $Hg^{+2}$ ;  $Fe^{+3}$ - $Co^{+2}$ ;  $Fe^{+3}$ - $Ni^{+2}$ ;  $Fe^{+3}$ - $Cd^{+2}$ ;  $Fe^{+3}$ - $Zn^{+2}$  and  $Fe^{+3}$ - $Pb^{+2}$  can also be separated out at pH 2.5. The metal ion understudy in a binary mixture may be separated at pH 6.5 from each other like  $Hg^{+2}$ - $Cd^{+2}$ ;  $Hg^{+2}$ - $Zn$ ;  $Hg^{+2}$ - $Ni^{+2}$ ;  $Hg^{+2}$ - $Co^{+2}$ ;  $Hg^{+2}$ - $Cu^{+2}$ ;  $Hg^{+2}$ - $Pb^{+2}$ . Similarly, using the appropriate pH, the separation of the binary mixture is possible which has different distribution ratios [38]. With increase in pH the negatively charged nature of sorbent surface increases which leads to increase in the electrostatic attraction between charged metal ions and negatively charged copolymer and resulted in increase in exchanging metal ions. Decrease in removal of metal ions at lower pH is due to the higher concentration of  $H^+$  ions presented in the reaction mixture which compete with metal ions for the sorption sites on the ion exchanger surface.

The *p*-NP-4,4'-MDA-F copolymer resin is a cation exchange resin and the equilibrium may be expressed in terms of mass action law and the relative amount of metal ions in the resin phase are determined by the relative concentrations of these ions in the bulk of the solution.



$$K = \frac{[\text{H}^+][(\text{Resin OH}^-)\text{M}^+]}{[(\text{Resin OH}^-)\text{H}^+][\text{H}^+]}$$

Equilibrium constant (K) of this type are useful for comparing the relative affinities for a resin towards various ions. The strength of electrolyte and dielectric constant also affect the metal distribution or accumulation of resin. Thus, the present paper describes the novel ion-exchanger resins suitable for the desalination of waste water containing a high concentration of toxic metal ion contents.

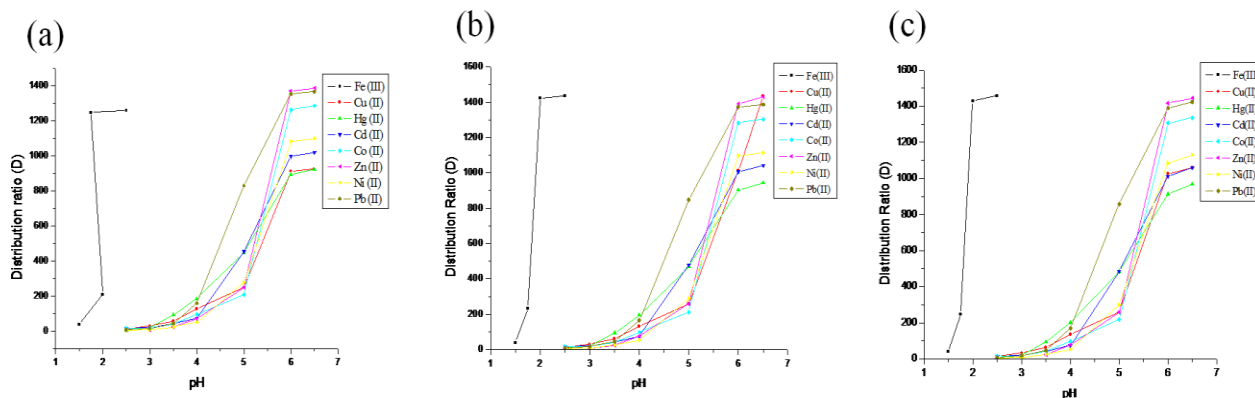


FIG. 4. (a-c) Distribution ratio (D)<sup>a</sup> of different metal ions as function of the pH<sup>b</sup> of *p*-NP-4,4'-MDA-F copolymer resins.

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

<sup>b</sup>[Mt(NO<sub>3</sub>)<sub>2</sub>] = 0.1 mol/l; volume = 2 ml; NaNO<sub>3</sub> = 1.0 mol/l; volume of electrolyte NaNO<sub>3</sub> = 25 ml; room temperature.

### 3.2 Effect of temperature and thermodynamic parameters

Effect of temperature on the adsorption of various metal ions on *p*-NP-4,4'-MDA-F resins was studied using optimizing conditions. The temperature was varied from 30 to 60 °C. It was observed that the adsorption of metal ions increases with the increase in temperature because  $\Delta G$  decreases with the rise in temperature of the solution (Fig. 5) [43]. This is due to endothermic ion-exchange reaction with cations [39]. The surface energy of *p*-NP-4,4'-MDA-F resin increases with temperature. Similar results have also been reported earlier for the adsorption of divalent cations with commercial resins Dowex 50 [39] and Amberlite IR 120 [40].

The values of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  were also calculated from the slope and intercept of the Van't Hoff plot of the adsorption of metal ions on the *p*-NP-4,4'-MDA-F resin, i.e. the linear variation of  $\ln K_d$  with reciprocal temperature  $1/T$  (Fig. 6) using the following relation.

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

Where,  $K_d$  is the distribution coefficient ( $\text{cm}^3/\text{g}$ ),  $\Delta S$  is the entropy change for the process and  $\Delta H$  is the enthalpy change for the process. The free energy of the adsorption and  $\Delta G$  was calculated using the following Vant Hoff equation:

$$\Delta G^{ads} = -RT \ln K_d \quad (10)$$

The determination of thermodynamic parameters for adsorption of various metal ions on *p*-NP-4,4'-MDA-F resin is given in Table 3. Value of  $\Delta H$  is negative which indicates an exothermic adsorption process and it shows that the chelation mechanism dominates [41]. The entropy ( $\Delta S$ ) is positive corresponding to an increase in degree of freedom of the system due to release of two hydrogen ions for the divalent metal ions under study [42]. The negative values of  $\Delta G$  indicate the feasibility of the process and also the spontaneity of the adsorption process.

Table 3. Thermodynamic parameters for metal ion adsorption on *p*-NP-4,4'-MDA-F-I resin.

Metal ions	T (K)	1/T ( $\text{K}^{-1}$ )	$K_d$	$\ln K_d$	$\Delta G$ (kJ $\text{mol}^{-1}$ )	$\Delta H$ (kJ $\text{mol}^{-1}$ )	$\Delta S$ (J $\text{K}^{-1} \text{mol}^{-1}$ )
$\text{Fe}^{+3}$	293	$3.30 \times 10^{-3}$	38.28	3.64492	-2.45952	-97.97	3.98
	303	$3.19 \times 10^{-3}$	38.86	3.65996	-2.55396		
	313	$3.09 \times 10^{-3}$	39.21	3.66893	-2.64471		
	323	$3.00 \times 10^{-3}$	39.50	3.67630	-2.73469		
$\text{Cu}^{+2}$	293	$3.30 \times 10^{-3}$	11.85	2.47232	-1.66827	-205.11	3.16
	303	$3.19 \times 10^{-3}$	12.07	2.49072	-1.73805		
	313	$3.09 \times 10^{-3}$	12.25	2.50552	-1.80608		
	323	$3.00 \times 10^{-3}$	12.68	2.54002	-1.889.45		
$\text{Hg}^{+2}$	293	$3.30 \times 10^{-3}$	7.53	2.01889	-1.36231	-391.39	3.35
	303	$3.19 \times 10^{-3}$	7.88	2.06432	-1.44051		
	313	$3.09 \times 10^{-3}$	8.17	2.10046	-1.5141		
	323	$3.00 \times 10^{-3}$	8.54	2.14476	-1.59542		
$\text{Cd}^{+2}$	293	$3.30 \times 10^{-3}$	15.02	2.70938	-1.82823	-188.13	3.35
	303	$3.19 \times 10^{-3}$	15.34	2.73046	-1.90534		
	313	$3.09 \times 10^{-3}$	15.71	2.75429	-1.98541		
	323	$3.00 \times 10^{-3}$	15.92	2.76757	-2.05871		
$\text{Co}^{+2}$	293	$3.30 \times 10^{-3}$	15.33	2.72981	-1.84202	-167.67	3.30
	303	$3.19 \times 10^{-3}$	15.65	2.75047	-1.9193		
	313	$3.09 \times 10^{-3}$	15.89	2.76569	-1.99362		
	323	$3.00 \times 10^{-3}$	16.18	2.78377	-2.07076		
$\text{Zn}^{+2}$	293	$3.30 \times 10^{-3}$	4.35	1.47017	-9.92044	-419.63	2.89
	303	$3.19 \times 10^{-3}$	4.48	1.49962	-1.04645		
	313	$3.09 \times 10^{-3}$	4.69	1.54543	-1.11401		
	323	$3.00 \times 10^{-3}$	4.97	1.60342	-1.19273		
$\text{Ni}^{+2}$	293	$3.30 \times 10^{-3}$	2.90	1.06471	-7.18444	-903.11	4.14
	303	$3.19 \times 10^{-3}$	3.18	1.15688	-0.80728		
	313	$3.09 \times 10^{-3}$	3.48	1.24703	-0.89891		
	323	$3.00 \times 10^{-3}$	3.87	1.35325	-1.00664		
$\text{Pb}^{+2}$	293	$3.30 \times 10^{-3}$	7.51	2.01623	-1.36051	-355.40	3.22
	303	$3.19 \times 10^{-3}$	7.78	2.05155	-1.43159		
	313	$3.09 \times 10^{-3}$	8.07	2.08815	-1.50522		
	323	$3.00 \times 10^{-3}$	8.41	2.12942	-1.58401		



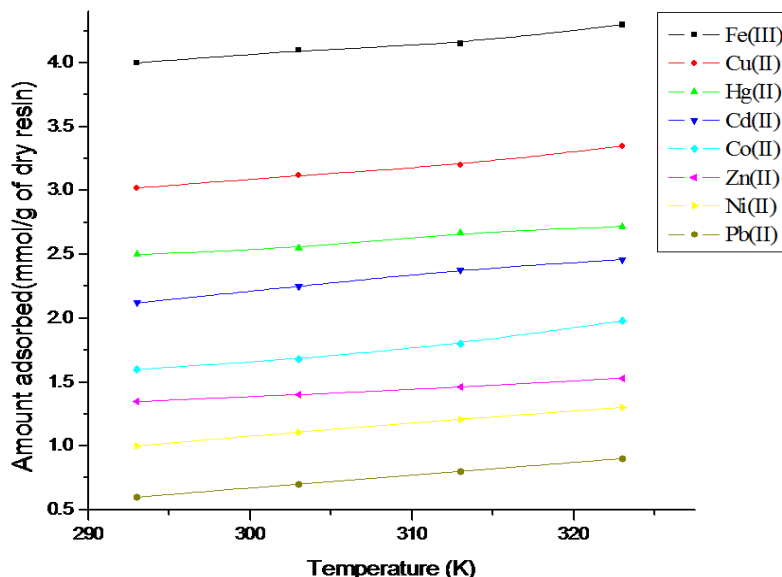


FIG. 5. Metal ion uptake capacity as a function of *p*-NP-4,4'-MDA-F-I as a function of temperature.

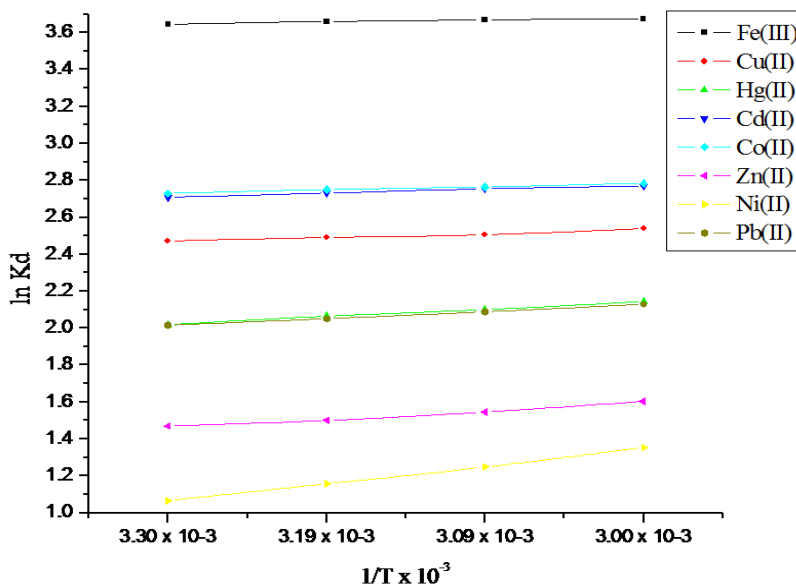


FIG. 6. Van't Hoff plot for the adsorption of metal ions on *p*-NP-4,4'-MDA-F-I resin.

3.3 Kinetic Model (Langergran equation)

When a single species is considered on a heterogeneous surface, the ion exchange phenomenon follows reversible first order kinetics [39]. The specific rate constant *K<sub>r</sub>* for the sorbent was determined by Langergren equation as follows.

$$\log(q_e - q) = \log q_e - (K_r \times t)/2.303 \text{ -----(11)}$$

Where *q<sub>e</sub>* and *q* (mmol/g) are the amounts of metal ions adsorbed at equilibrium and time, *t*(min) respectively. The straight line plot (fig. 7) of the log (*q<sub>e</sub>*-*q*) versus time, *t* (at 30 ± 2 °C) indicates the validity of Langergran equation for the system and explains that process follows first order kinetics. The values of *K<sub>r</sub>* were calculated from the slope of the plot (fig. 7) and found to be 8.167 × 10<sup>-3</sup>, 9.672 × 10<sup>-3</sup>, 15.009 × 10<sup>-3</sup>, 14.253 × 10<sup>-3</sup>, 17.371 × 10<sup>-3</sup>, 10.298 × 10<sup>-3</sup>, 17.271 × 10<sup>-3</sup>, 15.273 × 10<sup>-3</sup> for Fe<sup>+3</sup>, Cu<sup>+2</sup>, Hg<sup>+2</sup>, Zn<sup>+2</sup>, Cd<sup>+2</sup>, Co<sup>+2</sup>, Ni<sup>+2</sup> and Pb<sup>+2</sup> respectively [44, 45].

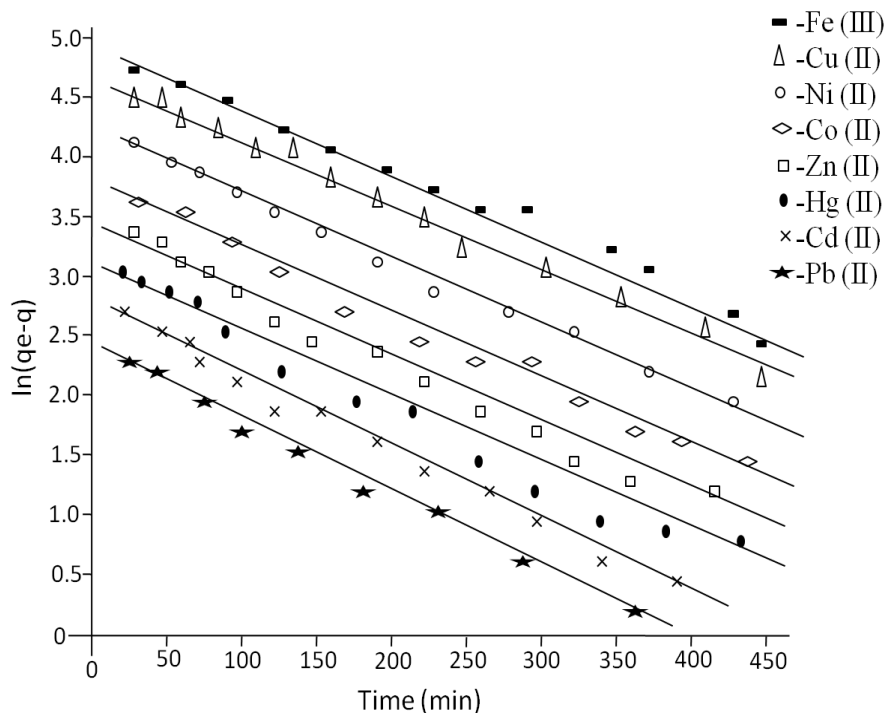


FIG. 7. Langergren plot for specific rate constant of metal ions on *p*-NP-4,4'-MDA-F-I resin

3.4 Sorption isotherms

To quantify the sorption capacity of the *p*-NP-4,4'-MDA-F for the removal of divalent cations, two isotherms namely Langmuir [46] and Freundlich [47] have been adopted (Table 4).

Table 4. Adsorption isotherm models.

Isotherm	Linear form	Plot
<b>Freundlich</b> $q_e = kF.C_e^{1/n}$	$\log q_e = \log K_f + 1/n \log C_e$	$\log q_e$ Vs $\log C_e$
<b>Langmuir</b> $q_e = \frac{Q^0 C_e}{1 + bC_e}$	$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0}$	$C_e/q_e$ Vs $C_e$

3.4.1 Freundlich model

Freundlich model is commonly used to describe the adsorption characteristics for the heterogeneous surface due to the variety of sorption sites or the varied nature of the adsorbate adsorbed on the surface. The linear form of Freundlich isotherm is given in Table 4. The linear plot of  $\log q_e$  vs.  $\log C_e$  indicates the applicability of Freundlich isotherm. The constants  $K_F$  and  $1/n$  relates to the measure of adsorption capacity and adsorption intensity respectively (Table 5). Values of  $1/n$  are lying between 0 and 1 and the  $n$ -value lying in the range of 1–10 confirms the favorable conditions for adsorption [48, 49, 50]. The higher fractional values of  $1/n$  signify that strong adsorption forces are operative on the system. The magnitude of  $1/n$  also gives indication of the favorability and capacity of the adsorbent/adsorbate system [51]. The adsorption capacity increases with increase in temperature suggesting that the metal ion uptake by copolymer is an endothermic process. Freundlich constants  $kF$  and  $n$  were calculated for all metal ions under study (Table 5).

3.4.2 Langmuir model

Langmuir isotherm model proposed quantitatively the formation of a monolayer adsorbate on the surface of the adsorbents. The Langmuir constants  $Q_0$  and  $b$  are related to sorption capacity and sorption energy respectively. Maximum sorption capacity ( $Q_0$ ) represents monolayer coverage of sorbent with sorbate and  $b$  represents the energy of sorption and should vary with temperature [45]. The linear plot of  $C_e/q_e$  vs.  $C_e$  indicates the applicability of Langmuir isotherm. The values of Langmuir constants are given in Table 2. In order to find out the feasibility of the isotherm, the essential characteristics of the

Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter,  $R_L$  [52, 53].

$$RL = \frac{1}{1 + bC_0}$$

Where,  $b$  is the Langmuir isotherm constant and  $C_0$  is the initial concentration of metal (mg/L). The  $RL$ -values between 0 and 1 indicate favorable adsorption (Table 5) [43]. The adsorbents have more surface area and higher pore volume is responsible for the effective adsorption capacity of the adsorbents.

Table 5. Adsorption isotherm data of various isotherm models.

Parameters	Metal ions							
	Fe(III)	Cu(II)	Hg(II)	Cd(II)	Co(II)	Zn(II)	Ni(II)	Pb(II)
<b>Langmuir constant</b>								
$Q^0$ (mmol/L)	0.126	0.159	1.148	1.123	0.112	2.131	1.453	2.857
$b$ (L/mg)	0.072	0.075	0.057	0.091	0.071	0.086	0.887	0.681
$R^2$	0.985	0.988	0.998	0.967	0.954	0.978	0.911	0.997
<b>Freundlich constant</b>								
$K_F$ (mmol/g)(L/g)	43.51	65.49	28.35	55.70	44.38	50.78	34.73	61.58
$n$	1.431	1.076	1.868	1.005	1.987	1.125	1.798	1.398
$R^2$	0.976	0.911	0.993	0.991	0.998	0.993	0.997	0.991

### 3.5 SEM analysis

The typical microphotograph at 2,000 magnifications from SEM of  $p$ -NP-4,4'-MDA-F-I is shown in Figure 8. The image clearly indicates a loosely close packed structure with high porosity or voids. The voids presented in the copolymer ligands may be responsible for the swelling behavior and reactivity of active sites buried in the polymer matrix and also responsible for exchange of metal ion. The image also showed a transition state between the amorphous and crystalline states. However, more predominantly, the copolymer is amorphous, because of the polycondensation reaction.

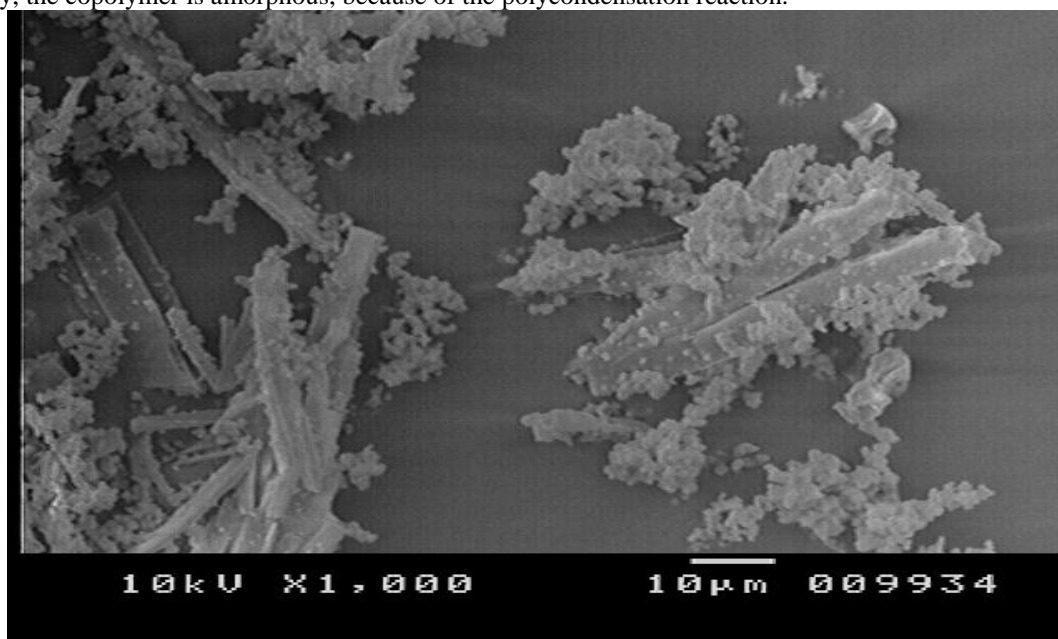


FIG. 8. Scanning electron micrograph of (SEM) of  $p$ -NP-4,4'-MDA-F-I copolymer resin.

### 3.6 Comparative study of resins

The strength of ion exchange capacities of various resins can be studied by comparing their ion-exchange capacities. The ion exchange capacity is the amount of ion that undergoes exchange in a definite amount of material, under specified experimental condition. The cation exchange capacity (CEC) of  $p$ -NP-4,4'-MDA-F-I copolymer has been calculated and found to be  $5.32 \text{ mmol.g}^{-1}$  which indicates that this copolymer resin is a better ion-exchanger or its ion exchange capacity is as equivalent as commercially available ion-exchangers and other reported copolymers (Table 6) [54,55].

Table 6. The ion exchange capacity of some ion-exchangers

Trade Name	Functional 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
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

#### IV. CONCLUSION

The resin shows lower percentage of moisture content as compared to other reported resins which indicates the high degree of cross linking in the resin so it become less dense and expected to be more porous. It is a selective chelating ion-exchanger resin 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>, Pb<sup>2+</sup> and Hg<sup>+2</sup> metal ions. These resins showed higher selectivity for Fe<sup>+3</sup>, Hg<sup>+2</sup>, Cd<sup>+2</sup> and Pb<sup>+2</sup> ions than for other metal ions understudy.

As the pH of the medium increases, the amount of metal ion adsorbed by the polymers also increases and follow the trend as Ni<sup>+2</sup> > Cu<sup>+2</sup> > Co<sup>+2</sup> > Pb<sup>+2</sup> > Zn<sup>+2</sup> > Cd<sup>+2</sup> > Hg<sup>+2</sup>. The Fe<sup>3+</sup> adsorption were studied in the pH range 1.5 to 2.5 and it also increases with increasing pH. From the result of distribution ratio, it can be observed that the polymer shows highest affinity for Fe<sup>3+</sup> whereas least affinity for Ni<sup>2+</sup>.

These copolymers showed higher selectivity for Fe<sup>3+</sup> at pH 2.5 as compared to other metal ions. The amount of metal ions taken up by *p*-NP-4,4'-MDA-F copolymer resins increases in the order *p*-NP-4,4'-MDA-F-III > *p*-NP-4,4'-MDA-F-II > *p*-NP-4,4'-MDA-F-I. It may be due to introduction of more and more ligand groups in the repeating unit structure of copolymer chain. Because of the considerable difference between the adsorption capacity at different pH, rate of metal uptake and distribution ratio at equilibrium; it may be possible to use these polymers for the separation of particular metal ions from their admixtures.

The adsorption follows both Langmuir and Freundlich isotherm models which indicates that beneficial adsorption occurs through monolayer mechanism involving ion-exchange/chelation phenomenon. Thermodynamic parameters show that adsorption process is exothermic and spontaneous.

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