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Metal ion binding and biological properties of copolymer resin derived from 2, 4-Dihydroxyacetophenone

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ABSTRACT

Copolymer resin (2,4-HADF-III) synthesized by the condensation of 2,4-dihydroxyacetophenone and dithiooxamide with formaldehyde in 3:1:4 mol ratio using hydrochloric acid as a reaction medium, were proved to be selective chelation ion-exchange copolymers for certain metals. The synthesized copolymer resin was characterized by elemental analysis, TGA, FTIR, electronic absorption and ^1H NMR spectroscopy. The physic-chemical parameters have been evaluated for the copolymer resin. The thermal stability of the copolymer was analyzed by thermo gravimetric analysis. The activation energy and the order of the reaction were calculated for 2, 4-HADF-III by the Freeman-Carroll method. 2, 4-HADF-III possesses antimicrobial activity for certain bacteria such as *Staphylococcus aureus*, *Escherichia coli*, and fungi *Aspergillus niger*, *Candida albicans*. The semi crystalline nature of the synthesized copolymer was established by scanning electron microscopy (SEM). The electrical property of the copolymer was also evaluated at various concentrations and temperatures.

Key words: copolymers; resins; ion-exchanger; antimicrobial screening; absorption.

INTRODUCTION

Polymers possess attractive applications for environmental pollution control, bioinorganic catalysts, hydrometallurgy, semiconducting devices, and metal recovery from dilute solutions [1-3]. Ion-exchangers are widely used for the treatment of radioactive wastes from nuclear power stations [4]. A series of cyano derivatives of N-alkyl and N-aryl piperazine were synthesized and their antimicrobial activities were evaluated against Gram-positive and Gram-negative strain *S. Aureus*, *P. Aeruginosa*, *S. Epidermidis*, *E.Coli* and antifungal activities against *A. Fumigantus*, *A. Flavus* and *A. Niger*. Few of the synthesized derivatives possess potent antibacterial activity and some of the compounds were reported for its cytotoxic activity [5]. Biological evaluation of novel nitrogen containing aniline formaldehyde resin has been studied and the compounds were reported as a potent antifungal and antibacterial agent [6]. Long chain aliphatic esters as well as organic and ferrocene containing Schiff bases were synthesized and reported to have good antitumor, anticancer and antioxidant also a candidate [7]. Poly [(2-hydroxy-4-methoxybenzophenone) ethylene] resin and its polychelates with lanthanides (III) were screened for antibacterial activity and the metal chelated compounds maintain better activity compared to the ligand [8]. A copolymer involving 2, 4-dichlorophenylmethacrylate and vinyl acetate was reported as a significant inhibitor for the growth of microorganisms [9]. In an earlier communication [10-13] from this department a number of such copolymers have been reported. However, no work has been carried out on the synthesis, characterization, ion-exchange and biological properties of the copolymer resins from 2, 4-dihydroxyacetophenone, dithiooxamide and formaldehyde.

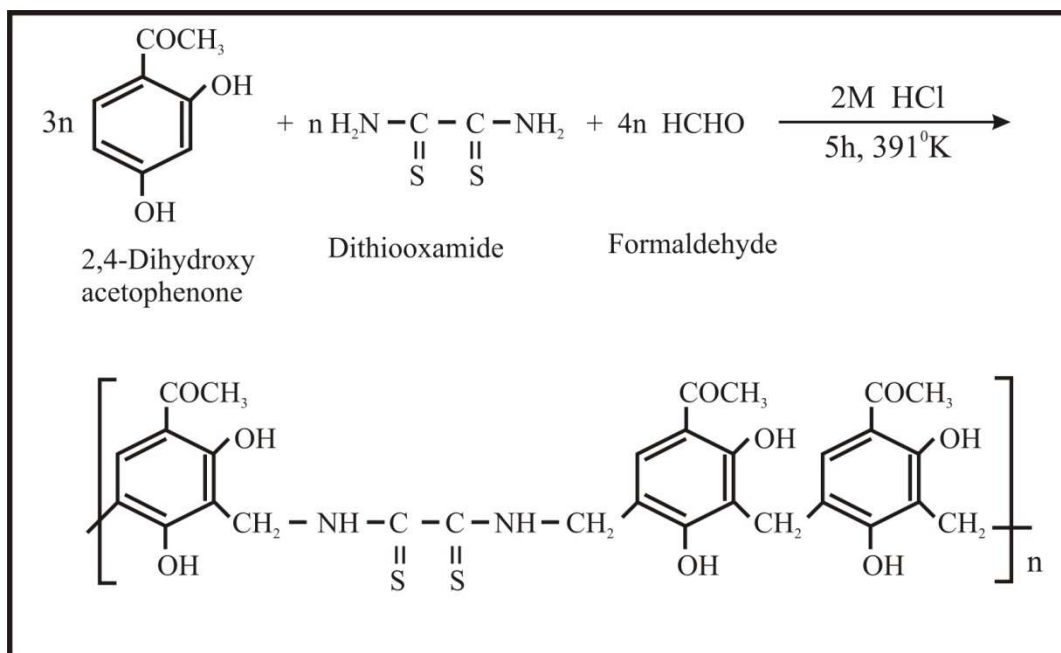
MATERIALS AND METHODS

Materials

2, 4-dihydroxyacetophenone (SRL, Mumbai) and dithiooxamide (Merck, India) were purified by rectified spirit, formaldehyde (37 %), metal chlorides and nitrates of selected metals (AR grade, Merck) were used as received. All the other chemicals, solvents and the indicators such as fast sulphon black F, methyl blue, xylenol orange and solochrome black were analytical grades procured from Qualigens Fine Chemicals, Mumbai, India. Standardized Na_2EDTA was used as a titrant for all complexometric titrations. Double distilled water was used in all the experiments.

Synthesis of 2, 4-HADF copolymer resin

The 2, 4-HADF-III copolymer resin was prepared by condensing 2, 4-HADF (5.58 gm, 0.3mol) and dithiooxamide (1.20 gm, 0.1mol) with formaldehyde (15 mL of 37 %, 0.4 mol) in the presence of 2M HCl (200 mL) as a catalyst at 391 K in an oil bath for 5 h with occasional shaking to ensure thorough mixing [14-17]. The solid resinous product obtained was removed immediately from the flask. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove unreacted monomers. Then it was extracted with diethyl ether to remove excess of 2, 4-dihydroxyacetophenone-formaldehyde copolymer which might be present along with 2, 4-HADF copolymer resin. The purified copolymer resin was finely ground and kept in a vacuum over silica gel. The yield of the copolymer resin was found to be 78 %. The dried resin sample finely ground and sieved to obtain uniform particles of 300 mesh size and stored in a polyethylene container. The sieved resin was used for further characterization. The reaction sequence of the synthesis of 2, 4-HADF-III copolymer resin is shown in Scheme 1.



Scheme 1. Synthesis of representative 2, 4-HADF-III copolymer resin

Ion-exchange properties

The ion-exchange properties of the 2, 4-HADF-III copolymer resins were determined by the batch equilibrium method [19]. The ion exchange properties of the 2, 4-HADF-III copolymer resin has been presented in this paper.

Determination of metal uptake in the presence of various electrolytes and different concentration

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 0.1M HNO_3 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 the required value. The mixture was again stirred at 30 °C for 24 hrs. The polymer was then filtered off and washed with distilled water. The filtrate and the washing were collected and then the amount of metal ion was estimated by titrating against standard EDTA (ethylene diamine tetra-acetic acid) at the same pH (experimental reading). The same titration has been carried out without polymer (blank reading). 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. The experiment was repeated in the presence of several electrolytes [18, 19].

The metal ion uptake can be determined as,

Metal ion adsorbed (uptake) by resin = (X-Y) Z mmol / gm.

Where,

'Z' ml is the difference between actual experimental reading and blank reading.

'X' mg is metal ion in the 2ml 0.1M metal nitrate solution before uptake.

'Y' mg is metal ion in the 2ml 0.1M metal nitrate solution after uptake.

By using this equation the uptake of various metal ions by resin can be calculated and expressed in terms of milliequivalents per gram of the copolymer.

Estimation of rate of metal ion uptake as function of time

In order to estimate the time require 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 25ml of 1M NaNO₃ solution). It was assumed that, under the given conditions, the state of equilibrium was established within 24 hrs [19]. The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to that at the state of equilibrium and it can be defined by the following relationship.

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

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

Percentage of metal ion adsorbed after 1 hr = (100X) / Y

Where,

'X' mg of metal ion adsorbed after 1 hr and 'Y' mg of metal ion is adsorbed after 25 hrs, then by Using this expression, the amount of metal adsorbed by polymer after specific time intervals was calculated and expressed in terms of percentage metal ion adsorbed. This experiment was performed using 0.1M metal nitrate solution of Fe³⁺ and Cu²⁺.

Evaluation of the distribution of metal ions at different pH

The distribution of each one of the seven metal ions i.e., Cu²⁺, and Fe³⁺ between the polymer phase and the aqueous phase was determined at 30 °C and in the presence of 1M NaNO₃ solution. The experiments were carried out as described above at different pH values. The distribution ratio, D, is defined by the following relationship²³.

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

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

Where,

'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.

Antimicrobial Screening

Biological assay depends upon a comparison of the inhibition of growth of microorganism by measuring the concentration of the sample to be examined with the known concentration of standard antibiotic. For the antimicrobial analysis the in vitro disc diffusion method has been employed. In this study the ligand and their chelates were tested for their effect on certain human pathogenic bacteria such as Gram-positive (*Aspergillus niger* and *Candida albicans*).

The nutrient agar medium was boiled and sterilized by autoclaving at 7 kg pressure (120 °C) for 20 min for the study of antibacterial activity. 20 mL media was poured into the sterilized Petri plates and kept at room temperature for a few minutes, and allowed to solidify in plates. It was then incubated for 12 h and inoculated with microorganism using sterile swabs. All of these manipulations were carried out with utmost care under aseptic conditions. The test

solution prepared by dissolving the compound in DMSO was filled with the media using a micropipette and incubated at 35 °C for 48 h. The same procedure was adopted for the antifungal studies in which potato dextrose agar was the medium.

During the course of time, the test solution diffuses and the growth of the inoculated microorganisms such as *Staphylococcus aureus*, *Escherichia coli*, *Aspergillus niger*, and *Candida albicans* were found to be affected. The activity developed on the plate was measured by measuring the diameter of the inhibited zone in millimetres. The drug ciprofloxacin was used as the standard for bacteria and nystatin for fungi.

RESULTS AND DISCUSSION

The copolymer resin is soluble in DMF, DMSO and is insoluble in almost all other organic solvents. The 2, 4-HADF-III copolymer which has been used in the present investigation was prepared by the reaction given in Scheme 1.

Ion-exchange properties

Batch equilibrium technique developed by Gregor et al. and De Geiso et al was used to study ion exchange properties of 2, 4-HADF-III copolymer resin. Two metal ions Fe^{3+} and Cu^{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) uptake time and c) pH of the aqueous medium, Among these three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymers similar to the earlier co-workers[23-26]. The details of experimental procedure are given below.

Effect of electrolyte and its ionic strength on metal uptake

We examined the influence of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} at various concentrations on the equilibrium of metal-resin interaction. Figure 1-4 shows that the amount of metal ions taken up by a given amount of copolymer depends on the nature and concentration of the electrolyte present in the solution. Generally as concentration of the electrolyte increases, the ionization decreases, number of ligands (negative ions of electrolyte) decrease in the solution which forms the complex with less number of metal ions and therefore more number of ions may available for adsorption. Hence on increasing concentration, uptake of metal ions may be increased, which is the normal trend. But this normal trend disturbed due to the formation of stable complex with more number of metal ions with electrolyte ligands, which decrease the number of metal ions available for adsorption, hence uptake decreases.

Electrolyte solution + metal ion solution + polymer \rightarrow electrolyte ligand - metal ion chelates + Polymer - metal ion chelates

If electrolyte ligand – metal ion complex is weak than polymer metal ion chelates, the more metal ion can form complex with polymer hence uptake of metal ion is more. But if this complex is strong than polymer – metal ion chelates, more metal ions form strong complex with electrolyte ligand which make metal uptake capacity lower by polymer.

In the presence of perchlorate, chloride and nitrate ions, the uptake of Fe^{3+} and Cu^{2+} 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 copolymer decreases with increasing concentration of the electrolyte [23, 24]. This may be explained on the basis of the stability constants of the complexes with those metal ions. The ratio of physical core structure of the resin is significant in the uptake of different metal ions by the resin polymer. The amount of metal ion uptake by the 2, 4-HADF-III copolymer resin is found to be higher when comparing to the other polymeric resins [1, 25].

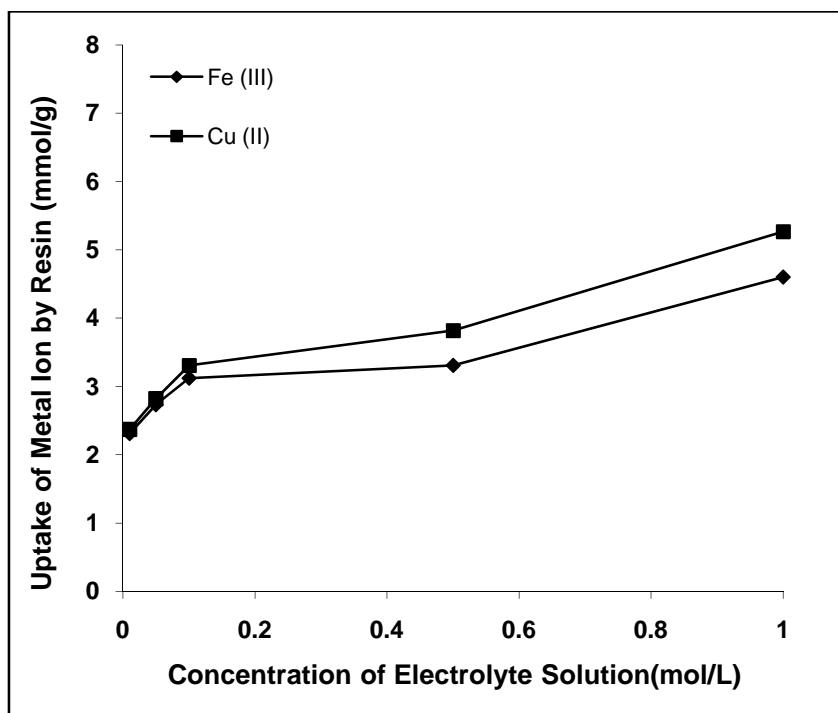


Fig.1 Uptake of several metal ions^a by 2, 4-HADF-III copolymer resin at five different concentrations of electrolyte NaNO₃ solution

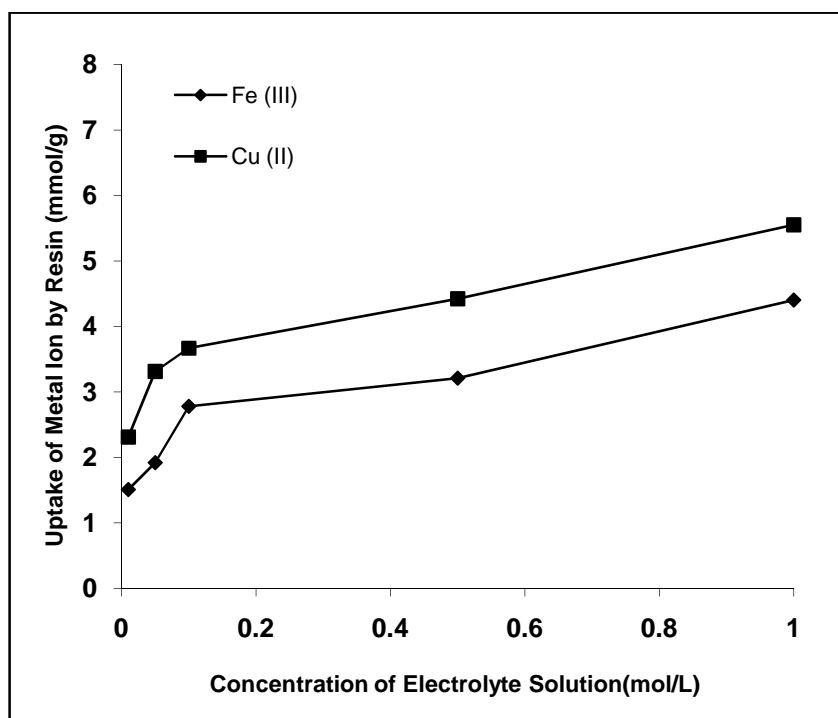


Fig.2. Uptake of several metal ions^a by 2, 4-HADF-III copolymer resin at five different concentrations of electrolyte NaCl solution

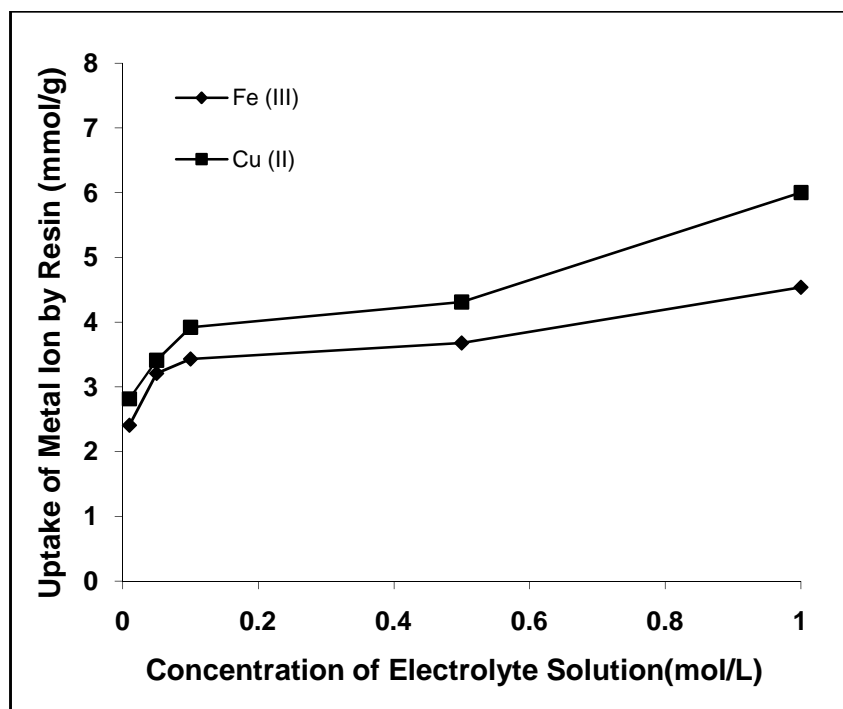


Fig.3. Uptake of several metal ions^a by 2, 4-HADF-III copolymer resin at five different concentrations of electrolyte NaClO₄ solution

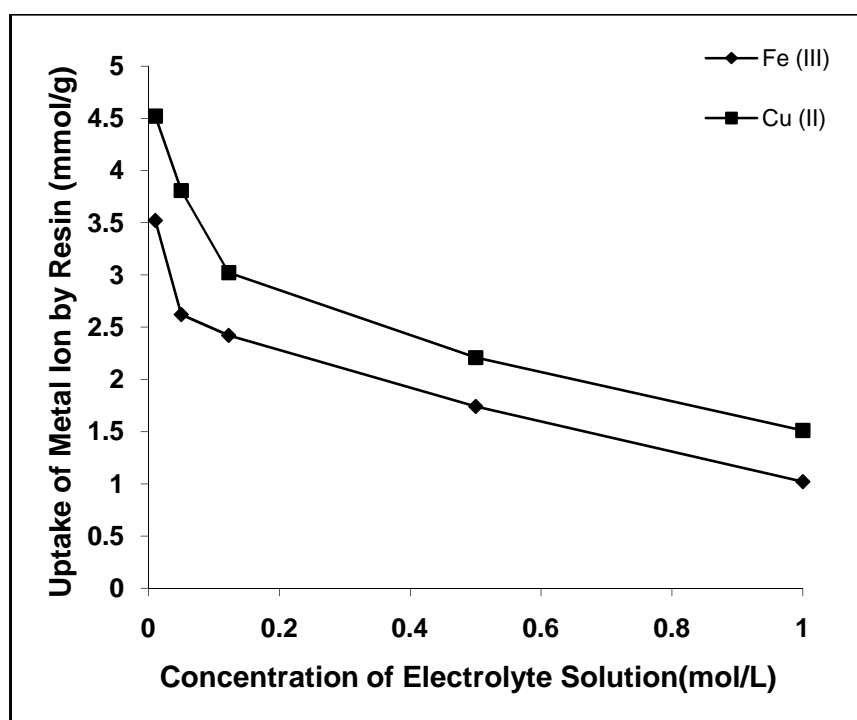


Fig. 4. Uptake of several metal ions^a by 2, 4-HADF-III copolymer resin at five different concentrations of electrolyte Na₂SO₄ solution

Estimation of the 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 to while operating as close to equilibrium conditions as possible. As shaking time increases the polymer gets more time for adsorption, hence uptake increases on the increasing in the time. Figure 5 shows the dependence of the rate of metal ion uptake on the nature of the metal. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given polymer. The result shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of the metal ion under given conditions. It is found that Fe (III) ions require about 3hrs for the establishment of the equilibrium, whereas Cu (II) ions required

about 5 or 6 hrs [23, 24]. The rate of metal uptake may depend upon hydrated radii of metal ions. The rate of uptake for the post transition metal ions exhibit other trend for Fe (III), the rate of uptake is in the comparable that of Cu (II) because of difference in 'd' orbital.

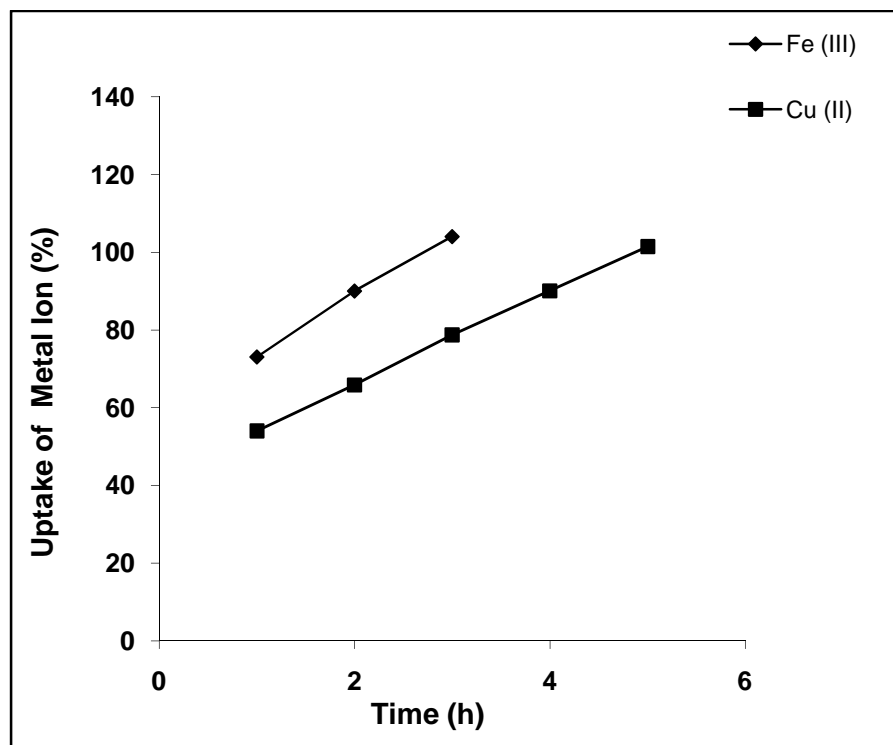


Fig.5. Comparison of the rate of metal ion^a uptake^b by 2, 4-HADF-III copolymer resin

Distribution ratios of metal ions at different pH

The effect of pH on the amount of metal ions distributed between two phases can be explained by the data given in Figure 6. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ion taken up by the 2, 4-HADF-III copolymer increases with increasing pH of the medium [24, 25]. The magnitude of increase, however, is different for different metal cations. The study was carried from pH 2.5 to 6.5 to prevent hydrolysis of metal ions at higher pH. For metal ion Fe³⁺ the highest working pH is 3, where distribution ratio is medium, since Fe³⁺ forms octahedral complex with electrolyte ligand, showing crowding effect (steric hindrance), which may lower the distribution ratio of Fe³⁺ ions. The value of distribution ratio at particular pH thus depends upon the nature and stability of chelates with particular metal ion. The data of distribution ratio show a random trend in certain cases [26]. This may be due to the amphoteric nature of the 2, 4-HADF-III resin. From the result it reveals that with decrease in atomic number, the ion uptake capacity is increased. The steric influence of the acetyl group and hydroxyl group in 2, 4-HADF-III resin is probably responsible for their observed low binding capacities for various metal ions. The higher value of distribution ratio for Cu (II) may be due to the formation of more stable complex with chelating ligands. Therefore the polymer under study has more selectivity of Cu²⁺ than other ions which form rather weak complex. While at pH 3 the copolymer has more selectivity of Fe³⁺ ions. The order of distribution ratio of metal ions measured in pH range 2.5 to 6.5 is found to be Fe (III) > Cu (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 [20]. For example, for the separation of Cu (II) and Fe (III) the optimum pH is 2.5, at which the distribution ratio 'D' for Cu (II) is 74.3 and that for Fe (III) are 530.4. The lowering in the distribution of Fe (III) was found to be small and, hence, efficient separation could be achieved [1, 26].

The strength of ion exchange capacities of various resins can be studied by comparing their ion exchange capacities. The ion exchange capacity (IEC) is a fundamental and important quantity for the characterization of any ion exchange material. It is defined as the amount of ion that undergoes exchange in a definite amount of material, under specified experimental conditions. The ion exchange capacity of 2, 4-HADF-III copolymer has been calculated, which was found to be 4.8 meq.g-1 which indicates that 2, 4-HADF-III copolymer resin is better ion exchanger than commercial phenolic and some polystyrene commercial ion exchangers.

For the strongly acidic cation exchange resin such as cross linked polystyrene sulphonic acid resins, the ion exchange capacity is virtually independent of the pH of the solutions. For weak acid cation exchangers, such as those containing carboxylate group, ionizations, occurs only in alkaline solution. Similarly weakly basic cation exchanger does not work above pH-9.

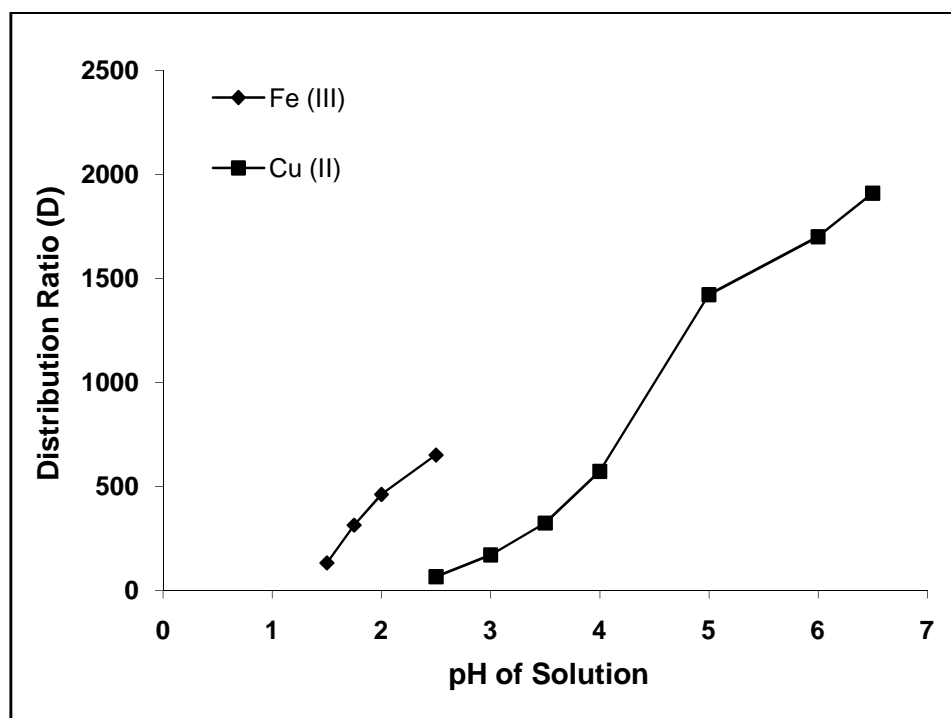


Fig.6. Comparison of the rate of metal ion^a (m) uptake^b at different pH

Antimicrobial Screening

The microbial screening results of 2, 4-HADF-III copolymer ligand are presented in Table 1; show higher activity is due to the donor atoms of the ligand and the π -electrons delocalization. This effect increases the lipophilic character, which favours the permeation through the lipid layer of the bacterial and fungal membranes [15]. The higher activity may also be due to the presence of -OH and the aromatic ring [26]. It is perceived that the factors such as solubility, conductivity, dipole moment and cell permeability mechanism may be alternative reasons for the increased activity of the metal complexes [25]. The ligand has good inhibition against the growth of Gram-negative bacteria which induces tumour. Hence the copolymer ligand may possess antitumor activity. The Gram-positive bacteria are both pathogenic and invasive. The copolymer has good inhibition characteristics against the growth of this pathogen. *Aspergillus niger* cause aspergillosis, the growth of the fungus is controlled by the copolymer chelates to some extent. The *Candida albicans* can penetrate into the intestinal walls and cause diseases. From the findings, the growth of *Candida albicans* is inhibited by the addition of 2, 4-HADF-III copolymer resin.

Table 1. Antimicrobial activities of 2, 4-HADF-III copolymer resin

Copolymer	Diameter of zone of inhibition (mm)			
	<i>S. Aureus</i>	<i>E. Coli</i>	<i>A. Niger</i>	<i>C. Albicans</i>
2, 4-HADF-III	18	19	20	19
Solvent (DMSO)	--	--	--	--

CONCLUSION

A copolymer 2, 4-HADF-III based on the condensation reaction of 2, 4-dihydroxyacetophenone and dithiooxamide with formaldehyde in the presence of acid catalyst was prepared. 2, 4-HADF-III is a selective chelating ion-exchange copolymer resin for certain metals. The copolymer resin showed a higher selectivity for Fe^{3+} and Cu^{2+} . The copolymer resin shows higher activity against certain bacterial strains such as *Staphylococcus aureus*, *Escherichia coli*, and fungal strains *Aspergillus niger* and *Candida albicans*.

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