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Der Pharmacia Lettre, 2012, 4 (5):1360-1366
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ISSN 0975-5071
USA CODEN: DPLEB4

Ion-Exchange Properties of 8-Hydroxyquinoline-Dithiooxamide-Formaldehyde Terpolymer Resin (8-HQDF)

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ABSTRACT

A number of ion-exchange resins have been synthesized by reacting 8-Hydroxyquinoline with dithiooxamide and formaldehyde in presence of 2M HCl as catalyst, proved to be selective chelating ion-exchange resin for certain metals. Chelation ion-exchange properties of the terpolymer resin was studied for Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions. A batch equilibrium method has been employed in the study of the selectivity of metal ions uptake involving the measurement 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 ions strengths. The terpolymer showed higher selectivity for Fe^{3+}, Cu^{2+}, and Ni^{2+} ions than for Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions.

Key words : Synthesis, Characterization, Resins Ion-exchange, Chelating properties, Metal ion uptake, Distribution ratio.

INTRODUCTION

Terpolymers find very useful applications as adhesives, high temperature flame resistant fibres, coating materials, semiconductors, catalysts and ion-exchange resins[1-3]. Ion-exchange resins have attracted much interest in the recent years due to their application in waste water treatment, metal recovery and for the identification of specific metal ions [4-5]. Chelating ion-exchange resin involving o-aminophenol with resorcinol and formaldehyde was reported by Penington and Williams [6]. De Geiso et al studied the chelation ion-exchange property of the resin synthesized from salicylic acid and formaldehyde [7]. They have studied the ion-exchange capacity and selectivity of salicylic acid formaldehyde copolymer with Fe^{3+} and UO_2^{2+} ions as a function of pH. Patel et al. [8,9] have prepared the terpolymer of salicylic acid / p-hydroxy benzoic acid and thiourea with trioxane in presence of acid catalyst with different molar proportions of monomers.

Kapadia et al [10,11,12] prepared ion-exchange resins from various phenolic derivatives like salicylic acid, gallic acid, β-resorcylic acid, anthranilic acid, 8-hydroxyquinoline and hydroquinone using DMF as solvent. They have studied their anion as well as cation-exchange properties towards various metal ions. Attachment of multidentate ligands to insoluble polymeric supports is a technique commonly utilized for the preparation of selective ion-exchange resins, which are capable of separation and purification of metal ions. The polymeric chelates of Ni (II), Co (II) and Cu (II) have been prepared from poly (salicylaldehyde-acrylate) divinylbenzene resin [13].

A number of terpolymers derived from phenol derivatives have been studied and reported along with chelating ion-exchange properties for example, Karunakaran et al [14] have synthesized terpolymer from o-nitrophenol-thiourea-formaldehyde and Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and UO_2^{2+} were used for chelation. Das [15] has derived terpolymer from thiosemicarbazone derivatives of phenolic compounds. Terpolymers of 8-hydroxyquinoline-formaldehyde-resorcinol/catechol were reported by shah et al [16,17] and chromatographic column separation for various metal ions such as Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} have carried out using the quinoline base resins. Dabrowski et al [18] have sufficiently removed trace impurities and toxic metals from industrial waste water by various ion-exchangers.

Moreover, synthetic resins derived from salicylic acid-dithioxamide/biuret-formaldehyde have attracted the attention of many researchers because of their versatile use as ion-exchangers [19, 20]. In continuation to our earlier work [21-25] the present communication deals with the systematic study of selectivity and capacity of terpolymer resins derived from 8-hydroxyquinoline-and dithiooxamide with formaldehyde in the ion-exchange reaction.

MATERIALS AND METHODS

Materials

The chemicals used were all of A.R. or chemically pure grade. The starting materials such as 8-hydroxyquinoline, dithiooxamide and formaldehyde were of Analar grade (Merck, India) and used as received.

Synthesis 8-HQDF terpolymer resin

The polymerisation reaction was carried out with different concentrations of 8-hydroxyqninoline, dithiooxamide and trioxane. Condensation of the reactants was carried out in the presence of an acid, like 2M HCl by heating at 130^0C on an oil-bath for six hours [19, 20]. The separated polymer was washed with hot water and finally with ether to remove excess of monomer and 8-hydroxyquinoline-formaldehyde polymer. The polymer was purified by dissolving it in 10% NaOH and reprecipitating it by dropwise addition of 1:1(V/V) HCl/ water. The process was repeated twice. The terpolymer sample thus obtained was washed with boiling water, dried and kept in vacuo over silica gel. The terpolymers (8-HQDF) thus synthesized were obtained in quantitative yields.

Different resin samples of 8-HQDF viz. 8-HQDF-1, 8-HQDF-2 and 8-HQDF-3 in the ratio (2:1:3), (3:1:5) and (4:2:7) were prepared using different molar ratio of reactants. The details of mole ratio of reactants, reflux temperature, time of reflux and percentage yield of product have been reported in our previous publication [25].

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 [25].

Ion-exchange properties

Ion-exchange properties of the 8-HQDF terpolymer resins were determined by the batch equilibrium method [26]. The ion-exchange properties of prepared 8-HQDF resins have been studied.

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

The terpolymer 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 0.1N HNO_3 or 0.1N NaOH. The suspension was stirred for a period of 24 h at 25^oC. 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 25^oC for 24 h and filtered [26]. The polymer 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 [27]. The blank was also estimated for the metal ion content. The amount of metal ion taken up by polymer in the presence of the given electrolyte of known concentration was calculated from the difference between blank reading and the reading in the actual experiment [26, 28].

The experiment was repeated in presence of several electrolytes of known concentration with seven different metal ions viz. Pb^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}. The same procedure was applied to all molar ratios of the terpolymer resins. The results with seven different metal ions are incorporated in Fig. 1-4.

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^oC in presence of 25 ml of 1M $NaNO_3$ 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 (Fig. 5).

Evaluation of the distribution of metal ions at different pH

The distribution of each one of seven metal ions Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} between polymer phase and aqueous phase was estimated at 25°C and in presence of 1M $NaNO_3$ solution. The experiments were carried out as described earlier at pH range 1.5 to 6.5. The distribution ratio (D) is defined by the following relationship: The results are presented in Fig. 6.

RESULTS AND DISCUSSION

In order to ascertain the selectivity of the 8-HQDF 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 8-HQDF system are as shown in Figs 1 to 3. From this study carried out with seven metal ions under limited variation of experimental conditions. Certain generalizations may be made about the behaviour of the four polymer samples selected for ion-exchange study.

Influence of electrolyte on metal uptake

Examination of Fig. 1-4 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^{3+}, Cu^{2+} and Ni^{2+} ions increases with increasing concentration of the electrolytes, whereas in presence of sulphate ions the amount of above mentioned ions taken up by the teropolymers decreases with increasing concentration of electrolytes [29–31]. Moreover, the amount of Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} decreases with increasing concentration of Cl^-, NO_3^- and SO_4^{2-} ions [31-33]. This may be explained in terms of the stability constants of the complexes with Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} metal ions form with these anions [31–34]. SO_4^{2-} might form rather strong complexes with Fe^{3+}, Cu^{2+} and Ni^{2+} while NO_3^- and Cl^- might form weak complexes and therefore, might not be expected to influence the position of the Fe^{3+}, Ni^{2+} and Cu^{2+} chelate equilibrium as much as SO_4^{2-}. The sulphate and chloride might form rather strong complexes with Co^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} and therefore, might be expected to influence the position of Co^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} complex equilibrium. This type of trend has been observed by other earlier workers in this field [31,35]. It is also observed that the amount of metal ions taken up by the 8-HQDF terpolymer resins increases in the order:8-HQDF -1 < 8-HQDF-2 < 8-HQDF-3 < 8-HQDF-4. This observed order may be due to introduction of more and more ligand groups (dithiooxamide monomers) in the repeating unit of the terpolymer resins.

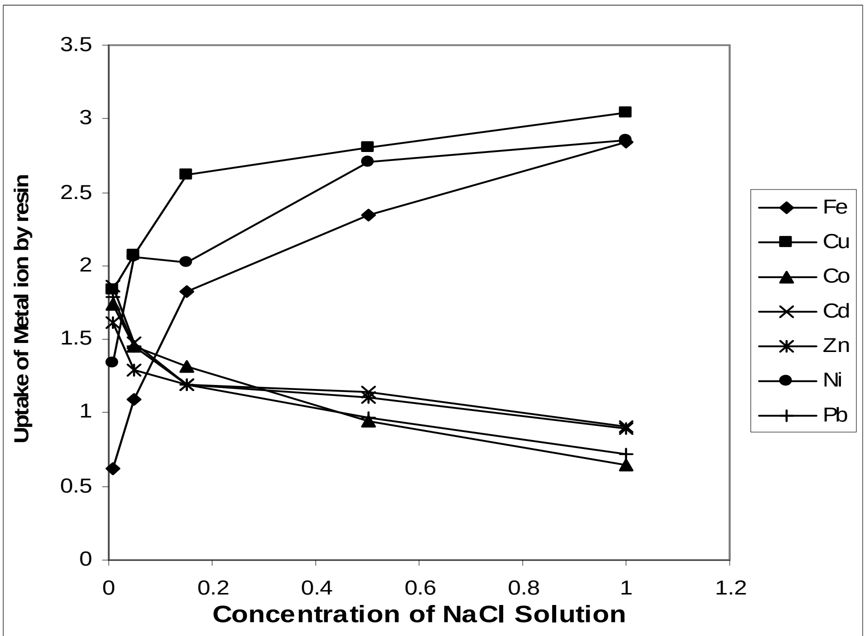

Fig.1. Uptake of several metal ions by 8-HQDF terpolymer resin at five different concentrations of electrolyte solution NaCl

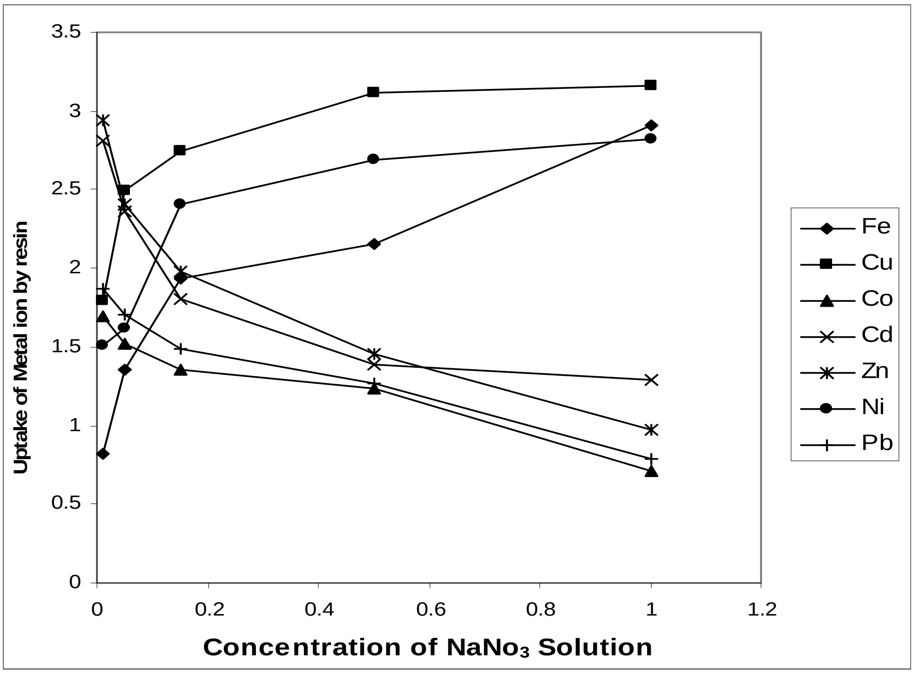

Fig.2. Uptake of several metal ions by 8-HQDF terpolymer resin at five different concentrations of electrolyte solution $NaNo_3$

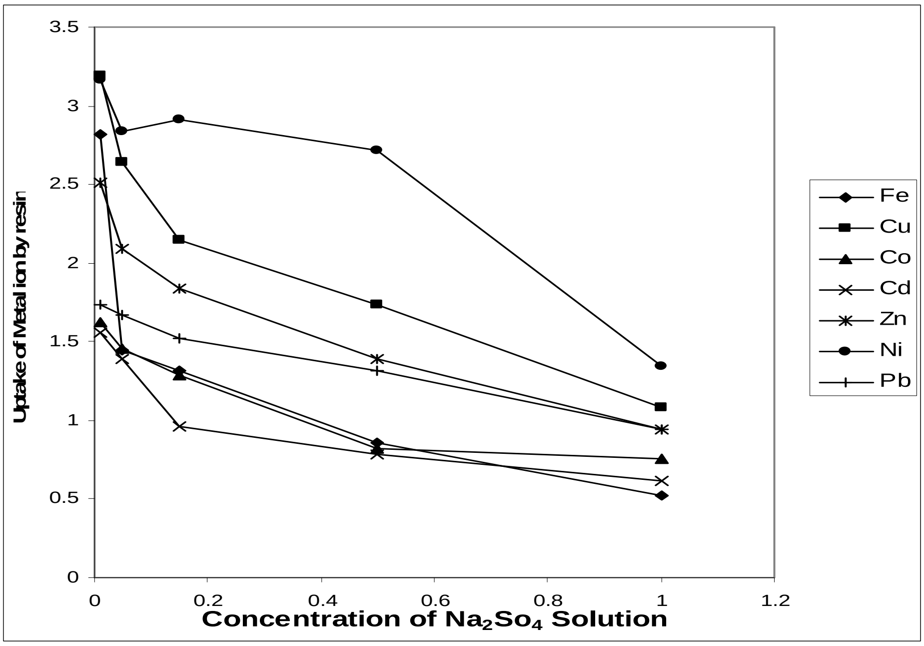

Fig.3. Uptake of several metal ions by 8-HQDF terpolymer resin at five different concentrations of electrolyte solution $NaCIO_4$

Evaluation of the rate of metal uptake

The rate of metal adsorption by 8-HQDF 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. Observation of Fig. 5 shows that the rate of metal ion uptake depends on the nature of metal. These results also 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 plots show that Fe^{3+} ions require about 4 h for the establishment of equilibrium where as Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} require about 5 h for equilibrium. Cd^{2+} and Pb^{2+} required the highest time, that is, 7 h to attain equilibrium. The rate of metal ion uptake follows the order : $Fe^{3+} > Cu^{2+} > Ni^{2+} = Co^{2+} = Zn^{2+} > Cd^{2+} > Pb^{2+}$. This type of trend has also been observed by earlier workers in the field [31, 36]. Comparison of the rate uptake of given metal ion by terpolymers is made on the basis of data presented in Fig. 2. It reveals that the rate of metal uptake by the terpolymer follows the order : 8-HQDF-4 > 8-HQDF-3 > 8-HQDF-2 > 8-HQDF -1.

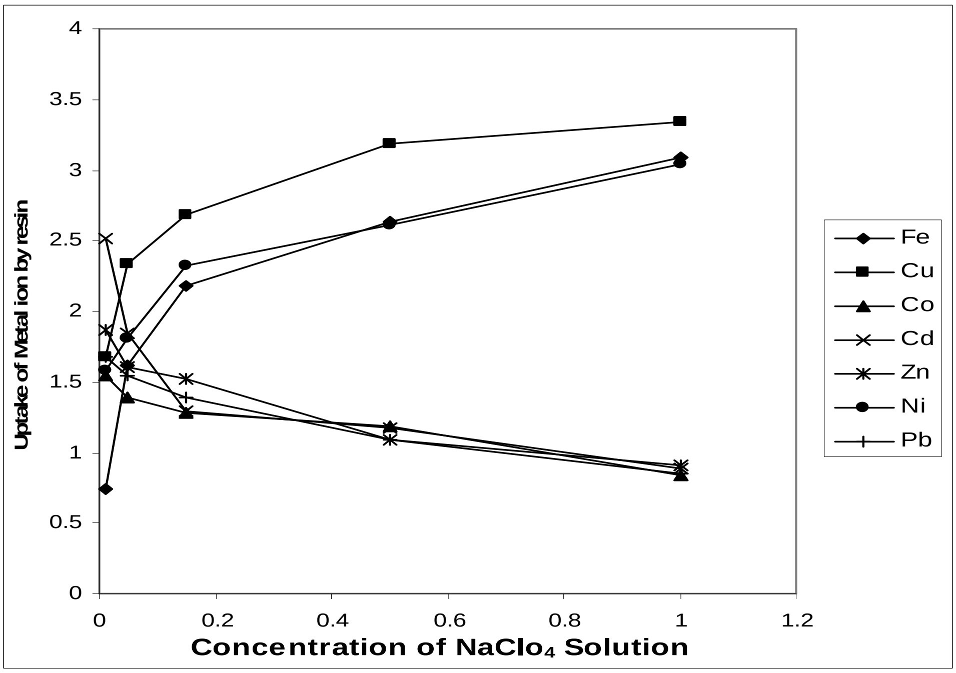

Fig.4. Uptake of several metal ions by 8-HQDF terpolymer resin at five different concentrations of electrolyte solution Na_2SO_4

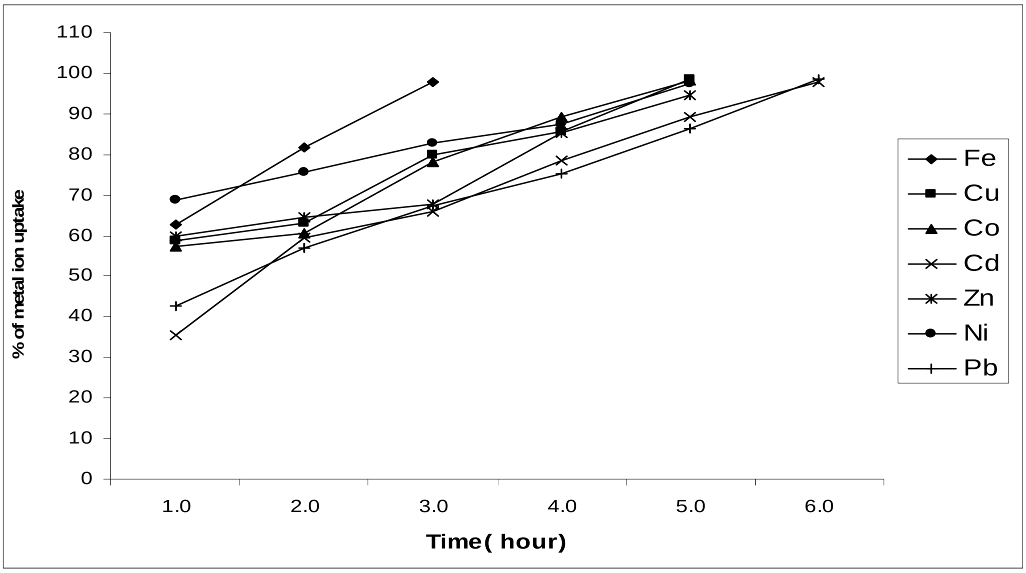

Fig.5. Comparisons of the rate of metal ion uptake by 8-HQDF terpolymer resin

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. 6. Examination of plot indicates that the relative amounts of metal ion taken up by the terpolymer resin at equilibrium increase with the increase of pH of the medium [31, 36].

The study was carried out only up to pH 6.5 in order to prevent hydrolysis of the metal ions at higher pH. In case of Fe^{3+} the highest working pH is 2.5. The results indicate that terpolymer resin samples take up Fe^{3+} ions more selectively than any other metal ions under study. The lower distribution ratio of Fe^{3+} may be attributed to steric hindrance [37-40]. Among the other metal ions, Cu^{2+} and Ni^{2+} ions are taken up by the teropolymers more selectively. The other four metal ions Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} have low distribution ratio over the pH range 3 to 6.5. This could be attributed to low-stability constants, that is, the weak ligand stabilization energy of the metal complexes [34].

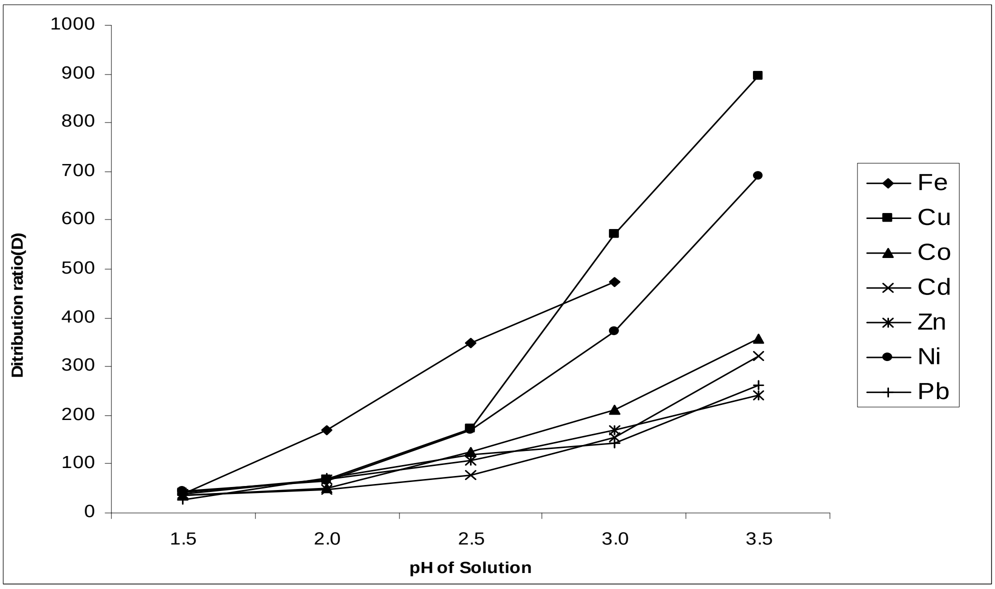

Fig.6. Distribution ratio (D) of various metal ions as function of different pH by 8-HQDF terpolymer resin

The reported order of selectivity of a cation exchange resin for divalent metal ions by Irving et al. [40] is as: Pd > Cu > Ni > Co > Zn > Cd > Fe > Mn > Mg.

In the present study the observed order of distribution ratio of divalent ions measured in the range of pH from 3 to 6.5 was found to be $Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$.

This order partly matches with above trend. 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 4 for the separation of Pb^{2+}, Co^{2+} and Cu^{2+} using 8-HQDF terpolymer resins with their distribution ratios 117.6, 125.6 and 172.5 respectively.

CONCLUSION

1. It is selective chelating ion-exchange resin for Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} metal ions.
2. These resins showed a higher selectivity for Fe^{3+}, Cu^{2+} and Ni^{2+} ions as compared to Zn^{2+}, Cd^{2+} and Pb^{2+} ions.
3. These polymers showed higher selectivity for Fe^{3+} at pH 2.5 as compared to other metal ions.
4. The amount of metal ions taken up by the 8-HQDF terpolymer resins increases in the order:

8-HQDF-1 < 8-HQDF-2 < 8-HQDF-3 < 8-HQDF-4. It may be due to the introduction of more and more 8-hydroxyquinoline monomers in the repeating unit of the terpolymer resins.

Acknowledgement
One of the author W. B. Gurnule thanks to University Grant Commission, New Delhi for financial support.

REFERENCES

[1] B. L. Rivas, H. A. Maturana, M. J. Molina, M. R. Anton, M. Rosa, I. F. Pierola, *J. Appl. Polym. Sci*, **1998**, 67, 1109-1118.
[2] W. B. Gurnule, D. B. Patle, *Der Pharma Lett*, **2011**, 3(6), 250-256.
[3] A. N. Egorov, Y. L. Sukhorukov, G. V. Plotnikova, A. K. Khaliullin, *Rus. J. Appl. Chem*, **2002,** 75, 152-155.
[4] L.K. Orazzhanova, M. G. Yash Karova, I. A. Bimendina, S. D. Kudaibergen, *J. Appl. Polym. Sci*. **2003**, 87, 759-764.
[5] A. A. Atia, A. M. Domia and K. Z. Elwakeel, *React. Funct. Polym*. **2005**, 65, 267-275.
[6] L. D. Pennington, M. B. Williams, *Ind. Eng. Chem*, **1959**, 57, 759-762.
[7] R. C. Degeiso, L. G. Donaruma, E. A Tomic, *Anal. Chem*, **1962,** 34, 845-847.
[8] W. B. Gurnule**,** Sonali S. Dhote, *J. Der Pharma Chemica*, **2012**, 4(2), 791-799.
[9] M. M. Patel, R. Manavalan, *J. Indian Chem. Soc*. **1984,** 61, 490-494.

[10] M. V. Vyas, R. N. Kapadia, *Ind. J. Technol*, **1981,** 18, 411-415.
[11] W. B. Gurnule, S. S. Rahangdale, *Der Pharm. Chem*, 2011, 3(4), 314-322.
[12] S. Amin, R. N. Kapadia, *J. Sci. Ind. Res*, **1997**, 56, 540-544.
[13] K. A. Nandekar, J. R. Dontulwar, W. B. Gurnule, Der Pharma, Chem, **2012**, 4(4), 1644-1652.
[14] M. Karunakaran, A. Burkanudeen, *Orient J. Chem*, **2002**, 18, 65-68.
[15] S. C. Das, *J. Indian Chem. Soc*. **2000**, 77, 66-69.
[16] B. A. Shah, A. V. Shah, B. N. Bhandari, *Asian J. Chem*, **2004,** 16, 1801-1810.
[17] B. A. Shah, A. V. Shah, B. N. Bhandari., *Asian J. Chem*, **2003,** 15, 117-125.
[18] A. Dabrowski, Z. Hubicki, P. Podkoscielny. E. Robens., *Chemosphere*, **2004**, 56, 91,-106.
[19] T. K. Pal, R. B. Kharat, *Ind. J. Chem*, **1989**, 28(A), 55-58.
[20] T. K. Pal, R. B. Kharat, *Die Angew Makromol Chemie*, **1989**, 173, 55-68.
[21] W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal, R. B. Kharat, *Synth. React. Inorg. Met. Org. Chem*. **2003**, 33(7), 1187-1205.
[22] W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal, R. B. Kharat, *React. Funct. Polym*. **2003**, 55, 255-265.
[23] W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal, R. B. Kharat, *Prog. Cryst. Grow. Charact. Mat*. **2002**, 45, 155-160.
[24] R. H. Gupta, A. B. Zade, W. B. Gurnule, *J. Appl. Polym. Sci*. **2008**, 109(5), 3315-3320.
[25] S. S. Katkamwar, A. B. Zade, W. B. Gurnule, *J.Appl. Polym. Sci*. **2009**, 113(5), 3330.
[26] W. B. Gurnule, M. B. Thakare, *Der Pharma Chemica*, **2011,** 3(5), 236-242.
[27] G. H. Jeffery, J. Mendham, R.C. Denney, J. Bassett, Vogel's Text Book of Quantitative Inorganic Analysis, 5th Edition, John Wiley and Sons Inc., New York NY 10158, **1989.** [28] W. B. Gurnule, *Inter. J. Envirn. Res*, **2012,** 1(1), 16-25.
[29] W. B. Gurnule, *J. Sci. Tech. Res*, **2012**, 2, 14-22.
[30] U. K. Samal, P. L. Nayak, S. Lenka, *J. Appl. Polym. Sci*, **1993**, 47, 1315.
[31] J. R. Patel, D. H. Sutaria, M. N. Patel, *High Perform. Polym*, **1994**, 6, 201.
[32] J. Bjerrum, G. Schwarzenbach, L. G. Sillen, ''Stability constants of Metal- ion Complexes'', Vol-I, 83, the Chemical society, London, **1958**.
[33] F. A. Cotton, G. Willkinson, Advanced Inorganic Chemistry, 3rd Edition, Wiley, 594, New York, **1972.**
[33] S. L. Davadov, N.A. Plate, *Coord. Chem. Rev*, **1975**, 16, 195.
[34] J. S. Parmar, M.R. Patel, M.M. Patel, *Angew. Makromol. Chem*. **1981**, 105, 75.
[35] W. B. Gurnule, H. D. Juneja, L. J. Paliwal, *Indian J. Chem*. **2000,** 39A , 1110.
[36] R. C. De Geiso, L. J. Donaruma, E.A. Tomic, *J. Org. Chem*. **1962,** 27, 1424.
[37] R. C. De Geiso, L. J. Donaruma, E.A. Tomic, *Anal. Chem*. **1962,** 34, 845.
[38] J. R. Patel, D. H. Sutaria, M.N. Patel, *High Perform. Polym*. **1994,** 6, 123.
[39] H. Irving, R. J. Williams, *Chem. Rev*.**1956**, 56, 271.