Asian Journal of Chemistry Vol. 16, Nos. 3–4 (2004), 1801–1810

Recovery of Transition Metal Ions from Binary Mixtures by Ion-exchange Column Chromatography using Synthesized Chelating Resin Derived from *m*-Cresol

BHAVNA A. SHAH*, AJAY V. SHAH and BHARAT N. BHANDARI
Department of Chemistry, South Gujarat University, Surat-395 007, India

Chelating ion-exchange resin was synthesized from oxine 8-hydroxyquinoline-formaldehyde-*m*-cresol. The physico-chemical properties like % moisture content, true density of resin (d_{res}), apparent density of resin (d_{col}), void volume fraction, total exchange capacity, rate of exchange, interruption test, salt splitting capacity, thermal stability, resin stability, pH study for metal ions and effect of metal ion concentration on exchange capacity were measured. The resin was characterized by FT-IR, ^{1}H-NMR spectra and TGA. The quantitative separation of metal ions from the mixture of cadmium(II)-copper(II), lead(II)-zinc(II), copper(II)-zinc(II) and nickel(II)-zinc(II) was accomplished by selective sorption on column at optimized K_d values.

Key Words: Chelating Resin, *m*-Cresol, Recovery, Ion exchange column, Transition metal ions.

INTRODUCTION

Ion exchangers have established their place in analytical chemistry due to their resistance to heat, radiation and their differential selectivity for metal ions. These compounds have shown great promise in analytical chemistry because of their potentiality in separation of metal ions.

In recent years, interest has been focused on the removal of industrial discharge of heavy metal ions from contaminated or waste water effluents, due to their well known toxicity. Therefore, special attention has been given by various investigators to develop methods for water purification based on low cost materials like chitosan, fly-ash, biomass etc. Recently, the removal of various metal ions such as copper and nickel by using polymethacrylate micro beads carrying ethylenediamine[1] and resin prepared from methacrylic acid-ethyleneglycol-dimethacrylate[2] have been reported.

Solid-phase extraction is now one of the interesting areas in analytical chemistry. Anchoring the active site to a solid support in polymer matrix provides an immobilized active surface capable of selective and quantitative separation of cations from aqueous solutions. These solid phase extraction systems can be used in the application of imidazolylazo resin for the preconcentration and separation of copper(II) and zinc(II) in biological samples after microwave assisted treatments[3]. Inorganic ion-exchange materials are found to have better ion-exchange characteristics. In order to explore the analytical potentiality of thorium iodate cation exchanger, its ion-exchange properties were studied for copper(II), lead(II), nickel(II) and mercury(II) ions[4]. Chelating resin prepared by polycondensation of 8-hydroxyquinoline and biuret with formaldehyde in presence of 2 M HCl as catalyst was found to be a selective for certain metals[5].

EXPERIMENTAL

8-Hydroxyquinoline (National Chemicals, extra pure 99%) was used as received. Formaldehyde (37%) (Qualigens Fine Chemicals, Mumbai) was used as received. *m*-Cresol (Sisco, Mumbai, extra pure 98%) was purified by distillation. DMF, chloroform, methanol, benzene, toluene, acetate salts of copper(II), zinc(II) and lead(II) and chloride salts of nickel(II) and cadmium(II) used in the present work were of analytical grade and with purity better than 99%.

Resin synthesis

(A) Resin synthesis was carried out as follows:

(i) In the first step, 8-hydroxyquinoline ground to a fine powder (0.1 mol), was taken in 250 mL round bottom flask and dissolved in DMF solvent (25 mL) to give a clear yellow solution. Formaldehyde (0.25 mol) was added and stirred until a red solution was obtained.

A solution of *m*-cresol (0.1 mol) in 10 mL of DMF was added to the above solution and stirred for 3 h. The mixture was refluxed on a water bath with constant stirring for 3–5 h and then on a sand bath for 10–12 h until a viscous solution was obtained with the formation of a hard mass of resin.

(ii) Curing of resins: Hard mass of resin was poured into a beaker containing 250 mL of liquid paraffin at 80°C and stirred sufficiently to produce small droplets, which gelled to resin beads. The resin was separated by filtration from liquid paraffin, rinsed with chloroform and washed thoroughly with soap solution to remove paraffin. The resin was washed with DMF and finally with water to remove monomer impurities[6]. The resin was then sealed and cured at 100°C for 24 h.

(iii) The synthesized resin (OFCR) was characterized by FT-IR, ^{1}H-NMR and TGA methods. Infrared spectra of synthesized resin sample had been scanned in KBr pellets on Shimadzu FT-IR spectrophotometer model-8201 PC. The ^{1}H-NMR spectrum was taken in DMSO-d_6 solvent on "Bruker-DPX-200 spectrometer" at 200 MHz with a sweep time of 10 min at room temperature. The internal reference used was TMS. Mettler TA 4000 system (Switzerland) was used to obtain the thermogram of the present resin sample.

(iv) Resin pretreatment: To convert the resin samples to H^+ form, each resin sample having uniform particle size (100 mesh) was equilibrated with 2 M HCl solution for 24 h and washed with deionized water till it was freed from chloride by testing with silver nitrate solution. The H^+ form of resin was used for further studies.

(B) K_d values for metal ions in presence of electrolyte solutions

The dry resin samples (0.25 g) were suspended in the electrolyte solution of tartaric acid (50 mL) of different known concentrations. The pH of the suspension was adjusted to the desired value and the resin was equilibrated for 24 h. To the suspension, 2 mL of (5 mg/mL) solution of the metal ion under study was added. The pH was again adjusted to the desired value. The mixture was further equilibrated for 24 h and then filtered. The solid was washed with water. The filtrate and washings were combined and examined for the metal-ion concentration.

$$K_d = \frac{\text{mmol of metal ion on resin}}{\text{mmol of metal ion in soln.}} \times \frac{\text{vol. of solution}}{\text{wt. of dry resin}}$$

(C) Ion-exchange chromatography

(i) Packing of column: A calibrated 100 mL burette was used as chromatographic column, in which well soaked hydrated resin having uniform particle size was packed with a plug of glass wool at the bottom of column. The formation of air pockets in the column should be avoided during the filling and therefore deionized water was added to the column to a depth of several inches before the resin slurry was passed into the column.

The slurry (1 : 2 resin : water) was poured along the walls of the column, allowing the particles to settle so as to form the compact resin bed. The column length was about 17 cm. When the resin had settled, the effluent screw clamp was opened and water was allowed to flow down up to 1 cm. on the top of the bed. The column was used for different types of binary mixtures of heavy metals separation systems.

(ii) Loading of column: The superior selectivity towards multivalent cations exhibited by chelating resins has been demonstrated in column experiment by using K_d values. Selective elutions on resin column were carried out for equimolar mixture of two metal ion systems. Separations were carried out by taking mixture of metal ion solution in concentration ratio of 1 : 1 (10 mL of 1 mg/mL concentration of each). The mixtures of metal solutions were passed through the column at a flow rate of 1 mL/5 min.

(iii) Elution: Tartaric acid having different concentration at different pH as eluting agent was used for different systems. For each column the optimized condition of concentration and pH of eluting agent was known from the K_d values.

RESULTS AND DISCUSSION

Spectral characterization of OFCR

The FT-IR spectrum of OFCR is shown in Fig. 1. The strong band at 3400 cm^{-1} is due to ν(O—H) stretching of phenolic group. The presence of medium strong band at 2920 cm^{-1} is due to ν(C—H) stretching of methylene and methyl group. The bands at 1605 cm^{-1} and 1500, 1470 cm^{-1} can be assigned to ν(C=N) heterocyclic ring and ν(C=C) aromatic ring stretching respectively. A band at 1470 cm^{-1} is due to the δ(C—H) deformation of methylene group. The presence of a medium strong band at 1380 cm^{-1} is due to δ (O—H) in- plane-bending of aromatic phenolic group and a band at 1250 cm^{-1} is due to the aromatic ν(C—O) stretching. A single band at 1300 cm^{-1} can be assigned to the δ(C—H) bending of aromatic methyl group (Ar—CH_3). A medium strong band at 830 cm^{-1} is assigned to the δ(C—H) bending of 1, 2, 3, 4 tetra-substituted benzene ring.

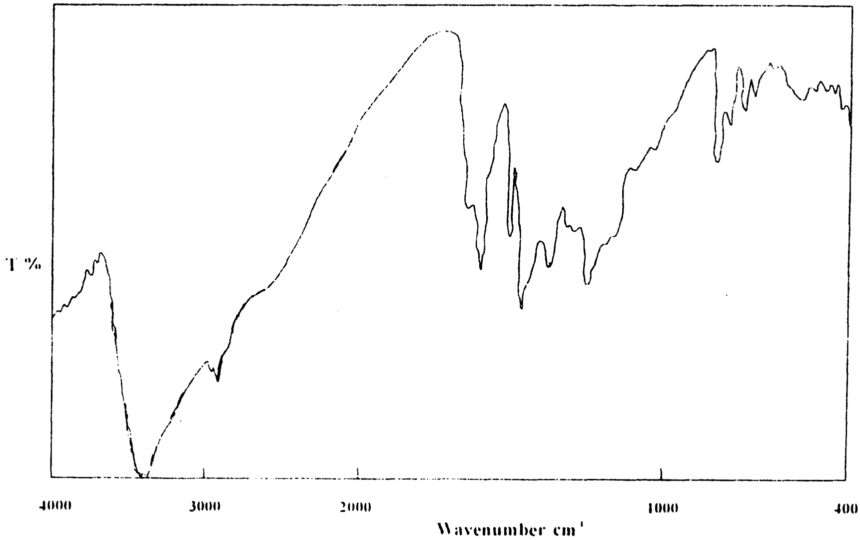

Fig. 1. FT-IR spectra of OFCR

^{1}H-NMR of the resin is shown in Fig. 2. Peaks at δ 6.5–8.6 ppm correspond due to protons of aromatic segment in resin. The peaks observed at 8.1–8.6 ppm (broad) are due to 3Ar—H of fused aromatic rings. 3Ar—H of *ortho, meta* and *para* to the —OH group appear at δ 6.5–7.5. A sharp singlet at 5.3 ppm appears due to two protons of —OH group. 2H of methylene group (Ar—CH_2—Ar) appear at δ 4.07 ppm and a peak at 2.5 ppm is due to three proton of methyl group (—CH_3).

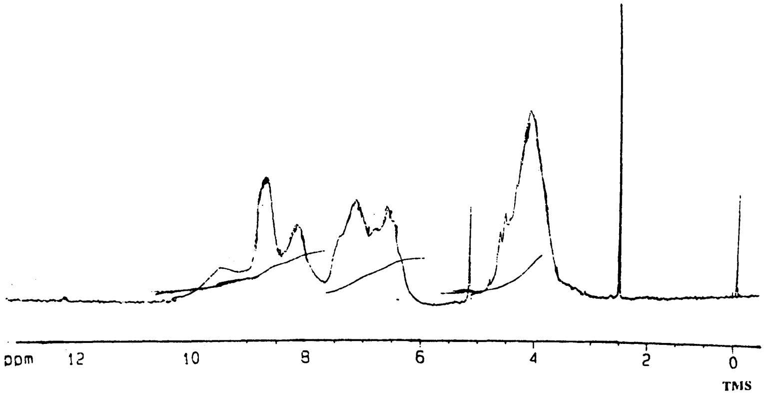

Fig. 2. ^{1}H-NMR of OFCR

In Fig. 3, the thermogram exhibits two step degradation. The first decomposition step involving a loss of about 19.87% weight begins at 150°C and proceeds up to 400°C. The second decomposition step begins at 500°C and extends up to 894°C involving a weight loss of about 96.17%. The maximum rate of weight loss occurs at 250°C and 650°C for the steps one and two respectively. Physico-chemical properties of ion-exchange resin are given in Table-1.

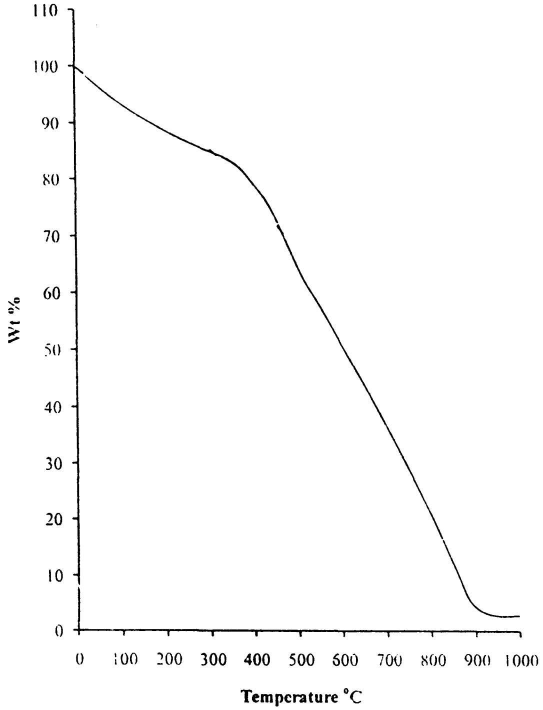

Fig. 3. Thermogram of OFCR

TABLE-1

PHYSICO-CHEMICAL PROPERTIES OF ION-EXCHANGE RESIN

Properties	Values
(%) Moisture content	8.05
(%) Solid	91.95
True density (d_{res}) g/cm^3	0.46
Apparent density (d_{col}) g/mL	0.21
Void volume fraction	0.54
Sodium exchange capacity mmol/g dry resin	4.73
Concentration of fixed iono-genic group, meq/cm^3	2.00
Volume capacity mmol/cm^3	0.92

pH titration study

The effect of pH on sodium exchange capacity shows that the resin exhibits good cation exchange capacity above pH 12.0. Thus the cation exchange capacity is pH dependent. The effect of pH on metal ions shows the maximum chelating capacity for nickel(II) at pH 6.0, for copper(II) and cadmium(II) at pH 5.0 and for zinc(II) and lead(II) at pH 4.0 (Fig. 4). An increase in pH increases the negatively charged nature of the sorbent surface. This leads to an increase in the electrostatic attraction between positive substrate and negative sorbent and results in increase in the adsorption of metal ions. The decrease in removal of metal ions at lower pH is apparently due to the higher concentration of H^+ ions present in the reaction mixture which compete with the metal ions for the sorption sites on the sorbent surface. Decrease in sorption at higher pH is due to the formation of insoluble hydroxy complexes of metal ions.

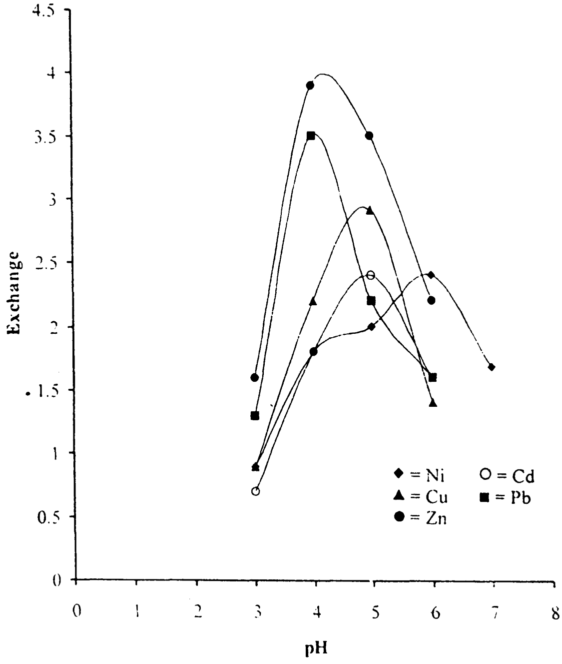

Fig. 4. Effect of pH on metal ion capacity for OFCR

The resin shows lower exchange capacity for nickel(II) than the other metal ions. Therefore, separation of nickel(II) would be clear from binary mixture using K_d values.

Rate exchange for metal ions

The exchange of metal ions on resin exhibits the time dependent phenomenon. Fig. 5. shows the study of the rate of exchange of metal ions on OFCR resin. The graph shows that the times required for 50% of exchange ($t_{1/2}$) for nickel(II), copper(II), zinc(II), cadmium(II) and lead(II) are at 47, 45, 50, 56 and 39 min respectively. The shorter time for 50% exchange indicates the faster rate of exchange. For this reason the resin may be used for chromatographic separation of metal ions from binary mixture or removal of toxic metals from the water. Finally, kinetics of metal ion-exchange mainly depends on the physical properties of the resins.

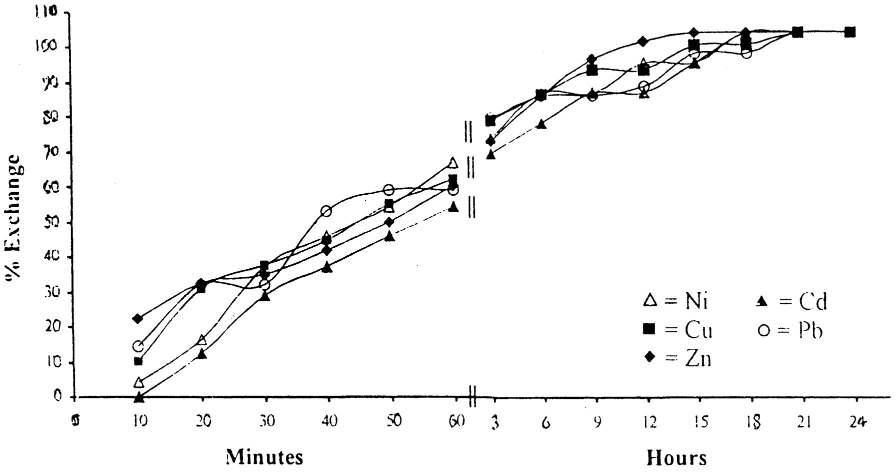

Fig. 5. Rate of exchange for metal ion on OFCR

Effect of concentration of metal ions on metal exchange capacity

Uptake of metal ions by the resin increases in proportion to the concentration of metal ion solution. The saturation of the resin takes place at 0.2 M concentration.

K_d values for metal ions in presence of electrolyte solutions

Effect of different concentrations of organic electrolyte on metal ion uptake by the synthesized resin was studied. The quantitative separation of metal ions from the mixture of cadmium(II)-copper(II), lead(II)-zinc(II), copper(II)-zinc(II) and nickel(II)-zinc(II) was accomplished by selective sorption on column at optimized K_d values from Table-2.

Chromatographic recovery of metal ions

Cadmium is a metal of current toxicological concern. The main toxic effect of cadium is local irritation in the respiratory tract. Zinc is an essential trace element for mammals, plants and lower forms of organisms but at higher concentrations it is also toxic[7]. The 5-amino salicylic acid group was anchored on guar backbone in dioxane medium. This ion selective chelating resin has been used in column chromatographic separation of copper(II) and iron(II)[8]. There are reports of radio-chemical separation of silver ion employing cerium(IV) molybdate ion-exchanger[9].

TABLE-2
K_d VALUES OF METAL IONS ON OFCR IN TARTRATE MEDIA AT VARIOUS MOLARITIES AND pH

Metal ion	Tartaric acid contration (M)	K_d values in tartaric acid at different pH				
		3.0	3.5	4.0	5.0	6.0
Ni(II)	0.1	99.0	89.8	67.0	53.0	50.0
	0.2	67.0	59.0	55.0	49.0	40.0
	0.3	24.0	20.0	—	—	—
	0.5	11.0	3.0	9.0	—	—
	1.0	1.7	—	—	—	—
Cu(II)	0.1	786.0	402.3	301.9	129.2	73.2
	0.2	305.7	251.7	78.0	15.0	8.0
	0.3	92.2	59.0	7.0	2.0	—
	0.5	—	—	—	—	—
	1.0	—	—	—	—	—
Zn(II)	0.1	999.5	542.3	411.3	212.0	59.0
	0.2	495.3	370.0	210.0	150.2	41.0
	0.3	312.0	222.5	95.3	50.0	—
	0.5	98.0	57.0	—	—	—
	1.0	12.0	0.9	—	—	—
Pb(II)	0.1	1000.7	353.0	542.0	375.0	95.7
	0.2	542.0	300.0	102.0	90.0	51.2
	0.3	314.0	151.0	23.0	19.0	10.9
	0.5	59.0	27.0	12.5	—	—
	1.0	3.0	8.0	2.0	—	—
Cd(II)	0.1	395.0	217.7	119.9	34.0	19.0
	0.2	125.0	195.0	82.0	25.0	25.0
	0.3	75.0	25.0	11.0	2.0	—
	0.5	51.3	—	—	—	—
	1.0	15.2	—	—	—	—

All systems exhibit clean separation in Figs. 6–9. The recovery of each metal ion was achieved on the basis of metal ion capacities and K_d values at optimized condition. The results of recovery of transition metal ions from binary mixtures by ion-exchange column chromatography using synthesized resin are given in Table-3.

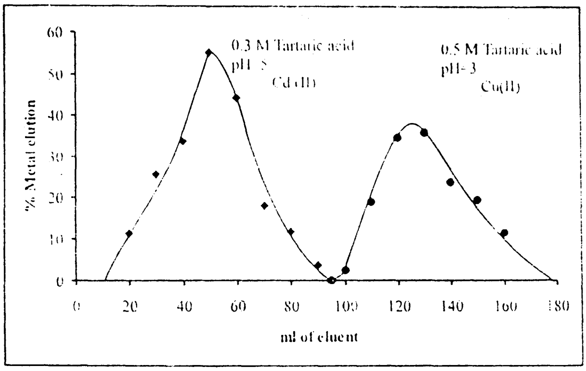

Fig. 6. Separation of Cd(II) and Cu(II) on OFCR

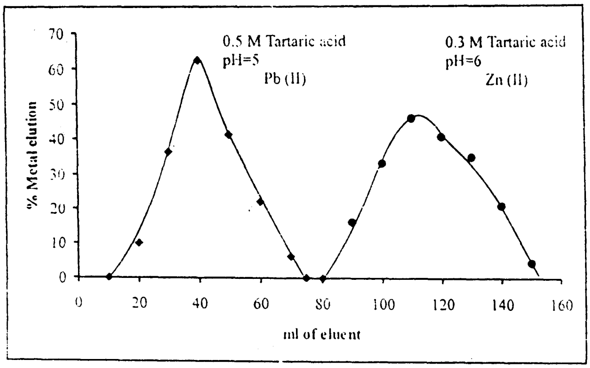

Fig. 7. Separation of Pb(II) and Zn(II) on OFCR

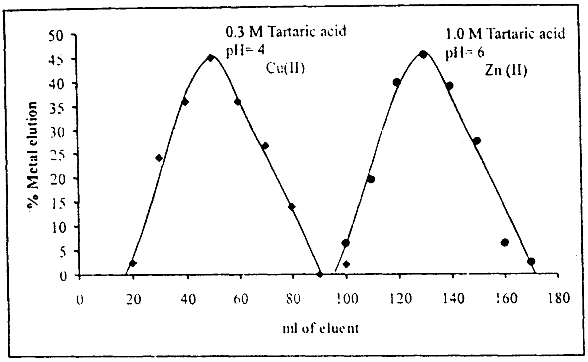

Fig. 8. Separaton of Cu(II) and Zn(II) on OFCR

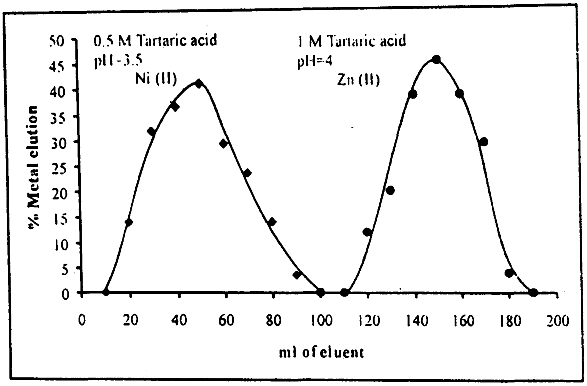

Fig. 9. Separation of Ni(II) and Zn(II) on OFCR

TABLE-3
OPTIMIZED CONDITIONS AND RECOVERY OF METAL IONS FROM BINARY MIXTURES BY COLUMN CHROMATOGRAPHY

Concentration and pH of tartaric acid and recovery of metal ions	Systems							
	Cd(II)–Cu(II)		Pb(II)–Zn(II)		Cu(II)–Zn(II)		Ni(II)–Zn(II)	
	Cd(II)	Cu(II)	Pb(II)	Zn(II)	Cu(II)	Zn(II)	Ni(II)	Zn(II)
Concentration (M)	0.3	0.5	0.5	0.3	0.3	1.0	0.5	1.0
pH	5.0	3.0	5.0	6.0	4.0	6.0	3.5	4.0
Recovery (%)	96.8	83.2	89.1	98.0	96.8	93.49	97.0	94.0

REFERENCES

1. A. Denzili, G. Ozkan and M.Y. Arica, *J. Appl. Polym. Sci.*, **78**, 81 (2000).
2. H. Hari Prasad, K.M. Popat and P.S. Anand, *Indian J. Chem. Tech.*, **9**, 385 (2002).
3. B. Mandal, D. Das and A.K. Das, *Indian J. Chem. Soc.*, **78**, 89w (2001).
4. M.J. Kunhikrishnan and C. Janardanan, *Indian J. Chem. Tech.*, **9**, 420 (2002).
5. W.B. Gurnule, H.D. Juneja and L.J. Paliwal, *Indian J. Chem.* **39A**, 110 (2000).
6. F. Vernon and K.M. Nyo, *Anal. Chim. Acta*, **93**, 203 (1977).
7. B. Mondal and A.K. Das, *Indian J. Chem. Tech.*, **10**, 489 (2003).
8. S. Loonker, S.K.Guar, K. Daga, V. Gupta and P. Mishra, *Asian J. Chem.*, **14**, 395 (2002).
9. Z.R. Turel and R.D. Bhagat, *J. Indian Chem. Soc.*, **27**, 425 (1995).

(*Received*: 9 March 2004; *Accepted*: 10 June 2004) AJC-3446