ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Synthesis of a novel chelating resin containing hexylthioglycolate group and a few of its applications

Preeti R. Dwivedi*, J.K.Verma and Chitra R. Kamath
Inorganic Research Laboratory, K.J.Somaiya College of Science and Commerce,
Vidyanagar, Vidyavihar, Mumbai-400077, India

Manuscript Info

Manuscript History:

Received: 28 August 2014
Final Accepted: 25 September 2014
Published Online: October 2014

Key words:

Chelating resin, batch equilibrium, column chromatography, recovery of metals from industrial wastewater and PCB scrap solution, selective elution.

****Corresponding Author***

Preeti R. Dwivedi

Abstract

A chelating resin having sulphur as the donor atom has been synthesized by suspension polymerization of highly cross-linked styrene, divinylbenzene and methyl methacrylate and was characterized on the basis of elemental analysis, FTIR, SEM, TGA and physico-chemical parameters. The adsorption properties of the synthesized resin (SR) were compared with two commercially available resins viz., a chelating resin (C1) containing thiol group and another chelating resin (C2) containing thio-uronium group. In Chromatographic column separations, for a binary mixture of Zn (II) and Cd (II) and for a ternary mixture of Zn (II), Cd (II) and Hg (II), the SR manifested slightly higher recovery values of the heavy metal ions in comparison to C1 and C2. Similarly, for the recovery of Zn (II), Cd (II) and Ni (II) from industrial wastewater samples and for the recovery of Cu (II) and Ni (II) from printed circuit board (PCB) scrap solution, the performance of SR was found to be somewhat better as compared to both C1 and C2.

Introduction

The removal of toxic metal ions from various industrial effluents is vital as the toxicity of metal ions poses serious health hazards to humans as well as other living organisms [1]. Among various methods for the removal of heavy metal ions such as liquid-liquid extraction, precipitation, electrolytic concentration, membrane filtration, ion-exchange and adsorption, the last one is generally preferred because of its high efficiency, ease of handling and availability of different sorbents [2].

An ion-exchange resin is an insoluble matrix normally in the form of tiny beads fabricated from an organic polymer substrate. The sorption characteristics of the metal ions depend upon the size of the chelate ring with a given metal atom, number of donor atoms per binding site of the functional group, type of donor atoms, oxidation state of the metal ion, pH of the system etc. Studies have revealed that sulphur containing ligands are more selective with high bond stability towards the noble and heavy metal ions, because sulphur, a member of the third period, having low-lying empty 3d orbitals, exhibits markedly different bonding properties compared to nitrogen and oxygen [3].

The removal of heavy metal ions by chelating resins using batch equilibration method has acquired wide acceptance because of the availability of a wide variety of sorbent phases and their high degree of selectivity, high loading capacity and enhanced hydrophobicity [4]. Various chelating resins containing sulphur as a donor atom have been synthesized and reported in literature. Such resins contain different functional groups, for example, dithizone [5], bicine [6], poly [4-vinyl (2-hydroxyethyl) sulphide] [7], dithiocarbamate [8], 2-amino-6-nitro-benthiazole and thiosemicarbazide [9], diphenyl disulphide [10], hexylthioglycolate [11], etc. supported on a suitable copolymer matrix such as poly-(styrene-divinyl benzene). Such tailor-made chelating resins then have been successfully employed for selective separation of noble and heavy metal ions vis-à-vis removal of heavy metals from industrial effluents / printed circuit board scrap solution.

The purpose of the present work is to synthesize a novel hexylthioglycolate (HTG) chelating resin (SR) by polymerization of styrene, methyl methacrylate (MMA) and divinylbenzene (DVB) and to investigate the sorption behaviour of heavy metal ions viz., Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II), and Pb (II) by complexometric titration using standard EDTA solution at different pH values and different time intervals. The adsorption properties, separation of binary and ternary mixture of heavy metal ions and recovery of heavy metal ions from industrial wastewater samples and from printed circuit board (PCB) scrap solution for SR were compared with two commercially available resins viz., a chelating resin (C1) containing thiol group and another chelating resin (C2) containing thio-uronium group.

2 Experimental

2.1. Apparatus and reagents

With the help of elemental analysis, the percentage of elements such as C,H,O,S present in the synthesized chelating resin (SR) were determined by using Thermofinnigan elemental analyser, Model FLASH EA 1112 series. The FTIR spectrum of the SR was scanned in KBr pellets on Bruker spectrophotometer Model 3000 Hyperion microscope with vertex 80, in order to identify the various linkages and functional groups. The thermal behaviour of SR was investigated by using Perkin Elmer thermogravimetric analyser Model Diamond (TGA/DTA) at a heating rate of 10^0C/min in static nitrogen atmosphere. An image of the surface of SR was produced by using Scanning Electron Microscopy (Joel- JSM 7600F Model).The physicochemical parameters viz., percent moisture content, solid percent, true and apparent densities, void volume fraction, hydrogen ion capacity and sodium exchange capacity of SR were evaluated according to the methods cited in literature [12].

Styrene (Sty), methyl methacrylate (MMA), and divinylbenzene (DVB) used were of 98% purity as supplied by Aldrich Sigma (India). The commercial chelating resins (C1 and C2) containing thiol group and thio-uronium group respectively were procured from Ion-exchange India (Pvt.) Ltd., Mumbai. All other chemicals, solvents and indicators used were of AR grade from Merck India and Loba Chemicals Company. Double distilled water was used throughout the present work.

2.2 Synthesis of hexylthioglycolate (HTG) chelating resin

The copolymer beads were prepared by suspension polymerization of styrene (18.86 mL; 0.164 mol), divinylbenzene (8.5 mL; 0.062 mol) and MMA (10.18 mL; 0.092 mol) in the presence of toluene (4mL) as diluent, gelatine (1 g) as stabiliser and benzoyl peroxide (BPO) as an initiator in a round bottom flask at 80^0C for 8 hours with continuous stirring using a magnetic stirrer. The beads were filtered off on Buchner funnel, washed with water and ethanol and dried under vacuum at 60^0C for 48 hrs.

A mixture of the copolymer beads (23 g), sodium boronhydride (2 g; 0.052 mol), zinc chloride (9.0 g; 0.066 mol) and N,N'-dimethyl aniline (8.5 g; 0.070 mol) in tetrahydrofuran (100 mL) was then refluxed for 2 hours in a round bottom flask on a boiling water bath . The reaction mixture was poured into an ice-cold and previously blended mixture of 100 mL of 10% aqueous ammonium chloride and 100 mL of chloroform with continuous stirring and then filtered off. The filtered resin was washed with acetone, water and finally with methanol and dried under vacuum at 60^0C for 48 hrs. The resin beads thus obtained were found to contain hydroxyl group as confirmed by FTIR analysis.

Next, the copolymer beads containing hydroxyl group were treated with 0.1M potassium permanganate in 2% sodium hydroxide at 60^0C by stirring for 2 hours using a magnetic stirrer, then filtered on Buchner funnel and washed with 12 M HCl, water and finally with acetone. The product was dried under vacuum at 60^0C for 48 hours and was found to contain carboxylic group as confirmed by FTIR analysis.

The resin beads containing carboxylic group were then refluxed with 50 g of 1,6–hexandiol containing 2 mL of 18 M sulphuric acid as a catalyst, for 24 hours at 60 – 70^0C. The beads were filtered using Buchner funnel and washed with hot methanol.

The filtered resin beads were finally refluxed with 100 mL thioglycolic acid at 60-70^0C for 24 hours containing 2 mL of 18 M sulphuric acid as a catalyst. The product was collected by suction filtration, washed with 12 M HCl, water and acetone successively and dried in vacuum at 60^0C for 48 hours to yield the dried product. The product was found to contain hexylthioglycolate functional group on the basis of FTIR analysis.

The synthesis of the resin beads is schematically represented in Fig. 1.

2.3. Stability Studies

The stability of SR was checked by soaking 1 g of resin each in 2M HCl, 0.1M HNO_3 and 0.05M NaOH separately for 48 hrs. The soaked resin was filtered through a sintered glass crucible (G3), washed with double distilled water, dried in vacuum at 80^0C for 1 hour and then weighed again.

2.4. Swelling Studies

The dry resin (1 g) was allowed to stand up in double distilled water for 48 hours, then filtered off by suction and lightly pressed between filter paper to remove surface moisture. The resin was then dried at 80^0C for 11 hours after which its weight was recorded. The water regain value (WRV) was calculated from the difference in the weight of wet and dry resin by using the following formula:

$$\text{WRV} = \frac{(\text{Weight of wet resin} - \text{Weight of dry resin})}{\text{Weight of dry resin}}$$

2.5. Metal Ion-exchange Studies

The metal ion-exchange properties of SR, C1 and C2 were studied by batch equilibration method as reported in the literature [13].

Metal Ion Uptake as a Function of pH and time

The metal ion uptake of metal ions viz., Co (II), Pb (II), Ni (II), Cd (II), Cu (II), Zn (II) and Hg (II) was studied by adding 0.5 g of dry resin to 25mL of the respective metal ion (1mg/mL) solution buffered at the requisite pH. After equilibrating for 24 hours, the mixture was filtered and the resin was thoroughly washed with distilled water. The sorbed metal ions were then completely eluted using 40 mL of 2N HCl solution.

In order to estimate the optimum time, a series of experiments were carried out in which the dry resin (0.5g) was added to 25mL of a given metal ions solution buffered at an optimum pH in the range of 3.5 to 11. After equilibrating for different intervals of time, each mixture was filtered and washed thoroughly with double distilled water. The sorbed metal ions were completely eluted by 40mL of 2N HCl solution.

The amount of each metal ion present in the solution and retained on the resin was determined by complexometric titration with a standard EDTA solution.

2.6. Packing of the Column

In a glass column (25 Cm length and 1.0 Cm internal diameter), the slurry of H^+ form of resin (1 g) was poured slowly along the wall of the column to form a compact resin bed. The outlet was then opened and care was taken to keep water level above the top of the resin bed. The column was conditioned at pH 6 using 0.2 M acetate buffer solution before commencing further column operations.

2.7. Recovery of the Heavy Metal Ions from Industrial wastewater samples

Prior to use, the resins- SR, C1 and C2 were converted into sodium form as per the procedure [14] cited in literature. The resin beads were rinsed with 1N HCl to remove the undesired metals and then washed with 1M NaOH and finally washed repeatedly with double distilled water until the pH of the effluent in each case dropped to 10.

Three different glass columns of each of length 25 Cm and 1 Cm internal diameter were packed with 0.5 g of the resins viz., SR, C1 and C2 in the sodium form. Each resin column was equilibrated with about 25 mL of 0.2 M acetate buffer. Then 10 mL of the industrial wastewater samples containing either Zn (II) or Cd (II) or Ni (II) were introduced separately in to the first, the second and the third columns respectively. After that approximately 150 mL of the respective eluting agent for a given metal ion was passed through the column at a flow rate of 0.5 Cm^3/min., the concentration of each metal ion in eluent was determined by complexometric titration.

2.8. Recovery of Cu (II) and Ni (II) from Printed Circuit Board (PCB) scrap solution

Among the wastes that contain Cu (II) and Ni (II), one of the most complex recyclable material is electronic scrap like printed circuit boards, which generally contain 10-30% Cu (II) as well as plastic and other metals like Ni (II), Pb (II), Sn (II), etc. Recovery of Cu (II) and Ni (II) from PCB scrap solution was carried out as follows.

Approximately 10g of the waste PCB were crushed manually and were leached using 500 mL of ammonical alkaline solution [5M NH_3 – 1M $(NH_4)_2SO_4$] in one litre round bottom flask. The flask was immersed in a thermostat water bath maintained at 60^0C and the reactants were stirred for 24 hours [15]. After completion of the extraction, the solution was filtered to remove the solid impurities. The resultant solution was diluted to 250mL with double distilled water and was labelled as the leach solution. Next, 10 mL of the leach solution was passed through a column of 25 Cm length and 1 Cm internal diameter containing 1.0 g of the dried resin in the sodium form. 150 mL of 7M H_2SO_4 and 0.25M tartaric acid solutions were used as eluting agents and were passed through the column successively with a flow rate of 0.5 Cm^3/min for the elution of Cu (II) and Ni (II) respectively. The recovery of Cu (II) and Ni (II) in eluent was determined by complexometric titration method.

3. Results and discussion

3.1. Characterization of SR

The synthesized HTG-resin (SR) was insoluble in water and common organic solvents suggesting the formation of a cross-linking structure. Resin beads of 36-44 mesh size only were used throughout the work.

The results of the elemental analysis for SR have been recorded in Table 1. The empirical formula of the repeating unit was found to be $C_{30}H_{38}O_4S$. The theoretically calculated values of %C, %H, %O and %S as are in good agreement with the experimentally obtained values (as given in parentheses in Table 1).

FTIR spectrum of SR is depicted in Fig. 2. The broad band at 3103.70 Cm^{-1} is due to the stretching of methylene group (C-H). A medium peak appearing at 2905.70 Cm^{-1} is assigned to aromatic ring stretching modes. A medium band appearing at 2945.17 Cm^{-1} is due to the $-CH_2-$ linkages present in resin. A sharp strong band at 1705.47 Cm^{-1} is due to the presence of ester linkage. A broad peak appearing at 2565 Cm^{-1} shows the presence of S-H stretching vibrations. The stretching vibrations at 665.82 Cm^{-1} show the presence of C-S group. A sharp peak at 1208.23 cm^{-1} is due to the presence of thiocarbonyl group. The medium band of C=C ring stretch is found at 1400.11 cm^{-1} and sharp weak band for C=C stretch appears at 918.14 Cm^{-1}.

The thermogram of SR, shown in Fig. 3, reveals that the resin sample undergoes degradation in one step. The degradation of the resin starts at about 300^0C and extends up to 450^0 C involving 84.86 % weight loss with constant heating rate of 10^0 C per minute in nitrogen atmosphere. Thus, SR is found to possess robust thermal stability.

The physical integrity of the resin was observed with SEM. In Fig. 4, the white bar at the bottom of the scanning electron micrographs represents the scale.

The physicochemical parameters of SR are presented in Table 2. The water regain value of the synthesized resin was found to be 0.6689 g/g. The stability of the SR towards 2M HCl, 0.1M HNO_3 and 0.05M NaOH was examined. The resin samples showed no significant loss in weight after stability studies. Thus, the resin was considered stable in both acidic and alkaline media.

3.2. Metal Ion Uptake as a function of pH and time

The distribution of metal ions for SR between the resin and the aqueous phase was determined by equilibrating for 24 hours at room temperature at various pH values. It is assumed that the equilibrium state is attained under given conditions in 24 hours. The results of such study have been plotted in Fig.5. The plots reveal that the amount of uptake of each metal ion by the resin increases with the rise in pH of the aqueous phase. Fig.5 also demonstrates that the maximum ion-exchange capacity for Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and Pb (II) is observed at the pH values of 3.5, 10, 11, 6, 8, 3.5 and 5 respectively. Furthermore, it is also observed that Cu (II) is more effectively taken up by SR than the other metal ions. The metal ions viz., Pb (II) and Zn (II) showed selective uptake at acidic pH values. Finally, it is clearly seen that the distribution ratios of Co (II) and Ni (II) in the pH range of 3 - 11 are higher than the distribution ratios of both Hg (II) and Cd (II).

The distribution ratios of all the metal ions for C1 and C2 were similarly determined as in case of SR. The order of the distribution ratios of the metal ions for the SR and C2 was found to be the same as given below:

Cu (II) > Pb (II) > Zn (II) > Co (II) > Ni (II) > Hg (II) > Cd (II).

While for C1, the order of their distribution ratios was evaluated to be as given below:

Cu (II) > Pb (II) > Co (II) > Zn (II) > Ni (II) > Hg (II) > Cd (II).

Table 3 presents the data generated for maximum adsorption of each of the seven metal ions studied at their respective pH values for SR, C1 and C2. From the data, it can be concluded that SR is the most effacious resin than both C1 and C2 and C2 is better than C1 with regard to uptake of the metal ions studied.

Fig.6 depicts the plots of % of metal ion uptake with regard to time of equilibration in hours. These plots reveal that Cu (II) and Hg (II) ions required shortest time i.e. about 9 hours, whereas Zn (II) and Pb (II) required 10 hrs. Furthermore, Co (II) and Cd (II) required about 11 hours, while Ni (II) requires 12 hours to reach the equilibrium. Thus, the rate of metal ion uptake for SR follows the order:

Cu (II) = Hg (II) < Zn (II) < Co (II) = Pb (II) = Cd (II) < Ni (II).

For C1, the order for the rate of metal ion uptake is found to be:

Hg (II) = Cd (II) < Cu (II) < Pb (II) = Zn (II) = Co (II) = Ni (II)

For C2, The order for the rate of metal ion uptake is:

Cu (II) = Pb (II) = Co (II) = Cd (II) < Ni (II) = Hg (II) = Zn (II)

Table 4 records the data to the optimum time in hours for maximum metal ion uptake as evaluated for the seven metal ions by the resins – SR, C1 and C2. From the data, it can be concluded that the rate of metal ion uptake by commercially available resin viz., C2 is the fastest, whereas commercially available resin C1 is the slowest. However, the synthesized resin (SR) manifests as an intermediate kinetics with respect to metal ion uptake.

3.3. Chromatographic Separations

For the separation of binary mixture of Zn (II) and Cd (II), 10 mL of 1:1 mixture of Zn (II) and Cd (II) were passed through the resin column at pH 6 using 0.2M acetate buffer at a flow rate of 0.5 $cm^3 min^{-1}$. Separation of Zn (II) and Cd (II) was achieved with the help of selective elution technique by first passing 150 cm^3 of 0.5 M HCl as an eluent for Zn (II)followed by 150 cm^3 of 1 M HNO_3 for elution of Cd (II). For the synthesized resin, the recovery of Zn (II) was found to be 98.10 % while that for Cd (II) it was 96.05 %, whereas, for C1 the recovery of Zn (II) and Cd (II) was 95.45% and 92.88% and for C2 the recovery for the same was 97.27% and 94.28% respectively (Fig. 7). The result shows that the synthesized resin is much better than commercial C1 and C2 resins.

In the separation of ternary mixture of Zn (II), Cd (II) and Hg (II), 10 mL 0f 1:1:1 mixture of Zn (II), Cd (II) and Hg (II) were passed through the column at pH 3 using 0.2M acetate buffer at a flow rate of 0.5 $Cm^3 min^{-1}$. Here Hg (II) was retained on the column, whereas Zn (II) and Cd (II) were found in column effluent. The Hg (II) was eluted with 150 cm^3 of 5 % thiourea in 1 M $HClO_4$. The column effluent containing Zn (II) and Cd (II) were passed through the column at pH 5 using 0.2 M citrate-phosphate buffer. Zn (II) was eluted first with 150 mL of 0.5 M HCl at a flow rate of 0.5 Cm^3min^{-1}. Further, Cd (II) was eluted with 150 mL of 1 M HNO_3 and finally, Hg (II) was eluted with 150 mL of 5 % thiourea in 1 M $HClO_4$ each at a flow 0.5 $Cm^3 min^{-1}$. With synthesized resin (SR), the recoveries of Zn (II), Cd (II) and Hg (II) were found to be 98.73 %, 98.68% and 98.48 % respectively which are marginally higher compared to the recovery values for these metal ions with commercial resins C1 and C2. In case of the commercial resin C1 the recoveries of Zn (II), Cd (II) and Hg (II) were 95.45%, 92.88% and 96.29% respectively, while for C2 the recoveries of the same were 97.27%, 94.28% and 96.29% respectively. Thus, the recovery values for Zn (II), Cd (II) and Hg (II) with C1 and C2 are slightly lower than those obtained with the synthesized resin (SR) in the present work (Fig.8).

No cross contamination was observed in any of the separations under study.

3.4 Recovery of Zn (II), Cd (II) and Ni (II) from Industrial Wastewater

According to column procedure, Zn (II) was eluted with 0.5M HCl with a flow rate of 0.5 Cm^3min^{-1} and its recovery was found to be 98.92 %. Similarly, Cd (II) was eluted with 1M HNO_3 with the same flow rate and its recovery was 99.50%. Lastly, Ni (II) was eluted with 0.25M tartaric acid with the same flow rate and its recovery was 98.17 %.

According to fig. 9 for C1 and C2, the recovery of Zn (II), Cd (II) and Ni (II) from industrial wastewater were 98.20%, 98.51% and 96.71% and 98.20%, 99.50 % and 97.36% respectively.

Thus the synthesized HTG-resin can be used to remove the toxic metal ions from industrial wastewater efficiently.

3.5. Recovery of Cu (II) and Ni (II) from PCB scrap solution

With the help of complexometric titrations, recovery of Cu (II) and Ni (II) were calculated. For the synthesized resin, Cu (II) was recovered to the extent of 97.52%, whereas Ni (II) 96.74%. While for C1 and C2, the recovery of Cu (II) was 95.86% and 96.69% respectively and for Ni (II) the recovery was 93.50% and 95.93% respectively (Fig.10).

3.6. Reusability of Resin

The polymeric chelating resin can be used again and again repeatedly. The resin was recovered back to its original form by desorption process using a 1:3 mixture of concentrated HNO_3 and HCl. After the repeated cycling with the mixture the resin was washed thoroughly with distilled water. It was then ready for reuse. Furthermore, it was experimentally established that the amount of metal ion taken up by the recycled polymer is no way inferior to the freshly prepared resin.

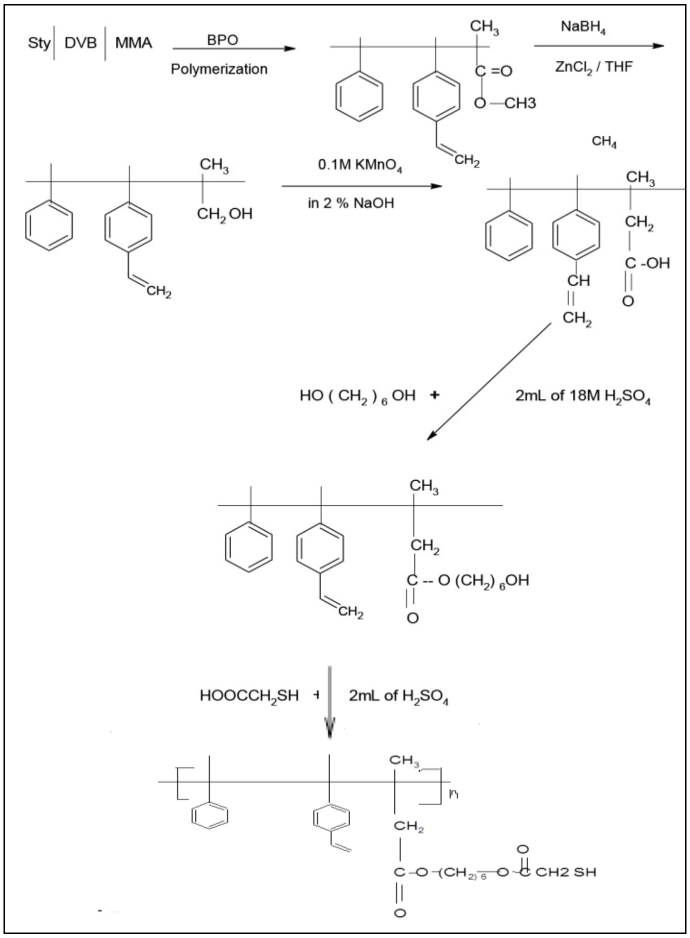

Fig.1: Synthesis of SR

Table 1: Elemental analysis of SR

Elemental analysis calculated (%) and found (%) parenthesis			
C	H	O	S
72.80 (72.50)	7.70 (7.01)	12.95 (10.23)	6.47 (5.46)

Table 2: Physico-chemical parameters of SR

Properties	**Values**
Moisture (%)	1.5890
Solid (%)	98.411
True density (dry resin) g/cm^3	0.667
Apparent density (dry resin) g/cm^3	0.7273
Void volume (%)	16.59%
Hydrogen ion capacity (meq/g dry resin)	0.5
Sodium exchange capacity (meq/g dry resin)	1.7

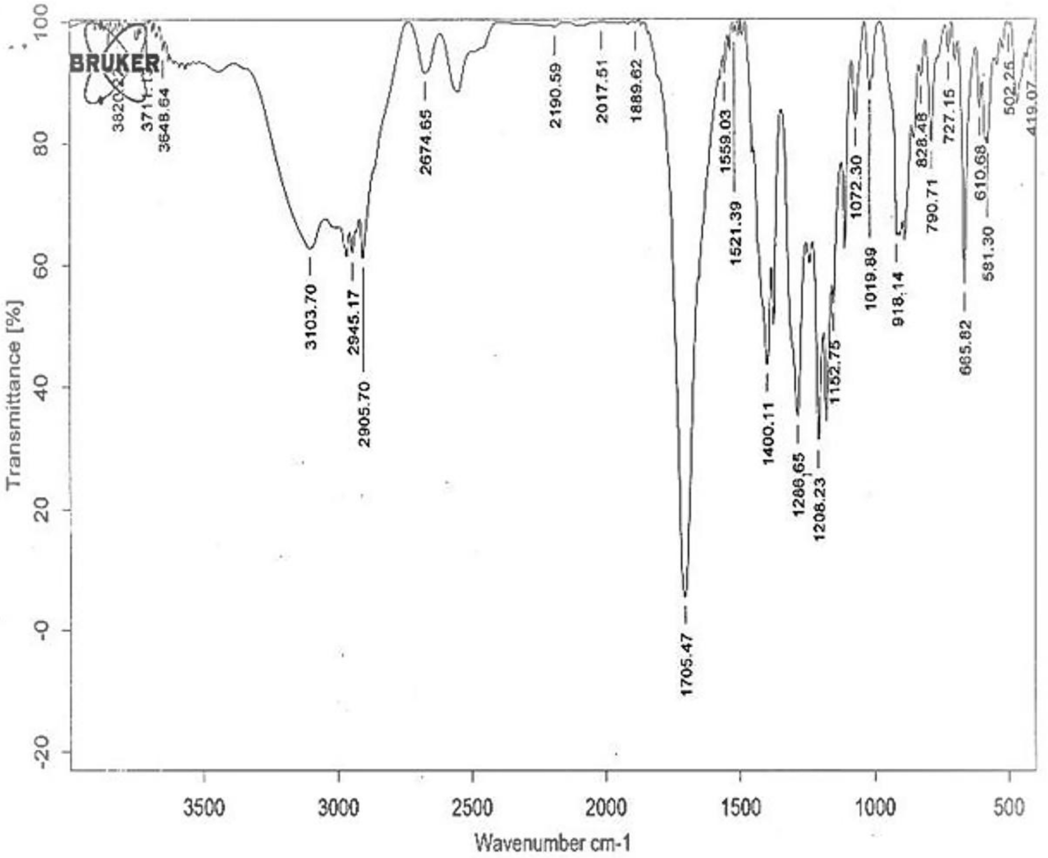

Fig.2: FTIR of SR

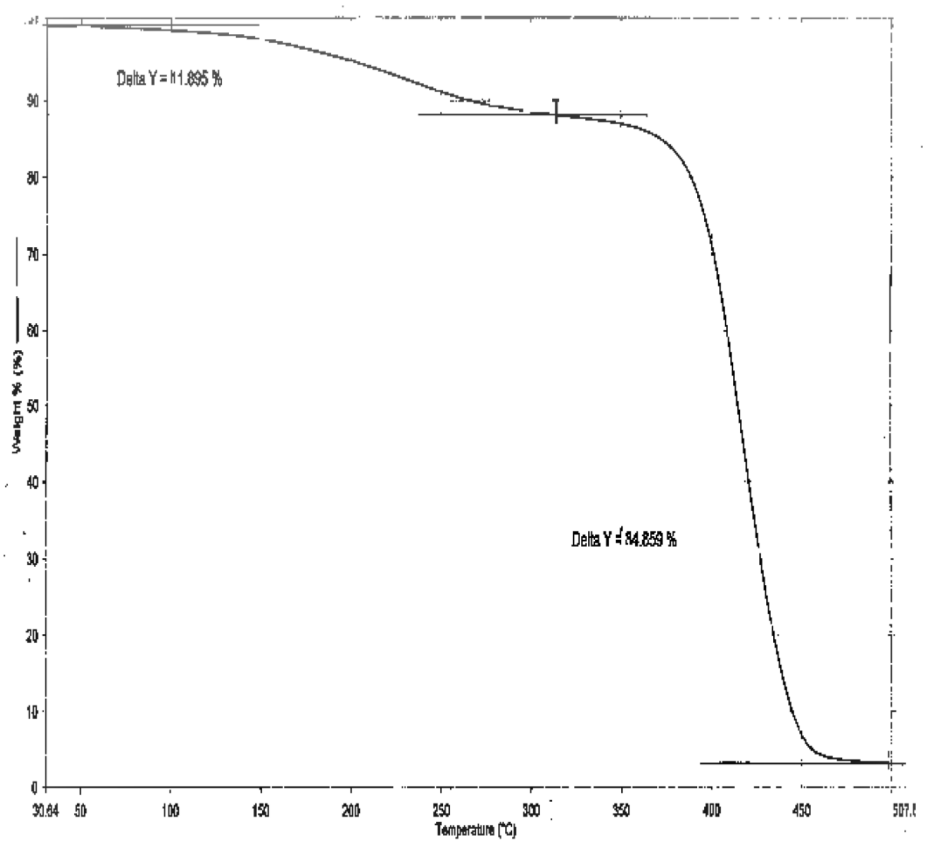

Fig.3: TGA of SR

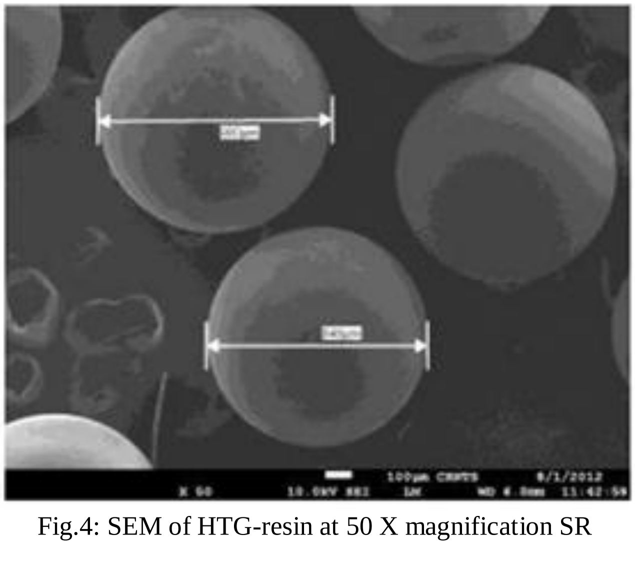

Fig.4: SEM of HTG-resin at 50 X magnification SR

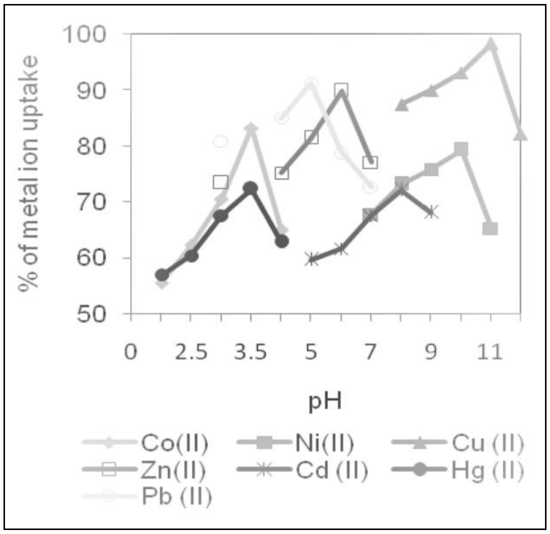

Fig.5: Effect of pH on metal ion uptake by SR

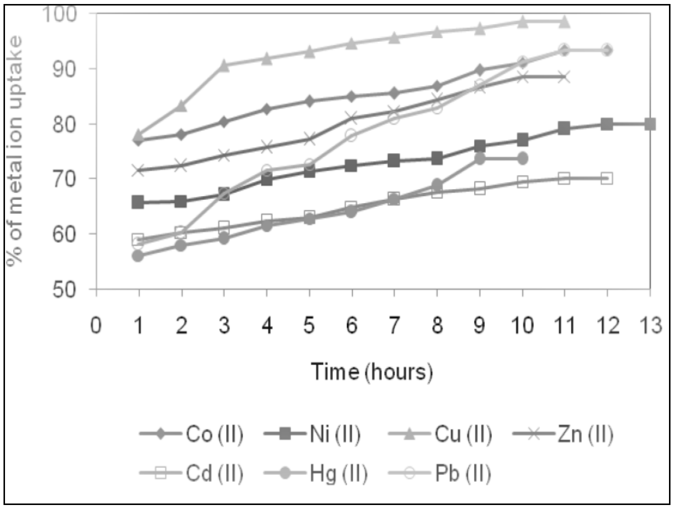

Fig.6: Rate of metal ion uptake as a function of time by SR

Table 3: Maximum adsorption of heavy metals for SR, C1 and C2 at respective optimum pH values

Metal ions	**Opti-mum pH**	**Maximum adsorption (%)**		
		SR	**C1**	**C2**
Cu(II)	11	98.31	92.62	97.80
Pb(II)	5	91.28	81.94	87.13
Zn(II)	6	89.9	79.97	82.36
Co(II)	3.5	83.18	80.38	82.24
Ni(II)	10	79.25	73.55	75.06
Hg(II)	3.5	72.3	71.01	72.22
Cd(II)	8	72.09	64.89	69.47

Table 4: Optimum time for metal ion uptake in case of SR, C1 and C2

Metal ions	**Optimum Time (hours)**		
	SR	**C1**	**C2**
Cu(II)	09	10	09
Pb(II)	10	11	09
Zn(II)	10	11	10
Co(II)	11	11	09
Ni(II)	12	11	10
Hg(II)	09	09	10
Cd(II)	11	09	09

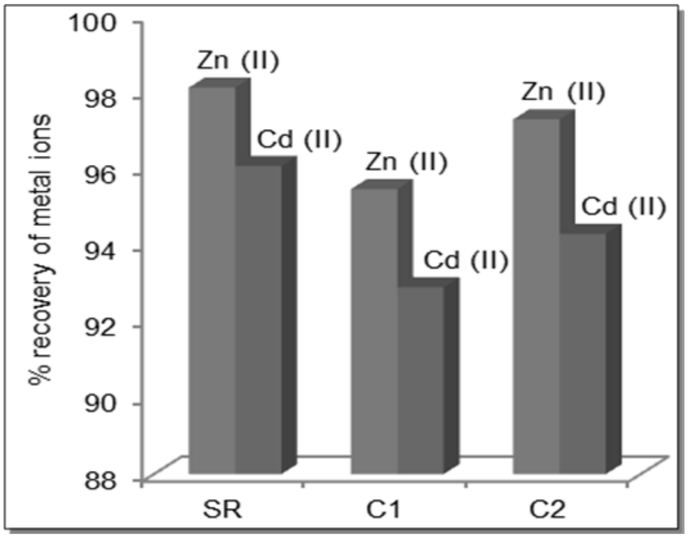

Fig.7: Recovery of Zn (II) and Cd (II) from their binary mixture using SR, C1 and C2

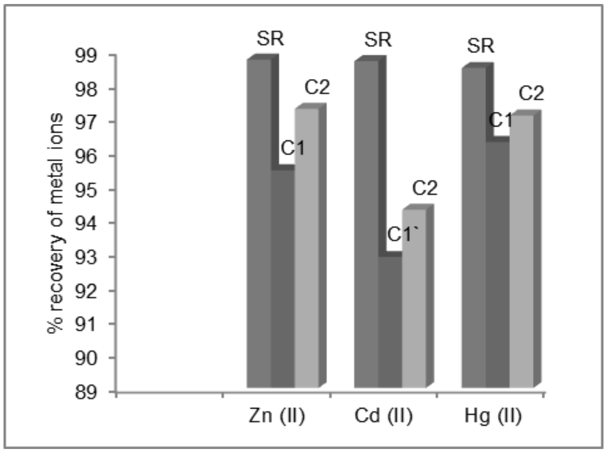

Fig.8: Recovery of Zn (II), Cd (II) and Hg (II) from their ternary mixture

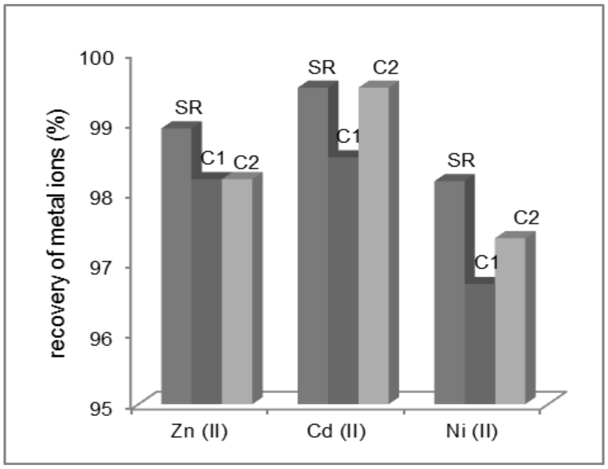

Fig.9: Recovery of Zn (II), Cd (II) and Ni (II) from Industrial wastewater using SR, C1 and C2

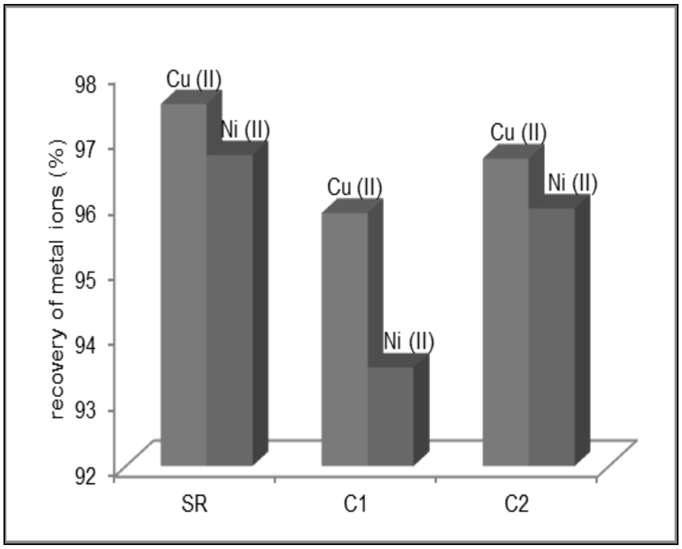

Fig.10: Recovery of Cu (II) and Ni (II) from PCB scrap solution using SR, C1 and C2

4. Conclusions

The synthesized novel chelating resin (SR) derived from 1, 6-hexanediol and thioglycolic acid was found to be useful as a cation-exchanger for divalent heavy metal ions. With the help of FTIR, the structure of SR was confirmed. TGA of SR revealed that the degradation of the resin involved a single step at 350^0C (upto 450^0C) showing its good thermal stability. SEM showed the morphology of the resin. The order of distribution ratios of the metal ions for SR and for C1 is the same: Cu (II) > Pb (II) >Zn (II) > Co (II) > Ni (II) > Hg (II) > Cd (II), while for C2 it is: Cu (II) > Pb (II) > Co (II) > Zn (II) > Ni (II) > Hg (II) > Cd (II). In Chromatographic column separations, for a binary mixture of Zn (II) and Cd (II), recoveries for SR, C1 and C2 were evaluated to be 98.10% and 96.05%; 95.45% and 92.88% and 97.27% and 94.28% respectively. For a ternary mixture of Zn (II), Cd (II) and Hg (II), the recoveries for SR, C1 and C2 were found to be: 98.73%, 98.684% and 98.48%; 95.45%, 92.88% and 96.29%; 97.27%, 94.28% and 96.29% respectively. The recoveries of Zn (II), Cd (II) and Ni (II) from industrial wastewater samples with SR, C1 and C2 as obtained 98.92%, 99.50% and 98.17%; 98.20%, 98.51% and 96.71%; 98.20%, 99.50% and 97.36% respectively and those for Cu (II) and Ni (II) from PCB scrap solution were evaluated to be 97.52% and 96.74%; 95.86% and 93.50% and 96.69% and 95.93% respectively. Thus the synthesized chelating resin (SR) containing hexylthioglycolate as a functional group manifested slightly superior recovery values of heavy metal ions in comparison to commercially available resins viz., C1 having thiol group and C2 having thio-uronium group.

Acknowledgements

The authors are thankful to the SAIF, IIT Bombay, for extending the instrumental facilities pertaining to FTIR, SEM, TGA and Elemental Analysis. Thanks are also due to Mr. Sandeep Maru, Manager of Jalaram Metal Finishers Company, and Mr. Nitin Patil of Jonhson Matthey Company for providing the industrial wastewater samples. The authors also extend their grateful thanks to Dr.Sanjay Mendeley of Ion-Exchange India (Pvt.) Ltd., Mumbai, for readily providing the two samples of commercial chelating resins (C1 and C2) for this study.

References:

1. Singh, A. V., Sharma, N. K., Rathore, A. S. *Environmental technology*, **(2012),** 53, 423-480.

2. Mahmoud, M. E., Osman, M. M., Hafez, O. F., Hegazi, A. H., Eimely, E. *Desalination*, **(2010),** 251, 23-30.

3. Tuzen, M., Narin, I., Soylak, M., Elci, L. *Anal Lett*, **(2004),** 37, 473-482.

4. Ismael, A. R., Edbey, K. M. *J. Chem Pharm Res*., **(2010),** 3, 459-466.

5. Scamai, S., Kartal, S., Yilmaz, Y., Scamai, M., Soykan, C. *Chem Engineering J*, **(2012),** 181-182, 746-753.

6. Dev, K., rao, G. N. *Talanta*, **(1995),** 42, 591-599.

7. Rongjan, Qu., Sun, S., Wang, C., Cheng, G. *European Polymer J*, **(2006),** 42, 254-258.

8. Shabaan, A. F., Fadel, D. A., Mahmoud, A. A., Elkomy, M. A., Elbahy, S. M. *J Environ Chem Engineering*, **(2013),** 1, 208-217.

9. Mohamed, A., Riswan, A., Duraisamy, J. K., Burkanudeen, A. R. *J Hazardous Materials,* (2013), 248-249, 59-68.

10. Dwivedi, P. R., Verma, J. K. *e-journal of Chemistry*, **(2014),** 7, 57-63.

11. Dwivedi, P. R., Verma, J. K. *Int. J. Of Chemical and Environmental Engineering,* **(2014),** 5, 57-64.

12. Helfferich, F. Ion-Exchange, Mc Graw-Hills, New York, 1962.

13. Vogel, A. Textbook of Quantitative Chemical Analysis, 5th Edition, Longman, UK, **1989.**

14. Koivula, R., Letho, J., Pajo, L., Gale, T., Leinone, H. *Hydrometallurgy,* **(2000)**, 56, 93-108.

15. Sridhar, V., Verma, J. K.., Kumar, S. A. *Hydrometallurgy,* **(2009)**, 99, 124-126.