A novel chelating resin with diphenyl disulphide functional group: Synthesis, sorption, separation and recovery of some heavy metal ions

Preeti R. Dwivedi* and J.K.Verma

Inorganic Research Laboratory, K.J.Somaiya college of Science and Commerce, Vidyanagar, Vidyavihar, MUMBAI-400077, India

Abstract: *A novel chelating resin containing diphenyl disulphide as a functional group, supported on poly-(ethylacrylate-acrylonitrile-divinylbenzene) was synthesized by suspension polymerization and characterized by elemental analysis, physico-chemical properties thermal studies, FTIR studies and scanning electron microscopy. With the help of batch equilibrium technique, the selectivity and binding capacities of chelating resin were measured towards certain metal ions in different electrolyte concentration, wide pH range and different time intervals. The maximum adsorption capacities of the resin for Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and Pb (II) were evaluated to be 24.27, 24.59, 24.02, 24.52, 23.94, 22.46 and 19.26 mg g^{-1} respectively at pH 7, 10, 11, 6, 8, 3.5 and 5 respectively. With the help of chromatographic separations, the recoveries of Zn (II) and Cd (II) were found to be 99.05% and 98.68% respectively from their binary mixture. In case of ternary mixture of Zn (II), Cd (II) and Hg (II) the recoveries as obtained were 98.10%, 98.02% and 97.9% respectively. The synthesized resin was also used to recover Zn (II), Cd (II) and Ni (II) from industrial wastewater samples each containing a single metal ion, and Cu (II) and Ni (II) from Printed Circuit Board (PCB) scrap.*
Keywords: *Chelating ion-exchange resin, sorption studies, column chromatography and elution.*

1. Introduction

It is well known that various dissolved toxic metal ions, species or compounds in industrial wastewaters and natural waters pose severe environmental and health problems to ecological systems as well as human life [1]. Toxic heavy metals such as lead (Pb), mercury (Hg), cadmium (Cd), nickel (Ni), etc. tend to accumulate and concentrate in the environments leading to severe health problems [2]. Several methods have been widely applied for removal, extraction, separation and pre-concentration of heavy metal ions from wastewaters as well as other environmental samples [3].

Chelating resins are designed for selective adsorption, separation and pre-concentration of metal ions and usually employed in wastewater treatment, in the recovery and removal of metal ions and in accurate analysis of heavy metal ions [4, 5].

Chelating resins are polymers with covalently bound functional groups containing one or more donor atoms which are capable of forming complexes directly with metal ions and can also be used in the separation of metal ions from solutions. Since sulphur containing groups are soft bases, resins with sulphur containing functional group are useful for the removal of soft acids like Cu, Pb, Cd, etc. [6].

Chelating resins containing bis-(2-aminophenyl) disulphide [7], dithiocarbamate sporopollenin derivative [8], mixture of sulphadiazine and trimethylolphenol [9], thiosemicarbazide [10], and chitosan-phenyl thiourea [11] have been used to investigate the adsorption properties and also applied for selective separation of specific metal ions.

The present paper deals with the synthesis and characterization of a novel chelating resin containing diphenyl disulphide derived from poly-(ethyl acrylate-acrylonitrile-divinyl benzene) and highly cross-linked polystyrene. This resin has been studied for its sorption behaviour towards heavy metal ions viz., Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and Pb (II) and in the separation of heavy metal ions from binary and ternary mixtures, industrial wastewater and printed circuit board (PCB) scrap solution.

2. Experimental
2.1 Chemicals

Diphenyl disulphide (DPDS), ethyl acrylate, styrene, acrylonitrile and divinylbenzene used were from Aldrich-Sigma. All the metal salts were procured from Merck and Loba Chemie Company. Double distilled water was used throughout the work.

2.2 Preparation of DPDS resin

DPDS micro beads were prepared by a suspension polymerization process by placing 250 mL distilled water, 8 mL of 2 % gelatine solution,

2.0 g calcium carbonate, 12 g anhydrous sodium sulphate and toluene in a three necked round bottom flask fitted with a condenser, a mechanical stirrer and a thermometer. With stirring 3 mL styrene, 8.5 mL ethyl acrylate, 38 mL acrylonitrile and 0.5 g benzoyl peroxide (initiator) were added. The reaction temperature was maintained at 85^0C. After 6 hours, beads were filtered off using a Buchner funnel, washed successively with hot water, methanol and 1 M HCl and dried under vacuum for 72 hours.

The resin beads were then converted into beads containing hydroxyl group according to literature [12]. The product thus obtained was refluxed with 6 g of diphenyl disulphide containing 6 mL of 18 M H_2SO_4 as a catalyst for 52 hours at 85-90^0C in a round bottom flask with continuous stirring using a magnetic stirrer. The beads were filtered and washed first with hot methanol and then with distilled water and dried in vacuum for 36 hours. The synthesis of the resin beads is represented schematically in Fig. 1.

Fig.1: Schematic synthesis of DPDS-resin
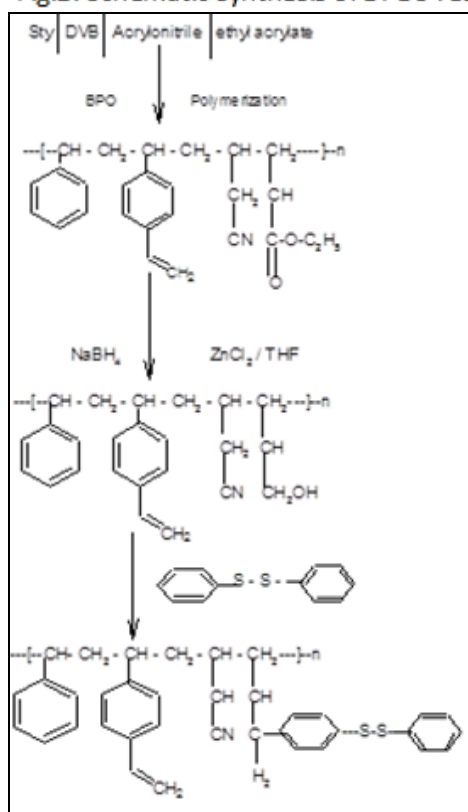
2.3 Uptake measurements by Batch methods
2.3.1 Preparation of solutions

All metal ion solutions used in the experimental studies were prepared in double distilled water. A stock solution of EDTA (0.02 M) was prepared and standardized against a solution of $MgSO_4.7H_2O$ using Erichrome Black T as an indicator. The pH of metal ion solution was adjusted by using a buffer of acetic acid and ammonia (pH 2.5-12).

2.3.2 Sorption Experiments

By batch method, under controlled pH, the sorption equilibrium was attained by shaking 0.5 g of dry resin in 25 mL of aqueous metal ion solution. After 24 hours solution was filtered and leached with 30 mL of 2N HCl. The metal ion concentration of the leached solution was measured by complexometric titrations with standard EDTA solution.

The rate of loading of metal ions on the resin was determined by shaking 0.5 g of dry resin with 25 mL of metal ion solution at optimum pH for different time intervals. The solution was filtered and the sorbed metal ions were completely eluted by 30 mL of 2N HCl. The metal ion concentration was measured by complexometric titrations with standard EDTA solution.

To determine the metal ion uptake in the presence of electrolyte of different concentrations, 0.25 g of dry resin was suspended in an electrolyte (25mL) viz., NaCl, KCl, $NaNO_3$ and Na_2SO_4 of known concentrations viz., 0.01 M, 0.1 M and 0.5 M at optimum pH. After equilibrating for 24 hours, 2 mL of 0.1 M metal ion solution was added and again equilibrating for 24 hours. The metal ion content was determined by complexometric titration against standard EDTA solution. The amount of metal ion taken up by the polymer in the presence of given electrolyte then could be calculated from the difference between the actual titration value and that of the blank.

2.4 Column Separations

A glass column of 25 cm length and 1 cm internal diameter was packed with the slurry of H^+ form of resin (1 g). The column was equilibrated at required pH using 0.2 M acetate buffer.

Separations of binary mixture of Cd (II) and Zn (II) and ternary mixture of Zn (II), Cd (II) and Hg (II) were attempted at optimised conditions.

2.4a Recovery of Heavy Metal Ions (Zn, Cd and Ni) from Industrial Wastewater samples

With the help of ion-exchange resin, metal ions viz., Zn (II), Cd (II) and Ni (II) from industrial wastewater can be easily removed. Prior to use, all the resin was converted in the sodium form, as per the procedure cited in literature [13]. Three different glass columns of length 25 cm and 1 cm internal diameter were packed with 1.0 g of those resin and equilibrated with about 25 mL of 0.2 M acetate buffer. Then 5 mL of the industrial wastewater samples containing each of the ions viz., Zn (II), Cd (II) and Ni (II) were introduced in to individual columns separately. After eluting the metal ion sorbed on the resin with respective

eluting agents, the concentration of each metal ion in eluent were determined by complexometric titrations.

2.4b Recovery of Copper and Nickel from Printed Circuit Board (PCB) scrap

Leach liquor from Printed Circuit Board scrap was prepared according to literature [14]. 10mL of leach solution was passed into a column (25 cm length, 1 cm id) containing 1 g of sodium form of resin. 7M H_2SO_4 and 0.25M tartaric acid as an eluting agent for copper and nickel respectively were passed through the column at a flow rate of 0.5 cm^3/min. The recovery of copper and nickel metal ion in eluent was determined by complexometric titration method.

3. Results and Discussions

The chelating resin was synthesized from 36-44 mesh sized beads of ethyl acrylate-acrylonitrile-divinylbenzene copolymer through the steps shown in Fig.1. The results of elemental analysis showed the presence of 10.1% sulphur as reported in Table 1.

Analysis Calculated (%) Found (%)			
C	H	N	S
79.2 (78.09)	6.42 (6.27)	2.5 (2.41)	11.74 (10.1)

Table1. Elemental Analysis of DPDS-resin

Based on analytical data the empirical formula of the repeating unit was found to be $C_{36}H_{35}NS_2$. The physicochemical parameters of the synthesized resin were evaluated and are presented in Table 2.

Properties	Values
Moisture (%)	1.3047
Solid (%)	98.70
True density (dry resin) g/cm³	0.589
Apparent density (dry resin) g/cm³	0.7096
Void volume (%)	16.99 %
Hydrogen ion capacity (meq/g dry resin)	0.62
Sodium exchange capacity (meq/g dry resin)	1.2

Table 1: Physicochemical parameters of DPDS-resin

The linkages and the functional groups present in the resin were confirmed through FTIR analysis (Fig. 2). The appearances of a band at 2931.39 cm⁻¹, 2868.88 cm⁻¹ and 1406.38 cm⁻¹

showed the presence of (C-H) stretching vibrations, -CH₂- symmetrical stretching vibrations and vinyl group respectively. A sharp band at 1185.69 cm⁻¹, a weak band at 676.18 cm⁻¹ and a band at 491.33 cm⁻¹ indicate the presence of thiocarbonyl group, C-S group and S-S stretching group respectively.

The thermograph of DPDS resin, shown in Fig.3, reveals that the sample undergoes degradation in one step. A maximum weight loss equivalent to 48.605% took place in the temperature range from 325⁰C to 400⁰C with constant heating rate of 10⁰C per minute in nitrogen atmosphere.

The morphology of the synthesized resin was investigated by scanning electron microscopy, where white bar at the bottom represents the scale (Figs. 4 and 5).
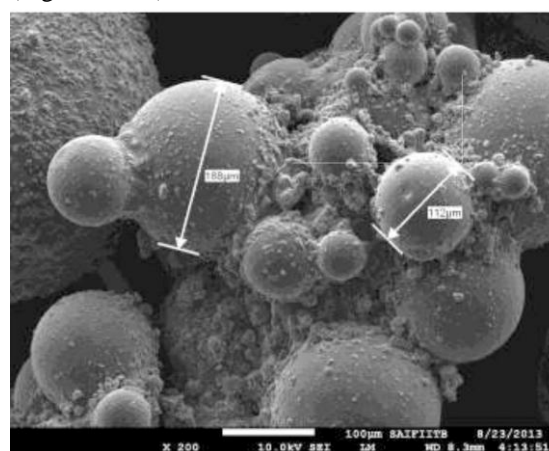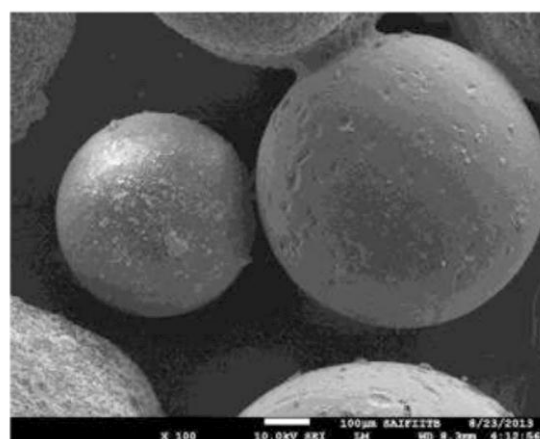

Fig.4: SEM of DPDS-resin

Fig. 5: SEM of DPDS-resin

5.1 Effect of pH on metal ion uptake

The sorption of various metal ions viz., Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and Pb (II) on chelating resin at various pH values was investigated and the results are shown in Fig.6. The metal ion uptake was found to be dependent on pH
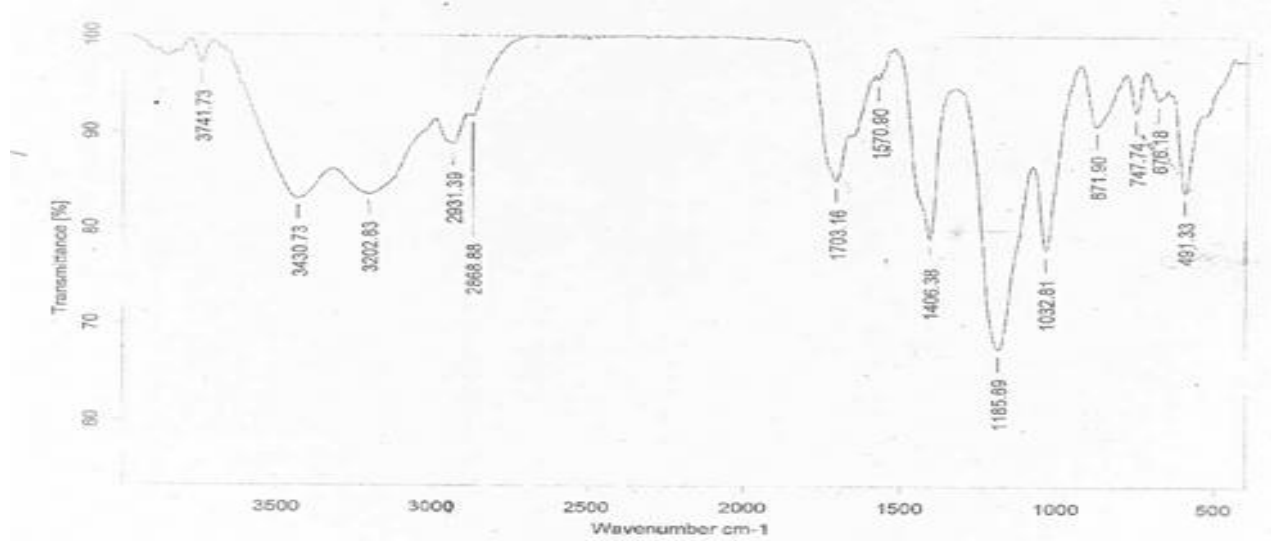
Fig.2: FTIR of DPDS-resin

of the medium. For each metal ion, there is an optimum pH at which maximum intake of metal ion takes place. The maximum ion-exchange capacity for Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and Pb (II) is observed at a pH 7, 10, 11, 6, 8, 3.5 and 5 respectively. The order of distribution ratio of the metal ions is:

Cu (II) > Pb (II) = Co (II) > Zn (II) > Ni (II) > Cd (II) > Hg (II)
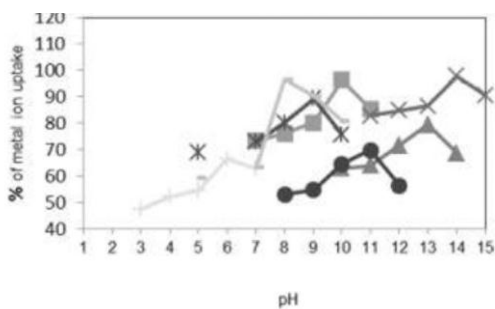(98%)   (96%) (96%) (89%) (79%)   (69%)   (66%)

for maximum adsorption of metal ions as evaluated in Table 3.

Fig.7: Effect of time on metal ion uptake

Fig.6: Effect of pH on metal ion uptake

5.2 Effect of time on metal ion uptake

Fig.7 shows adsorption rates of heavy metal ions by the synthesized resin as a function of time. To determine the rate of loading of seven metal ions viz., Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and Pb (II) on the resin, batch experiments were carried out at optimum pH. The time required
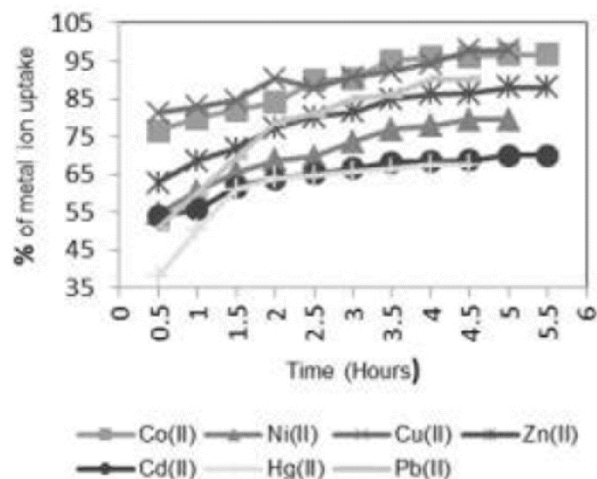
Among seven metal ions taken for study Pb (II) and Hg (II) required shortest time i.e., about 4 hours, whereas, Cu (II) and Ni (II) require 4.5 hours and Co (II), Cd (II) and Zn (II) required longest time i.e. about 5 hours to reach the equilibrium. Thus, the rate of metal ion uptake for the synthesized resin follows the order:

Pb (II) = Hg (II) < Cu (II) = Ni (II) < Co (II) = Cd (II) = Zn (II)
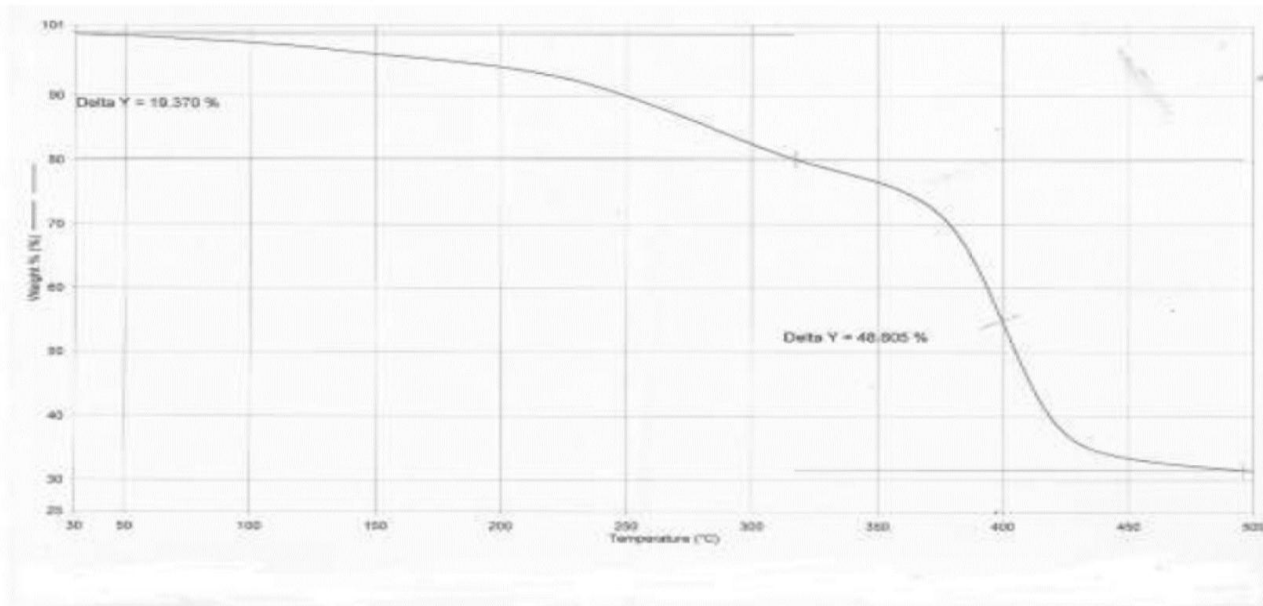
Fig.3: TGA of DPDS-resin

5.3 Study of the Effect of Different Electrolytes on Metal ion Uptake

The data obtained for resin with different electrolytes with various concentrations (Table 4) reveals that the amount of metal ion taken for a given amount of resin sample depends on the nature and concentration of electrolyte present in the solution. In presence of chloride ions, the amount of Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and Pb (II) increases with increasing concentration of electrolyte, while in presence of nitrate and sulphate ions, the amount of the same metal ions decreases with increasing concentration. (Fig.8-11).The order of uptake of metal ions by the resin in presence of electrolyte at different concentration follows the order:

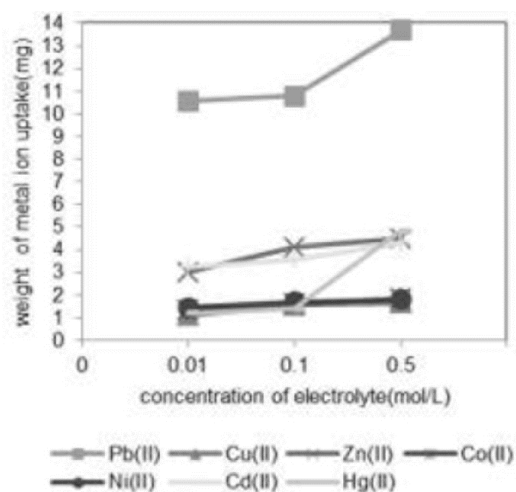Pb (II) > Hg (II) >Cd (II) > Zn (II) > Cu (II) > Ni (II) > Co (II)

Fig.8: Effect of KCl on metal ion uptake

Metal ions	Cu (II)	Co (II)	Pb (II)	Zn (II)	Ni (II)	Cd (II)	Hg (II)
Time(hours)	4.5	5	4	5	4.5	5	4

Table 3: Time required by the for maximum adsorption

4.5 Chromatographic Separations
4.5.1 Separation of Binary Mixture of Zn (II) and Cd (II)

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 column at pH 6 using 0.2M acetate buffer at a flow rate of $0.5 cm^3 min^{-1}$. Separation was achieved with the help of selective elution technique by first passing 150 mL of 0.5

MHCl as an eluent for zinc followed by150 mL of 1 M HNO_3 for elution of cadmium. Recovery of Zn (II) and Cd (II) were found to be 99.05% and 98.68% respectively.

(b) Separation of Hg (II), Cd (II) and Zn (II)

In the separation of ternary mixture of Zn (II), Cd (II) and Hg (II), 10 mL 0f 1:1:1 mixtures of Hg (II), Cd (II) and Zn (II) were passed through the column at pH 3.5 using 0.2M acetate buffer at a flow rate of $0.5 cm^3 min^{-1}$. The mercury was eluted with 150 mL of 5 % thiourea in 1 M $HClO_4$. The zinc (II) was further eluted with 150 mL of 0.5 M HCl and cadmium (II) was eluted with 150 mL of 1 M HNO_3. The recoveries of Zn (II), Cd (II) and Hg (II) were found to be 98.10%, 98.02% and 97.8% respectively.
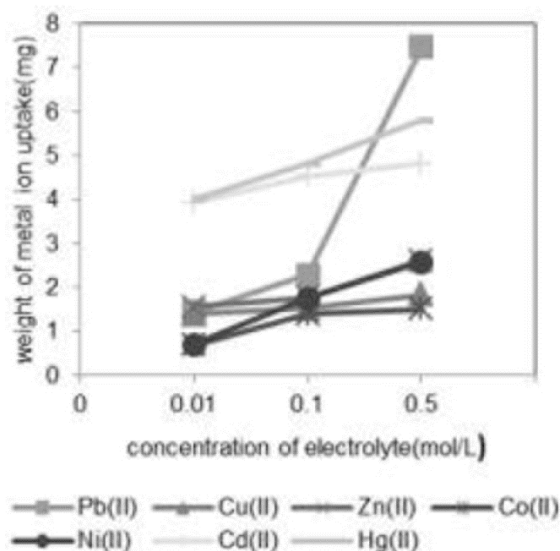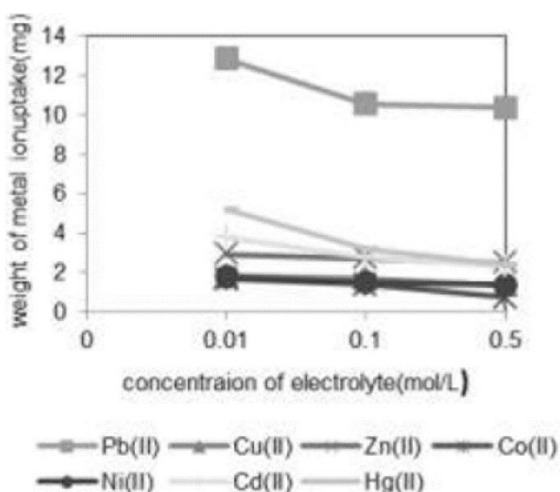
Fig.9: Effect of NaCl on metal ion uptake

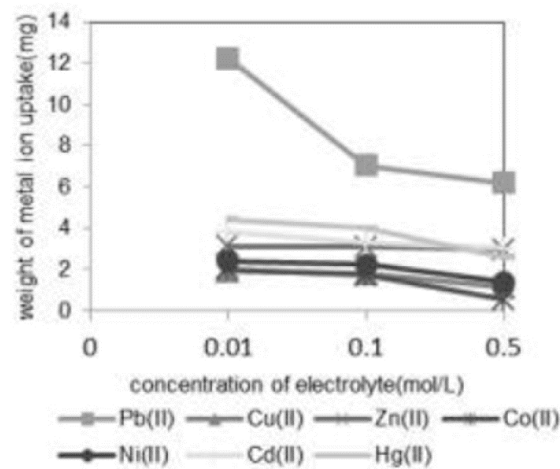Fig.10: Effect of $NaNO_3$ on metal ion uptake

Fig.11: Effect of Na_2SO_4 on metal ion uptake

4.5.2. Recovery of Zn, Cd and Ni from Industrial Wastewater

With the help of column chromatography the recovery of Zn (II), Cd (II) and Ni (II) from industrial wastewater was carried out individually. Zn (II), Cd (II) and Ni (II) were eluted with 0.5M HCl, 1M HNO_3 and 0.25M tartaric acid respectively at a flow rate of 0.5 cm^3/min. Recoveries of zinc, cadmium and nickel were found to be 97.83%, 99.35% and 97.55 % respectively.

4.5.3. Recovery of Copper and Nickel from Printed Circuit Board (PCB) scraps

The resin beads were successfully employed for the recovery of copper (98.21%) and for nickel (96.90%) from a leach solution prepared from PCB scrap.

I.   Conclusions

A novel chelating resin containing diphenyl disulphide synthesized from poly-(ethylacrylate-acrylonitrile-divinylbenzene) beads was characterized by elemental analysis and physicochemical properties. The presence of functional group and linkages required for the resin structure was confirmed by FTIR analysis. TGA revealed the one step degradation of the resin showing good thermal stability for the resin. The order of distribution ratio of the metal ions studied was found to be: Cu (II) > Pb (II) = Co (II) > Zn (II) > Ni (II) > Cd (II) > Hg (II). It has been demonstrated that the chromatographic separation of binary mixture viz., Zn (II) and Cd (II) and ternary mixtures of Zn (II), Cd (II) and Hg (II) can be done successfully as per the procedures developed. Furthermore, Zn (II), Cd (II) and Ni (II) from industrial wastewater samples were recovered using the resin. Finally, Cu (II) and Ni (II) from PCB scrap were also be separated using the resin effectively.

Acknowledgements

Metal ions	Concentration of electrolytes (mol/L)	Weight of metal ion uptake in presence of electrolytes			
		KCl	NaCl	NaNO$_3$	Na$_2$SO$_4$
Pb^{+2}	0.01	10.56	1.45	12.84	12.22
	0.1	10.77	2.28	10.56	7.04
	0.5	13.67	7.46	10.36	6.19
Cu^{+2}	0.01	1.08	1.39	1.84	1.90
	0.1	1.55	1.52	1.73	1.78
	0.5	1.65	1.84	1.38	1.14
Zn^{+2}	0.01	3.0	1.56	2.94	3.13
	0.1	4.09	1.77	2.74	3.07
	0.5	4.49	2.61	2.53	2.94
Co^{+2}	0.01	1.32	0.69	1.69	2.0
	0.1	1.59	1.39	1.41	1.70
	0.5	1.83	1.51	0.76	0.53
Ni^{+2}	0.01	1.46	0.70	1.81	2.40
	0.1	1.70	1.76	1.51	2.23
	0.5	1.81	2.58	1.40	1.40
Cd^{+2}	0.01	3.23	3.93	3.82	3.81
	0.1	3.59	4.53	2.81	3.28
	0.5	4.29	4.82	2.35	3.02
Hg^{+2}	0.01	1.20	4.01	5.22	4.41
	0.1	1.40	4.81	3.21	4.01
	0.5	4.81	5.81	2.41	2.61

Table 3: Evaluation of the effect of different electrolytes on the uptake of several metal ions of HTG resin

M^{+2}(NO$_3$)$_2$: 0.1M; volume: 2 mL; volume of electrolyte: 25mL; weight of resin: 25 mg ; time 24 h; temperature:25-30^{0}C

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