SYNTHESIS OF ENVIRONMENTAL FRIENDLY CHELATING ION EXCHANGE RESIN SPECIFIC FOR ZINC

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ABSTRACT

An environmental friendly hydrophilic chelating resin based on naturally occurring polysaccharide, chitosan has been synthesized, characterized and the molar distribution coefficient values of different metal ions viz., Co(II), Ni(II) Cu(II), Zn(II), Ca(II), U(VI) and W(VI) on this resin were determined as a function of pH in the range 3-10. The quantitative separation of zinc-cadmium mixture was achieved on the resin at pH 9.

Key words: Chitosan, Chelating resin, Molar distribution coefficient.

INTRODUCTION

Recent global attention has shown serious concern towards discernible environmental disruptions, which have threatened the sustenance of human race on the earth. The removal of heavy metals from aqueous stream represents a significant industrial waste problem. Heavy metals such as Cu, Zn, Cd, Fe and Hg deteriorate not only the main water streams but also contaminate the downstream water bodies.

Chelating ion exchange resins having specific chelating groups attached to a polymer backbone have recently found great applications in separation and concentration of metal ions as floataids, flocculants, depressant, in the extraction and concentration of metals from sea water and in clarification of industrial waste water[1-3]. Most of the chelating resins in use are very expensive. Therefore, attention has been focused on the synthesis of various chelating resins, which are able to remove unwanted metal ions at low cost.

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Among various bisorbents, chitin is the second most abundant natural biopolymer after cellulose[4]. Chitosan is produced by alkaline N-deacetylation of chitin, which is widely found in the exoskeleton of shellfish and crustaceans. Chitosan possess the ability to form complexes with transition metal ions due to the presence of the amino group of the 2-amino-2-deoxy-D-glucose unit[5-7]. However, it is not very selective. Further, chemical modification of chitosan has been made to improve its selectivity and capabilities for metal ions[8]. Therefore, in continuation of our work on environmental friendly chelating resins[9-11], we report here the synthesis, characterization and adsorption ability of dithiocarbamate derivative of chitosan (DTC-CH).

EXPERIMENTAL

Reagents

Chitosan powder of 100 mesh size was obtained from Central Institute of Fisheries Technology, Cochin (India). Epichlorohydrin and carbon disulphide were obtained from Merck. All the metal salts and solvents were AR grade materials and used without further purification.

Physical measurements

Infrared spectra were recorded on Shimadzu IR-400 spectrophotometer using KBr pellets. A Perkin Elmer-2380 atomic absorption spectrophotometer was used for the quantitative determination of metal ions where as uranium was estimated on Shimadzu model UV-160A U.V. spectrophotometer. Nitrogen and sulphur analysis was done using Vario EL III CHNS analyzer.

Synthetic procedures

Synthesis of crosslinked chitosan

Chitosan (1.79 g) powder was soaked in dioxane for one hour in a conical flask, 1.8 mL of epichlorohydrin and 0.92 g of sodium hydroxide was added into it with continuous stirring. The flask was then sealed and kept in an oven for 6 h at $50^{o}C$. The product obtained was filtered and washed with dioxane, 80% aqueous methanol and finally with solvent ether. It was dried in an oven at $50^{o}C$ for 2 h.

Synthesis of dithiocarbamate derivative of chitosan (DTC-CH)

Crosslinked chitosan (2.35 g) was taken in a round bottom flask and 20 mL of

40% NaOH (w/v) was added into it drop wise. The reaction mixture was stirred magnetically at 45°C for 2 h. Carbon disulphide (3 mL) was then added into the reaction mixture and the stirring was further continued for 6-7 h at 45°C. The reaction product was filtered and treated successively with 0.1 N HCl, 0.1 N NaOH and 0.1 N HCl. Finally, it was washed with pure methanol and dried in vacuum (Fig. 1).
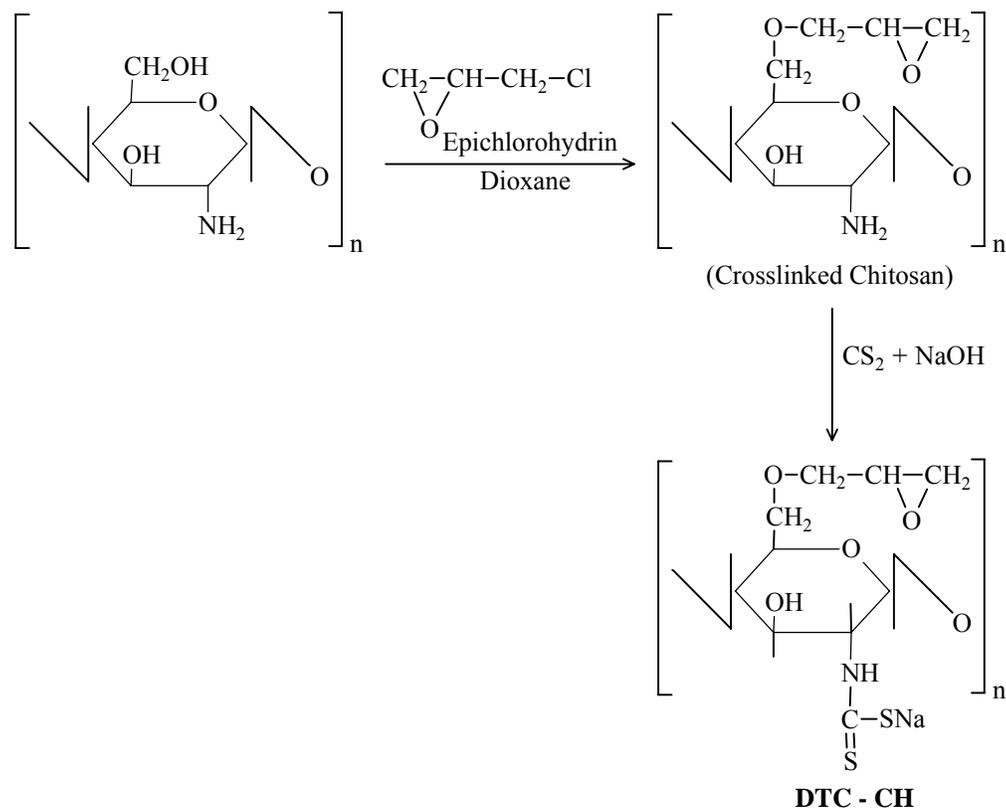

Fig. 1: Scheme for the synthesis of dithiocarbamate derivative of chitosan (DTC-CH)

Analysis for metal uptake

A batch equilibration technique was employed for the investigation of metal uptake by the resin. The method involved equilibrating H^+ form of resin with 1 mL of 1000 ppm metal ion solution corresponding to 1 mg metal ion and a known volume of sodium acetate – acetic acid buffer (pH range 4-7) or NH_4OH-NH_4Cl buffer (pH range 8-10). Two phases were separated after equilibration and an aliquot of filtrate was analyzed for metal concerned by atomic absorption spectrophotometer. The calibration curves for different metals were

plotted using standard metal solutions and the unknown concentration of metal ions was determined from these curves. The distribution coefficient values (K_d) were then calculated using following formula:

$$K_d = \frac{\text{Amount of metal ions in resin/g resin}}{\text{Amount of metal ion in solutiom/mL of solution}}$$

Column separations

A 10 cm long glass column of uniform diameter was used for the column separation of metal ions. It was packed with slurry of DTC-CH in DMF to a column height of 2-3 cm. The column was equilibrated with NH_4OH—NH_4Cl buffer of pH 9. A mixture of 20 mL aliquot containing 10 mL of Zn(II) and Cd(II) metal ions each were loaded on the column at a flow rate of 2 mL/min. The column was washed with the same buffer solution and the sorbed metal ions were eluted with 0.1 N HC1. 5 mL of fractions were collected and were analyzed for metals concerned by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

In the infrared spectra of crosslinked chitosan, a broad peak at 3680-3000 cm^{-1} ascribed to ν (N-H) and ν (0-H) vibrations and a band at 1600 cm^{-1} was assigned to (N-H) bending vibrations. In the infrared spectra of dithiocarbamate derivative of chitosan, a broad band at 3625-3000 cm^{-1} was assigned to ν (O-H) + ν (N-H) vibrations. A strong peak at 990 cm^{-1} was attributed to ν (C-S) vibrations. The resin characteristics, viz., moisture content, bulk density, nitrogen content, sulphur content and degree of crosslinking/ substitution are given in Table 1 and pH titrations are represented in Fig. 2, which confirmed the synthesis of resin.

Table 1: Resin characteristics

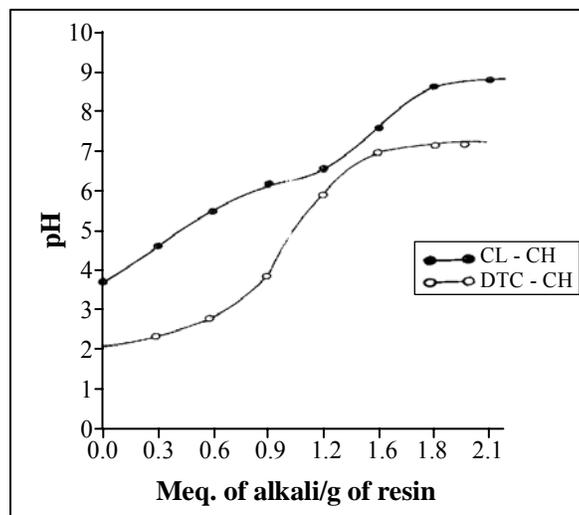| Resin	Moisture content (%)	Bulk density (g/cm³)	Sulphur content (%)	Nitrogen content (%)	Degree of crosslinking/substitution (%)
CL-CH*	3	0.363	-	2.83	47
DTC-CH	1.3	0.555	20.45	2.38	88
*Crosslinked chitosan					

**Fig. 2: pH titration curve for crosslinked chitosan and DTC-CH**

Uptake of metal ions by the resin

The chitosan was crosslinked with epichlorohydrin to stabilize it at a lower pH level. The molar distribution coefficient values for cobalt (II), nickel (II), copper (II), cadmium (II), calcium (II), uranium (VI) and tungsten (VI) metal ions with DTC-CH resin are summarized in Table 2.

Table 2: K_d values of different metal ions on DTC-CH resin

pH	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	U(VI)	W(VI)	Ca(II)
3	425	390	1147	1020	1782	533	706	44
4	519	470	2236	2840	2869	1947	1784	89
5	1393	1950	**5520**	7236	**6969**	3205	**3114**	**124**
6	2181	**2151**	3009	**11022**	5320	**4802**	1828	70
7	**2663**	1697	1297	8492	3776	3086	1321	40
8	1884	636	997	2011	1576	1170	1005	-
9	1361	410	650	726	576	470	570	-
10	610	250	550	615	480	310	380	-

The adsorption of metal ions on the resin depends on the pH values. The experimental results depict that the molar distribution coefficient values first increase, attains a maximum value and further increase in the pH leads to a decrease in K_d values. The selectivity sequence of metal ions on DTC-CH resin at the pH of their maximum adsorption is as follows and the values are depicted in Fig. 3.

$$Zn(II) > Cd(II) > Cu(II) > U(VI) > W(VI) > Co(II) > Ni(II) > Ca(II)$$
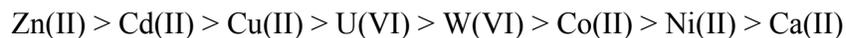
This order also represents the order of decreasing adsorption of metal ions on DTC-CH resin.
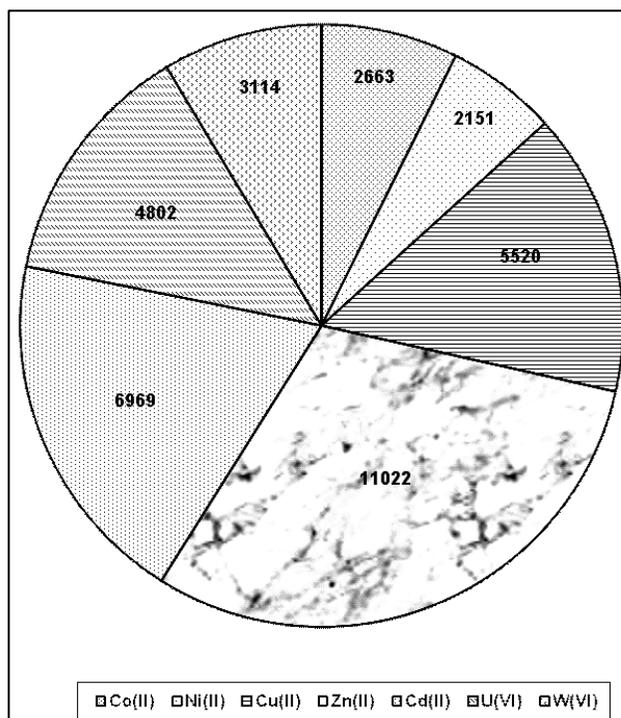

Fig. 3: K_d values of different metal ions at pH of their maximum adsorption

The resin exhibits maximum adsorption for cobalt at pH 7, nickel, zinc and uranium at pH 6, copper, cadmium, tungsten and calcium at pH 5. The most effective pH range for the resin was 5-7 as revealed from the results and there was a decline in adsorption capacity at higher pH values.

The pH of chitosan prepared from lobster shells has been reported to be between 6.2 and 6.8. The experimentally observed decrease in the metal ion adsorption at higher pH was

explained by Schmuhl et al.[12]; as the rapid changes in protonated and unprotonated forms of chitosan derivative.

The results suggest that the adsorption capability of DTC-chitosan is found to be satisfactory for zinc, cadmium, copper and uranium metal ions. The resin exhibits specificity for Zn(II) ions and a selective separation of copper(II) ($K_d = 3009$), Ni(II) ($K_d = 2151$), Cd(II) ($K_d = 5320$) and Co(II) ($K_d = 2181$) can be affected from Zn(II) ($K_d = 11022$) at pH 6.

The synthesised resin shows little adsorption for alkaline earth metal, i.e. calcium. Therefore, the resin can be utilised for the separation of transition and highly charged metal ions from alkaline earth metals and the disadvantages of the most widely used resin, Chelex-100 (its high cost and similar affinity for transition as well as alkaline earth metals) can be overcome to a great extent by utilizing the synthesised resin. Any interference in the form of hydroxide ions is not seen at higher pH values.

Separation of metal ions by the resin

A study of distribution coefficient values of various metal ions suggests that there are separation possibilities for a large number of metal ions on the dithiocarbamate resin. The difference in the K_d values between the Zn(II), Cu(II) and Cd(II) metal ions are large enough to permit good separation on columns (Fig. 4). Zinc-cadmium separations were achieved at pH 9 using column mode of operation. Cadmium ions being less strongly held by the resin moved down the column more rapidly and were collected before zinc (Fig. 5).
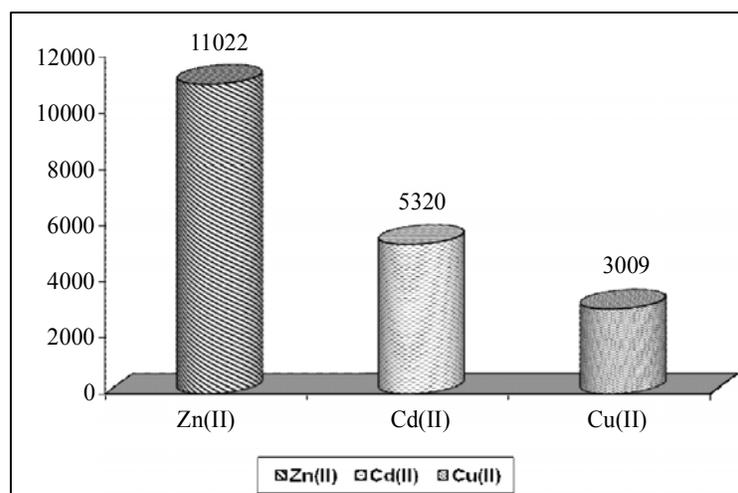

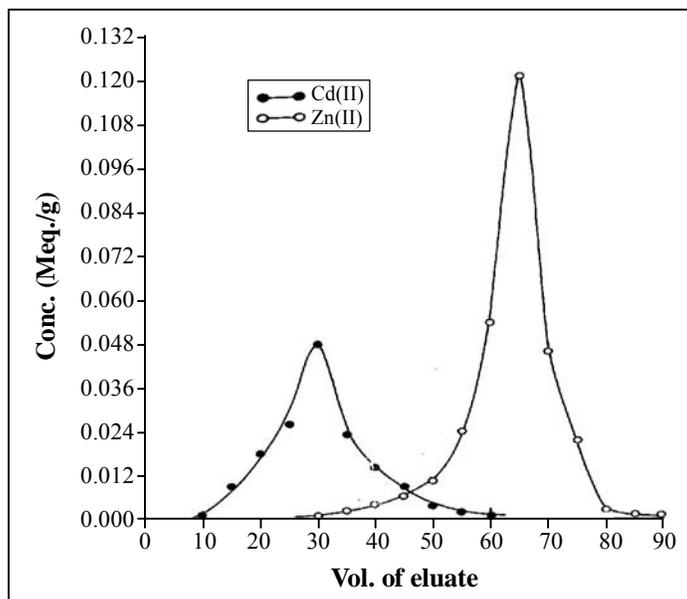**Fig. 4: Adsorption behavior of Zn(II), Cd(II) and Cu(II) at pH 6**

Fig. 5: Column separation of Zn (II) and Cd (II)

CONCLUSION

The chelating polymer based on chitosan is hydrophilic, more compatible with metal ion solutions, cheap, easily available and environment friendly (biodegradable).

(i)   It is specific for zinc. Zinc is most of the time associated with cadmium and it can be used to separate cadmium and zinc.

(ii) The optimum pH for the resin for different metal ions in between 5-7.

(iii) The advantage of dithiocarbamate group is its ability to quantitatively concentrate a large number of trace elements, while not complexing alkali and alkaline earth metal ions.

(iv) The synthesized resin thus can be utilized for the clarification of waste water from metals like zinc, cadmium, copper and uranium.

ACKNOWLEDGEMENT

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