

## Extraction of Lead by Dithiocarbamate Derivative of Chitosan

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### ABSTRACT

Lead extraction was done by means of ion selective resin synthesized from Dithiocarbamate derivative of chitosan. The separation is carried out by column chromatography. IR spectra, nitrogen content [done by Kjeldhal method] and pH titration [by Batch method] were made for resin characterization. Resin characteristic viz. moisture content, bulk volume, specific bulk volume, ion exchange capacity were also determined by standard methods. Metal uptake analysis was done by using batch method using Atomic Absorption Spectrophotometer. The distribution coefficient values at different pH were determined from batch method. Pb[II] shows maximum distribution coefficient at pH 8.0 and Dg value at this pH is 12941.

**Keywords:** chitosan, resin, lead, separation, Dg values.

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### INTRODUCTION

It is widely distributed in lithosphere and is also encountered in atmosphere and hydrosphere. Its most common form in the environment is  $Pb^{+2}$ . Concentration of lead in natural water increases mainly through anthropogenic activities. In addition, a some what more subtle source however is pottery utensils. One theory for the decline of roman empire proposes that the function of much of the population was impaired by chronic lead poisoning originated from wine stored in lead glazed vessels.

In aquatic systems, lead has been found to be quite toxic to many organisms even at small concentrations. Toxicity of lead is however, extremely dependent on the hardness which antagonizes its toxic effects. In animals and men lead accumulates mainly in bone from where it can be excreted very slowly. A concentration of 0.8 ppm of lead in the blood is considered to be threshold concentration for lead poisoning. The toxicity of lead is more acute in infants and children than in the adult. The recommended maximum lead concentration in drinking water is 0.05 mg/l.

Resins are useful in metal recovery. Ion exchange chelating [3] resin are often used in removal, preconcentration and determination of various metal ions in aqueous solution. Dithiocarbamate derivate of Chitosan [1] was used for removal of lead. The methods for detection of lead in water involve test [6] with various reagents like Thiourea, Potassium chromate, Dithiozone, Benzidine, Sodium rhodizonate. Laboratory studies on these reagents were conducted in view of their adaptability for field [4] determination, stability, ease and sensitivity of test at different dilutions specially near permissible limit. But it has been found that sodium rhodizonate is most suitable reagent [5] because other reagents used are not suitable due to their complexity, instability, interferences by other cations. So sodium rhodizonate [0.02g] along with citric acid [0.002g] was used as a modified test.

### MATERIALS AND METHODS

#### Synthesis of Crosslinked chitosan

1.79 g (0.01 mol) of chitosan [2] was taken in a conical flask and soaked in dioxane, for one hour. 1.8 ml (0.023 mol) of epichlorohydrin and 0.92 g (0.023 mol) of sodium hydroxide was added into the conical flask with continous shaking. The conical flask was then sealed and kept in an oven for 6 hours at 50°C.

The product formed was filtered and The washing was continued till the filterate was free from chloride ions and it was no more alkaline. Finally it was washed with solvent ether. The washed product was dried in an oven at 50°C for 2 hours. The crosslinked chitosan was thus formed.

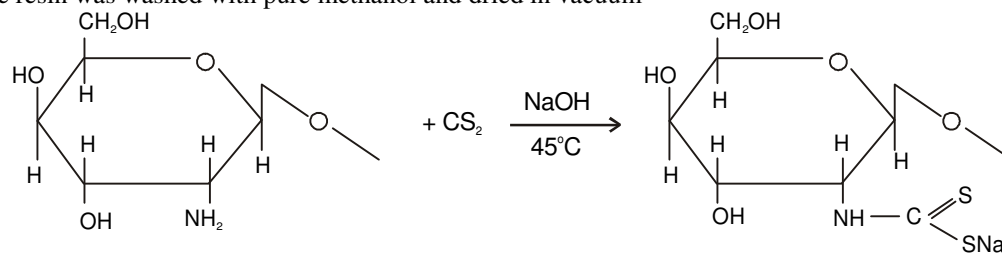
It was further used for derivatization.

2.35 g (0.01 mol) of crosslinked chitosan was taken in a round bottom flask and 20 ml of 40% NaOH (W/v) was added to it dropwise. The reaction mixture was stirred magnetically at 45°C for 2 hours. 3 ml (0.049 mol) of carbondisulphide was then added to the reaction mixture and the stirring was further continued for 6 – 7 hours at 45°C.

The product formed was filtered on buchner funnel and washed with 80% methanol containing nitric acid (to remove the inorganic impurities and excess alkali). It was then successively treated with 0.1N HCl, 0.1N NaOH and

was finally suspended in 200 ml portion of 0.1N HCl. Supernatant liquid was decanted and the resin was washed 5 – 6 times to remove the suspended impurities. The washing was continued till the supernatant liquid was clear and free from acid.

Finally, the resin was washed with pure methanol and dried in vacuum



### Synthesis of dithiocarbamate derivative chitosan

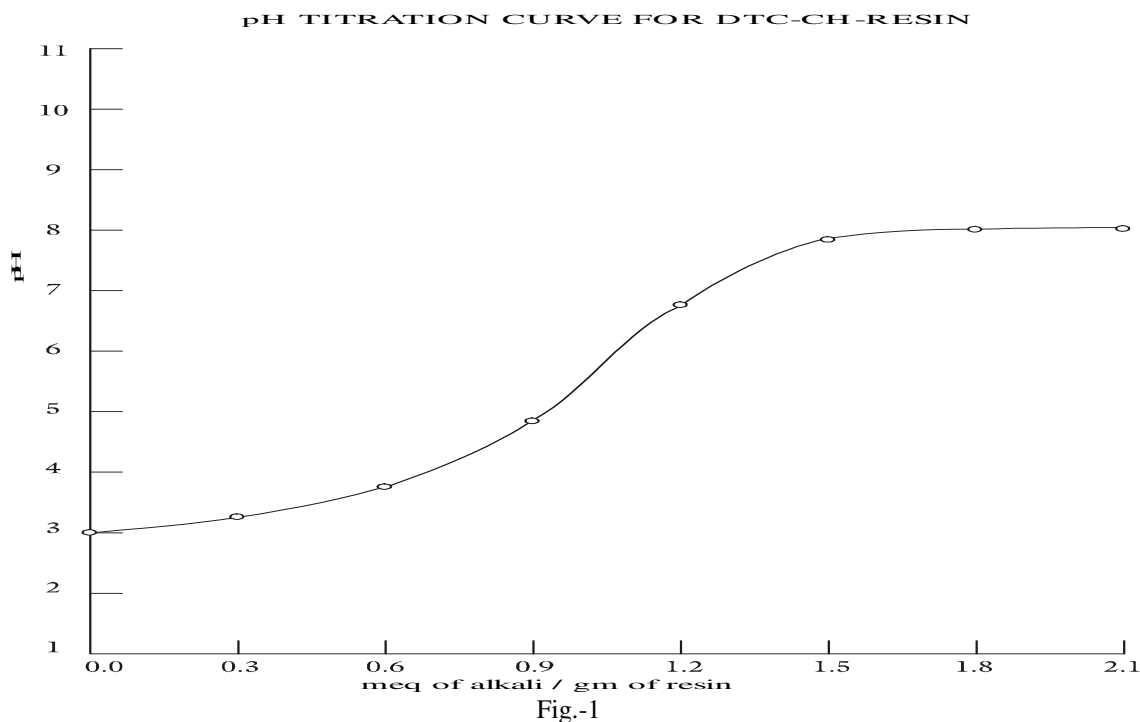
#### Characterization of Dithiocarbamate derivative of Chitosan

The resin characterization of dithiocarbamate derivative of chitosan was done by Kjeldahl method which was used nitrogen estimation. Sulphur estimation was done by Messenger's method. Back titration method was used for determination of ion exchange capacity and characteristics of resin was determined by bulk density, moisture content specific bulk volume, degree of crosslinking and the result are shown in Table -1.

Table -1

Nitrogen content	Sulphur content	Bulk density g/cm <sup>3</sup>	Specific bulk volume cm <sup>3</sup> /g	Degree of crosslinking	% Degree of substitution	Moisture content
2.3%	20.45%	0.555	1.8	47	88	1.3%

The ion exchange capacity using Back titration for Dithiocarbamate derivative of chitosan was found to be 1.540meq/g of H form of dry resin. pH titration curve using Batch method was done and the result is shown in Fig.-1.



### Pb UPTAKE ANALYSIS AND DETERMINATION OF ITS Dg VALUE

A Batch equilibrium method was used for the metal uptake investigation by the resin. In this method appropriate amounts of 0.2M CH<sub>3</sub>COOH and 0.2M CH<sub>3</sub>COONa were added to glass stoppered flasks to get the buffers of 5 – 7 pH and appropriate amounts of 0.2M NH<sub>4</sub>OH and 0.2M NH<sub>4</sub>Cl were also added to glass stoppered flasks to get the buffers of 8 to 9 pH. 0.0552 g of dry resin and 1 ml of 1000 ppm of lead nitrate solution corresponding to 1 mg of Pb(II) was then added to each flask. The total volume in each case was kept at 40 ml. The contents were equilibrated by magnetic stirring for 1 hour and then filtered. The filterates were analysed for the remaining Pb(II) concentration by A.A.S. The results are given in Table-2.

Table-2: Dg values for Pb(II) on DTC – CH resin

pH	Concentration of Pb(II) in filtrate (ppm)	Amount of Pb(II) in solution (mg)	Amount of Pb(II) in resin (mg)	Dg ml g <sup>-1</sup>
5	6.5	0.26	0.74	254
6	6.9	0.276	0.724	276
7	5.3	0.212	0.788	2693
8	1.326	0.05304	0.94696	12941
9	1.815	0.0726	0.9274	9257

Dg values were calculated using the standard formula, as-

$$Dg = \frac{\text{Amount of metal ion in resin phase / gm of dry resin}}{\text{Amount of metal ion in solution / ml of solution}}$$

### Efficiency of the resin

For determining the efficiency of the resin, column chromatography was used. A 20cm height and 1.5cm diameter column was used in which about 2 to 3cm height dithiocarbamate derivative was added. For assessing the efficiency of the resin varying increasing amounts of the metal solution i.e lead nitrate solution of 5 to 50 ppm solution was added at the pH of 8.0 which is its maximum adsorption. In this resin the metal ion is not simply exchanged instead it forms a chelate or ion pair, the formation of which is pH dependent. Then the filtrate were analysed for remaining lead by atomic adsorption spectrophotometer. The resin was then eluted by using pH solution of 5. The resin is then regenerated and can be used again. The result of resin efficiency is given in Table-3.

Table-3

Concentration of Pb(II) before adsorption (ppm)	Concentration of Pb(II) in filtrate after adsorption (ppm)	Amount of Pb(II) adsorbed (ppm)	% Efficiency
5	0.1	4.8	96
10	0.4	9.6	96
20	0.7	19.3	96
30	1.1	28.9	96.3
40	1.5	38.5	96.2
50	2.1	47.9	95.8

In the IR spectra of dithiocarbamate - chitosan derivative, a band at 3640 – 3000 cm<sup>-1</sup> was assigned to  $\bar{\nu}$  (O–H) +  $\bar{\nu}$  (N–H) stretching vibrations, and a very strong peak at 1140 cm<sup>-1</sup> was assigned to  $\bar{\nu}$  (C–S) IR spectra of newly synthesised chelating derivatives were recorded using Shimadzu IR – 400 spectrophotometer. Spectrophotographic grade KBr was used for preparation of pellets.

In the IR spectra of crosslinked chitosan, primary NH<sub>2</sub> group gives two peaks at 3500 and 3400 cm<sup>-1</sup> while O – H group gives a peak at 3600 cm<sup>-1</sup>. In our case the three peaks merged together to give a broad peak at 3680 – 3000 cm<sup>-1</sup> assigned to  $\bar{\nu}$  (N – H) and  $\bar{\nu}$  (O – H) vibrations, and a band at 1600 cm<sup>-1</sup> is assigned to  $\bar{\nu}$  (N – H) bending = S). This peak confirmed the synthesis of dithiocarbamate derivative.

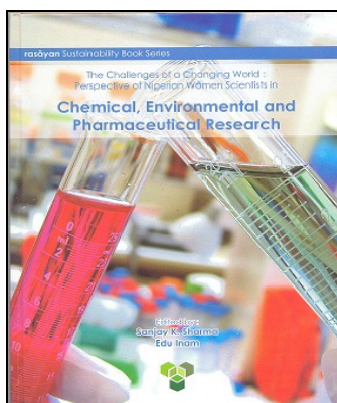
The theoretical metal exchange capacity in meq/g of DTC-CH resin is 0.1meq/g. Pb(II) shows maximum distribution co-efficient at pH 8.0 and Dg value at this pH is 12941. At pH 8 efficiency of the resin for Pb(II) was determined varying the concentration of the metal at the pH of its maximum adsorption. It has been experimentally determined that nearly 96% efficiencies were recorded for the metal concentration in the range of 5 ppm to 50 ppm.

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