ALUMINIUM EXTRACTION BY MEANS OF DIHYDROXIMATE OF IMINODIACETIC ACID DERIVATIVE OF CHITOSAN

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ABSTRACT

Aluminium extraction was studied by means of ion selective chelating ion exchange resin synthesized form cross linked chitosan functionalized with iminodiaceticacid dihydroximate. The separation is carried out by column chromatography. IR spectra, nitrogen content (calculated by Kjeldahl method) and pH titration (using batch method) were made for resin characterization. Resin characteristics such as moisture content, bulk density, specific bulk volume and ion exchange capacity were also determined by standard methods. Metal uptake analysis was done by batch method using atomic absorption spectrophotometer. The distribution coefficient values at different pH levels were determined from batch method. Estimation of Al (III) was done by U.V. Spectrophotometer at 535nm. Aluminium showed maximum Dg value at pH 2.0.

INTRODUCTION

The presence of inorganic contaminants, especially heavy metals in environment, continues to be one of the most pervasive environmental issue of this time. Elevated levels of heavy metals in water can be attributed to both natural and anthropogenic sources. Several disaster of metal poisoning episodes have been recorded from time to time, which have caused great ecological damage and led to the large number of human casualties. Therefore, present situation strongly calls for more newer methods for the removal of the toxic metals. There is necessity to develop quick and reliable methods for analysis of metal pollutants particularly in remote areas where accurate laboratory facilities are not available (AWWA 1985).

Aluminium as the third most abundant element of the earth and its wide distribution accounts for the presence of it in nearly all natural waters as soluble salt, a colloid or as insoluble compound. Its compounds are often used for removal of fluoride from groundwater, therefore, it is often present in alum treated water (Sax 1974, Chung 1990, Nieboer 1995). If its concentration exceeds the permissible limit it may be a cause of alzeimer disease which is characterized by memory loss, formation of neuritic plaque, etc. The permissible limit of aluminium in drinking water is 0.05 mg/L as laid down by WHO/ICMR (Packham 1988, APHA, AWWA, WEF 1992).

Aluminium was neither regarded as essential nor as a toxicant to human body. It is normally absent in drinking water, food, and vegetables but due to change in lifestyle in modern civilization, aluminium has started entering human body (Desai & Ganguly 1981). The toxic limit of aluminium in drinking water has unanimously been accepted as 200 μg/L (0.2 ppm) by WHO, UNICEF, European Commission and Government of India. The chemistry of aluminium in water is complex and influenced by pH, presence of fluoride, organic matter and other ligands. Dissociation of aluminium in water gives $Al(OH)_3$ and other hydroxide ions (Vallon 1977, Carson et al. 1987, Nieboer 1995).

At pH greater than 3, $Al(OH)_3$ gives $Al(OH)_4^-$, the aluminate ion. At extremely low pH it exists mainly as Al^{3+}, the major species are $Al(OH)^{2+}$, $Al(OH)^+$, and $Al(OH)_3$. Aluminium may form relatively stable complexes with fluorides, fulvic acids and other agents in addition to mono, di and

polymeric aluminium hydrates in surface waters which greatly affect the environmental toxicity of aluminium (Carson et al. 1987, Nieboer 1995). Common diseases caused by aluminium are:

1. Alzeimer's disease characterized by intellectual deterioration, memory loss
2. Neurofibrillary changes and formation of neurilic plaques
3. As neurotoxic element
4. Dementia and senility

Ion-exchange chelating resins are very often used in removal, preconcentration and determination of various metal ions in aqueous solutions. Resins are particularly useful in metal recovery. Determination and aluminium was successfully carried out using IDAAH-CH resin. For detection of aluminium in water, tests with various reagents like alizarin red-s, 8-hydroxiquinoline, aluminon, xylenol orange, eriochrome cyanine R, etc. were conducted at different dilution to assess the sensitivity of these tests near the permissible limit of aluminium in water. Except eriochrome cyanine R none of the reagents was found suitable for field application (because of their complexity and other limitation), but even eriochrome cyanine R cannot be used singly due to limitation like use of several ingredients and unstable colour. Therefore, modified test (eriochrome cyanine R along with 0.001g ascorbic acid) was preferred.

MATERIALS AND METHODS

Synthesis of Iminodiacetic Acid Dihydroximate Derivative of Chitosan (Fig. 1)

Synthesis of cross linked chitosan: 1.79 g (0.01 mole) of chitosan was taken in a conical flask and soaked in dioxane for one hour and 1.8 mL (0.023 mole) of epichlorohydrine and 0.92 g (0.023 mole) of sodium hydroxide were added into the conical flask with continuous shaking. The conical flask was then sealed and kept in an oven for 6 hours at 50°C.

The product formed was filtered and washed with dioxane and 80% aqueous methanol containing nitric acid to remove the inorganic impurities and excess alkali in the content. The washing was continued till the filtrate was free from chloride ions and 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 cross linked chitosan was, thus, formed. It was further used for derivatization.

Preparation of ester of iminodiacetic acid derivatives of chitosan: 29.5 g (0.1 mole) of iminodiacetic acid derivative of chitosan was taken in a 100 mL round bottom flask. Excess methanol was added to the acid was cooled to -5°C to -10°C. 1.6 mL thionyl chloride was then added and the temperature was raised to 40°C. The reaction mixture was kept at this temperature for 2 hours on rotavapour and dimethyl ester of iminodiacetic acid was, thus, formed.
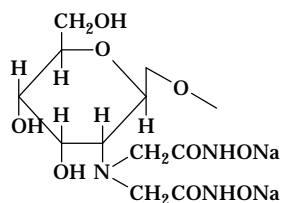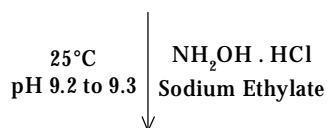
Preparation of dihydroximate of iminodiacetic acid derivative of chitosan (Fig. 1): 16.15 g (0.05 moles) of dimethyl ester of iminodiacetic acid derivative of chitosan and 3.45 g (0.05 moles) of methanolic solution of hydroxyl amine hydrochloride were taken in a round bottom flask and the reaction mixture was stirred on a magnetic stirrer at 25°C for five hours. The pH of the reaction mixture was then adjusted to 9.2-9.3 by sodium ethylate and sodium bicarbonate solutions. The dihydroximate of iminodiacetic acid-chitosan derivative was formed which was filtered on Buchner funnel and washed with 80% methanolic solution. The above resin was then successively treated with 0.1N HCl, 0.1N NaOH and was finally suspended in 200 mL portion of 0.1N HCl. The supernatant liquid was decanted and 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

Synthesis of Iminodiacetic acid derivative of chitosan
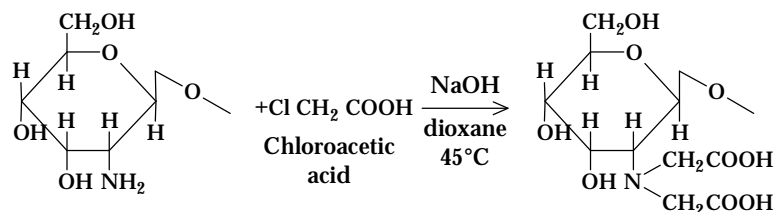
Iminodiacetic Acid - Chitosan
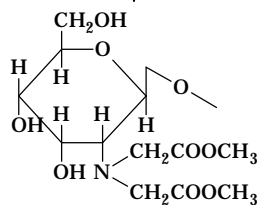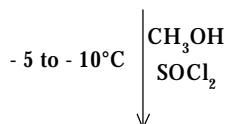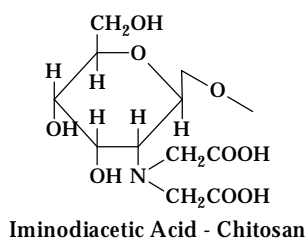
Ester of Iminodiacetic Acid - Chitosan

Synthesis of Iminodiacetic acid dihydroximate - Chitosan

Fig. 1: Synthesis of iminodiacetic acid derivative of chitosan and iminodiacetic acid dihydrximate.

washed with absolute alcohol and dried in vacuum.

Characterization of iminodiacetic acid dihydroximate-chitosan resin: For characterization of newly synthesized resin Kjeldahl method was used for nitrogen estimation, back titration method was used for determination of ion exchange capacity, and other characteristics like bulk density, moisture content, etc. were determined by standard methods, and data are summarized in Table 1.

The ion exchange capacity using back titration for iminodiacetic acid dihydroximate derivative of chitosan was found to be 2.819 meq/g of H^+ form of dry resin. pH titration curve using batch method is shown in the Fig. 2.

Metal uptake analysis and determination of Dg value for aluminium: A Batch equilibrium method was employed for the metal uptake investigation by the resin. In glass stopper conical flask, 0.0552g of dry resin and 1 mL of 1000 ppm of $Al_2(SO_4)_3.16H_2O$ solution containing 1 mg of Al(III) were taken. Then appropriate amount of 0.2 M CH_3COOH and 0.2 M CH_3COONa were added to glass stopper flasks to get the buffer solutions in the pH range 2-4. The total volume in each case was kept 40 mL. The contents were stirred magnetically for 1 hour and then filtered. The filtrate were analysed for the remaining Al(III) concentration by U.V. spectrophotometer. Al(III) estimation was done by eriochrome cyanine R method using U.V. spectrophotometer at 535 nm. The Dg values were calculated using the standard formula. Data are summarized in Table 2.

Meq of alkali/gm of resin
pH Titration Curve for IDAAH-CH-RESIN

Fig. 2: pH titratin curve for IDAAH-Ch resin.

$$Dg\ value = \frac{Amount\ of\ metal\ in\ resin\ per\ of\ dry\ resin}{Amount\ of\ metal\ ion\ in\ solution\ per\ mL\ of\ solution}$$

RESULTS AND DISCUSSION

IR spectra of newly synthesized chelating ion-exchange resin were recorded using Schimadzu IR-400 spectrophotometer, using standard methods. The IR spectra of cross linked chitosan derivative revealed 2 peaks at 3500 cm⁻¹ and 3400 cm⁻¹ corresponding to primary -NH_2 group. A peak at 3600 cm⁻¹ corresponding to OH group was also observed. A band at 1600 cm⁻¹ is assigned to (N-H) bending.

In the IR spectra of iminodiacetic acid dihydroximate, a band at 3620-3000 cm⁻¹ is assigned to (O-H) and (N-H) stretching vibrations, a peak at 1640 cm⁻¹ is seen due to C-O stretching and peak at 1580 cm⁻¹ disappears and the C-O stretch of ester at 1725 cm⁻¹ also disappears.

The theoretical metal exchange capacity in meq/g of IDAAH-CH resin is 0.644 meq/g. Al(III) shows maximum distribution coefficient at pH 2.0 and Dg value at this pH is 17373.

At pH 2.0 efficiency of the resin for aluminium was assessed varying the concentration of the metal at the pH of its maximum adsorption. Observations revealed that newly 96% efficiencies were recorded for the metal concentration in the range of 5 to 50 ppm.
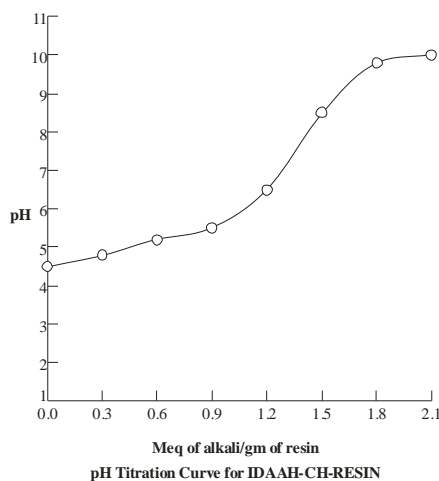
Table 1: Characteristic properties of resin (IDAAH-Ch)

Moisture Content	Nitrogen Content (%)	Bulk Density (g/cm^3)	Specific Bulk Volume (cm^3/g)	Degree of Crosslinking %	Degree of Substitutions %
2.10	6.37	0.357	2.80	47	56

Table 2: Values for Al^{3+} on IDAAH-Ch resin.

pH	Concentration of Al(III) in filtrate (ppm)	Amount of Al(III) in solution (mg)	Amount of Al (III) in resin (mg)	Dg mL g-I
2	1.0028	0.0401	0.9599	17373
3	1.3640	0.0552	0.9454	12563
4	1.8365	0.0734	0.9265	9151

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