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SYNTHESIS AND ANALYTICAL APPLICATION OF NEW POLYSACCHARIDE CHELATING RESIN CONTAINING NITRILOTRIACETIC ACID

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ABSTRACT

A new polysaccharide chelating resin was synthesised by anchoring nitrilotriacetic acid (NTA). The resin was characterized by FTIR and elemental analysis. The resin is found to be stable in acidic as well as basic medium. Physicochemical properties of the resin are examined. Because of its greater selectivity and higher exchanger properties, chelating ion exchanger as well as weakly acid cation exchanger guar gum nitrilotrlacetic acid find tremendous application in waste water treatment and the quantitative results have been given for removal of heavy metal from the reference solution. The distribution coefficient of Cu^{2+}, NI^{2+}, Zn^{2+} and Pb^{2+} at different pH was systematically studied using batch equilibration method.

Key words: Polysaccharide, Cation exchanger resins, Heavy metal ion, Distribution coefficient, pH effect.

INTRODUCTION

Wastewater or contaminated water is a big environmental problem all over the world. The presence of heavy metals in the environment is a cause of concern due to their acute and long term toxicity. The removal of heavy metals from aqueous streams represents a significant industrial waste problem[1]. Although various inorganic salts and trace elements are required to maintain normal good health, they can be toxic above threshold levels. Toxicity generally results when an excessive concentration is presented to an organism over a prolonged period of time and when the metal is present in an unusual biochemical form. Toxicity may also result, when the metal is presented to the organism by way of unusual route[2]. Heavy metals pollution may be traceable to industrial activities such as smelting of ores or refining of metals, from both of which metals may be introduced into the air, water and soil. The bioavailability of metals in natural waters is often related to the dissolved free metal concentration[3]. Ion exchange processes have found a valuable place in the treatment of

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metal wastes from plating, metal working and other industrial processes where the discharge of toxic metals may violate the environmental regulations[4,5]. In recent year, the chelating polymer resin have been of interest to chemists due to their application in the field of metal ion separation[6,7], wastewater treatment[8-12], mine water treatment[13] and pollution control[14]. Similar experiment was carried by Lobosova et al.[15], who synthesised Lewatit TP 214 chelating resin[15], and Gawale and Marathe[16] also synthesised Indion 225H cation exchanger resin.

The present research paper describes the synthesis of guar-gum nitrilotriacetic acid cation exchanger resin (GNTA).The exchanger has been found to be very selective for Cu^{2+}, NI^{2+}, Pb^{2+} and Zn^{2+}.

EXPERIMENTAL

Reagent and chemicals

All the reagents and chemicals used were high purity commercial products and were used as such. The functionalization of polysaccharide guar gum with nitrilotrlacetic acid group via epichlorohydrin has been described in an Ease German patent[17]. However, we have employed Porath's method[18] of functionalisation of polysaccharides.

Perkin-Elmer Model 460 Atomic absorption spectrophotometer was used for quantitative determination of trace metals. For different metal ions, standard wavelengths of main resonance line and air acetylene flame were used.

Procedure

Synthesis of guar-gum nitrilotriacetic acid (GNTA) cation exchanger resin 32 g guar-gum powder (0.2 mole anhydroglucose unit, AGU) was suspended in 60 mL dioxane. While stirring the reaction mixture on a magnetic stirrer, 5 mL of 20% aqueous NaOH solution were added followed by 9.25 g (0.1 mol) of epoxychloropropane and the mixture was stirred for 5 hrs. at 60°C. After keeping it over night, compound was filtered and washed with dioxane and ether. This form of functionalized guar-gum can be stored at 25°C for long time. It can be activated by reaction with sodium hydroxide by converting the chlorohydrin functionality into an epoxide group, when it is required to be loaded with a ligand.

Since the functionalisation was to be done immediately, a drop of phenolphthalein was added to the dioxane suspension of guar-gum chlorohydrin, followed by drop wise addition of 20% aqueous sodium hydroxide with stirring at 50°C till the appearance of the pink colour. The 0.2 mole of nitrilotriacetic acid (NTA) was added drop wise and stirred for

4 hrs, and left overnight. Guar-gum incorporating NTA group was filtered, washed with HCl-methanol, and finally with ether and dried.

Characterization of the resin

Moisture content determination

1 g of resin, free from surface moisture, was kept on a watch glass over ammonium chloride in vacuum desiccators for several days until the constant weight was obtained.

The physico-chemical properties like moisture content, density, ion exchange capacity and thermal stability were studied according to the literature methods[19] and the results are presented in Table 1.

Table 1

Colour	Light brown
Moisture content	18 %
Density	1.35 g cm^{-3}
Total ion exchange capacity	2.94 Meq/g
Thermal stability	265˚C

K_d Values for metal ions

The procedure adopted for removal of heavy toxic metal ion is as follows -

A 50 mL aliquot of effluent was taken in a clear beaker. The pH was adjusted using sodium bicarbonate and hydrochloric acid. 80 mg of guar nitrilotriacetic acid (GNTA) resin was added to the solution and stirred on a magnetic stirrer for one hour. The solution was then filtered through Whatman filter paper No. 40. The residue on the filter paper was equilibrated with 4N HCl, and the solution was filtered through Whatman filter paper No. 42. The volume was made up to 250 mL with distilled water.

The heavy metal ion concentration in the filtrate was estimated using atomic adsorption spectrophotometer. The distribution coefficients (K_d) were calculated using the formula:-

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

RESULTS AND DISCUSSION

IR data

The FTIR spectrum of guar-gum nitrilotriacetic acid are characterized by –COOH and >N- stretching vibrations 1020-1200 cm^{-1} for C-N stretching band, 1250-1350 cm^{-1} for aliphatic tertiary amine, 1651 cm^{-1} for β- keto ester stretching, 2927 cm^{-1} for COOH group and 3400-3600 cm^{-1} for –OH bond.

Effect of pH on distribution coefficient

To estimate the Cu^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} removal capacity of GNTA resin at different pH, removal capacity after 120 h was determined at various pH values from acidic to alkaline. The relative preference for various metal ions in GNTA is pH dependent. The distribution coefficients of various metal ions are given in Table 2.

Table 2: Distribution coefficients and % removal of various metal ions at different pH

pH	Cu^{2+}	% Removal	Ni^{2+}	% Removal	Zn^{2+}	% Removal	Pb^{2+}	% Removal
2	1090.06	68.02	944.73	62.24	961.52	65.23	493.16	49
3	2038.52	79.91	986.36	65.81	1098.26	68.18	547.71	51.66
4	2536.28	83.19	1145.39	69.09	1253	70.97	614.63	54.53
5	3329.78	86.06	1631.64	76.10	13.29	72.74	781.35	57
6	4922.28	90.57	1500.40	74.54	1646.37	76.26	540.54	51.33
7	2692.63	84.01	1437.6	73.72	1323	72.08	599.64	53.92
8	2394.48	82.37	1100.32	68.22	952.96	65.03	497.18	49.24

The perusal of the results shows that the distribution coefficient value (Table 2) first increase and then decrease with increasing pH. Due to principle of selectivity, the order of distribution ratio of divalent ions measured in the range pH 2-8, which was found to be Cu > Zn > Ni > Pb. It has been found that the percentage removal of Cu, Zn, Ni, and Pb are maximum at pH 6, 6, 5 and 7, which is maximum and shown in Fig. 1. It has been found that the percentage removal of Cu is 90.57 % at pH 6, which is maximum. Similarly, a maximum 76.10 % removal was observed at pH 5 for Ni and, 76.26 % removal was observed at pH 6 for Zn and, 53.92% was observed for Pb as shown in Fig. 1. Difference in distribution coefficient at the same pH for different metal ions suggests possible strategy for separation of these ions from their mixtures.

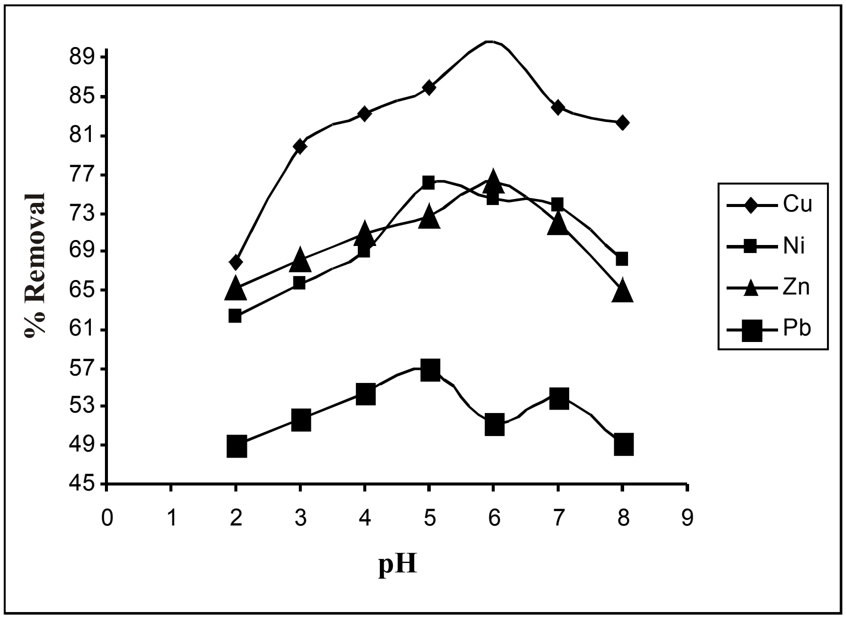

Fig. 1: Removal of Cu, Ni, Zn and Pb at different pH

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