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SYNTHESIS AND APPLICATIONS OF NEW TAMARIND 1-AMINO-2-NAPHTHOL-4-SULPHONIC ACID (TANSA) RESIN

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ABSTRACT

A new polysaccharide chelating resin was synthesized by anchoring 1-amino-2-naphthol-4-sulfonic acid. The synthesized resin was characterized by FTIR and elemental analysis by Atomic Absorption spectroscopy. The various physicochemical properties of the resin were examined and found that resin is stable in acidic as well as basic medium. Because of it's greater selectivity and higher exchanger properties (chelating ion exchangers as well as weakly acid cation exchanger), tamarind 1-amino-2-naphthol-4-sulfonic acid (TANSA) resin finds tremendous applications in waste water treatment and quantitative results have been given for removal of heavy metals from the reference solutions. The distribution coefficients of Fe^{2+}, Pb^{2+}, Cu^{2+} and Cd^{2+} at different pH were systematically studied using batch equilibration method.

Key words: Polysaccharide based resin, Heavy metal ions. Distribution coefficient, pH effect.

INTRODUCTION

As waste volumes have grown, it has become necessary to remove heavy metals from process effluents. Some of these metals are relatively valuable, making it economical to recover them. During the last 20 years, several new ion-exchange resins have been developed that are selective for heavy metals. Recently, recovery has become widely recognized as a way to reduce waste treatment costs. Metal salts dissolve in water and split into ions, which carry an electric charge. The ionic forms of dissolved metals, cations, carry a positive charge. Ions can be modified or removed using ion-exchange[1]. Much effort is devoted to the removal of heavy metals from industrial effuents and waste water, mainly because of increasing environmental problems resulting from excessive potential of chelating ion-exchange resin for separation and pre-concentration of metal ions has been firmly established[2-6]. The selectivity of the resin for metal ions depends on the nature of functional groups of the complexing agents. Polymeric resin are used in hydrometallurgy

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waste water treatment purification of metal salt solutions and various analytical method[7-10]. Various inorganic salts and trace elements are essential to maintain health but their excessive concentrations over a prolonged period of time are toxic and hazardous to environment[11].

Dowex 1-x8 is useful for separation of copper and nickel[12]. A series of malonamide ligand has been anchored to a vinyl benzylchloride / divinylbenzene copolymer, which is effective in removal of various metal ions from aqueous solutions[13,14].

EXPERIMENTAL

Reagents and chemicals

All the reagents and chemicals used were high purity commercial products and were used as such. The functionalisation of polysaccharide tamarind with trimethylamine group via epichlorohydrin has been described in an East German patent [10]. However, we have employed Porath's method[11]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.

Synthesis of tamarind 1-amino-2-naphthol-4-sulphonic acid (TANSA) resin

32 g Tamarind powder (0.2 mole anhydroglucose unit, (AGU) was taken in round bottom flask and slurried 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 mole) of epoxychloropropane (chlorohydrin) and the mixture was stirred for 5 hrs at 60^{o}C.

After keeping it overnight, the compound was filtered and washed with dioxane and ether. This form of functionalised tamarind can be stored at 25^{o}C for long time. It can be activated by reaction with sodium hydroxide (NaOH) by converting the chlorohydrin into an epoxide group. In the dioxane suspension of tamarind chlorohydrin, dropwise 20% aqueous sodium hydroxide was added with stirring at 60^{o}C.

It was followed by addition of 23.92 g (0.1 mole) of 1-amino- 2-naphthol- 4-sulphonic acid and stirring for 4 hrs and left over night. Tamarind incorporating 1-amino, 2-naphthol-4-sulphonic acid group was filtered, washed with HCl- methanol and finally with ether and dried. The yield of free flowing dark purple TANSA resin is 36.5 g and the degree of substitution (DS) is 0.49

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 a constant weight was obtained.

The physicochemical properties like moisture content, density, ion exchange capacity and thermal stability were studied according to the literature methods[14] and the results are presented in Table 1.

Table 1: Physicochemical properties of resin

Property	Value (S.D.)
% Moisture content	20
Scientific weight capacity	1.84 meq g^{-1}
% Nitrogen content	3.80
% Sulphur content	15.25
True density	1.05 g cm^{-1}

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 clean beaker. The pH was adjusted using sodium bicarbonate and hydrochloric acid. 80 mg of tamarind 1-amino-2-naphthol-4-sulfonic acid (TANSA) resin was added to the solution and it was 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. Then 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 –

$$(K_d) = \frac{\text{Amount of metal ion in resin phase/g of resin}}{\text{Amount of metal ion in solution phase/mL of solution}} \qquad \ldots(1)$$

RESULTS AND DISCUSSION

IR Data

The FTIR spectrum of tamarind 1-amino-2-naphthol-4-sulfonic acid (TANSA) are characterized by 3452.3 cm^{-1} stretching band (3200-3500 cm^{-1}) for –OH and >NH group; 2923.9 cm^{-1} for –C=H stretching band for bicyclic aromatic system (2900-3050 cm^{-1}), 2854.5 cm^{-1} for -C-H stretching band of aliphatic system (2800-3000 cm^{-1}). 1608.5 cm^{-1} for C=C stretching of aromatic system (1400-1600 cm^{1}), 1377cm^{-1} for C-H bending in aliphatic system (1350-1480 cm^{-1}) and 1250-1100 cm^{-1} for S=O stretching.

The distribution coefficient of various metal ions are given in Table 2

Table 2: Effect of pH on metal ion exchange capacity

pH	Pb^{2+}	% Removal	Fe^{2+}	% Removal	Cu^{2+}	% Removal	Cd^{2+}	% Removal
2	1168.83	45	731.25	33.86	955.21	40.07	389.33	21.41
3	1599.22	52.82	859.75	37.61	**3310.76**	**69.85**	482.33	25.25
4	2225.91	60.90	1408.30	49.64	2194.61	60.57	**2234.43**	**61**
5	3723.65	72.27	**3035.71**	**68**	2031.63	58.71	1787.72	55.58
6	**8392.85**	**85.45**	2585.49	60.5	1677.01	54	1200.70	45.66
7	5846.56	80.36	1816.92	56.14	1353.06	48.64	949.07	39.91
8	3406.59	70.45	1474.18	50.78	1330.04	48.21	677.43	32.26

Effect of pH on distribution coefficient

To estimate the Pb^{2+}, Fe^{2+}, Cu^{2+} and Cd^{2+} removal capacity of TANSA resin at different pH, removal capacity was determined after 120 h at various pH values from acidic to alkaline range. The relative preference for various metal ions in TANSA is pH dependent.The perusal of the results shows that the distribution coefficient value (Table 2) first increases 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 was found to be $Pb^{2+} > Cu^{2+} > Fe^{2+} > Cd^{2+}$. It has been found that the percentage removal of Pb^{2+}, Cu^{2+}, $Fe^{2+}$and Cd^{2+} are maximum at pH 6, 3, 5 and 4 (Fig. 1). It has been found that the percentage removal of Pb^{2+} is 85.45% at pH 6, which is maximum. Similarly, a maximum 69.85% removal was observed at pH 3 for Cu^{2+} and 68% removal was observed at pH 5 for Fe^{2+} and 61% was observed for Cd^{2+} at pH 4. Difference in distribution coefficient at the same pH for different metal ions suggests possible strategy for separation of these ions from their mixtures.

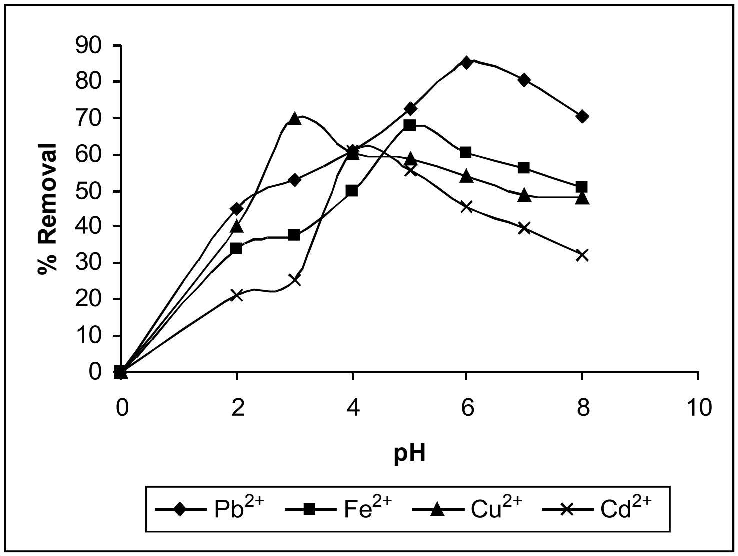

Fig 1: Removal of Pb^{2+}, Fe^{2+}, Cu^{2+} and Cd^{2+} at different pH

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