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Synthesis of a guaran-sulphonic acid cation-exchanger and its application in metal ion removal from underground mine water of the Rajpura Dariba Mines, Udaipur, India

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Abstract

A sulphonic acid group has been incorporated in guaran or galactomannan polysaccharide in order to develop a hydrophilic flocculant cum cation exchanger. Cis-hydroxyl groups present in the guaran matrix help flocculating the metal ions along with their cation exchange by the sulphonic acid functional group. The resin has been employed for removal of transition and toxic metal ions from reference aqueous solution and from the underground mine water of the Rajpura Dariba mines, Hindustan Zinc Limited, Udaipur, India.

Keywords: Hydrophilic flocculant; Cation exchanger; Transition metal ion removal

1. Introduction

Most commonly used chemical flocculants are basically designed to remove suspended solids and colloidal impurities, and they do not remove the dissolved solids to a large extent. For the removal, separation and recovery of metal ions from industrial effluent, ion exchange technology has proved to be cost effective compared to chemical precipitation and solvent extraction techniques. For the effluent to be discharged to a sewer or for its reuse, it has to be treated with selective ion exchangers [1]. Chelating resins take up heavy metal ions preferentially to alkali and alkaline earth metal cations [2,3], but chelating ion exchangers behave chromatographically so that it is not practical for the streams containing more than one metal [4]. Therefore, a strong acid cation exchange resin has been selected for the treatment of such streams. Various ion-exchange techniques have been reviewed for such applications. Due to rising prices of petroleum products, galactoman-

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nan matrix has been selected for the development of inexpensive and easily disposable cation-exchange resin incorporating a sulphonic acid functional group.

The guaran polysaccharide is an abundantly available local agricultural product. The resin has been used for the removal of trace metal ions from mining effluent from Hindustan Zinc Limited, Udaipur, India. Trace metal ion removal studies have also been done using a synthetic reference solution.

2. Experimental

All the reagents and chemicals used were high-purity commercial products and were used as such. A guaran-sulphonic acid derivative was synthesized in the laboratory by a modified Porath method for polysaccharide functionalization.

A digital ECIL pH meter and Perkin-Elmer atomic absorption spectrophotometer were used in the study for trace metal ion analysis. For different metal ions standard wavelengths of the main resonance line and air-acetylene flame were used.

2.1. Procedure

2.1.1. Synthesis of galactomannan sulphonic acid cation exchange resin

To prepare the cation exchange based on guaran or galactomannan polysaccharide, it was first treated with sodium 1,2-epoxypropyl-sulphonate, which was in turn prepared by the reaction of epichlorohydrin with sodium bisulphite. It was accomplished by the following two steps:

1. Preparation of sodium 1,2-epoxypropylsulphonate: 20.8 g (0.2 M) of sodium bisulphite were dissolved in a minimum quantity of distilled water in a 250 ml R.B. flask. 18.5 g (0.2 M) of epichlorohydrin were added dropwise and stirred for 4 h. The product sodium 3-chloro-2-hydroxypropylsulphonate was crystallized on cooling. Colourless, water-soluble crystals having an MP of 272°C were obtained. The product sodium 3-chloro-2-hydroxypropyl-sulphonate was taken in a 250 ml R.B. flask, and a 50% aqueous solution of sodium hydroxide was added until the pH reached 9.5. Stirring was continued for an hour. The product thus obtained was sodium 1,2-epoxypropylsulphonate and was used as such for further reactions with guaran.

2. Preparation of 2-hydroxypropyl-3-sodium sulphonate ether of guaran polysaccharide: 162 g (one anhydrohexose unit) of the purified guaran were taken in a 1 l R.B. flask and slurried in dioxane. Eight milliliters of 50% aqueous solution of sodium hydroxide were added to the flask. Sodium 1,2-epoxypropylsulphonate prepared as above was added to this solution with constant stirring. The solution was further stirred for 4 h at 60°C. The product was filtered under vacuum and washed with 80% methanol containing a few drops of hydrochloric acid. Finally it was washed with pure methanol to remove inorganic impurities. The product 2-hydroxypropyl-3-sodium sulphonate ether of guaran polysaccharide was a free flowing colourless powder. The yield was 201.7 g.

2.1.2. Determination of cation exchange capacity of the resin

The cation exchange capacity was determined by the method described by Helfferich [5], and it was found to be 9.5 meq/g.

2.2. Experiments on removal of metal ions from the reference solution

A reference solution having the following characteristics was prepared. Appearance: clear; pH 4.8; metal ion concentrations (in ppm): Pb^{2+}, 8; Zn^{2+}, 67; Cu^{2+}, 12; Fe^{2+}, 48; Cd^{2+}, 36; Mg^{2+}, 22.

A 50 ml aliquot of reference solution was taken in a clear beaker. The pH was adjusted using sodium bicarbonate and hydrochloric acid. Twenty milligrams of guar-sulphonic acid resin were added to the solution and stirred on a magnetic stirrer for 1 h. 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 concentrations in the filtrate as well as in the

Table 1
Percentage removal values of metal ions of reference solution on guar-sulphonic acid cation exchanger

pH	Pb^{2+}	Zn^{2+}	Cu^{2+}	Fe^{2+}	Cd^{2+}
5.0	83.2	50.1	62.5	80.4	57.4
6.0	86.1	59.2	89.5	86.0	65.3
7.0	100.0	98.2	90.3	98.2	72.6

Table 2
Distribution coefficient values of metal ions of reference solution on guar-sulphonic acid cation exchanger

pH	Pb^{2+}	Zn^{2+}	Cu^{2+}	Fe^{2+}	Cd^{2+}
5.0	2.5 $\times 10^4$	0.5 $\times 10^4$	8.33 $\times 10^3$	2.05 $\times 10^4$	6.76 $\times 10^3$
6.0	3.1 $\times 10^4$	7.25 $\times 10^3$	4.26 $\times 10^4$	3.07 $\times 10^4$	9.41 $\times 10^3$
7.0	—	27.3 $\times 10^3$	4.65 $\times 10^4$	27.3 $\times 10^4$	1.32 $\times 10^4$

residue were estimated using an atomic absorption spectrophotometer. The percentage removal of the metal ions and their distribution coefficients on the guaran-sulphonic acid resin were calculated. The results are given in Tables 1 and 2.

2.3. *Experiments on removal of metal ions from the underground mine water of Rajpura Dariba mines*

The underground mine water of the Rajpura Dariba mines had the following characteristics:

- Appearance: dirty brown; pH: 4.84
- Metal ion concentrations (in ppm): Pb^{2+}, 0.69; Zn^{2+}, 7.23; Cu^{2+} , 0.77; Fe^{2+} , 1.03; Cd^{2+}, 0.12; Ca^{2+} , 177.6; Mg^{2+} , 93.12.
- Other (in ppm): fluoride 0.9; cyanide 0.09; sulphate 986.4
- Total hardness: 876 ppm

The same procedure was adopted for the metal ion removal studies as stated above in case of the reference solution. The results of percentage removal of the metal ions and their distribution coefficients on the guaran-sulphonic acid resin are given in Tables 3 and 4.

Table 3
Percentage removal values of metal ions of underground mine water of Rajpura Dariba mines on guar-sulphonic acid cation exchanger

pH	Pb^{2+}	Zn^{2+}	Cu^{2+}	Fe^{2+}	Cd^{2+}
5.0	91.06	55.37	86.4	97.5	100.0
6.0	100.0	66.0	92.5	99.0	100.0
7.0	100.0	99.4	100.3	100.0	100.0

Table 4
Distribution coefficient values of metal ions of underground mine water from the Rajpura Dariba mines on guar-sulphonic acid cation exchanger

pH	Pb^{2+}	Zn^{2+}	Cu^{2+}	Fe^{2+}	Cd^{2+}
5.0	5.09 $\times 10^4$	6.23 $\times 10^3$	3.18 $\times 10^4$	19.6 $\times 10^4$	—
6.0	—	9.69 $\times 10^3$	6.19 $\times 10^4$	50.5 $\times 10^4$	—
7.0	—	88.8 $\times 10^4$	—	—	—

3. Results and discussion

The derivatives of guaran can be used as floc-culant cum metal ion scavenger from effluent of the mineral and metallurgical industries. Primary and secondary treatments of effluent from metallurgical industries considerably reduce the concentration of undesired metal ions in the form of insoluble hydrous oxides followed by their adsorption and flocculation. However, such treatments still leave behind the residual metal ion concentration at a level considered unsafe for discharge into natural streams [6,7]. Therefore, it becomes necessary to develop a more sophisticated tertiary treatment method to remove the toxic metal ions. Cation exchangers can effectively reduce the toxic metal ion concentration to a desired safe limit [8]. Ion selective exchangers are also used to remove toxic and expensive metal ions from effluent containing large concentrations of alkali and alkaline earth metal ions [9].

Rajpura Dariba deposits from Hindustan Zinc Limited are multimetal sulphides of a non-ferrous metal group [10]. Mine water is usually first neutralized by lime treatment. For its reuse in beneficiation plants, we have developed an ion exchanger based on a locally available polysaccharide guaran. The functionalization of guaran has been done by a modified Porath method [11].

The guar-sulphonic acid cation exchanger reduced the concentration of toxic and expensive metal ions to a level much below the permissible discharge limit [12]. Presence of cis-hydroxyl groups in the galactomannan polysaccharide helps the binding and flocculation of metal ions. The resin can be used on a large scale in batch operation. Pore size in the resin can be controlled by adjusting the degree of crosslinking, and the resin with proper crosslinking can be used as column material.

In a preliminary study a column of the crosslinked resin (degree of crosslinking raised from 1:0.2 to 1:1 with epichlorohydrin while retaining the sulphonic group substitution) was prepared after digesting it with an excess of 1 N hydrochloric acid and transferring sufficient resin to fill a 1 cm diameter column to a depth of 8 cm. The resin column was then washed with several bed volumes of demineralized water. Five milliliters of the reference metal ion solution were passed through the column at a flow rate of 2 ml/min. The column was washed with 20 ml of deionized water, and washing was rejected. Then the metal ions were eluted quantitatively with different strengths of acids. Zn^{2+} was eluted with 0.05N HCl; Fe^{2+} with 0.5 N HCl; Cu^{2+} with 2.5N HCl; Cd^{2+} with 0.5 N HNO_3 and Pb^{2+} was eluted with 1N HNO_3. Then the resin column was washed thoroughly with demineralized water. It could be reused up to five cycles with recovery better than 95%. After elution, the resin can be finally disposed of either by burying it or by incineration, as it is based on a biopolymer. Considering the four-cycle use, the cost of resin for treatment of 10001 of reference solution is $4 at the laboratory level.

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