

Recovery of boron and rare metals from sea water by chemically-modified novel chitosan resins

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1. BACKGROUND

Though boric acid in low concentration level is essential to vegetation, it stunts plant growth at a concentration greater than about 5mg/l. Boron contamination of natural waters by wastewater from boron mines [1], and from desulfurizing equipment in coal-fired steam power stations [2] is an environmental concern around the world. Therefore, the concentration of boron in wastewater must be reduced to levels permitted. Separation technologies for removal and recovery of boric acid in water are mainly employ chelating resin or solvent extraction.

Recently, chitosan biopolymer, which consists of D-glucosamine with β -(1,4) bonds, has attracted much attention as an adsorbent because chitosan is biodegradable and a possible environmentally friendly alternative to currently used polystyrene-based resins. Inukai *et al.* [3-5] prepared a chitosan resin modified by saccharides and N-2,3-dihydroxypropylchitosan resin and found that germanium(IV) was selectively adsorbed on the resins through a complex formation between germanium(IV) and the hydroxy groups of the saccharides.

This study aims to develop an environmentally friendly resin for boron recovery. Chitosan resins modified by various saccharides (henceforth SMC) were prepared in anticipation of the interaction between borate and the hydroxy groups of the saccharides. The adsorption characteristics of boron on the chitosan resins are quantitatively investigated in detail for the purpose of the removal of boron from a boron mine and the desulfurizing equipment in coal-fired steam power stations, and compared with

those of a commercial chelating resin with N-methyl-(polyhydroxyhexyl) amino group (Duolite ES371).

To enhance the capacity and selectivity for metal adsorption, on the other hand, many metal ligands were chemically introduced to the amino or hydroxyl groups in chitosan, and such resins with metal selectivity have been developed [6]. Though the polystyrene-supported sulfonic acid resin is nonselective, the metal selectivity of the sulfonic acid resin may be changed by replacing polystyrene by a chitosan matrix. Researchers were interested in the anticoagulant activity of sulfonated chitosan [7], but adsorption of metal on chitosan-supported sulfonic acid resin has not been examined so far.

In the present work, we prepare also a novel chitosan-supported sulfonic acid resin modified by propane sultone and the adsorption of metal ions is examined by using both the crosslinked chitosan-supported sulfonic acid resin (henceforth PSC) and a crosslinked chitosan resin (henceforth CLC). The metal selectivity of PSC is also discussed.

Fibrous or granular chelating adsorbents containing amidoxime groups have been used in the recovery of uranium from seawater [8]. Though amidoxime resins have excellent metal selectivity, the resins prepared so far were polystyrene- or polyacrylonitrile-supported ones. These resins are not readily disposed of. Choi [9] first reported the introduction of the amidoxime group to the chitosan. However, the preparation method of the amidoxime chitosan was not described, and the adsorption ability of uranium ion on the amidoxime resin was only described. Lee *et al.* [10] prepared a membrane composed of an amidoxime derivative of chitosan for the pervaporation separation of water-ethanol.

We prepare another novel resin organized from an amidoxime derivative of chitosan (henceforth AO-b-1) in the present work and the adsorption characteristics of metal ions are examined. Though the adsorption characteristics of metal ions on the amidoxime resin and fiber have been studied, in the previous papers [11-12], we found that the chitosan matrix as well as the functional groups affected the metal selectivity.

2. RESULTS

The following information is obtained.

(1) The number of amino groups per dry-weight of the chitosan resins is found to be larger than that of Duolite ES371. Values of pK_a of amino group modified by saccharide and a free amino group are considered to be similar.

(2) It is found that the adsorption mechanism is a complex formation between boron which exists as boric acid or borate in an aqueous solution and the vicinal diol groups of the branched saccharide. The apparent adsorption equilibrium constants of boric acid-diol complex and borate-diol salt complex are determined. The adsorption isotherms of boron correlate well with the Langmuir equation, and the order of the saturated adsorption capacity of boron on the SMC resins corresponds to that of the degree of substitution on SMC resins.

(3) In the low acidic region, the metal selectivity of PSC is similar to that of CLC. The role of the sulfonate is considered to be enriching the metal concentration in the neighborhood of the chitosan matrix. At the same time, since hydrogen ion is also enriched in a thin layer near the surface of the resin, the characteristic adsorption curves of PSC shift to a higher pH region compared with those of CLC.

(4) The adsorption equilibrium constants of metal on PSC and CLC are evaluated taking into account formation of metal-amine complexes. The adsorbed species are free metal ions. In the case of copper, $CuNH_3^{2+}$ is also adsorbed. The maximum adsorption capacity for PSC is 1.6 times higher than that of CLC.

(5) In the high acidic region, the maximum adsorption capacity for PSC is lower than that for CLC because of steric hindrance.

(6) The adsorption of metal ions except copper is retarded in the lower pH range because of electrostatic

repulsion between the protonated resin and the metal cations. The metal ions are adsorbed by forming chelates coordinated by nitrogen atoms of primary amino groups and oxygen atoms of oxime groups on the resins.

(7) AO-b-1 resin retards the adsorption of nickel ion compared with PSC and the maximum adsorption capacity of copper ion for AO-b-1 is 1.6 times as much as that for PSC. Thus, amidoxime chitosan resin is found to be an excellent adsorbent with a high adsorption capacity and selectivity for copper ion. Alkali-treated AO-b-1 resin shows the highest capacity of copper adsorption.

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