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TECHNICAL NOTE

Adsorption Characteristics of Metal Ions on Chitosan Chemically Modified by D-Galactose

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ABSTRACT

The adsorption characteristics of metal ions on chitosan chemically modified by D-galactose were examined. The pH dependency on the distribution ratio was found to be affected by the valency of the metal ion, and the apparent adsorption equilibrium constants of the metal ions were determined. The order of adsorption of the metal ions is Ga > In > Nd > Eu for the trivalent metal ions and Cu > Ni > Co for the divalent metal ions. It is believed that amino and hydroxyl groups in the chitosan act as a chelating ligand.

Key Words. Adsorption; Chemically modified chitosan; Metal; Galactose

INTRODUCTION

It is well known that chitosan behaves as a natural chelating polymer and is a good adsorbent for metal ions. To enhance the selectivity between the metal ions, the amino group in chitosan has been chemically modified to be converted into other functional groups, e.g., ascorbic (1, 2), carboxybenzyl (3), carboxymethyl (4–7), dithiocarbamate (8), hydroxybenzyl (9),

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oxoglutaric (10, 11), phosphoryl (12, 13), and pyridylmethyl group (14, 15).

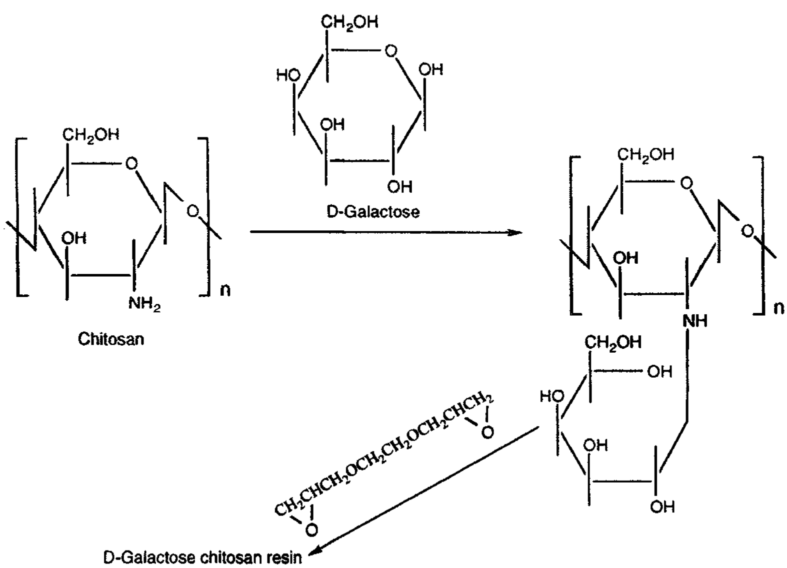
Recently, the interaction between saccharides and metal ions has attracted practical interest from the viewpoint of a biological model (16). In the present study we synthesized chitosan modified by D-galactose, which is a kind of saccharide, and examined the adsorption characteristics of metal ions on the modified chitosan.

EXPERIMENTAL

Materials

Chitosan from crab shells was purchased from Nakalai Tesque and used without further purification. Chitosan modified by D-galactose was prepared according to the method by Yalpani and Hall (17) as shown in Scheme 1.

The product obtained was identified by its IR spectrum. The product was then crosslinked with ethylene glycol diglycidyl ether in aqueous media at 333 K for 4 hours. The chitosan resin obtained was washed with ethanol and then methanol, and finally dried in vacuo. The other reagents were of guaranteed reagent grade.



SCHEME 1

Adsorption of Metal Ions on Chitosan Resin

The resin was ground and sieved to 100–120 mesh size. The sieved resin, 50 mg, was placed in an Erlenmeyer flask, to which was added 20 mL of 0.1 mol/dm^3 hydrochloric acid/sodium acetate buffer solution containing a metal chloride whose concentration was 5×10^{-4} mol/dm^3 except for Ga and In (1×10^{-3} mol/dm^3). The mixture was shaken at 303 K for 24 hours to attain equilibrium. The equilibrated mixture was centrifuged, and then the metal concentration in the supernatant was analyzed by atomic absorption spectrophotometry (Shimadzu AA 660) for transition metals or by the Arsenazo III method for lanthanoides. The quantity of metal ion adsorbed by the resin was calculated by subtracting the metal concentration in the supernatant from the initial concentration. The distribution ratio, D, is defined as the ratio of the concentration of the metal ion adsorbed on the dry adsorbent to its equilibrium concentration in an aqueous solution.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between D and pH for various metal ions. Galactose chitosan could adsorb the metal ions well. D increased with pH. The plots for the trivalent metal ions, Ga(III), In(III), Nd(III), and Eu(III), gave straight lines with a slope of 3. Slopes for the divalent metal ions, Cu(II), Ni(II), and Co(II), changed from two in the low pH

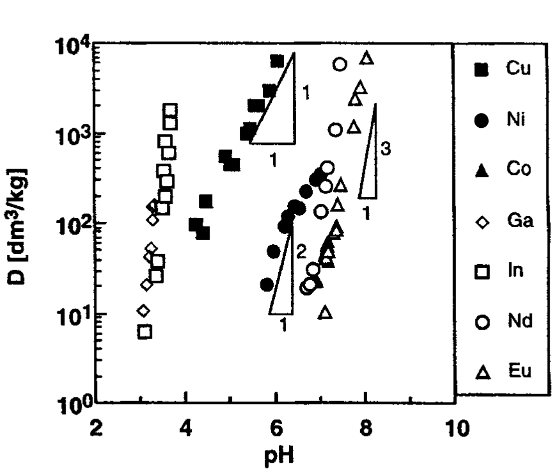


FIG. 1 Plots of distribution ratio against equilibrium pH.

TABLE 1
Apparent Adsorption Equilibrium Constant

Metal	log K'_M
Cu(II)	−8.41
Ni(II)	−12.1
Co(II)	−13.8
Ga(III)	−7.93
In(III)	−8.27
Nd(III)	−18.9
Eu(III)	−20.1

range to unity in the high pH range. This is considered to be caused by the decrease in the free metal ion in the high pH range due to the formation of the metal–acetate complex. The pH dependency on D was found to be affected by the valency of the metal ion in the same manner as in the solvent extraction with a chelating reagent. The order of the adsorption of the metal ions is Ga > In > Nd > Eu for the trivalent metal ions and Cu > Ni > Co for the divalent metal ions. This tendency for the divalent cations nearly parallels that on crosslinked chitosan (18). From these results it is expected that amino and hydroxyl groups in the chitosan act as a chelating ligand.

From analogy of the solvent extraction of metal ions with a chelating reagent, the following adsorption equilibrium is assumed:

$$M^{n+} + n\text{HR} \rightleftharpoons \text{MR}_n + n\text{H}^+, \qquad K_M \tag{1}$$

where HR represents the ligand moiety included in a glucosamine unit and K_M is the adsorption equilibrium constant.

In the low pH region, the concentration of the free metal ions is assumed to be approximated to the total concentration in the aqueous phase. In addition, the concentration of uncoordinated HR is assumed to be approximated to its initial concentration. The logarithm of D can be expressed by Eq. (2),

$$\log D = n\text{pH} + n \log[\text{HR}]_0 + \log K_M \tag{2}$$

$$= n\text{pH} + \log K'_M \tag{3}$$

where K'_M (= $[\text{HR}]_0^n K_M$) is an apparent adsorption equilibrium constant.

Equation (3) shows that the relation between log D and pH gives a straight line with a slope equated to the valency of the metal. This coincided with the experimental results shown in Fig. 1. Table 1 lists the values of K'_M for the metal ions tested.

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