Preparation of Chitosan Derivatives Containing Methylthiocarbamoyl and Phenylthiocarbamoyl Groups and Their Selective Adsorption of Copper(II) over Iron(III)*

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Adsorption techniques using chelating resins have been widely applied to the fields of analytical and separation chemistry. A large number of chelating resins have been developed so far, and some of them are commercially available. In recent years, from the viewpoint of environmental safety, much attention has been paid to the adsorption of metal ions on various kinds of biomass, such as alginic acid, cellulose, chitin, and chitosan. Among these natural polymers, chitin is the most abundant natural amino polysaccharide, and is estimated to be produced annually almost as much as cellulose. It has become of great interest not only as an underutilized resource, but also as a new functional material of high potential in various fields. Chemical modifications of chitosan have been noted owing to the presence of reactive amino groups in addition to hydroxyl groups. So far, we have also attempted to develop various types of chitosan derivatives for the adsorption and separation of specified metals.

The development of a selective resin for copper(II) is important from the viewpoint of not only metal ion-separation and detection in hydrometallurgy, but is also of biological interest. In earlier reports, we discussed our determination of the adsorption order of various metal ions by the crosslinked original chitosan (CLC). In general, a metal ion with a higher electron charge, such as iron(III), tends to be adsorbed at a lower pH compared with one with a lower electron charge, such as silver(I) and copper(II), as also seen in the adsorption of metal ions by a chelating resin, such as an iminodiacetic acid type. The adsorption order of copper(II) and iron(III) on CLC was also similar to that on an iminodiacetic acid type of chelating resin. Therefore, CLC has not been applicable as an adsorbent in the selective separation of copper(II) from a solution containing much iron(III), which is very important for the recovery of copper(II) in the fields of hydrometallurgy and analytical chemistry.

Recently, we found that a new chitosan derivative, N-(2-pyridylmethyl)chitosan, by introducing a pyridyl group to chitosan, can selectively adsorb copper(II) over iron(III). In the study, it was elucidated that pyridine introduced to chitosan plays an important role to cause a selective adsorption of copper(II) over iron(III).

In the present work, N-(methylthiocarbamoyl)chitosan (MTC) and N-(phenylthiocarbamoyl)chitosan (PTC) were newly synthesized to examine the selectivity toward metal ions from a 1 mol dm⁻³ (M) aqueous ammonium nitrate solution.

Experimental

Reagents

Chitosan (trade name, Chitosan 100 L), produced and marketed by Katokichi Co., Ltd., Japan, was used without further purification; the deacetylated degree was 100%. Alkylthiocyanic acid derivatives were supplied from Tokyo Kasei Co., Ltd., and were used without further purification. Chitosan derivatives with and introduced a methylthiocarbamoyl or phenylthiocarbamoyl group were synthesized by a conventional method. That is, these chitosan derivatives were prepared by a reaction of chitosan with a 10-fold excess of alkylthiocyanic acid in a mixture of aqueous acetic acid and methanol at room temperature. After 24 h, the product was filtered and washed with diethyl ether and ethanol to remove any excess alkylthiocyanic acid, and then with deionized water to neutrality. The final product was identified based on the IR spectra. In the IR spectra, the characteristic peaks appeared at around 2045 cm⁻¹ due to the resulting C=S linkage. The spectrum of the carbamoyl group showed a broad band at 3200 – 3600 cm⁻¹ assigned to ν(N–H) of the secondary amino groups. The degree of substitution was determined to be over 0.9 by the C/N ratio of an elemental analysis. The molecular structures of these chitosan derivatives are shown in Fig.1. All aqueous solutions were prepared with distilled and deionized water.

Adsorption procedure

Equilibrium adsorption experiments were performed by shaking 50 mg of the chitosan derivatives in 15 ml of the aqueous solution with a shaker (120 strokes per min) and incubating it at 30°C for 24 h. The aqueous solution was prepared by dissolving 1 mmol dm⁻³ of metal nitrate in 1 mol dm⁻³ aqueous ammonium nitrate solution, which was added to keep the ionic strength in the aqueous phase constant. The pH was adjusted by adding a small amount of nitric acid and ammonia. After equilibrium was reached, the chitosan derivatives were separated by filtration, and then the equilibrium concentration of the metal ion was determined by using a Hitachi Model z-8000 polarized Zeeman atomic absorption spectrophotometer.
absorption spectrophotometer. The amount of adsorbed metal ion was calculated from the concentration change in the aqueous solution before and after equilibration by taking account of the solution volume and the weight of the adsorbent. Here, the distribution ratio \(=D \text{ [cm}^3 \text{ g}^{-1}]\) was defined as the ratio of the amount of metal ion adsorbed (mol g\(^{-1}\)) to the equilibrium metal concentration (mol dm\(^{-3}\)). The equilibrium pH was measured by using a TOA electronics Model HM-30S pH meter.

Results and Discussion

Typical experimental results of the effect of pH on the distribution ratio of Ag(I), Pb(II), Cu(II), Ni(II), Cd(II), Hg(II), Fe(III), Pd(II), and Au(III) from 1 M aqueous ammonium nitrate solution on MTC and PTC are shown in Figs. 2 and 3, respectively. The order of selectivity to metal ions in the adsorption on MTC was as follows: Ag > Hg = Au > Pd > Cu > Cd > Fe > Pb > Ni, while that on PTC is Ag > Hg ≥ Au > Cu > Pd > Pb > Cd > Ni. In the adsorption on PTC, iron(III) was not adsorbed at all. The order of selectivity on MTC and PTC agrees with that expected from HSAB concepts, except for copper(II). However, the very high selectivity of MTC for copper(II) over other base metal ions, including iron(III), should be noteworthy. In both adsorbents, the ligating group is the same and the only difference is the structure of the alkyl group of an alkylthiocarbamoyl group introduced to chitosan, i.e., whether it is a methyl or phenyl group. The selectivity for copper ion is considered to be due to this difference.

As shown in Fig. 2, the adsorption of copper(II) and iron(III) on MTC depends on the pH in a low-pH region, suggesting that these metals are adsorbed by chelate formation accompanied by releasing hydrogen ions. Nickel(II), lead(II), mercury(II), and cadmium(II) were almost independent of the pH, indicating that MTC acts as a coordination adsorbent toward these metals. On the other hand, the adsorption for most of the metal ions, including copper(II) on PTC, is independent of the pH, as shown in Fig. 3.

Figure 4 illustrates the relationship between the equilibrium pH and the logarithm of the distribution ratio of copper(II) and iron(III) on MTC and CLC for a comparison. It is noteworthy that the adsorption of copper(II) on MTC shifts to a lower pH by 4 units compared with CLC, while iron(III) adsorption slightly shifts to a higher pH. In general, iron(III) is adsorbed in a lower pH range than copper(II), since iron(III) has a higher electric charge than copper(II). Nevertheless, the order of selectivity of copper(II)/iron(III) was reversed in the adsorption on MTC; that is, copper(II) with less electric charge than iron(III) was selectively adsorbed at a lower pH. This adsorption characteristics suggests that MTC is useful for the selective separation of copper(II) from a copper solution containing large amounts of iron(III).

The selective adsorption of copper(II) over iron(III) may be attributed to the difference in the affinity of the sulfur atom (–S–) in the thiocarbamoyl group introduced to chitosan for copper(II) and iron(III), since the nitrogen atom derived from chitosan is common. In addition, as is evident from the HSAB concept, copper(II) is classified as a border-line acid. Therefore, it is considered that copper(II) may exhibit a high affinity for –SH classified as a border-line base. Thus, we presumed that MTC with an S, N-bidentate ligand has selectively adsorbed copper(II) over iron(III), because it seems that MTC behaves as a monoprotic and probably bidentate ligand in metal adsorption. In order to recover copper(II) adsorbed on MTC, the desorption from MTC was investigated.
desorbed from MTC by a single batchwise treatment with 1 M hydrochloric acid for 24 h.

In conclusion, it was found that copper(II) adsorption on MTC occurred at a lower pH by 4 units than that on CLC or PTC, and that MTC adsorb selectively copper(II) at a lower pH by 2 over iron(III). MTC is expected to be an effective and selective adsorbent for copper ion.

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References