Solvent Extraction of Some Metal Ions with Lipophilic Chitosan Chemically Modified with Functional Groups of Dithiocarbamate

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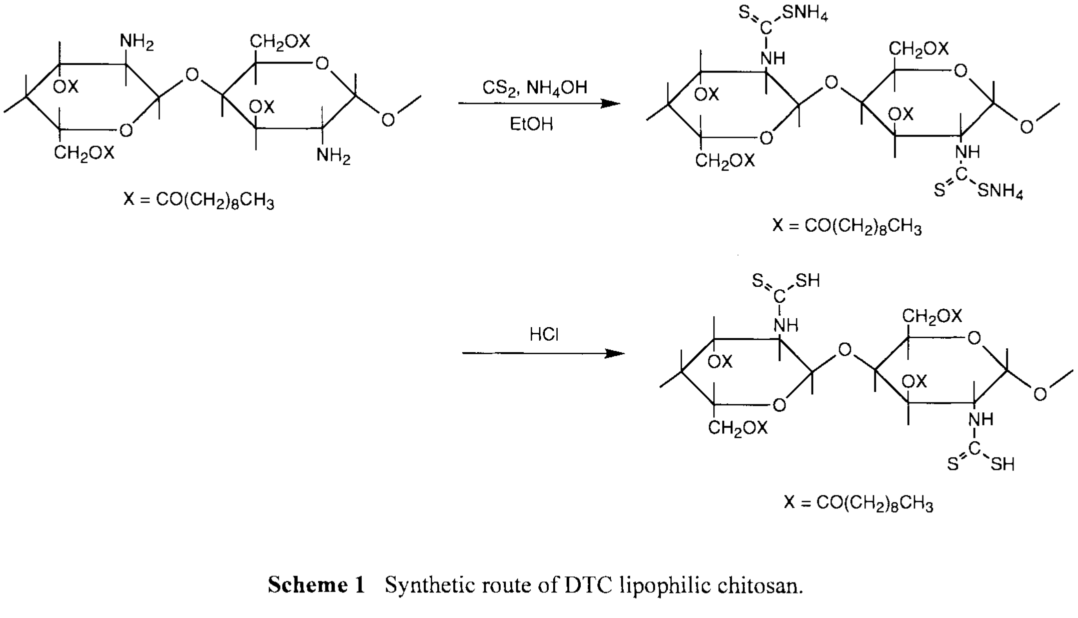
O,O'-Didecanoylchitosan chemically modified with functional groups of dithiocarbamate was prepared. The extent of the immobilization of the functional groups onto one glucosamine unit of chitosan was 96%. It was soluble not only in chloroform and toluene but also in hexane and kerosene. Its solvent extraction behaviors for some base metal ions were examined. The order of the selectivity to these metal ions was found to be as follows: Cu(II)>>Ni(II)>>Fe(III)>Co(II)>Zn(II). The high selectivity to copper and nickel over iron is noteworthy.

In the previous works, we demonstrated that chitosan is an interesting natural adsorbent for metal ions with much superior selectivity compared with conventional commercial chelating resins[1] and that the adsorption power and selectivity are further enhanced and improved by incorporating some functional groups such as some complexanes,[2,3] oxine[4,5] and dithiocarbamate[6] by chemical modification of primary amino groups. In relation to the chemical modification of primary amino groups, it is recommended to make raw material chitosan lipophilic or solubilize in organic diluents to facilitate the chemical modification and improve the extent of immobilization of functional groups.[7] On the other hand, the lipophilic chitosan is expected to work as a solvent extraction reagent for metal ions. However, there had been no works on the solvent extraction with lipophilic chitosan and its chemically modified derivatives. From the viewpoints as such, in the previous work, we prepared *O,O'*-didecanoylchitosan, a lipophilic chitosan soluble in chloroform and toluene, to investigate its solvent extraction behavior for metal ions.[8]

In the present work, we prepared *O,O'*-didecanoylchitosan chemically modified with functional groups of dithiocarbamate, abbreviated as DTC lipophilic chitosan, hereafter, to elucidate its solvent extraction behaviors for some base metal ions.

O,O'-Didecanoylchitosan was prepared according to the method proposed by Nishimura et al.[7] and the details of the preparation is reported elsewhere.[8] The immobilization of functional groups of dithiocarbamate on *O,O'*-didecanoylchitosan was carried out by interacting with carbon disulfide in ethanol according to the synthetic route shown in Scheme 1 as follows. *O,O'*-didecanoylchitosan (1.0 g) was dissolved in ethanol (200 cm$^{3)}$ with stirring. Carbon disulfide (5.0 g) was added to this mixture with stirring at 37 °C for 24 h, and 5.0 g carbon disulfide was further added together with 3.0 cm^3 ammonia water. The same operation was further repeated again after 24 h, followed by 24 h stirring after which 0.1 M (M = mol dm^{-3}) hydrochloric acid was added for neutralization of the reaction mixture. After removing ethanol together with unreacted carbon disulfide by evaporation in vacuum, chloroform was added to the mixture, which was washed with water until the washings became neutral pH. After drying the mixture over magnesium sulfate followed by evaporation in vacuum to remove the chloroform, brown solid material (1.02 g) was obtained as the final product. The identification was carried out by means of infrared spectroscopy.

The final product was found to be soluble not only in chloroform and toluene but also in kerosene and hexane. The sulfur content in the final product was measured by using a Mitsubishi Chemicals model TOX-10Σ total halogen analyzer, from which the extent of the immobilization of the functional group onto



Scheme 1 Synthetic route of DTC lipophilic chitosan.

glucosamine unit of *O,O'*-didecanoylchitosan was evaluated as high as 96 % while it was only 25 % in the case of the immobilization onto chitosan, the solid feed material.[6]

Solvent extraction tests for some base metals were carried out batchwise at 30 °C as follows. DTC lipophilic chitosan (2.3 kg m^{-3}) in kerosene was shaken in a flask together with equal volume of aqueous mixtures of 0.1 M nitric acid and 0.1 M HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid) solution containing 0.1 mM individual metal ion for 24 h to attain equilibrium. The metal concentrations in the aqueous phase were measured by using a Seiko model SAS 7500 atomic absorption spectrophotometer. The metal concentrations in the organic phase were calculated from those in the aqueous phase before and after the extraction.

Figure 1 shows the plot of % extraction of some base metal ions against equilibrium pH. This figure shows that copper(II) and nickel(II) are selectively extracted over iron(III), cobalt(II) and zinc(II), and that the high selectivity to copper(II) and nickel(II) over iron(III) should be noteworthy. This result may be attributable to the functional groups of dithiocarbamate immobilized onto polymer matrices of chitosan as a typical soft Lewis base excluding ferric ion, a typical hard Lewis acid.

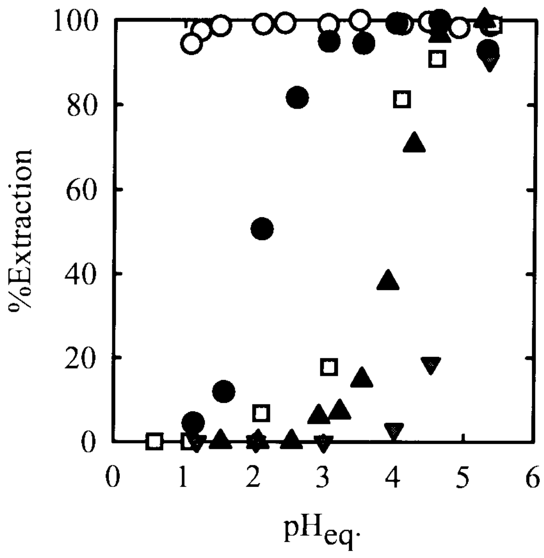


Figure 1. %Extraction of some base metals vs equilibrium pH (pH$_{eq.}$) in the solvent extraction with DTC lipophilic chitosan in kerosene. ○: Cu(II), ●: Ni(II), □: Fe(III), ▲: Co(II), ▼:Zn(II).

Stripping test of the loaded copper was carried out from 2.3 kg m^{-3} DTC lipophilic chitosan in kerosene containing 0.1 mM copper by using varying concentration of sulfuric acid solution. The % stripping is shown in Table 1.

Table 1. Stripping of copper from loaded solvent with varying concentration of sulfuric acid solution

[H_2SO_4] mol dm^{-3}	0.23	1.8	3.6
% stripping	39	82	85

Although it is not perfect, majority of copper can be stripped from the loaded solvent with high concentration of sulfuric acid.

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