

Selective Adsorption of Palladium(II), Platinum(IV), and Mercury(II)  
on a New Chitosan Derivative Possessing Pyridyl Group

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Crosslinked N-(2-pyridylmethyl)chitosan was newly synthesized by crosslinking N-(2-pyridylmethylidene)chitosan of the intermediate compound before reducing it so that the adsorptive activity is not lowered by the crosslinking. The pyridylmethylchitosan selectively adsorbed palladium(II), platinum(IV), and mercury(II) over base metals from hydrochloric acid.

Chitosan has been widely applied as an effective coagulating agent in activated sludge plants and for recovering proteins from food processing factories because of its excellent adsorption behaviors. Muzzarelli et al.<sup>1,2)</sup> carried out many studies on the chromatographic separations of metal ions with some chitosan derivatives. However, since chitosan and its derivatives are soluble in acidic solution, these materials are unsuitable as such for the removal of metal ions from industrial wastes. Ohga et al.<sup>3)</sup> proposed to prepare resins by crosslinking metal-complexed chitosans to overcome this disadvantage. Thus far, a number of adsorbents for metals have been developed, however, few studies on adsorbents which contain plural nitrogen atoms as ligating ones have been reported on the adsorption of platinum group metals.

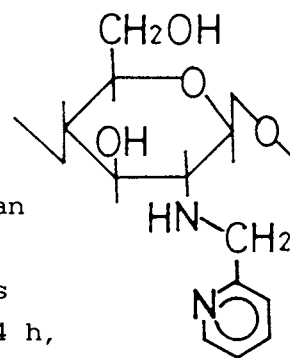
Recently, we have found that N-(2-pyridylmethylidene)chitosan can effectively adsorb various metal ions over the pH range of 3-8 from 1 mol dm<sup>-3</sup> of aqueous ammonium nitrate solutions.<sup>4)</sup> However, the N-(2-pyridylmethylidene)chitosan can not be used in a lower pH region (pH<2) because of its dissolution or the decomposition of its Schiff base in dilute acids. Therefore, the N-(2-pyridylmethylidene)chitosan was crosslinked, followed by its reduction to get the N-(2-pyridylmethyl)chitosan to be stable in the acidic solution, which is an important condition for its hydrometallurgical application.

In the present paper, the authors describe the preparation method and adsorption properties of the newly developed crosslinked chitosan deriv-

ative containing the substituted pyridine ring in order to enhance the adsorption ability and selectivity for metal ions, and show that the Schiff base is a useful amino-protecting group in the crosslinking reaction.

Chitosan (trade name: Chitosan 95L), produced and marketed by Katokichi Co. Inc. Japan, was used without further purification; the degree of deacetylation was 95%. Other reagents of reagent grade were used without further purification. All aqueous solutions were prepared with distilled and deionized water.

N-(2-Pyridylmethyl)chitosan was prepared by way of N-(2-pyridylmethylenidene)chitosan obtained through the Schiff base formation reaction between the amino groups of chitosan and 2-pyridinecarboxaldehyde by the conventional method. That is, N-(2-pyridylmethylenidene)chitosan was prepared by the reaction of chitosan with 10-fold excess 2-pyridinecarboxaldehyde 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 excess aldehyde and then with deionized water to neutrality. Thus, N-(2-pyridylmethylenidene)chitosan of a light yellow gel was obtained as the intermediate. This gel was immersed in dimethylsulfoxide to make it swell, followed by stirring in (chloromethyl)oxirane for 24 h. After filtration, the gel was crosslinked in 0.1 mol dm<sup>-3</sup> of aqueous sodium hydroxide solution at 80 °C for 24 h. Subsequently, the crosslinked N-(2-pyridylmethylenidene)chitosan was reduced with sodium borohydride for 24 h by gradually adding it to the aqueous solution. The final product, N-(2-pyridylmethyl)chitosan, was washed with ethanol and then with deionized water to neutrality. The intermediate and the final product were identified by IR spectra. In the IR spectra, characteristic peaks appeared at around 1635 cm<sup>-1</sup> and 859 cm<sup>-1</sup> due to the resulting C=N linkage and substituted pyridyl group, respectively. The degree of substitution was determined to be 0.90 by measuring the amount of hydrochloric acid adsorbed on N-(2-pyridylmethyl)chitosan.



About 0.1 g of the N-(2-pyridylmethyl)chitosan sieved to 100 mesh size and 20 ml of aqueous solution containing metal ion were shaken in a stoppered glass flask of 100 ml immersed in a thermostated water bath maintained at 30 °C overnight to achieve equilibration. The aqueous solution contained 1 mmol dm<sup>-3</sup> metal ion in 0.01-6 mol dm<sup>-3</sup> of hydrochloric acid. Initial and equilibrium metal concentrations in the aqueous solutions were determined by titration with EDTA or by using a Nippon

Jarrell-Ash model AA-782 atomic absorption spectrophotometer. The amount of adsorbed metal ion was calculated from the concentration change in the aqueous solution before and after the adsorption. The hydrochloric acid concentration was measured by neutralization titration.

Figure 1 shows the relation between the equilibrium concentration of hydrochloric acid and the adsorption percent of metal ion on the N-(2-pyridylmethyl)chitosan. As is evident from this result, it is noteworthy that N-(2-pyridylmethyl)chitosan has a higher selectivity than those of the conventional commercial chelating resins for palladium(II), platinum(IV), and mercury(II) over copper(II), nickel(II), cobalt(II), zinc(II), cadmium(II), and iron(III). Among these metals, iron(III), cobalt(II), zinc(II), and manganese(II) were not quite adsorbed on N-(2-pyridylmethyl)chitosan.

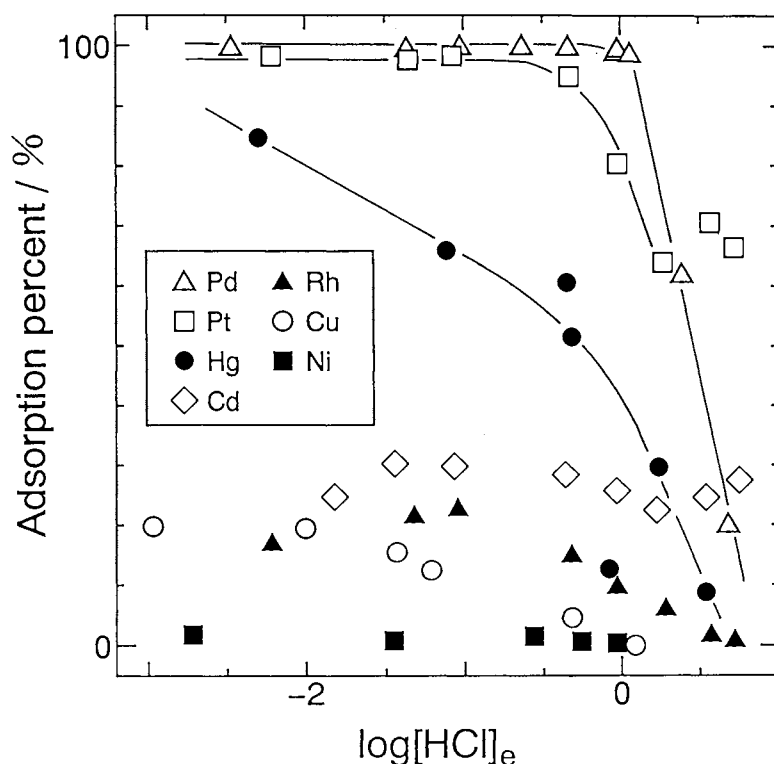


Fig.1. Effect of the hydrochloric acid concentration on the adsorption percent of various metals with the N-(2-pyridylmethyl)chitosan.

Figure 2 shows the adsorption isotherm of palladium(II) from 0.01 mol dm<sup>-3</sup> hydrochloric acid on N-(2-pyridylmethyl)chitosan and that of the crosslinked chitosan obtained by the method of Ohga et al.<sup>3)</sup> for comparison. The adsorption capacities for palladium were 5.8 mmol g<sup>-1</sup> and 2.1 mmol g<sup>-1</sup>, respectively; the adsorption capacity of N-(2-pyridylmethyl)-

chitosan is about three times that of the crosslinked chitosan. This suggests that the N-(2-pyridylmethyl)chitosan was crosslinked without a significant lowering of the adsorptive activity.

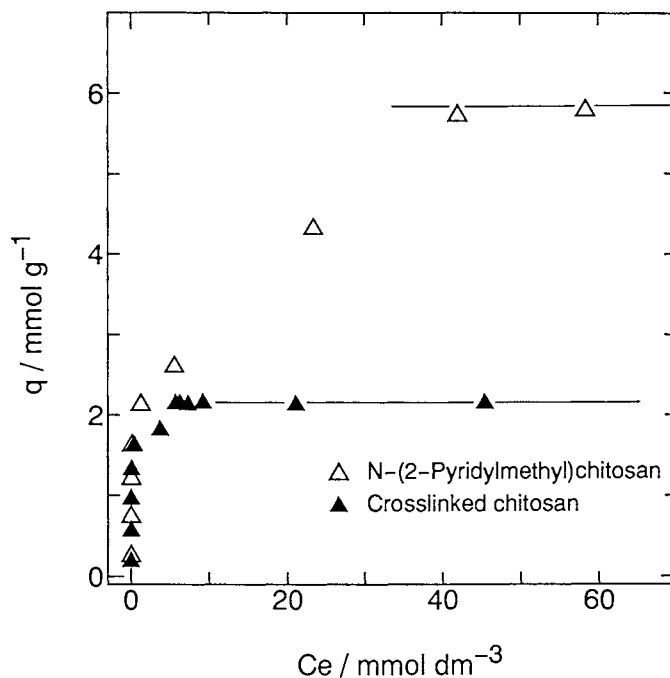


Fig.2. Adsorption isotherms of palladium(II) on the N-(2-pyridylmethyl)-chitosan and the crosslinked chitosan.

Consequently, these adsorption characteristics of N-(2-pyridylmethyl)chitosan which is synthesized by crosslinking the N-(2-pyridylmethylidene)chitosan possessing the Schiff base with (chloromethyl)oxirane are expected to be applicable to the commercial separation and purification of palladium(II), platinum(IV), and mercury(II) from hydrochloric acid containing base metals.

#### References

- 1) R.A.A. Muzzarelli, F. Tanfani, M. Emanuelli, and S. Mariotti, *Carbohydr. Res.*, **107**, 199 (1982).
- 2) R.A.A. Muzzarelli and A. Zattoni, *Int. J. Biol. Macromol.*, **8**, 137 (1986).
- 3) K. Ohga, Y. Kurauchi, and H. Yanase, *Bull. Chem. Soc. Jpn.*, **60**, 444 (1987).
- 4) P. Tong, Y. Baba, Y. Adachi, and K. Kawazu, *Chem. Lett.*, **1991**, 1529.

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