Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Adsorption of Some Platinum Group Metals on Some Complexane Types of Chemically Modified Chitosan

Katsutoshi Inoue[a]; Tomoo Yamaguchi[a]; Mineto Iwasaki[a]; Keisuke Ohto[a]; Kazuharu Yoshizuka[a]
[a] DEPARTMENT OF APPLIED CHEMISTRY, SAGA UNIVERSITY, HONJO-MACHI, SAGA, JAPAN

To cite this Article Inoue, Katsutoshi , Yamaguchi, Tomoo , Iwasaki, Mineto , Ohto, Keisuke and Yoshizuka, Kazuharu(1995) 'Adsorption of Some Platinum Group Metals on Some Complexane Types of Chemically Modified Chitosan', Separation Science and Technology, 30: 12, 2477 — 2489

To link to this Article: DOI: 10.1080/01496399508021396

URL: http://dx.doi.org/10.1080/01496399508021396

SEPARATION SCIENCE AND TECHNOLOGY, **30**(12), pp. 2477–2489, 1995

Adsorption of Some Platinum Group Metals on Some Complexane Types of Chemically Modified Chitosan

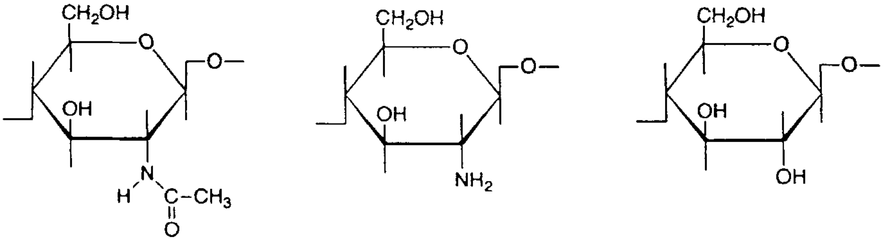
KATSUTOSHI INOUE, TOMOO YAMAGUCHI,
MINETO IWASAKI, KEISUKE OHTO,
and KAZUHARU YOSHIZUKA
DEPARTMENT OF APPLIED CHEMISTRY
SAGA UNIVERSITY
HONJO-MACHI, SAGA 840, JAPAN

ABSTRACT

A few kinds of complexane types of chemically modified chitosan, i.e., monocarboxymethylated chitosan (MCM-chitosan) and IDA- and DTPA-types of chitosan (IDA- and DTPA-chitosan) were synthesized to examine the adsorption of palladium(II), platinum(IV), and iridium(III) from hydrochloric acid solution as well as the elution of palladium and platinum and compared with those by crosslinked copper(II)-complexed chitosan (crosslinked chitosan). The adsorption of palladium(II) monotonously decreased with increasing hydrochloric acid concentration with all kinds of adsorbents. The adsorption of platinum(IV) also decreased with increasing hydrochloric acid concentration with all kinds of adsorbents except for DTPA-chitosan, with which it decreased in the low concentration region and increased in the high concentration region. The adsorption of iridium(III) also decreased with increasing concentration of hydrochloric acid with all kinds of adsorbents except for IDA-chitosan, but that on DTPA-chitosan was much smaller than other adsorbents. The adsorption on IDA-chitosan increased with increasing hydrochloric acid concentration in its low concentration region, and decreased in the high concentration region, different from other adsorbents. The magnitude of adsorption capacity of each adsorbent for palladium(II) was in the order MCM-chitosan = IDA-chitosan > DTPA-chitosan > crosslinked chitosan, while that for platinum(IV) was in the order, DTPA-chitosan > MCM-chitosan = IDA-chitosan > crosslinked chitosan. The elution of loaded palladium(II) and platinum(IV) with hydrochloric acid solution was much improved by chemical modification, especially that of platinum(IV) which was drastically improved by using IDA- and MCM-chitosan.

INTRODUCTION

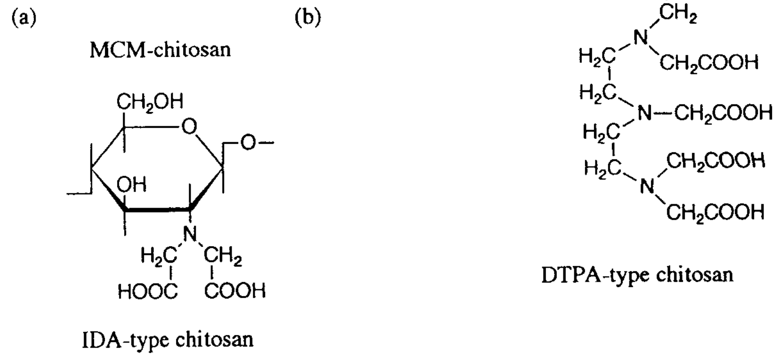
Much attention has been paid in recent years to the adsorption of microorganisms or biomass, such as algae and fungi, as well as on their cell components: alginic acid, chitin, cellulose, and so on (1). Among these, chitin is a main component consisting of shells of crustaceans, such as crabs, shrimps, prawns, insects, and so on, and is easily and cheaply prepared from their shells by removing other components, calcium and proteins, by treatment with acids and alkalines, respectively. Chitosan is also easily prepared from chitin by deacetylating its acetoamide groups with a strong alkaline solution. Consequently, they are very abundant and cheap forms of biomass, as is cellulose. The chemical structures of these biopolymers are illustrated in Fig. 1. It is well known that chitosan as well as chitin exhibits excellent adsorption behaviors for metal ions (2), and they have been utilized for the chromatographic separation of metal ions in the field of analytical chemistry. In previous work we conducted a fundmental investigation on the adsorption of some base metal ions from aqueous ammonium nitrate solution as well as palladium(II) and platinum(IV) on chitosan and crosslinked copper(II)-complexed chitosan, abbreviated as crosslinked chitosan hereafter, which was prepared by crosslinking the copper(II)-complexed chitosan by (chloromethyl)oxirane followed by washing with hydrochloric acid solution to removed the copper in order to avoid the significant loss of the loading capacity during crosslinking by protecting the adsorption sites from attack by the crosslinking agents and to maintain the polymer structure of the template of copper(II) to improve the selectivily (3).



chitin chitosan cellulose

FIG. 1 Chemical structures of chitin, chitosan, and cellulose.

We also synthesized three kinds of complexane types of chemically modified chitosan, i.e., monocarboxymethylated chitosan, *N*,*N*-dicarboxymethylated (or iminodiacetic acid type of chitosan), and diethylenetriaminepentaacetic acid type of chitosan (abbreviated as MCM-chitosan, IDA-chitosan, and DTPA-chitosan, respectively, hereafter) to investigate their adsorption behaviors for some base metals and rare earths (4). The chemical structure of these chemically modified chitosans are illustrated in Fig. 2. Based on MCM-chitosan, there are two possible carboxymethylations on the polymer chain of chitosan, i.e., at the primary amino groups or at the 6th position of hydroxyl groups. In the present work, from the practical point of view related to the recovery of previous metals from various wastes such as scraps of the electric and electronic industries, spent catalysts for the effluent gas of automobiles and for petrochemical industries, and so on, we investigated the adsorption behaviors of these chemically modified chitosans for palladium(II), platinum(IV), iridium(III), and rhodium(III) in hydrochloric acid solution as well as for iron(III) and aluminum(III) which are typical base metals coexisting as major components in the above-mentioned wastes.



(a) (b)

MCM-chitosan

IDA-type chitosan

DTPA-type chitosan

FIG. 2 Chemical structures of the complexane types of chemically modified chitosan.

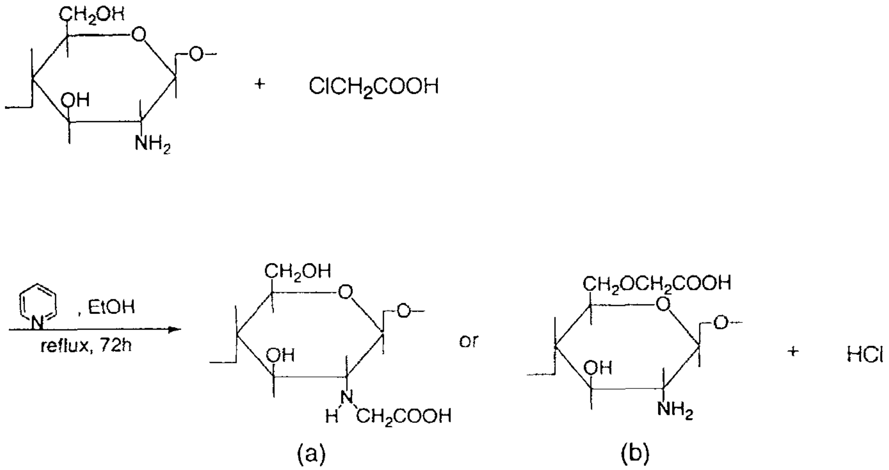
EXPERIMENTAL

Preparation of Chemically Modified Chitosan

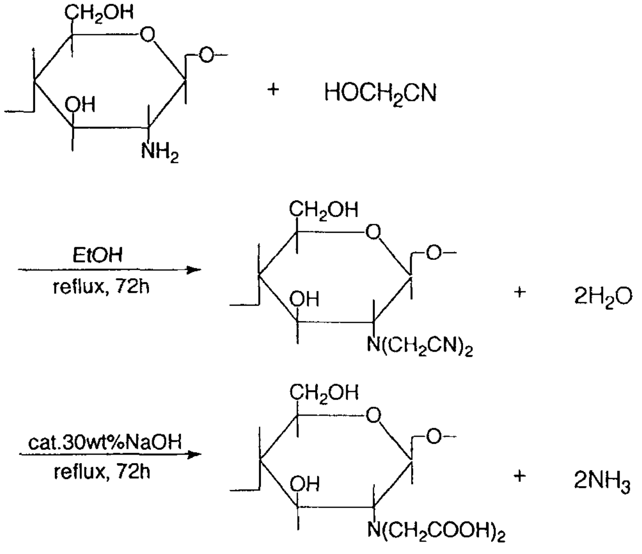
A sample of chitosan, the feed material, was kindly donated by Katokichi Co., Kan-onji, Japan, and was used as received after vacuum drying without further purification. The sample chitosan is produced from shells of prawns and is marketed under the trade name Chitosan 95L. Its degree of deacetylation is greater than 95%. It is made up of small, white, flake-shaped particles with a mean diameter of 0.12–0.25 mm.

MCM-chitosan was synthesized according to the route shown in Scheme 1: 18.0 g chitosan (equivalent to 0.11 mol gulucosamine units) and 20.7 g monochloroacetic acid (0.22 mol) were stirred together with 30 mL pyridine as the catalyst in 300 mL ethanol and refluxed under nitrogen atomosphere for 3 days. The product gel was washed, sequentially, with 0.5 mol/dm^3 sulfuric acid solution and deionized water after filtration, and again stirred in 0.3 mol/dm^3 acetic acid solution. After filtration, it was further washed, sequentially, with water, 1 mol/dm^3 aqueous sodium hydroxide solution, water, 0.5 mol/dm^3 sulfuric acid solution, and finally with water. It was dried in vacuo to a constant weight before use. The introduction of carboxylic groups was confirmed by its infrared spectrum. The degree of carboxymethylation, as measured by neutralization titration, was 94%.

IDA-chitosan was synthesized by two steps via *N*,*N*-dinitrated chitosan, the intermediate, according to the reaction shown in Scheme 2 as



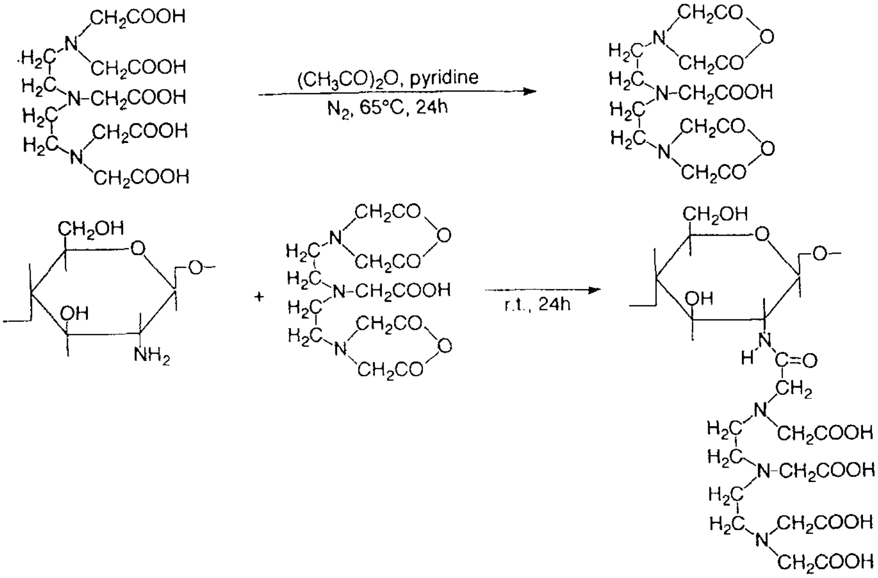
SCHEME 1 Synthetic route of MCM-chitosan.



SCHEME 2 Synthetic route of IDA-type chitosan.

follows. The latter was prepared by stirring 8 g chitosan (equivalent to 50 mmol glucosamine unit) together with a 170-mL aqueous solution of glycoronitrile (corresponding to about 1.6 mol) and a small amount of ethanol at 80°C for 3 days. After filtration and water washing, it was stirred in 300 mL of 30 wt% aqueous sodium hydroxide solution, also at 80°C, for 3 days and then hydrolyzed to obtain the IDA-type of chitosan, the final product. It was dried in vacuo after washing in the manner similar to MCM-chitosan before use. The introduction of nitrile groups in the intermediate product was confirmed from its infrared spectrum by the appearance of a new absorption band at 2200 cm^{-1}. The conversion of nitrile groups into carboxyl groups in the final product was confirmed by the disappearance of the above-mentioned absorption band and the appearance of new absorption bands at 1600–1700 cm^{-1}. The degree of conversion of primary amino groups into iminodiacetic acid groups, as measured by neutralization titration, was 50%.

DTPA-chitosan was synthesized according to the reaction shown in Scheme 3: 5 g chitosan (equivalent to 3 mmol glucosamine unit) was dissolved in 200 mL of 2 vol% aqueous acetic acid solution followed by the addition of 500 mL methanol. To this solution, 33 g diethylenetriaminepentaacetic acid (DTPA) anhydride (9 mmol) suspended in 100 mL methanol was added and stirred to undergo reaction at room temperature for 12



SCHEME 3 Synthetic route of DTPA-type chitosan.

hours. After filtration, the precipitate was washed with 0.5 mol/dm^3 aqueous sodium hydroxide solution to remove unreacted DTPA. Then it was washed, sequentially, with water and 50 mmol/dm^3 sulfuric acid solution and finally with water to neutral pH. It was dried in vacuo to constant weight before use. The degree of introduction of the functional group of DTPA, measured by the method mentioned above, was 34%.

Procedure

Crystals of palladium(II) chloride and hydrogen haxaplatinate(IV) hexahydrate, rhodium(III) trichloride tetrahydrate, and iridium(III) trichloride, kindly donated by Tanaka Noble Metals Industry Co., Tokyo, Japan, were used as received to prepare aqueous solutions by dissolving each of them in a hydrochloric acid solution. Reagent-grade iron(III) chloride hexahydrate and aluminum(III) chloride hexahydrate were used to prepare aqueous chloride solutions of these metals. The initial concentrations of all the platinum group metals were around 100 ppm while those of aluminum and iron were about 5 mmol/dm^3.

All experiments were carried out batchwise at 30°C as follows. Weighed amounts of the adsorbents (50 mg) were shaken together with 15 mL aqueous metal solution in a flask immersed in a water bath incubator maintained at 30°C. The metal concentration in the aqueous solution was measured by atomic absorption spectrochemical analysis by using a SEIKO model SAS-7500 atomic absorption spectrophotometer. The amount of adsorbed metal on each adsorbent was calculated from the metal concentrations in the aqueous solutions before and after adsorption and from the dry weight of the adsorbent.

Figure 3 shows plots of the amount of adsorbed palladium(II), platinum(IV), iridium(III), and rhodium(III) on DTPA-chitosan (*q*) against shaking time in the adsorption from 1.35 mol/dm^3 hydrochloric acid solution as a typical example. From Fig. 3 it is obvious that the adsorption of palladium(II) and iridium(III) attained equilibrium within 1 hour while it takes more than 10 hours for platinum(IV) to reach equilibrium and rhodium(III) is not appreciably adsorbed. Similar adsorption was observed on two other kinds of adsorbents. Based on these results, shaking was continued for more than 24 hours in subsequent experiments to attain equilibrium.

Elution tests of palladium(II) and platinum(IV) from the loaded adsorbents were carried out as follows: 0.3 g of the adsorbents was shaken with 60 mL of 10 mmol/dm^3 hydrochloric acid solution containing 300 ppm palladium(II) or platinum(IV) for more than 24 hours to load the metal. After water washing followed by drying in vacuo, 20 mg of the metal-loaded adsorbents was shaken in 15 mL of varying concentrations of hydrochloric acid solution for elution. From the metal concentrations

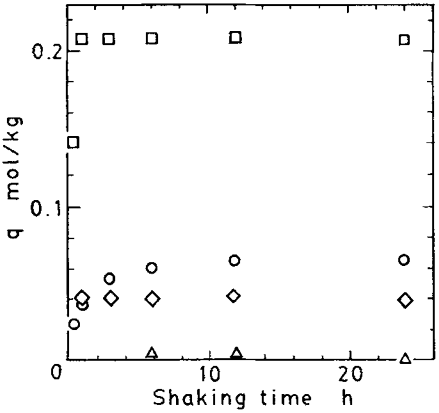


FIG. 3 Relationship between amount of adsorbed palladium(II) (□), platinum(IV) (○), iridium(III) (◇), and rhodium(III) (△) on DTPA-chitosan (*q*) and shaking time in the adsorption from 1.35 mol/dm^3 hydrochloric acid solution.

in the elutes and the amount of adsorbed metal, the percent elution was calculated for each metal and for each adsorbent.

RESULTS AND DISCUSSION

Effect of Hydrochloric Acid Concentration on Adsorption

The effect of hydrochloric acid concentration on the adsorption of the above-mentioned metals, i.e., on the distribution ratio [which is defined as the ratio of the amount of adsorbed metal per unit kg of the dried adsorbent (mol/kg) to the metal concentration (mol/dm^3) in the aqueous solution after adsorption], was examined on the three kinds of chemically modified chitosan and compared with that on the crosslinked chitosan.

Figure 4 shows plots of the distribution ratio of palladium(II) against the concentration of hydrochloric acid. It is obvious that the adsorption monotonously decreases with increasing hydrochloric acid concentration for all kinds of the adsorbents, and that the adsorption on DTPA-chitosan is greater than that of crosslinked chitosan, i.e., the former can more strongly adsorb palladium(II) than the latter. On the other hand, there appears to be no difference in adsorption between MCM-chitosan and IDA-type chitosan, and adsorption is smaller than that on crosslinked chitosan.

Figure 5 shows plots of the distribution ratio of platinum(IV) on four kinds of adsorbents against hydrochloric acid concentration. The adsorp-

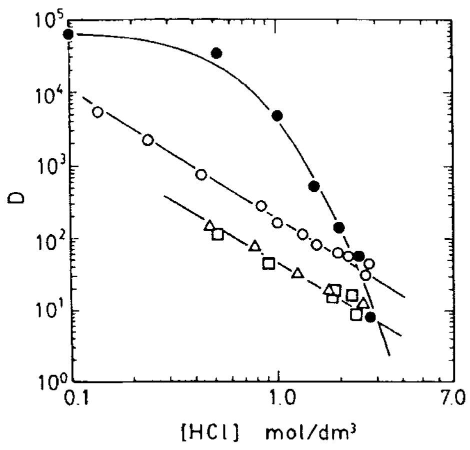


FIG. 4 Relationship between the distribution ratio of palladium(II) and hydrochloric acid concentration: MCM-chitosan (△), IDA-chitosan (□), DTPA-chitosan (●), crosslinked chitosan (○).

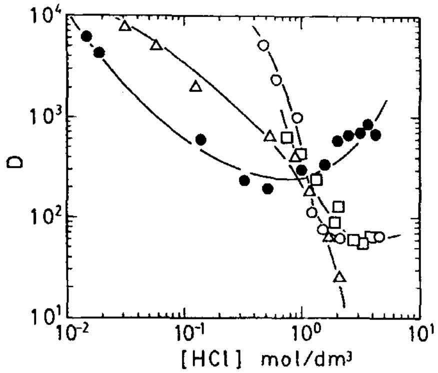


FIG. 5 Relationship between the distribution ratio of platinum(IV) and hydrochloric acid concentration. Keys are the same as those in Fig. 4.

tion on MCM-chitosan, IDA-chitosan, and crosslinked chitosan monotonously decreases with increasing hydrochloric acid concentration in a manner similar to palladium. On the other hand, in the case of DTPA-chitosan, adsorption decreases with increasing hydrochloric acid concentration in the low concentration region but increases with an increase in concentration, so it differs from the former three kinds of adsorbents. In the low concentration region, the adsorption on DTPA-chitosan is a little smaller than that on MCM-chitosan, which is also a little smaller than those on IDA-chitosan and crosslinked chitosan, which is different from the adsorption of palladium.

Figure 6 shows plots of the distribution ratio of iridium(III) on four kinds of adsorbents against hydrochloric acid concentration. The distribution ratio abruptly decreases with increasing hydrochloric acid concentration in the adsorption on MCM-chitosan and crosslinked chitosan, and the adsorption on DTPA-chitosan is remarkably smaller than these. Contrary to these three kinds of adsorbents, IDA-chitosan exhibits a very peculiar adsorption behavior; that is, the plots for this adsorbent lie on a convex curve very different from the curves of other adsorbents. This convex curve looks like the extraction curve of iridium(IV) with trioctylamine from hydrochloric acid solution as presented in the literature (5), where the extraction curve of trivalent iridium looks like the adsorption curves on MCM-chitosan and crosslinked chitosan. The convex adsorption curve might be attributable to the oxidation of trivalent iridium to its tetravalent state during chelating adsorption on IDA-type chitosan; similar phenomena have been frequently observed in chelating solvent extraction

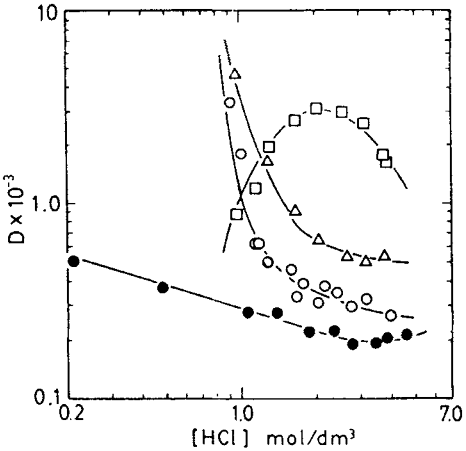


FIG. 6 Relationship between the distribution ratio of iridium(III) and hydrochloric acid concentration. Keys are the same as those in Fig. 4.

of cobalt, cerium, and manganese (6–9). Appreciable adsorption of rhodium(III), aluminum(III) and iron(III) was not observed under the present experimental condition on all of the adsorbents, suggesting the possibility of effective recovery of palladium, platinum, or iridium from various wastes by using some of the adsorbents developed in this work.

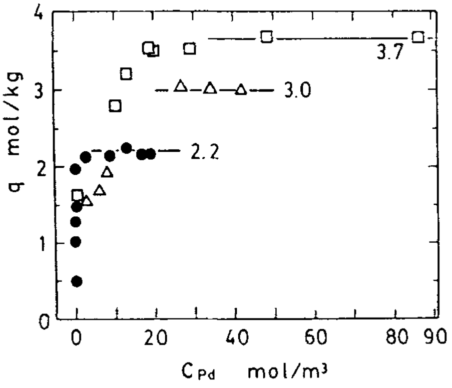


FIG. 7 Relationship between the amount of adsorbed palladium(II) (q) and palladium concentration in the aqueous solution after adsorption. Keys are the same as those in Fig. 4.

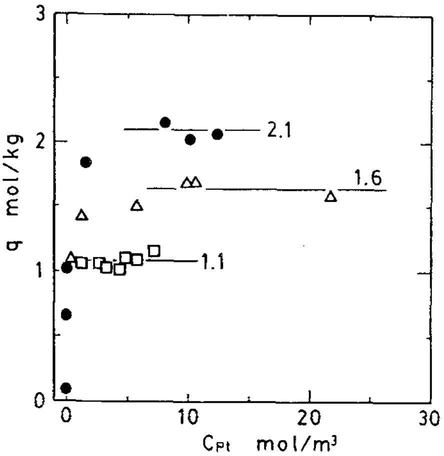


FIG. 8 Relationship between the amount of adsorbed platinum(IV) (q) and platinum concentration in the aqueous solution after adsorption. Keys are the same as those in Fig. 4.

Adsorption Isotherms of Palladium(II) and Platinum(IV)

Figures 7 and 8 show the relation between the amount of adsorbed palladium(II) and platinum(IV), respectively, from 10 mmol/dm^3 hydrochloric acid solution on the four kinds of the adsorbents and their concentration in the aqueous solution after adsorption. In both figures and for all of the adsorbents, the plots appear to lie on Langmuir-type adsorption isotherms which tend to approach certain constant values. The maximum adsorption capacities were evaluated for each adsorbent from these isotherms and for palladium(II) and platinum(IV) (listed in Table 1). The magnitude of the adsorption capacity of each adsorbent for palladium(II)

TABLE 1
Maximum Adsorption Capacities of Palladium(II) and Platinum(IV) on Each Adsorbent in the Adsorption from 10 mmol/dm^3 Hydrochloric Acid Solution

	$q_{\max}$ (mol/kg)			
	MCM-chitosan	IDA-chitosan	DTPA-chitosan	Crosslinked chitosan (3)
Pd(II)	3.0	3.7	2.2	2.2
Pt(IV)	1.6	1.1	2.1	1.6

is in the order MCM-chitosan = IDA-chitosan > DTPA-chitosan > crosslinked chitosan, while that for platinum(IV) is in the order DTPA-chitosan > MCM-chitosan = IDA-chitosan > crosslinked chitosan.

Elution of Palladium(II) and Platinum(IV) from the Loaded Adsorbents

Most adsorption, ion exchange, and solvent extraction processes of precious metals, palladium and platinum in particular, are irreversible and, consequently, are not necessarily appropriate for predicting the elution or stripping of these metals based on information of their adsorption or extraction behaviors. Difficulties of elution or stripping are frequently encountered when there is no choice except for burning off the metal-loaded adsorbents or solvents to recover the metal, which increases the costs of the recovery because of the consumption of expensive adsorbents or solvents and to the loss of some part of precious metals by volatilization with the burn-off gasses. For this reason, it is strongly desirable that the adsorbents or solvents free from any elution or stripping difficulties be developed. Elution tests were therefore carried out for the platinum(IV) or palladium(II) loaded adsorbents with varying concentrations of hydrochloric acid solution.

Figures 9 and 10 show plots of the percent elution of palladium(II) and platinum(IV), respectively, from the four kinds of adsorbents against the hydrochloric acid concentration. From these figures it is obvious that palladium(II) and platinum(IV) in particular are very difficult to elute from loaded crosslinked chitosan even at high concentrations of hydrochloric

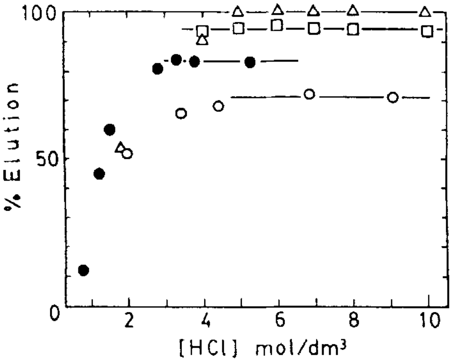


FIG. 9 Relationship between percent elution of palladium(II) from the palladium-loaded adsorbents and hydrochloric acid concentration. Keys are the same as those in Fig. 4.

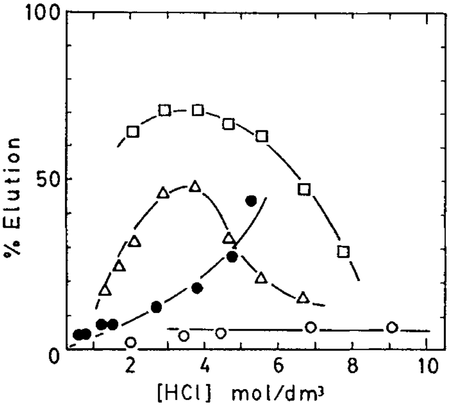


FIG. 10 Relationship between percent elution of platinum(IV) from the platinum-loaded adsorbents and hydrochloric acid concentration. Keys are the same as those in Fig. 4.

acid solutions; i.e., 70% and only about 5% of elution was achieved for palladium(II) and platinum(IV), respectively. Surprisingly, the elution characteristics were remarkably improved by chemical modification; that is, the maximum percent elution for palladium(II) was 100, 95, and 80, and for platrinum(IV) was 45, 70, and 45 from loaded MCM-chitosan, IDA-chitosan, and DTPA-chitosan, respectively.

REFERENCES

1. B. Volesky, *Trends Biotechnol.*, *5*, 96 (1987).
2. R. A. A. Muzzarelli, *Chitin*, Pergamon, London, 1977.
3. K. Inoue, Y. Baba, and K. Yoshizuka, *Bull. Chem. Soc. Jpn.*, *66*, 2915 (1993).
4. K. Inoue, K. Ohto, K. Yoshizuka, R. Shinbaru, Y. Baba, and K. Kina, *Bunseki Kagaku*, *42*, 725 (1993).
5. M. J. Cleare, P. Charlesworth, and D. J. Bryson, *J. Chem. Tech. Biotechnol.*, *29*, 210 (1979).
6. D. S. Flett, M. Cox, and J. D. Heels, *J. Inorg. Nucl. Chem.*, *37*, 2197 (1975).
7. P. Guesnet, J. L. Sabot, and D. Bauer, *Ibid.*, *42*, 1459 (1980).
8. T. Sekine, T. Ishii, and T. Fukaya, *Anal. Sci.*, *6*, 115 (1990).
9. T. Sekine and T. K. D. Nguyen, *Ibid.*, *9*, 361 (1993).

Received by editor October 5, 1994.