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

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To cite this Article Alam, M. Shafiqul , Inoue, Katsutoshi , Yoshizuka, Kazuharu and Ishibashi, Hideaki(1998) 'Adsorptive Separation of Rhodium(lll) Using Fe(Ill)- Templated Oxine Type of Chemically Modified Chitosan', Separation Science and Technology, 33: 5, 655 — 666

To link to this Article: DOI: 10.1080/01496399808544781

URL: http://dx.doi.org/10.1080/01496399808544781

SEPARATION SCIENCE AND TECHNOLOGY, 33(5), pp. 655-666, 1998

Adsorptive Separation of Rhodium(III) Using Fe(III)-Templated Oxine Type of Chemically Modified Chitosan

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ABSTRACT

The oxine type of chemically modified chitosan was prepared by the template crosslinking method using Fe(III) as a template ion. Batchwise adsorption of rhodium(III) on this chemically modified chitosan was examined from chloride media in the absence and presence of a large amount of tin(II). It was observed that the Fe(III)-templated oxine type of chemically modified chitosan shows better performance for rhodium adsorption than that of the original chitosan. When Sn(II) is absent from the solution, Rh(III) is hardly adsorbed on the modified chitosan and the order of selectivity of the adsorption of Rh(III), Pt(IV), and Cu(II) was found to be Pt(IV) $>$ Cu(II) $\approx$ Rh(III). On the other hand, adsorption of rhodium is significantly increased in the presence of Sn(II) and the selectivity order of the adsorption was drastically changed to Rh(III) $>$ Pt(IV) $\gg$ Cu(II), which ensures selective separation of Rh(III) from their mixture. Adsorption of Rh(III) increases with an increase in the concentration of Sn(II) in the aqueous solution, and maximum adsorption is achieved at a molar ratio, [Sn]/[Rh], of >6. The adsorption of Rh(III) decreases at a high concentration of hydrochloric acid. The maximum adsorption capacity was evaluated to be 0.92 mol/kg-dry adsorbent. Stripping tests of rhodium from the loaded chemically modified chitosan were carried out using different kinds of stripping agents containing some oxidizing agent. The maximum stripping of rhodium under these experimental conditions was found to be 72.5% by a single contact with 0.5 M HCl + 8 M HNO_3.

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INTRODUCTION

Rhodium is one of the most expensive platinum group metals (about US$210/ounce-troy in early 1997) and is indispensable for automobile catalytic converters in particular. 70% of the catalyst for purification of automobile exhaust gas is composed of a three-metal composite (Rh, Pt, and Pd) where the ratio of Pt/Rh is 5:1 to 10:1. A catalyst with a high quantity of Rh is better for purification. In the mining ore, Since the ratio of Pt/Rh is about 20:1 in mined ores, there is a lack of Rh as a natural resource. To solve the problem of this shortage in the amount of Rh, it is necessary to develop a more efficient recovery process for Rh from the spent catalyst as well as from mining ores.

Most of the leach liquor of platinum group metals are in chloride media, and in this media Rh is coordinated with the chloride ion to form various kinds of kinetically inert aquachloro complexes (1). The separation and purification of rhodium is one of the most difficult parts of processing platinum group metals. It is known that the addition of Sn(II) chloride to an aqueous solution containing Rh(III) results in the formation of dinuclear complexes between Rh and $SnCl_3^-$, reducing trivalent rhodium to the monovalent state (2–6). Since these complexes are more labile than aquachloro complexes of Rh(III), these complexes have a high affinity to 8-quinolinol-type ligands (6–8).

Chitosan has been used as an effective coagulating agent in activated sludge plants and for recovering proteins from food processing factories. Recently much attention has been drawn to the adsorption of metal ions on chitosan derivatives because this inexpensive polysaccharide acts as an excellent natural metal adsorbent with higher selectivity than conventional commercial chelating resins. However, most work is related to the adsorption of base metals, rare earths, and some toxic heavy metals (9–14). Only a few studies have been carried out on the separation of platinum group metals using chitosan derivatives, but successful adsorption and separation of rhodium has not been achieved (15, 16).

In the present work, a Fe(III)-templated oxine type of chemically modified chitosan [henceforth, Fe(III)-templated oxine chitosan] was prepared to examine the adsorptive separation of Rh(III) from chloride media containing Sn(II).

EXPERIMENTAL

Synthesis of Fe(III)-Templated Oxine Chitosan

A sample of chitosan, produced and marketed under the trade name Chitosan 95L, was kindly donated by Katokichi Co., Kan-onji, Japan, and was used as received without further purification. The degree of deacetylation of the sample chitosan was above 95%. The synthetic route to Fe(III)-templated oxine chitosan was nearly the same as in a previous paper (17) where Fe(III) was used instead of Ga(III) for templation. Chitosan (40 mmol) dissolved in 20 wt% aqueous acetic acid solution was stirred with 80 mmol 5-chloromethyl-8-quinolinol hydrochloride also dissolved in 20 wt% acetic acid solution at 80°C for 67 hours during which 1.43 mol triethylamine was added dropwise as a catalyst. Here, 5-chloromethyl-8-quinolinol hydrochloride was prepared by stirring 8-quinolinol and formaldehyde in concentrated hydrochloric acid solution with bubbling hydrogen chloride gas according to the method proposed by Kolobielski (18). The product was filtered and washed with diethyl ether and ethanol to remove excess 5-chloromethyl-8-quinolinol hydrochloride and triethylamine, and further washed with deionized water to neutral pH to obtain a yellow powder of the final product, the oxine type of chemically modified chitosan.

The oxine type of chemically modified chitosan was crosslinked according to the template crosslinking method to avoid its loss by dissolution in acidic media caused by the protonation of the quinoline nitrogen atom at low pH as well as deprotonation of the hydroxyl group of quinolinol at high pH. In template crosslinking though the target metal ion, i.e., the metal ion which should be slectively adsorbed should be used as the template metal ion, Fe(III) ion was used instead of Rh(III) ion for economic reasons of view in this experiment, because the atomic radii of these metal ions are close (Fe = 1.72 Å and Rh = 1.83 Å). To ensure the selectivity of the oxine type of chemically modified chitosan toward the Fe(III) ion, its adsorption on the uncrosslinked oxine type of chemically modified chitosan was examined prior to template crosslinking. It was found that the maximum amount of Fe(III) adsorption appears at pH ~1.3, and the maximum amount of adsorption of Fe(III) ion was determined as 0.77 mol/kg-dry adsorbent. This result ensures that Fe(III) ion is suitable as a templating ion owing to its high affinity for protecting the adsorption sites against attack by the crosslinking agents. In the crosslinking process, 50 mg of the oxine type of chitosan was stirred in 0.5 dm^3 dilute sulfuric acid solution containing 3.8 $mmol/dm^3$ Fe(III) nitrate at pH 1.3 to give rise to a Fe(III) chelate with oxine groups, which was then crosslinked with 75.3 mmol glycerolpolyglycidylether using 25 mmol zinc fluoroborate as a catalyst at 65°C for 110 hours. The powder product was filtered and washed with 0.2 dm^3 of 2 mol/dm^3 sulfuric acid solution to remove Fe(III) to obtain the final product, the Fe(III)-templated oxine chitosan. It was identified by its infrared spectrum, where characteristic peaks appeared at around 1504 and 1636 cm^{-1} due to the resulting C=C and C=N bonds, respectively. The average size of the powder product was around 0.1 mm.

Preparation of Aqueous Solutions

The aqueous metal solutions were prepared by dissolving $RhCl_3$ (Tanaka Kikinzoku Kogyo Co. Ltd., Tokyo, Japan) and stannous chloride (Wako Pure Chemical Industries Ltd., Osaka, Japan) in hydrochloric acid solution. Other chloride salts of Fe(III), Pt(IV), and Cu(II) were used for associated experiments. Hydrochloric acid, nitric acid, and sulfuric acid containing sodium sulfate were used as stripping agents accompanied with some oxidizing agents such as $KMnO_4$, H_2O_2, and HNO_3. All the chemicals employed in this work were of reagent grade.

Adsorption and Stripping of Metal Ions

The adsorption behavior of the original and Fe(III)-templated oxine chitosan for metal ions from chloride media was examined by batchwise experiments. It is noted that chitosan is totally dissolved in organic acids, such as acetic acid and formic acid, and partially soluble in some mineral acids, nitric, hydrochloric, and perchloric acids, in the 0.05–0.5 mol/dm^3 concentration range (10). Therefore, in this experiment, a higher concentration range (>0.5 mol/dm^3) of hydrochloric acid was chosen in which the original chitosan is not dissolved. The stripping tests were carried out using different kinds of stripping agents containing oxidizing agents. About 50 mg of the adsorbents and 0.015 dm^3 of aqueous solution containing metal ions were shaken in a stoppered glass flask immersed in a water bath maintained at 30°C for over 24 hours to attain equilibrium. After shaking, aqueous solution was separated from the adsorbent by filtration. Initial and equilibrium concentrations of metal ions in the aqueous solutions were determined by using a Seiko model SAS 7500 atomic absorption spectrophotometer for all experiments except those for stripping tests. Metal concentrations in the aqueous stripping solutions were determined by a Shimadzu model ICPS-1000 III sequential-type plasma emission spectrometer. The amount of metal ion adsorbed and the distribution ratio was calculated according to the following equations:

$$q = (C_i - C_e) \times L/W \tag{1}$$

$$D = q/C_e \tag{2}$$

where q = amount of metal adsorbed (mol/kg), D = distribution ratio (dm^3/kg), C_i = initial metal concentration in the aqueous solution (mol/dm^3), C_e = metal concentration in the aqueous solution after equilibrium (mol/dm^3), L = volume of aqueous feed solution (dm^3), and W = weight of dry adsorbent (kg).

RESULTS AND DISCUSSION

Adsorption of Rhodium in the Absence of Tin

Adsorption of Rh(III) from varying concentrations of hydrochloric acid was examined in the absence of Sn(II) prior to adsorption in the presence of Sn(II). In addition, adsorption of Cu(II) and Pt(IV) was also examined for comparison with Rh(III) adsorption. Figure 1 shows the logarithmic plot of the distribution ratio against hydrochloric acid concentration, where it was found that Pt(IV) was adsorbed most selectively. However, very poor adsorption behavior for Rh(III) and Cu(II) was observed. Such a poor adsorption for Rh(III) may be attributed to the complicated chemistry of Rh(III) in chloride solution. That is, Rh(III) gives rise to seven kinds of aquachloro complexes from hexa-aqua-rhodate $[Rh(H_2O)_6^{3+}]$ to hexa-chloro-rhodate $[RhCl_6^{3-}]$ among which hydrophilic aqua complexes which do not usually respond well to direct solvent extraction are predominant in the concentration region below 5 mol/dm^3 where extensive aquation takes place (1). Therefore, when Sn(II) is absent in the feed solution, only a small amount of Rh(III) is adsorbed over the whole concentration region of hydrochloric acid.

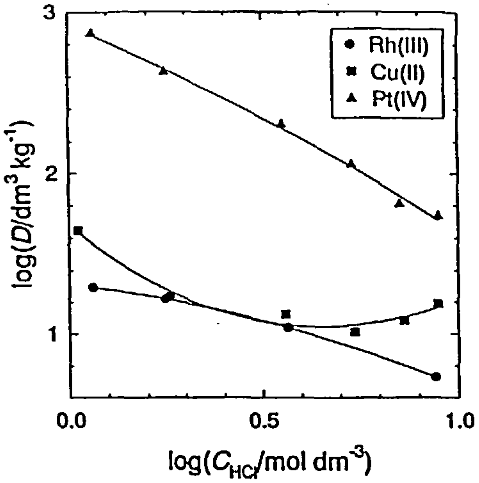


FIG. 1 Logarithmic plot of distribution ratio (D) against HCl concentration in the adsorption of metal ions on modified chitosan in the absence of Sn(II). Initial metals concentration in the aqueous solution is Rh(III): 9.7 × 10^{-4} mol/dm^3, Cu(II): 1.6 × 10^{-3} mol/dm^3, and Pt(IV): 5.1 × 10^{-4} mol/dm^3.

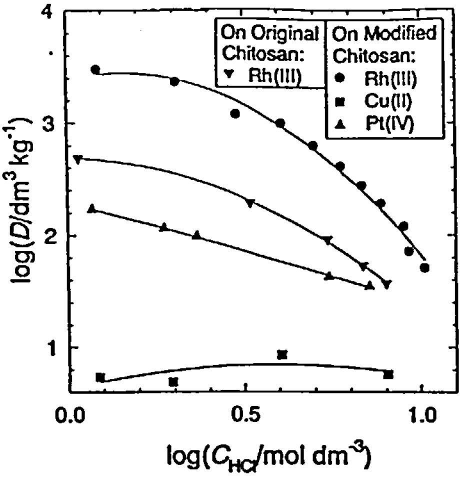


FIG. 2 Logarithmic plot of distribution ratio (D) against HCl concentration in the adsorption of metal ions on chitosan in the presence of Sn(II). Initial metals concentration in the aqueous solution is Rh(III): 9.7×10^{-4} mol/dm^3, Cu(II): 1.6×10^{-3} mol/dm^3, Pt(IV): 5.1×10^{-4} mol/dm^3, and Sn(II): 8.4×10^{-3} mol/dm^3.

Adsorption of Rhodium in the Presence of Tin

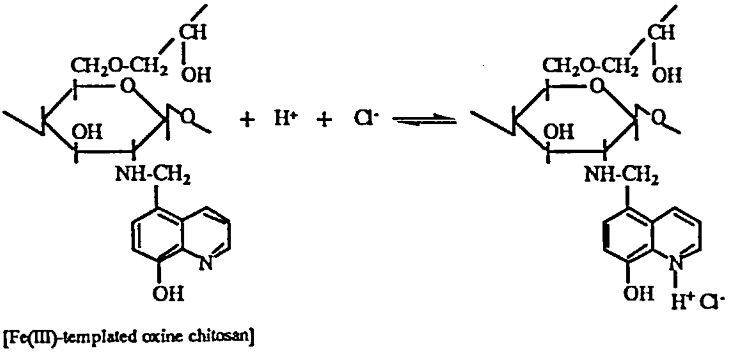
Figure 2 shows the logarithmic plot of the distribution ratios of Rh(III), Cu(II), and Pt(IV) on Fe(III)-templated oxine chitosan in the presence of Sn(II). It was found that the adsorption behavior of Rh(III) was significantly changed in the presence of Sn(II). However, Pt(IV) and Cu(II) demonstrated lower distribution ratios than the Sn(II) free system as mentioned before, which may be attributable to the coadsorption of Sn(II) on chemically modified chitosan (8). Of course, Sn(II) is also coadsorbed during Rh(III) adsorption, but the role of Sn(II) is rather important for activation of rhodium complexes which ultimately enhance overall rhodium recovery. This is because that when a large amount of Sn(II) is added to the feed solution, all trivalent rhodium complexes are reduced to the monovalent state by the oxidation of Sn(II) to Sn(IV) and is complexed with $SnCl_3^-$ anion according to Eqs. (3) and (4). These complexes are more labile than other kinetically inert chloride complexes of rhodium due to the strong π acid nature of $SnCl_3^-$ (19, 20).

$$RhCl_6^{3-} + 6SnCl_3^- \rightarrow [Rh(SnCl_3)_5]^{4-} + SnCl_6^{2-} + 3Cl^- \qquad (3)$$

$$RhCl_5(H_2O)^{2-} + 6SnCl_3^- \rightarrow [Rh(SnCl_3)_5]^{4-}$$
$$+ SnCl_6^{2-} + 2Cl^- + H_2O \qquad (4)$$

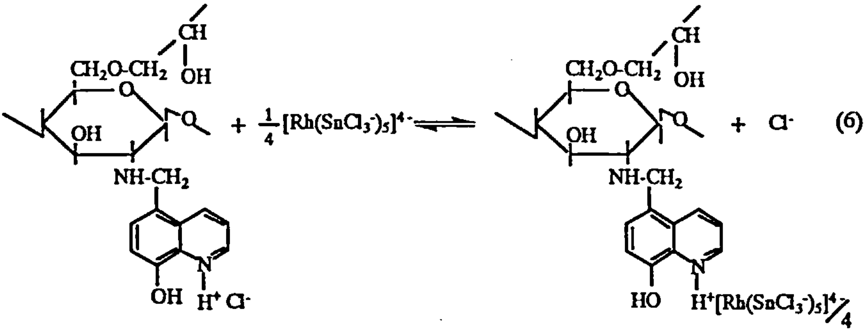
Therefore, almost quantitative adsorption of rhodium takes place when a large amount of Sn(II) is added to the chloride solution, though the adsorption decreases in the high chloride concentration region due to the mass effect of released chloride ion (Eq. 6).

Protonation:



(5)

Ion-pair formation:



(6)

The presumed adsorption reactions are shown by Eqs. (5) and (6), where the functional groups of oxine in the matrices of chitosan are first protonated by hydrochloric acid and then these protonated functional groups interact with anionic complexes of monovalent rhodium through ion-pair formation.

By adding a large amount of Sn(II) to the aqueous solution, the adsorption order is changed to Rh(III) > Pt(IV) ≫ Cu(II), which ensures selective separation of Rh(III) away from Pt(IV) and Cu(II). A similar tendency was observed for the extraction of Rh(III) from other platinum group metals with Kelex 100 (8). It was also found that the adsorption of Rh(III) on original chitosan is lower as a whole when compared with Fe(III)-templated oxine chitosan. Better adsorption on chemically modified chitosan can be attributed to the

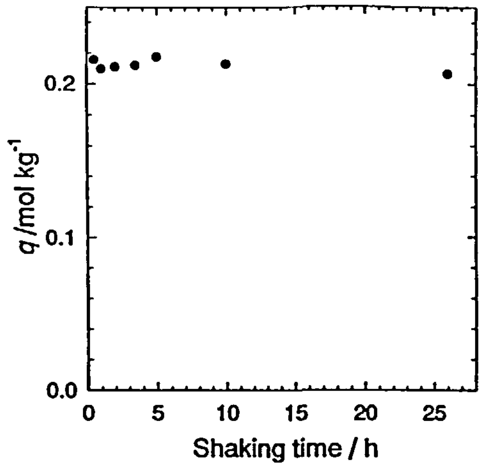


FIG. 3 Relationship between amount of rhodium adsorbed on the chemically modified chitosan and shaking time in the adsorption from 3.84 mol/dm^3 HCl solution. Initial metals concentration in the aqueous solution is Rh(III): 9.7 × 10^{-4} mol/dm^3 and Sn(II): 8.4 × 10^{-3} mol/dm^3.

strong affinity of the aqua-chloro complexes of rhodium to the functional group of oxine in the matrices of chitosan (6–8).

Figure 3 shows the plot of the amount of rhodium adsorbed on Fe(III)-templated oxine chitosan against shaking time in the adsorption from 3.84 mol/dm^3 hydrochloric acid solution as a typical example. From this figure it is obvious that the adsorption rate of rhodium is very fast, and the adsorption attained equilibrium within half an hour.

Effect of the Concentration of Tin Added on Rhodium Adsorption

Figure 4 shows the effect of the concentration of added Sn(II) on Rh(III) adsorption. It was found that Rh(III) adsorption increases with increasing Sn(II) concentration and tends to approach a constant maximum value at a molar ratio of [Sn]/[Rh] > 6. At [Sn]/[Rh] ≦ 6, rhodium gives rise to less active compounds with tin in the form of $[Rh(SnCl_3)_nCl^{3-}_{6-n}]$, where n = 1–5, while at a molar ratio of [Sn]/[Rh] > 6 it gives rise to monovalent compounds with tin like $[Rh(SnCl_3)^{4-}_5]$, which is more labile than the former and, hence, increases rhodium adsorption.

Maximum Adsorption Capacity of Rhodium

Figure 5 shows the relationship between the amount of Rh(III) adsorbed on Fe(III)-templated oxine chitosan and Rh(III) concentration in the aqueous

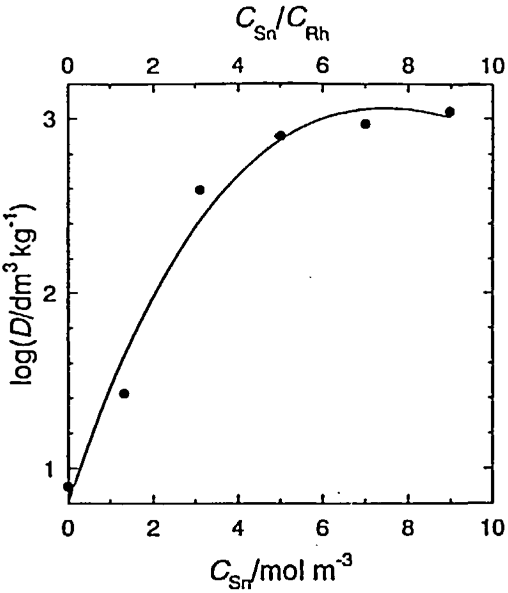


FIG. 4 Effect of the concentration of added Sn(II) on Rh(III) adsorption. Initial aqueous solution contains 9.7 × 10^{-4} mol/dm^3 Rh(III) in 1.2 mol/dm^3 HCl solution.

solution at the equilibrium state in 1.2 mol/dm^3 hydrochloric acid solution. The plots appear to lie on a Langmuir-type adsorption curve and tend to approach a constant value, from which the maximum adsorption capacity was evaluated to be 0.92 mol/kg-dry adsorbent, which is nearly the same value found by Inoue et al. (17) for Ga(III).

Stripping of Rhodium from Loaded Chitosan

The stripping of rhodium from the loaded modified chitosan was carried out batchwise by single contact with different kinds of stripping agents containing some oxidizing agents. In the previous study (8) on solvent extraction with Kelex 100, an oxine-type commercial chelating extraction reagent, it was found that rhodium stripping is very difficult because of the formation of a very stable complex of rhodium with the extractant. Since, as mentioned earlier, rhodium is adsorbed in the monovalent state, reoxidization to the trivalent state may be considered to facilitate stripping. Therefore, the oxidizing agents $KMnO_4$, H_2O_2, and HNO_3 were used to facilitate the possible stripping. Table 1 shows the results of rhodium stripping from the loaded Fe(III)-templated oxine chitosan. The maximum stripping under these experi-

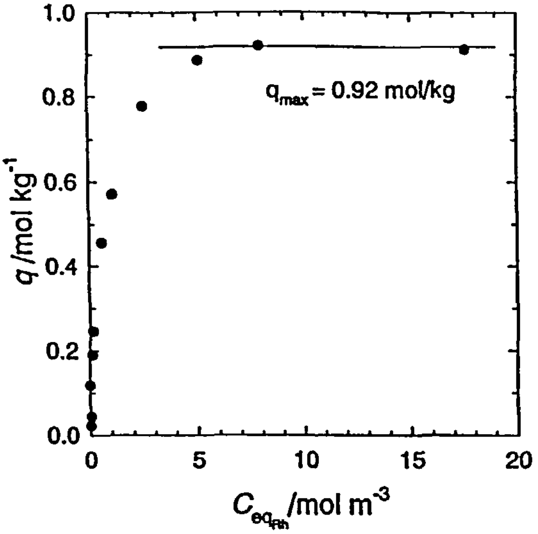


FIG. 5 Relationship between the amount of Rh(III) adsorbed on Fe(III)-templated oxine type of chemically modified chitosan and its equilibrium concentration in 1.2 mol/dm^3 HCl solution. Molar ratio of [Sn]/[Rh] = 6.

TABLE 1
Stripping of Rhodium (concentration of rhodium on the loaded modified chitosan is 0.29 mol/kg-dry adsorbent)

Stripping agent	% Stripping of Rh
1. 1.7 M H_2SO_4 + 0.5 M $KMnO_4$	44.0
2. 1.7 M H_2SO_4 + 1 M Na_2SO_4 + 1 M $KMnO_4$	16.7
3. 0.5 M HCl + 0.1 M $KMnO_4$	60.5
4. 1.7 M H_2SO_4 + 3 M H_2O_2	66.4
5. 1.7 M H_2SO_4 + 1 M Na_2SO_4 + 3 M H_2O_2	61.2
6. 0.5 M HCl + 3 M H_2O_2	60.7
7. 1.7 M H_2SO_4 + 2 M HNO_3	52.5
8. 1.7 M H_2SO_4 + 8 M HNO_3	70.2
9. 1.7 M H_2SO_4 + 12 M HNO_3	70.7
10. 1.7 M H_2SO_4 + 1 M Na_2SO_4 + 5 M HNO_3	67.2
11. 1.7 M H_2SO_4 + 1 M Na_2SO_4 + 12 M HNO_3	70.7
12. 0.5 M HCl + 8 M HNO_3	72.5
13. 0.5 M HCl + 12 M HNO_3	64.9
14. 5 M HNO_3	50.4
15. 10 M HNO_3	64.6
16. 12 M HNO_3	64.4

mental conditions was found to be 72.5% for a single contact with 0.5 M HCl + 8 M HNO_3.

CONCLUSIONS

Fe(III)-templated oxine type of chemically modified chitosan was prepared by the template crosslinking method to investigate its adsorption behavior for Rh(III) from chloride media containing Sn(II), together with the stripping of Rh(III) from the loaded adsorbent. The followings conclusions were reached.

1. When Sn(II) is absent from the solution, Rh(III) is hardly adsorbed on the modified chitosan. The order of adsorption for Rh(III), Pt(IV), and Cu(II) was found to be Pt(IV) $>$ Cu(II) $\approx$ Rh(III).
2. Adsorption of Rh(III) is significantly enhanced in the presence of Sn(II), and the selectivity order of adsorption was changed to Rh(III) $>$ Pt(IV) $\gg$ Cu(II), which ensures the selective separation of Rh(III) from their mixture.
3. Adsorption of Rh(III) increases with an increase in the concentration of Sn(II) in aqueous solution, and maximum adsorption is achieved at a molar ratio of [Sn]/[Rh] $>$ 6.
4. The adsorption of Rh(III) decreases at a high concentration of hydrochloric acid, and the maximum adsorption capacity was evaluated to be 0.92 mol/kg-dry adsorbent.
5. The Fe(III)-templated oxine type of chemically modified chitosan shows better performance for Rh(III) adsorption than does the original chitosan.
6. Stripping agents containing some oxidizing agents are able to strip rhodium from loaded chemically modified chitosan, and the maximum stripping of rhodium under these experimental conditions was found to be 72.5% by a single contact with 0.5 M HCl + 8 M HNO_3.

ACKNOWLEDGMENTS

This work was financially supported in part by a Iwatani Naoji Foundation Research Grant. The authors gratefully acknowledge the kind supply of the chitosan sample from Katokichi Co. Ltd., Japan as well as the kind provision of ICP analyses by the Industrial Technology Center of Saga, Japan.

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Received by editor April 7, 1997
Revision received July 1997