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UPTAKE PROPERTIES OF PALLADIUM FOR BIOPOLYMER MICROCAPSULES ENCLOSING CYANEX 302 EXTRACTANT

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ABSTRACT

An extractant having a strong affinity for palladium, *bis*(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302), was enclosed into microcapsules by mixing with a biopolymer, calcium alginate gel polymer. The uptake of Pd^{2+} and other metal ions in the microcapsules was investigated; a relatively large distribution coefficient of Pd^{2+}, $K_{d,Pd}$, of above 10^3 cm^3/g was obtained around 0.1 M HNO_3, and there was a large difference in K_d value between Pd^{2+} and other metal ions. The uptake of Pd^{2+} on microcapsules followed a Langmuir-type uptake isotherm. The microcapsules were packed into a column and then a separation of Pd^{2+} was performed.

Key Words: Uptake; Palladium; Biopolymer; Microcapsule; Cyanex 302; Alginate gel; Separation factor.

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INTRODUCTION

Special attention has been given to the separation and recovery of platinum group metals (PGMs; palladium, ruthenium, and rhodium) in relation to the partitioning of high-level liquid waste (HLLW) generated in nuclear fuel reprocessing processes (1,2).

A number of effective extraction methods using TBP, organophosphines, and amines have been developed for the separation of palladium (1). TBP extraction methods need to reduce HLW acidity to 0.5 *M* and to make the concentration of the salting-out reagent 4 *M* or more (3,4). Rare earth elements and actinoids will be extracted together with Pd by TBP under such conditions. It is possible to separate Pd from HLLW by means of organophosphines (5,6). This method is more attractive, because organophosphines do not require a salting-out agent and permit the extraction of Pd from solutions with nitric acid concentration up to 1 *M*. As for extractants, amines, and quaternary ammonium salts, certain difficulties can arise with Pd decontamination from Pu(IV) and Np(IV), which are well extracted by tertiary amines and quaternary ammonium salts (1). Technetium will be extracted together with Pd. The separation of these elements can be carried out at the backwashing stage.

In order to utilize these extractants having high affinity to Pd, the microencapsulation seems to be one of the most attractive techniques for the practical column operation. A few attempts for the encapsulation of extractants, 2-hydroxymes, and tri-*n*-octyl amine has been performed (7,8), but these procedures for preparation were rather complicated and the works were mainly focused on the characterization of physicochemical properties of microcapsules.

Organic binding polymers for the encapsulation have a number of advantages such as the simplicity of preparation procedure, high porosity, high content of active component, and mechanical strength (9,10). The gel network of the polymeric materials is further expected to increase the viscosity and to prevent the extractant from leaching out. Alginic acid is a biopolymer that occurs in brown seaweeds and has carboxyl groups capable of forming complexes with calcium ions (11). Recently, the gel-forming property of this polymer has led to its extensive use in biomedicine and biotechnology industry to immobilize or encapsulate enzymes, subcelluler organelles, and living cells (11–14). Thus, the prominent immobilizing ability of alginates seems to be applicable to the encapsulation of organic extractants. In this study, we have attempted to encapsulate Cyanex 302 extractant into the porous alginate gel polymer for the selective separation of Pd^{2+} (15,16). The present paper deals with the preparation of microcapsules enclosing Cyanex 302 and selective uptake of Pd^{2+} from nitric acid solutions.

EXPERIMENTAL

Preparation of Microcapsules

Sodium alginates (NaALG) with different viscosities of 100–150, 300–400, and 500–600 cP were obtained from Wako Pure Chemical Ind. Cyanex 302 (*bis*(2,4,4-trimethylpentyl) monothiophosphinic acid, HA) was supplied by Cyanamid and used without further purification.

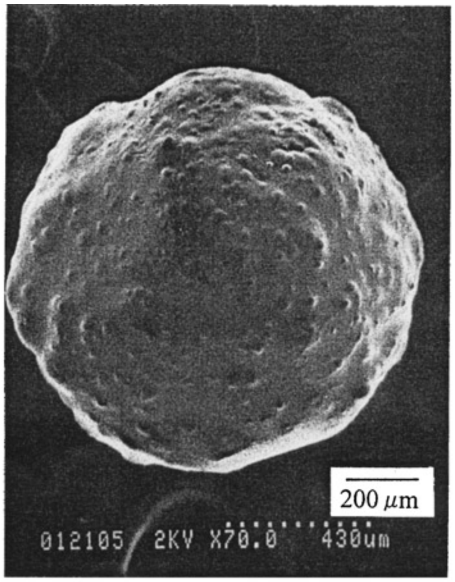
The calcium alginate gel microcapsules enclosing Cyanex 302 (abbreviated as HA-CaALG) were prepared as follows. HA extractant was kneaded with a viscous solution of 1.0 or 1.5 wt.-% NaALG and then kneaded sol was added dropwise to a 0.5 M $CaCl_2$ solution using a syringe with stirring at room temperature to form spherical gel particles. The mixing ratio of weight of HA extractant (g) to volume of NaALG solution (cm^3) was varied from 0.1/50 to 3.0/50 g/cm^3. After an overnight shaking, gel particles became rigid and turned an opaque white color. They were separated from the calcium solution, air-dried at 40°C for 2 d, and finally stored in a sealed vessel over a saturated NH_4Cl solution (humidity: 79% at 25°C). The microcapsules prepared under diferent conditions are listed in Table 1.

The surface morphology and physicochemical properties of HA-CaALG microcapsules were examined by scanning electron microscopy (SEM, Hitachi 4100-L), infrared spectrophotometry (IR, Hitachi 260-50), and electron probe microanalysis (EPMA, Hitachi X-650S). The specimens of microcapsule for SEM were air-dried at 40°C and coated with platinum. The accelerating voltage of electron beam was 10.0 keV. The microcapsule specimens dried at 40°C were embedded in the acrylic resin and coated with carbon for EPMA analysis. The accelerating

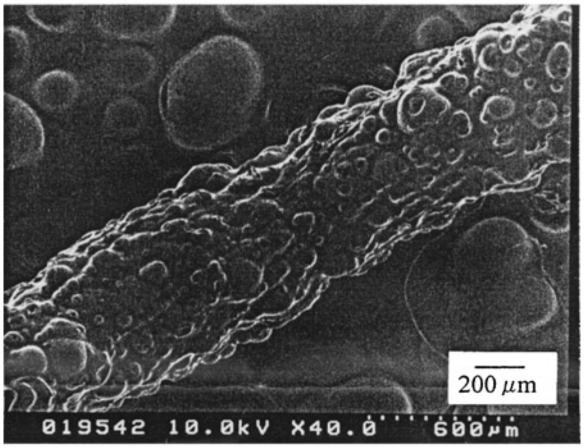
Table 1. Description of Microcapsules Used in This Study

Microcapsule	Component of Kneaded Sol	Mixing Ratio (HA/NaALG, g/cm^3)	Particle Size (mm)
HA-CaALG(I)	HA-1.5 wt.-% NaALG(500–600 cP)	3.0/50	1.6
HA-HALG[a]	HA-1.5 wt.-% NaALG(500–600 cP)	3.0/50	1.2
HA-CaALG(II)	HA-1.0 wt.-% NaALG(500–600 cP)	0.5/50	1.2
HA-CaALG(III)	HA-1.0 wt.-% NaALG(500–600 cP)	0.3/50	1.0
HA-CaALG(IV)	HA-1.0 wt.-% NaALG(500–600 cP)	0.1/50	0.90
HA-CaALG(V)	HA-1.0 wt.-% NaALG(300–400 cP)	0.1/50	0.91
HA-CaALG(VI)	HA-1.0 wt.-% NaALG(100–150 cP)	0.1/50	0.90
HA-CaALG(VII)[b]	HA-1.5 wt.-% NaALG(100–150 cP)	1.5/50	1.2

Gelling agent: 0.5 M $CaCl_2$: Drying temperature: 40°C.
[a] HA-CaALG treaded with 0.1 M HCl.
[b] HA-CaALG(VII) microcapsule was used for the elution experiment.



a) Spherical form



b) Columnar form

Figure 1. SEM images of HA-CaALG microcapsule dried at 40°C: a) spherical form and b) columnar form.

voltage and incident current were 15.0 keV and 10^2 pA, respectively. The accumulating time and energy range for EDS were 10^2 s and 0–10.24 keV, respectively.

The microcapsules with various shapes such as spherical, columnar, and fibrous forms were easily prepared by changing the way of dipping kneaded sol into calcium salt solution. Figures 1a and b show the SEM images of spherical and columnar microcapsules of HA-CaALG prepared from the kneaded sol of HA and 1.5 wt.-% NaALG solution with a mixing ratio of 1.5/50 g/cm^3. A number of oil drops of HA about 50 μm in diameter are seen to be uniformly encapsulated in the calcium alginate gel matrices. Here the oil drops of HA are encapsulated in the alginate gel matrices cross linked with Ca^{2+} ions, and the cross section of gel matrices has been reported to exhibit "egg-box structure," which brings about high porosity and mechanical strength of microcapsule (11,12).

The diameter of spherical microcapsules tended to increase with the content of HA enclosed; for example, the diameters of the microcapsules prepared at mixing ratio of 1.5/50 and 3.0/50 g/cm^3 were estimated to be 1.2 and 1.6 mm, respectively. The encapsulation at higher mixing ratio above 5.0/50 g/cm^3 resulted in an ooze of extractant through the wall of gel matrices. The acid treatment of microcapsules with 1 M HNO_3 led to an apparent contraction of about 8% in volume, probably due to the replacement of crosslinking cations of Ca^{2+} with H^+ in the gel matrices. The changes in viscosity of NaALG solution had no influence on the size of microcapsules.

Determination of Distribution Coefficient

The distribution coefficients of various metal ions for HA-CaALG microcapsules were determined by batch method. An aqueous solution (7 cm^3) containing 10^2 ppm metal ion was contacted with 0.070 g of microcapsules at 25 ± 1°C for 3 d, which was found to be sufficient for attaining equilibrium. The distribution of several metal ions was investigated using the radioisotopes, ^{137}Cs, ^{22}Na, ^{85}Sr, ^{60}Co, ^{152}Eu, and ^{241}Am. The γ-activity of the supernatant was then measured with a well-type NaI(T1) scintillation counter. A radioisotope ^{241}Am was obtained from the Radiochemical Centre (UK) as an oxide, and it was dissolved in HNO_3-HF solution by heating and diluted with 0.1 M HNO_3. The concentration of carrier-free ^{241}Am used for the distribution experiments was $2.1 \times 10^{-9} M$. A radioactive tracer ^{85}Sr was produced by the $^{86}Sr(\gamma, n)^{85}Sr$ reaction with 50 MeV bremsstrahlung from an linear accelerator (LINAC) in Laboratory of Nuclear Science, Tohoku Univ., and was dissolved with 0.1 M HNO_3. As for Pd, Ru, and Rh, their solutions were obtained by diluting standard solutions (5×10^3 ppm Pd^{2+} and 10^3 ppm Rh^{3+}: Wako Pure Chemical Ind., 10^3 ppm Ru^{3+}: Aldrich Chem. Inc.), and the concentrations of these metal ions were measured by atomic absorption spectrophotometry (AAS, SEIKO I. SAS 760).

The uptake percentage of metal ions removed from the solution, R (%), and the distribution coefficient, K_d (cm^3/g), are defined as

$$R = [(A_i - A_t)/A_i] \times 100 \quad (\%) \tag{1}$$

$$K_d = [(A_i - A_f)/A_f] \times V/m \quad (\mathrm{cm^3/g}) \tag{2}$$

where A_i, A_t, and A_f (cpm/cm^3) are the concentrations or counting rates at the initial stage, at time t, and at equilibrium, respectively; m (g) the weight of HA-CaALG microcapsule; V (cm^3) the volume of aqueous phase.

Breakthrough Curve and Elution Chromatogram

The HA-CaALG microcapsule (1 g) was previously degassed at reduced pressure in 0.1 M HNO_3 solution and then packed into a glass column (6 mm $\phi \times 200$ mm long) with a jacket thermostated at 25°C. The column volume of microcapsule was 3.0 cm^3. A feed solution containing 100 ppm Pd^{2+}/0.13 M HNO_3 was then passed through the column at a constant flow rate of 0.27 cm^3/min [space velocity $(SV) = 5.4$/h]. Every 5 cm^3 of the effluent was fractionated, and their Pd^{2+} concentrations were measured by AAS. A breakthrough curve was obtained by plotting the breakthrough ratio (C/C_0) against the effluent volume, where C_0 and C (ppm) are the Pd^{2+} concentrations of the initial solution and the effluent, respectively. The elution of Pd^{2+} was performed by flowing HCl solution above 5 M as an eluent.

RESULTS AND DISCUSSION

Uptake Rate of Pd^{2+}

The uptake rate of Pd^{2+} was examined by using HA-CaALG microcapsules prepared at different mixing ratios of HA and NaALG. Figure 2 shows the effects of equilibration time on the uptake percentage, R(%), of Pd^{2+} on microcapsules prepared from kneaded sols with different content of HA. The uptake rate of Pd^{2+} on microcapsules tended to increase with content of HA enclosed, and relatively large R values above 95% were obtained within 2 d for the microcapsules prepared at the mixing ratio of 3.0/50 g/cm^3. The CaALG gel matrices can be altered to alginic acid (HALG) ones by acid treatment of microcapsule with 0.1 M HCl solution. The uptake rate for the microcapsule treated with 0.1 M HCl was slightly larger than that for the untreated one in the initial stage within 1 d, probably due to the contraction of gel matrices in volume. The increase in viscosity of NaALG resulted in a slight enhancement of the uptake rate. Unless otherwise noted, the microcapsules prepared at the mixing ratio of HA to NaALG (500–600 cP) of 3.0/50 g/cm^3 were used in the subsequent experiments.

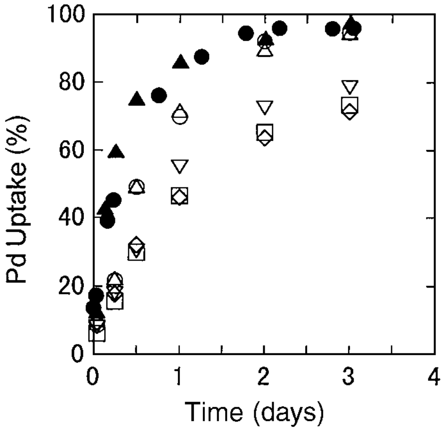


Figure 2. Uptake rate of Pd^{2+} on microcapsules prepared from different mixing ratios and viscosities of sodium alginate. (●): HA-CaALG(I), (▲): HA-CaALG(I) treated with 0.1 *M* HCl, (○): HA-CaALG(II), (△): HA-CaALG(III), (▽): HA-CaALG(IV), (□): HA-CaALG(V), (◇): HA-CaALG(VI); V/m, 100 cm^3/g; 100 ppm Pd^{2+}/0.13 *M* HNO_3; 25°C.

Distribution of Various Metal Cations

The affinity of various metal cations, Pd^{2+}, Cs^+, Na^+, Sr^{2+}, Co^{2+}, Eu^{3+}, Am^{3+}, $Ru(NO)^{3+}$, and Rh^{3+}, for HA-CaALG microcapsule was examined in the presence of HNO_3. Figure 3 shows the effect of initial concentration of HNO_3

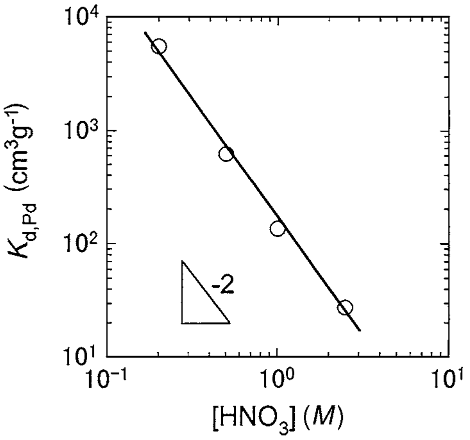


Figure 3. Effect of initial concentration of HNO_3 on distribution coefficient of Pd^{2+}. V/m: 100 cm^3/g, HA-CaALG(III); 100 ppm Pd^{2+}; 25°C; 3 d.

Table 2. K_d Values of Various Metal Cations for HA-CaALG Microcapsules

	K_d/cm^3 g^{-1}								
[HNO_3]/M	Pd^{2+}	$Ru(NO)^{3+}$	Rh^{3+}	Na^+	Cs^+	Sr^{2+}	Co^{2+}	Eu^{3+}	Am^{3+}
0.001	—	—	—	2.0	8.5	4.5×10^2	3.4×10^2	4.7×10^3	5.8×10^3
0.01	—	—	—	4.7	4.2	2.9×10^2	45	1.6×10^3	1.6×10^3
0.10	—	—	—	4.6	7.9	4.7	8.5	3.2	8.0
0.20	5.5×10^3	46	17	—	—	—	—	—	—
0.50	6.2×10^2	30	6.4	—	—	—	—	—	—
1.0	1.4×10^2	22	7.6	1.2	3.1	0.10	1.1	0.30	0.90
2.5	28	—	—	—	—	—	—	—	—

V/m 100 cm^3/g; [M^{n+}] 100 ppm, [Am^{3+}] 2.1×10^{-9} M; 25°C; 3 d. The final concentration of metal ions can be estimated from Equation (2). The K_d units are cm^3 of metal solution/grams of wet alginate microcapsule.

on distribution coefficient of Pd^{2+}. A logarithmic plot of distribution coefficient of Pd^{2+} against HNO_3 concentration gave a linear relation with a slope of -2.0, indicating that the uptake of Pd^{2+} with HA proceeds by following extraction reaction:

$$2(HA)_{2,org} + Pd^{2+}_{aq} \rightleftharpoons Pd(HA_2)_{2,org} + 2H^+_{aq} \tag{3}$$

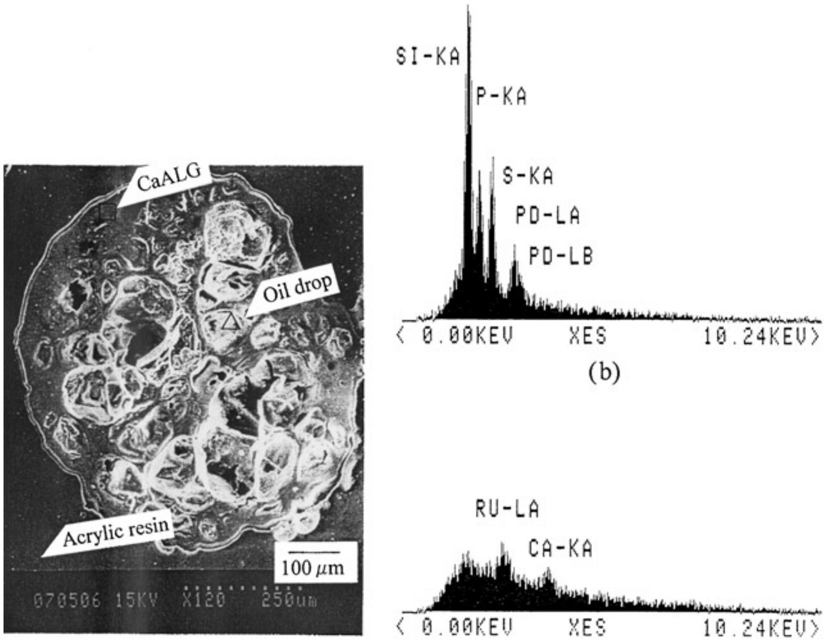
The authors have examined the uptake behavior of alginate polymer gels and found that the CaALG gel exhibited poor adsorbability toward Pd^{2+} in the presence of 0.1–3 M HNO_3. In the case of microcapsule of HA-CaALG, the Pd^{2+} ions seemed to be preferentially extracted with HA extractant in this concentration range of HNO_3.

The K_d values of various cations are summarized in Table 2. In the presence of 0.2–1.0 M HNO_3, K_d values of Pd^{2+} were much higher than those for other metal ions. For example, the separation factors of $Pd^{2+}/Ru(NO)^{3+}$ and Pd^{2+}/Rh^{3+} ($\alpha_{Pd/Ru} = K_d(Pd^{2+})/K_d(Ru(NO)^{3+})$ and $\alpha_{Pd/Rh} = K_d(Pd^{2+})/K_d(Rh^{3+})$) were estimated to be $6.4 \sim 1.2 \times 10^2$ and $18 \sim 3.2 \times 10^2$, respectively. Among platinum group metals, the uptake of $Ru(NO)^{3+}$ ions was somewhat higher than that of Rh^{3+}, due to the ion-exchange adsorption of CaALG gel matrices.

At lower concentrations of HNO_3 below 0.01 M, the K_d values of divalent and trivalent cations tended to increase markedly, and the K_d value increased in the order of Na^+, $Cs^+ \ll Co^{2+} < Sr^{2+} \ll Eu^{3+}$, Am^{3+}. The increase in K_d values of multivalent cations at lower HNO_3 concentration is due to both extraction and ion exchange in the microcapsule; these cations were extracted with HA and exchanged with crosslinking Ca^{2+} ions in gel matrices.

Uptake of Pd^{2+} and $Ru(NO)^{3+}$ in Microcapsule

The microcapsule was contacted with 10^2 ppm Pd^{2+}/10^2 ppm $Ru(NO)^{3+}$/10^2 ppm Rh^{3+}/0.13 M HNO_3 solution. The treated specimen was embedded in the acrylic resin, and the cross section of microcapsule was analyzed with EPMA. Here the acrylic resin was only used for the fixation of treated specimen for EPMA analysis. Figure 4a–c show the SEM image of the cross section of treated microcapsule and energy dispersive X-ray spectra (EDS) for oil drop and alginate matrices. The constitutional elements of P and S for Cyanex 302 and the extracted Pd^{2+} ions were detected in EDS spectrum for oil drop (Fig. 4b). The concentrations of Ca, Ru, and Rh were under detection limit of 0.3 wt.-%, indicating low extractability of HA toward these metal cations in the presence of 0.13 M HNO_3. In the CaALG gel matrices, small amounts of Ru were incorporated, probably due to the ion exchange adsorption (Fig. 4c). The maximum uptake capacity of Pd^{2+} for



(a) (b) (c)

Figure 4. EDS spectra for cross section of microcapsule treated with Pd-Ru-Rh solution. a) SEM image of cross section of microcapsule: △, point of EDS analysis for HA; □, point of EDS analysis for CaALG. b) EDS spectrum for oil drop of HA. c) EDS spectrum for CaALG gel matrices.

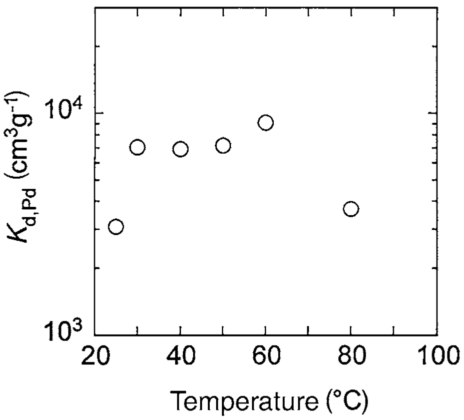


Figure 5. Effect of reaction temperature on K_d value of Pd^{2+}. V/m: 100 cm^3/g, HA-CaALG(III); 100 ppm Pd^{2+}/0.13 M HNO_3; 3 d.

the microcapsule (HA-CaALG(III)), prepared at the mixing ratio of 0.3/50 g/cm^3, was estimated to be 0.42 mmol/g from the Langmuir-type uptake isotherm.

Effect of Temperature on Pd^{2+} Uptake

The effect of reaction temperature on K_d of Pd^{2+} for the microcapsule is shown in Figure 5. The K_d value tended to increase with temperature up to 60°C. Relatively large K_d values above 7.0×10^3 cm^3/g were obtained at 30–60°C due to the apparent contraction of microcapsule. Oil drops were oozed from the wall of alginate gel matrices at 80°C, resulting in a considerable lowering of K_d value.

Effect of Acid Treatment on Pd^{2+} Uptake

The chemical durability of adsorbent was an important factor for the treatment of HLLW. In order to evaluate the acid resistance of microcapsules, the uptake behavior of Pd^{2+} was examined by using the specimens treated at different concentrations of HNO_3 and HCl up to 13 M. Figure 6 shows the comparison of $R(\%)$ values of Pd^{2+} for the microcapsules treated with HNO_3 and HCl. Relatively large R values above 99% were obtained for the specimens treated with HCl up to 8 M. In contrast, after treatment with HNO_3, the uptake ability gradually decreased with increasing its concentration, indicating the oxidative decomposition of Cyanex 302 extractant (15). These findings suggest that the microcapsules should be used at lower concentration of HNO_3 below 1 M and the concentrated HCl solution is effective for the elution of Pd^{2+} loaded on the column of microcapsule.

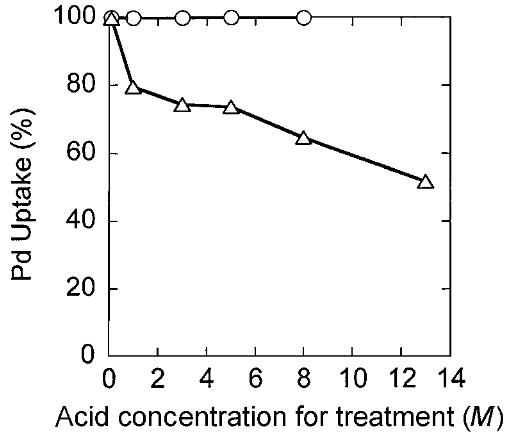


Figure 6. Uptake of Pd^{2+} for microcapsules treated with different concentrations of HNO_3 and HCl. (○) specimen treated with HCl, (△) specimen treated with HNO_3; V/m: 100 cm^3/g, HA-CaALG(III); 100 ppm Pd^{2+}/0.13 M HNO_3; 25°C; 3 d.

Breakthrough and Elution Properties of Pd^{2+}

The HA-CaALG microcapsules were packed in the glass column and were used for the removal of Pd^{2+} ions. The breakthrough curve of Pd^{2+} is shown in Figure 7. The breakthrough curve rose gently, indicating relatively low uptake rate

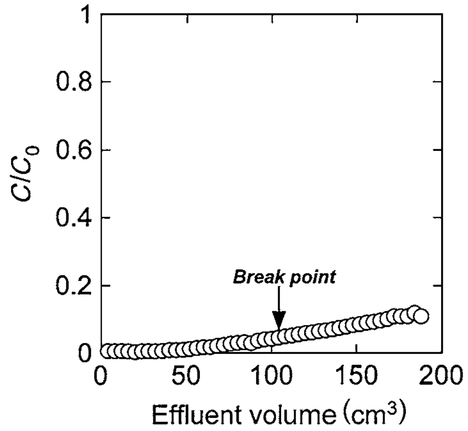


Figure 7. Breakthrough curve of Pd^{2+} through a column packed with HA-CaALG microcapsule. Column: 1 g HA-CaALG(III) microcapsule; feed: 100 ppm Pd^{2+}/0.13 M HNO_3; flow rate: 0.27 cm^3/min (SV: 5.4/h); 25°C.

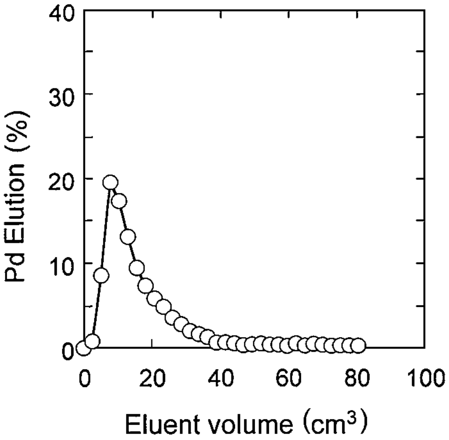


Figure 8. Elution chromatogram of Pd^{2+} through HA-CaALG column. Column: 0.5 g HA-CaALG(VII) microcapsule; amount of Pd^{2+} loaded: 0.43 mg; eluent: 8 *M* HCl/0.05 *M* HNO_3; flow rate 0.11 cm^3/min (*SV* 6.4/h); 25°C.

of Pd^{2+} in microcapsules. The 5% breakthrough was estimated to be 108 cm^3 [bed volume (BV) $=$ 36]. The breakthrough capacity (*B.T.Cap.*) and the uptake amounts of Pd^{2+} after flowing 200 cm^3 [BV $=$ 67] of feed were evaluated to be 9.5×10^{-2} and 0.17 mmol/g, respectively. The value of *B.T.Cap.* for microcapsule was about three times larger than that for copper ferrocyanide-CaALG composite (17).

The Pd^{2+} ions incorporated in the microcapsules were readily eluted by flowing concentrated HCl solution above 5 *M*. Figure 8 shows an elution chromatogram of Pd^{2+} obtained by passing 8 *M* HCl solution through the column packed with HA-CaALG(VII) microcapsules. The elution parameters, that is, retention volume (V_R) and total elution percentage, were evaluated to be 7.5 cm^3 and 99.4%, respectively. The microcapsule still exhibited high uptake ability after flowing HCl solution.

Thus, a relatively large break point and favorable elution chromatogram were obtained by using the HA-CaALG column. The HA extractant was immobilized in the alginate gel matrices, which are expected to prevent the extractant from leaching out (18); anomalous behavior due to the loss of extractant was not observed in this experiment. The column packed with HA-CaALG microcapsule was thus effective for the selective separation and recovery of Pd^{2+}.

CONCLUSIONS

The extractant of *bis*(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302, HA) was encapsulated in calcium alginate (CaALG) gel polymer.

The uptake of Pd^{2+} for HA-CaALG microcapsule was attained within 2 d, and the uptake rate increased with content of extractant and viscosity of alginate. The distribution of Pd^{2+} depended on HNO_3 concentration, and a relatively large $K_{d,Pd}$ value of above 10^3 cm^3/g was obtained around 0.1 M HNO_3. In the presence of 0.2–1.0 M HNO_3, the separation factors of Pd^{2+} and other cations such as $Ru(NO)^{3+}$ and Rh^{3+} were estimated to be $6.4 \sim 3.2 \times 10^2$. The continuous separation of Pd^{2+} ions was accomplished through the column packed with HA-CaALG microcapsules. The microencapsulation techniques with calcium alginate gel polymer can be considered applicable to various extractants.

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