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Adsorptive Separation of Palladium from a Simulated Nuclear Waste Solution with Activated Carbon Fibers

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Abstract: Adsorptive separation of palladium from a nitric acid solution was performed by using a pitch-based activated carbon fiber modified with NaOH (NaOH-ACF). The NaOH-ACF showed a markedly improved adsorption performance for the palladium ions as compared with the untreated ACF. It also showed a much higher preferential adsorption for the palladium ion over the rhodium and rhenium ions. The equilibrium capacity of the NaOH-ACF for palladium was $1.25 \text{ meq} \cdot \text{g}^{-1}$. The breakthrough behavior obtained by using the bed packed with the NaOH-ACF showed a complete separation of palladium from the coexisting ions of rhodium and rhenium. The spent bed was eluted effectively with nitric acid and a palladium nitrate with a purity of higher than 99% could be recovered.

Keywords: Carbon fibers, adsorption, palladium, chemical treatment

INTRODUCTION

Activated carbon fiber (ACF) has long been reviewed as an excellent adsorbent for various separation and purification processes due to its novel properties such

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as a high specific surface area, a high adsorption capacity, and a highly micro-porous structure (1–3). Furthermore, it has different reactive functional groups on its surface, which can be used for an ion exchange of various ionic substances. The functional groups or surface conditions of ACFs can be modified chemically, depending on the application purpose (4–10). Shim et al. (4) studied a modification of an ACF with HNO_3 and NaOH for a metal adsorption. They reported that the treatment of an ACF with an acid or a base solution changed the surface properties by creation of new functional groups and modified the structural properties of the adsorbents, thereby leading to an improvement in the metal adsorption performances. Ko et al. (5) carried out the ozone treatment of an ACF for the purpose of Cr (VI) and Cu (II) adsorption. The application of ACFs for the recovery of precious metals has also been reviewed in published literature (10–12). Fu et al. (10, 11) introduced a reductive property of an ACF for the adsorption of Pt (IV). Chen and Zeng (12) accomplished an improvement of the reduction capacity of an ACF by modifying the ACF with some chemicals. They suggested that a combination of the reductive property of an ACF and different redox potentials of metal ions could achieve a selective separation of metals from solutions.

The recovery of the platinum group of metals such as palladium (Pd), rhodium (Rh) and rhenium (Re), and a transition element such as technetium (Tc-99) from spent nuclear fuel (SNF) is an important issue from the financial and ecological points of view, due to the economic values of noble metals and the radio-toxicity of technetium. Some research results have been reported in relation to the separation of noble metals and Tc-99 from nuclear wastes. Lee et al. (13) reported the results on a possibility for a selective precipitation of palladium from a simulated fission product solution by using ascorbic acid. The separation of palladium from waste streams by using anion exchangers has been also carried out by other researchers (14–16). However, when considering that the purity of a noble metal recovered is crucial for its value, more selective separation methods with a quantitative approach need to be developed.

In this study, we tentatively performed an adsorptive separation of palladium from a simulated nuclear waste solution by using an ACF. The ACF was modified with NaOH to improve its adsorption capacity, and then its physical properties were characterized. The equilibrium characteristics for a mixed solution of Pd, Rh, and Re, which is a chemical analogue of Tc, were investigated to evaluate the adsorption performances of the NaOH -modified ACF. Finally, the breakthrough and elution characteristics of the palladium in the ACF-packed bed were investigated to recover the palladium of a high purity.

EXPERIMENTAL

A pitch-based ACF with an average diameter of 12 μm (Osaka Gas Co., FN-200PS-15) was modified with a NaOH solution to improve its adsorption

capacity. 5 g of ACF was immersed into 1 L of 1 M NaOH solution for 24 hrs. It was filtered and washed with distilled water and then dried at 110°C for 24 hrs. The Boehm titration method (17) was used to evaluate the acidity, which comes mainly from carboxylic, lactonic, and phenolic groups, on the surfaces of the ACF samples before and after the NaOH treatment. The carbon, hydrogen, nitrogen, and sulphur contents of the ACFs before and after the NaOH treatment were analysed by using a Carlo Erba 1160 elemental analyzer. The ash content was calculated from the amount of residue after the calcination of the ACF sample to 900°C using a thermogravimetric analyzer (TA Instruments SDT 2960). The rest from the initial mass of the sample was assumed to be the oxygen content.

The surface area and the pore volume of the samples were evaluated by a N₂ sorption analysis on a Micromeritics ASAP 2010. Pore size distribution was calculated by using the BJH (Barrett, Joyner and Halenda) formulism. X-ray diffraction patterns for the ACF samples were collected on a Siemens D-5000 diffractometer with a Cu K_α radiation. The surfaces of each ACF sample were also observed by a scanning electron microscope (SEM) on a JEOL JSM 5200 attached to an energy dispersive spectroscope (EDX).

Adsorption equilibrium tests were performed for single and multicomponent solutions containing Pd, Rh and Re ions in 0.5 M nitric acid solution. Pd(NO₃)₂ and Rh(NO₃)₃ were used for the Pd and Rh sources, respectively, while Re₂O₃ was used for the Re source after being dissolved in 0.5 M nitric acid solution. The experiment for measuring an equilibrium isotherm was carried out by the following procedure. A certain amount of the single or multicomponent solution was loaded into a vial which already included a measured amount of the ACF. The vial was then placed in a shaker vibrating at 100 cycles/min inside a thermostatic water bath kept constant at 25°C for 24 hrs. From our pretests, the equilibration time of 24 hrs was observed to be enough for equilibrium. The volume and concentration of each test solution were held constant at 20 mL and 100 ppm, respectively. The mass of ACF samples varied in the range between 0.002 and 0.3 g. The equilibrated solutions were filtered for concentration analysis by using a 0.2 µm syringe filter. The equilibrium measurement was repeated at least three times for each point, and an average value of those measurements was taken as a final isotherm point.

Breakthrough curves were obtained for the single and multicomponent solutions by using a jacketed glass column (ID = 11 mm, bed length = 150 mm, bed volume = 14.25 cm³). 2.35 g of the preconditioned ACF was dispersed in the pure water and then packed into the column from the top. A nylon screen was attached at the bottom of the column to prevent the release of the ACF samples and to ensure the water flow from the column. After packing the ACF sample, the top end of the column was sealed and connected to a fractional collector for sampling. The packed bed was kept constant at 25°C by using a water jacket. Then the test solution was fed from the bottom of the column to avoid a channeling effect by

using a micro pump with a flow rate of 1.9 to $8.2 \text{ cm}^3 \cdot \text{min}^{-1}$, which is equivalent to a linear velocity of 2.0 to $8.6 \text{ cm} \cdot \text{min}^{-1}$. The effluent samples were collected with a fractional collector. The solution phase concentrations were measured by using an atomic absorption spectrophotometer (AAS, GBC Co. Model 906). The ACF loaded with metal ions was characterized by SEM, XRD, and EDX to confirm the state of the adsorbed metals.

RESULTS AND DISCUSSION

Effect of NaOH Treatment on the Adsorption of Palladium

The adsorption of metal ions onto an ACF is influenced by its physical and chemical properties. Among them, structural properties of the ACF such as surface area and pore size distribution are very important along with its functional groups. The treatment of an ACF with NaOH will likely modify its surface characteristics such as structural and chemical properties for a better adsorption of palladium.

NaOH treatment process for an ACF is assumed to involve several steps. First, when an ACF is immersed in a NaOH solution, Na^+ ions are attracted to the ACF due to their surface negative charge. Then, the ACF preoccupied with Na^+ ions is surrounded by OH^- ions which are believed to proceed with oxidation reactions to form functional groups on the surfaces of an ACF. Figure 1 is the zeta potential of the ACF before the NaOH treatment by using a zeta meter (Zetasizer 4, Malvern Co) in the pH range of 2 and 11. It shows that the point of zero charge (PZC) for the ACF is found at around

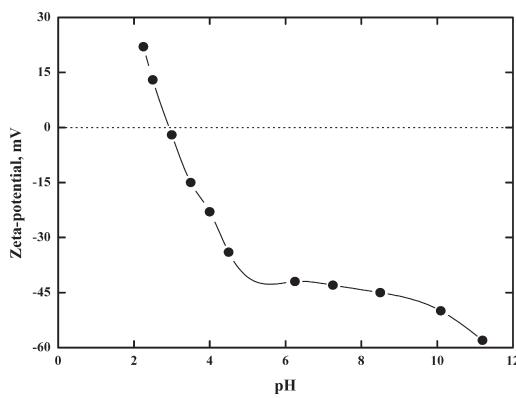
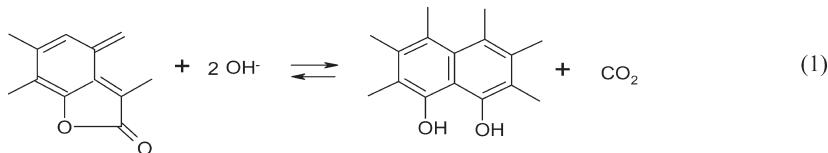


Figure 1. Zeta potential of the Raw-ACF showing a point of zero charge (PZC).

pH = 3, which justifies the assumption of negative surface charges of the ACF.

In this article, the untreated ACF is denoted by Raw-ACF, while the NaOH-treated one is denoted by NaOH-ACF. The SEM images of the Raw-ACF and NaOH-ACF samples are illustrated in Fig. 2. The NaOH treatment of the ACFs is shown to give quite different surface characteristics.

The concentrations of the acidic functional groups on the surfaces of the Raw-ACF and NaOH-ACF were measured by the Boehm titration method, and the results are summarized in Table 1. Total acidity increased from $0.97 \text{ meq} \cdot \text{g}^{-1}$ to $1.74 \text{ meq} \cdot \text{g}^{-1}$ by the NaOH treatment. This can be attributed to the increase of the concentration of phenolic group from $0.20 \text{ meq} \cdot \text{g}^{-1}$ to $1.41 \text{ meq} \cdot \text{g}^{-1}$ by the NaOH treatment. The concentration of the carboxylic group was almost unchanged. It is considered that some phenolic groups can be formed by the deformation of lactonic functional group by hydroxyl ions as follows (5):



Other phenolic groups might be generated by the oxidation reaction of active site of carbon with hydroxyl ion as follows (12, 18):



The chemical compositions of the Raw-ACF and the NaOH-ACF samples are shown in Table 2. The carbon content of the ACFs decreased by the NaOH treatment, while the oxygen and hydrogen contents increased. The decrease in the carbon content is possibly attributed to the oxidation reaction as shown in Eq. (1). On the other hand, the increase in the oxygen and

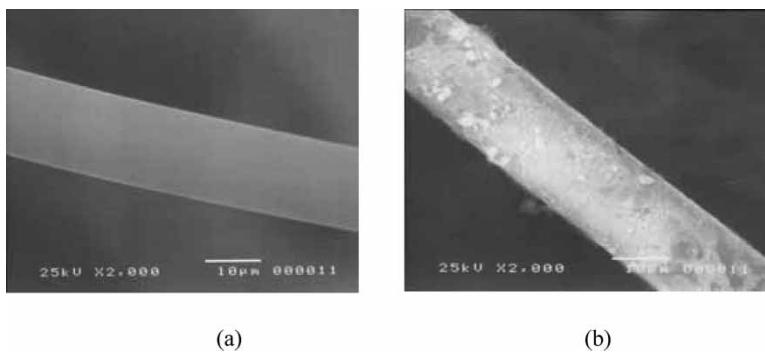


Figure 2. SEM images of ACFs: (a) Raw-ACF and (b) NaOH-ACF.

Table 1. Boehm titration data for Raw-ACF and NaOH-ACF

Samples	Functional Group (meq · g ⁻¹)			
	Carboxyl	Lactone	Phenol	Total
Raw-ACF	0.31	0.46	0.20	0.97
NaOH-ACF	0.29	0.04	1.41	1.74

hydrogen contents are obviously due to the reaction of the ACF with hydroxyl ions to form phenolic groups as given in Eqs. (1) and (2).

The nitrogen adsorption and desorption isotherms for the Raw-ACF and NaOH-ACF adsorbents are shown in Fig. 3. The isotherms exhibit a typical Type I behavior for both of the ACFs, indicating that the ACFs used in this work mainly have micropores. The inset in Fig. 3 shows the pore size distribution curves for the Raw-ACF and NaOH-ACF calculated from their desorption isotherms by using the BJH formulism. The centered pore diameters for the Raw-ACF and NaOH-ACF are 1.41 nm and 1.39 nm, respectively. The BET surface areas and pore volumes are also summarized in Table 3.

As previously reported (4, 5), it is shown that all the values of the physical properties for the Raw-ACF such as the specific surface area, pore volume and pore diameter reduced in some degree after the NaOH treatment. When we refer to the results reported by other researchers (4, 5), it might be attributed to the decomposition of some pores by NaOH treatment (4) or to the pore-blocking by the sodium ions of initiator NaOH (5). More exact explanation in this regard would require further study.

In order to evaluate the effect of the NaOH treatment on the adsorption of palladium, the adsorption isotherms of the Raw-ACF and the NaOH-ACF for palladium were obtained. Figure 4 shows that the adsorption performance of the ACF is substantially enhanced by the NaOH treatment. Adsorption capacities obtained by modeling the data with the Langmuir equation are 1.30 meq · g⁻¹ for NaOH-ACF and 0.42 meq · g⁻¹ for Raw-ACF.

Table 2. Elemental composition of pitch-based ACF before and after NaOH treatment

Samples	Elemental analysis (wt.%)					
	C	H	O	N	S	Ash
Raw-ACF	88.97	1.06	8.78	0.43	0.60	0.16
NaOH-ACF	86.51	1.34	10.99	0.42	0.57	0.17

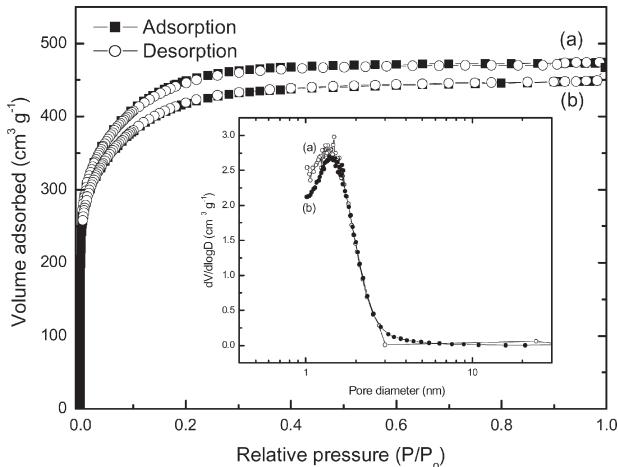
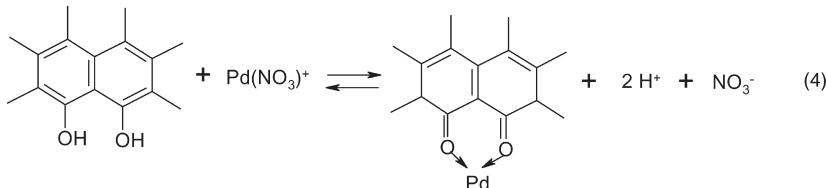
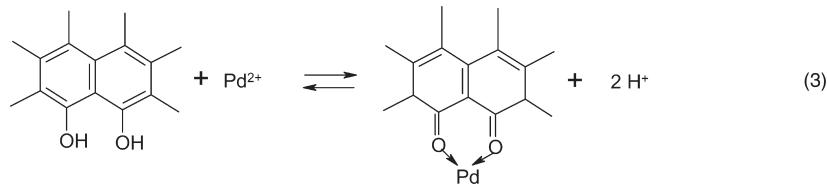


Figure 3. N₂ adsorption and desorption isotherms for (a) Raw-ACF and (b) NaOH-ACF. The inset shows the pore size distribution curves calculated from the desorption isotherms using the BJH formulism of the corresponding ACF.

The increase of the palladium adsorption capacity after the NaOH treatment can be explained to be due to the increase of the total acidic functional groups, even though the adsorption capacity of the NaOH-ACF for Pd does not exactly fit to the total acidity of the NaOH-ACF. The palladium ions in 0.5 M nitric acid solution exist mainly in the form of Pd²⁺ and PdNO₃⁺ (19). The electrochemically oxidized carbon fibers adsorb a palladium ion via ion exchange and redox reactions between the Pd²⁺ or PdNO₃⁺ ion and the acidic functional groups as follow:



Similar adsorption-reduction mechanism was reported for silver ions on an activated carbon fiber by Yue et al. (20) who had studied a surface

Table 3. Experimental data of N_2 sorption for the Raw-ACF and NaOH-ACF

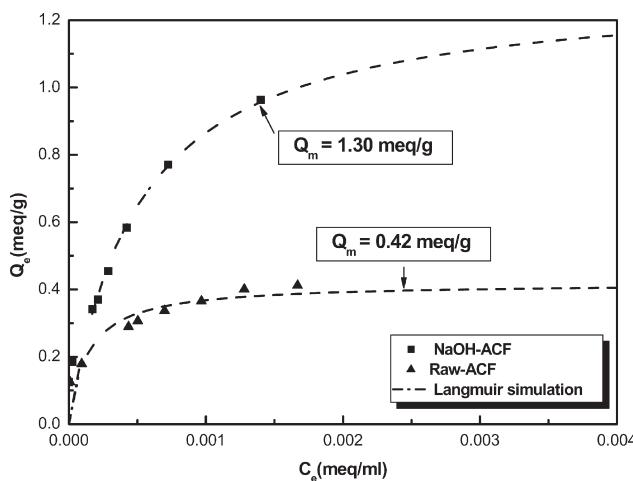
Sample	S_{BET} ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)		Centered pore diameter (nm)
		Micro	Total	
Raw-ACF	1255	0.679	0.734	1.41
NaOH-ACF	1151	0.631	0.695	1.39

characterization of electrochemically oxidized carbon fibers. The adsorption capacity is known to be proportional to the number of acidic sites on the ACF surfaces. On the other hand, the reduction capability of an ACF is reportedly mainly related to the number and reactivity of edge sites of the graphite micro crystals, which are formed during the carbonization-activation process (10).

Figure 5 shows the XRD pattern for the ACF equilibrated with the mixed solution of the palladium, rhodium and rhenium ions. The peaks of the XRD pattern coincide with the characteristic peaks of palladium metal ($2\theta = 40, 46, 68, 82, 86$), indicating that the adsorbed phases are mainly palladium metals along with some impurities undetectable by the XRD. The XRD analysis result justifies the assumption that the palladium ions are reduced to metals on the ACF surfaces.

Adsorption Isotherms in Mixed Solution

Multicomponent adsorption isotherms of Pd, Rh, and Re on the ACF were obtained to evaluate the adsorption capacity and the equilibrium constants.

**Figure 4.** Equilibrium isotherms and modeling examples for an adsorption of palladium with the Raw-ACF and the NaOH-ACF.

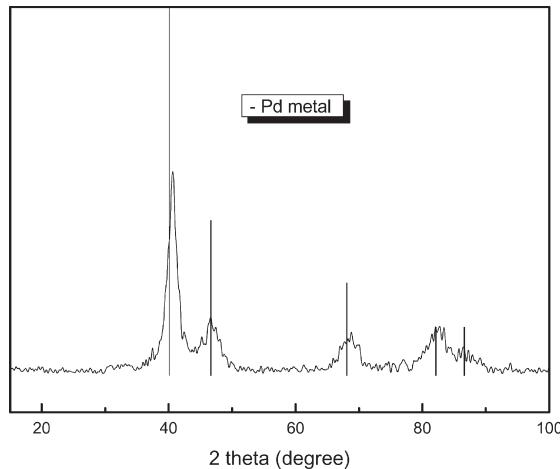


Figure 5. XRD pattern of the NaOH-ACF after being equilibrated with the solution containing palladium, rhodium and rhenium ions.

Experimental data were modeled by the Langmuir equation (21). The experimental values and their modeling results are shown in Fig. 6 for Pd, Rh, and Re ions on the NaOH-ACF.

It can be seen from the isotherms that the ACF has a much higher preference for the Pd ion over the Rh and Re ions. The isotherms were modeled by

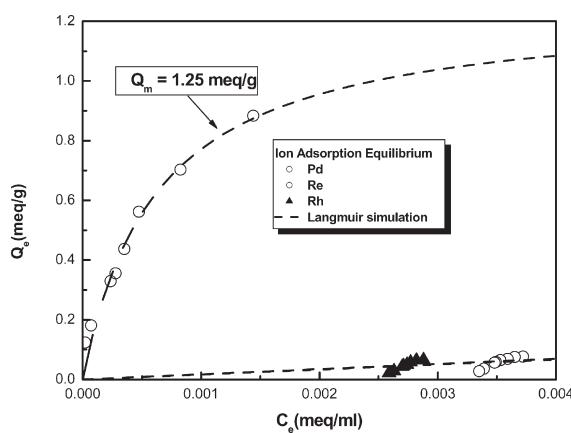


Figure 6. Ion adsorption equilibrium curves for NaOH-ACF in the mixed solution of palladium, rhodium and rhenium ions. The quantity of adsorbent treated with 1 M NaOH is 0.01~0.3 g; the concentration of eluting HNO₃ solution is 0.5 M; the solution concentrations for Pd, Rh, and Re ions are all 100 ppm; and the solution volume is 20 cm³. The dotted lines express the Langmuir correlation.

the Langmuir equation with high regression values. The loading capacity of the Pd ion in the three-component system was calculated to be $1.25 \text{ meq} \cdot \text{g}^{-1}$ of ACF by the Langmuir equation. Another model constant (b) representing a degree of affinity for the Pd ion was 1.597. On the other hand, in the case of the Rh and Re ions, unfavorable adsorption isotherms with significantly lower uptakes were observed. This implies that the Rh and Re ions would not have much impact on the adsorption of the Pd ion from the mixture. The Re ions in the nitric acid solution exist in the form of ReO_4^- . Since the ACF surface has acidic functional groups which act as cation exchange sites, ReO_4^- ions can not approach the ACF surface easily. The Rh ions in the nitric acid solution reportedly exist in the form of oligomers or in the most non-ionic stable form of $\text{Rh}(\text{NO}_2)_3(\text{H}_2\text{O})_3$ (22), which are hard to be adsorbed or exchanged with the other ions. Therefore, the ACF selectively adsorbs the Pd ions over the Rh and Re ions.

In order to confirm the composition of the adsorbed phase on the ACF, the ACF samples were analyzed with EDX and the results are given in Table 4. It was found out that most of the adsorbed phases were composed of palladium, while less than 0.09% was rhodium. This can be regarded to be consistent with the results obtained from the multicomponent adsorption isotherms.

Breakthrough Behavior

In the breakthrough experiments, the flow rate of the feed solution was set to $6.2 \text{ cm}^3 \cdot \text{min}^{-1}$ corresponding to the linear velocity of $6.5 \text{ cm} \cdot \text{min}^{-1}$ which was found to be the optimum flow rate for a maximum utilization of the bed (shorter length of mass transfer zone) in the pretests using a 100 ppm palladium solution. The effect of the coexisting ions on the optimum flow rate was not considered, since the adsorption of other coexisting ions of Re and Rh ions occurred only in a small amount compared to Pd ion. Figure 7 shows the breakthrough behavior of the mixed solution of Pd, Rh and Re ions in the column packed with 2.35 g of preconditioned NaOH-ACF. The breakthrough curve for the Pd ion is very steep, which means that a mass transfer is fast and thus the utilization of the bed is effective. As expected in the equilibrium isotherms of Fig. 6, the NaOH-ACF bed adsorbs

Table 4. EDX analysis showing the composition of adsorbed components on the NaOH-ACF

Element	Atomic Ratio	Concentration (wt.%)
C	1.0000	86.23
Rh	0.0001	0.09
Pd	0.0179	13.68
Re	—	—
Total		100.00

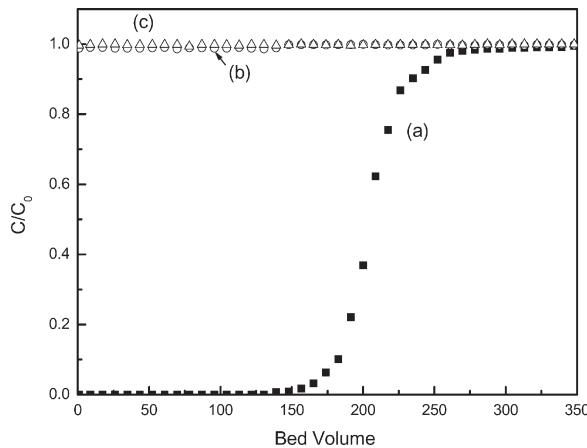


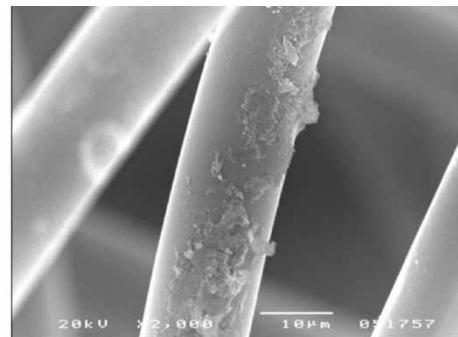
Figure 7. Breakthrough behavior of the mixed solution of palladium, rhodium and rhenium ions in NaOH-ACF bed. The quantity of adsorbent treated with 1 M NaOH is 2.35 g; the concentration of eluting HNO₃ solution is 0.5 M; the solution concentrations for Pd, Rh, Re ions are all 100 ppm; the effluent flow rate is 6.2 cm³ · min⁻¹; the column inside diameter is 1.1 cm; and the bed length is 15 cm (Bed Volume = 14.25 cm³).

preferentially the Pd ion where the adsorbed phase is composed of about 130 mg of Pd per g of ACF (2.45 meq · g⁻¹) and very tiny amounts of Rh and Re. The bed capacity for Pd was found to exceed much more the equilibrium capacity for Pd in the batch system (1.25 meq · g⁻¹). It is quite different from a general concept that fixed beds retain less quantity of ions compared with the batch wise equilibrium system due to diffusion problems. However, we could confirm the reliability of the data through repeated tests.

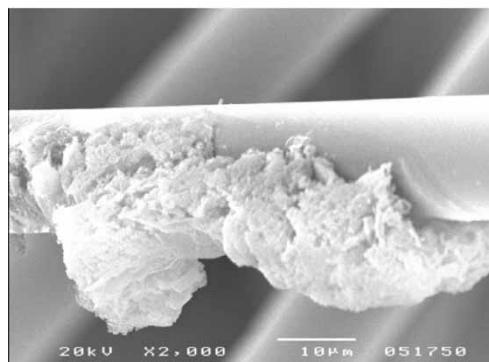
In order to find any reasons for this, we compared the SEM images for the surfaces of the Pd-loaded ACF samples after the batch test (a) and the column test (b), respectively, as shown in Fig. 8. The sample (b) contains bigger clusters on the surfaces than the sample (a), which means that the adsorbed palladium on the ACF surface provides another adsorption site for palladium ions. Although it is assumed to be due to the different conditions between the two adsorption systems such as a solution to solid ratio, the exact reasons could be explained after a more sophisticated study in this regard. In spite of some unclear phenomena, it is clear that Pd can be separated from the mixture. When the breakthrough point is 0.7% of the initial palladium concentration, the throughput is almost 140 BV.

Desorption Behavior

In order to test the possibility of a Pd recovery from the loaded ACF bed equilibrated with a Pd solution, desorption experiments were carried out by



(a)



(b)

Figure 8. SEM photos for the surfaces of the Pd-loaded ACFs after batch test (a) and after column test (b).

using three different chemicals: nitric acid, hydrochloric acid, and ammonium chloride. Desorption characteristics were investigated by varying the solution concentration for each chemical. Figure 9 shows the desorption characteristics of eluting solutions as a function of concentration. Among these three chemicals, nitric acid was the most effective. The degree of desorption was proportional to the solution concentration and about 45% of Pd was observed to be desorbed with 20 cm^3 of the 5 M nitric acid solution. The desorption was performed with the same column and flow rate as in the adsorption step. As a result, about 97% of the adsorbed palladium (88.2% in the first desorption step and 8.6% in the second desorption step) was recovered through the two desorption steps by using 5 M and 6 M of nitric acid solutions, respectively, as shown in Fig. 10. The elution of rhenium and rhodium was so little that palladium with a purity of more than 99% was recovered.

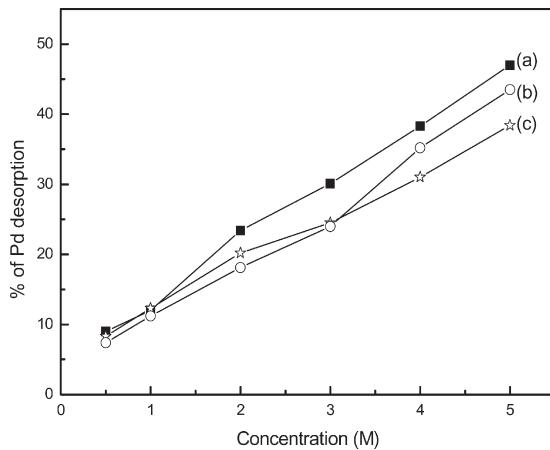


Figure 9. Desorption performances of palladium adsorbed on the NaOH-ACF for the eluting solutions of (a) HNO_3 , (b) HCl , and (c) NH_4Cl , respectively. The quantity of adsorbent preloaded with Pd is 2.35 g; the effluent flow rate is $6.2 \text{ cm}^3 \cdot \text{min}^{-1}$; the column diameter is 1.1 cm; and the bed length is 15 cm (Bed Volume = 14.25 cm^3).

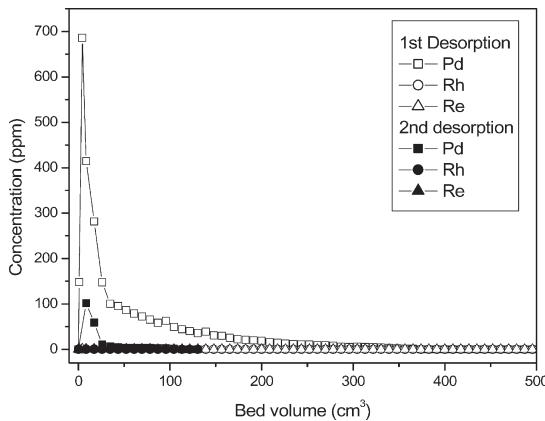


Figure 10. Elution behavior of the palladium, rhodium and rhenium from the loaded NaOH-ACF bed with nitric acid solutions.

CONCLUSIONS

The ACF was modified with NaOH and used to successfully recover palladium from its mixture with rhodium and rhenium in a nitric acid solution. The isotherms of the NaOH-ACF showed a remarkably improved adsorption performance for the palladium ions when compared with the

Raw-ACF. The NaOH-ACF showed a much higher preference for the palladium ion over the rhodium and rhenium ions. The equilibrium adsorption capacity of palladium on the NaOH-ACF was 1.25 meq per unit gram of adsorbent. The breakthrough behavior obtained by using a packed column showed a complete separation of the palladium ion from the rhodium and rhenium ions. The throughput of the bed was almost 140 BV when 0.7% of the initial palladium concentration was considered as a breakthrough point. The adsorbed bed was eluted effectively with a nitric acid solution, and the palladium nitrate with purity of higher than 99% could be recovered.

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