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Selective Separation of Pd(II), Rh(III), and Ru(III) Ions from a Mixed Chloride Solution Using Activated Carbon Pellets

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ABSTRACT

We performed batch adsorption tests with a view to separate Pd(II), Rh(III), and Ru(III) in chloride media using commercial activated carbon pellets (0.8 SUPRA, Norit) as adsorbent. The adsorption mechanism of Pd(II) [as $PdCl_3(H_2O)^-$ or $PdCl_4^{2-}$] and Ru(III) (as $RuCl_5^{2-}$) is explained by the ionization and adsorption model whereby the protonated basal plane of carbon interacts with the palladium or ruthenium species in solution. On the other hand, Rh(III) existing in solution as either hexa-aqua-rhodate $Rh(H_2O)_6^{3+}$ or penta-aqua-chloro-rhodate $RhCl(H_2O)_5^{2+}$ was adsorbed by interacting with the oxygen functional groups on the carbon surface. In general, the activated carbon pellets exhibited a strong affinity for Pd(II) in a wide range of HCl concentration (0.005–2.0 M). It was easy to remove Pd(II) selectively from a ternary solution (1.5–2.0 M HCl) containing equal metal concentrations (120 mg/L) using 0.2–0.3 g of dry carbon. We found that adsorption of Rh(III) and Ru(III) occurred simultaneously within a narrow solution pH range (2.3–2.6) but the overall adsorption rate of Rh(III) was threefold higher than that of Ru(III). The adsorption capacities of Pd(II), Rh(III), and Ru(III) in the single-component solutions were found to be 27, 15, and 4 mg/g, respectively. Finally, we found that adsorption of the metals was accompanied by an increase in solution pH up to 8.8 and was reversible at high HCl concentration. Except for Ru(III), all other metals fit the Langmuir isotherms.

Key Words. Activated carbon; Adsorption; Palladium; Rhodium; Ruthenium

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INTRODUCTION

Platinum group metals (PGMs) such as palladium, rhodium, and platinum have continued to be used as autocatalysts for exhaust gas treatment. Ruthenium is one of the metals, along with other PGMs, commonly found in power reactor nuclear wastes. The level of worldwide consumption of palladium, rhodium, and ruthenium has by far exceeded the extraction rate of these precious metals from primary ores mainly due to their scarcity and high production costs (1). Therefore, it has become necessary to recover these precious metals from spent autocatalysts and to recycle them in industry. However, the fact that these precious metals occur in the form of alloys (~10:4:1, Pt:Pd:Rh), or as a mixture in nuclear wastes, make it difficult to separate their solubilized ions in a mixed solution. Recently, Cote et al. (2) developed 8-hydroxyquinoline derivative extractants for the separation of PGMs while Freiser et al. (3) and Yan et al. (4) reported on the solvent extraction of palladium and rhodium, respectively. In addition, Inoue et al. (5) tried the adsorption and separation of rhodium using chemically modified chitosan but reported that it was difficult.

To date, scarcely any literature exists about selective adsorption of PGMs from multicomponent chloride solutions using activated carbons. It is known that activated carbon adsorbents exhibit a larger surface area of active sites and are less toxic than most adsorbents or extractants, besides being extremely cheap. Presently, the industrial application of activated carbons is limited to gold recovery (6), mainly due to the difficulty associated with developing specialized carbon adsorbents in the absence of empirical and theoretical models to predict their adsorption behavior. However, numerous authors have recently reported results from the preparation of activated carbons which would react with specific organic (7) and inorganic molecules (8). Research interest in activated carbon material as an alternative to extractants and ion-exchange resins is undoubtedly gaining importance.

In this study we applied a commercially available activated carbon (SUPRA) from Norit Company (USA). Like other steam-activated carbons from peat, SUPRA is mostly basic in nature and carries oxygen functional groups of the "oxo" (C_xO_y) type after activation (9, 10). Our choice of a base carbon is based on the fact that it contains many delocalized basal plane electrons (Lewis-type basic sites) (11) and acidic sites of oxygen groups. We anticipated that at high acid strength the protonation of delocalized planes of carbon would result in ion-pair complexation with palladium species while at moderately acidic conditions the cationic species of rhodium would react with oxygen moieties to form ionic complexes. Therefore, in this report we seek to demonstrate that selective adsorption of Pd(II), Rh(III), and Ru(III) ions from a mixed chloride solution onto an activated carbon surface is possible, depending on the proton concentration in the bulk solution.

EXPERIMENTATION

Reagents

High-grade standard solutions for analytical use of $PdCl_2$, $RhCl_3$, and $RuCl_3$ were purchased from Kishida Chemicals Co. Japan, and used as received without further purification. Activated carbon pellets (SUPRA) were purchased from Norit Co., USA.

Batch Adsorption and Desorption Tests

Activated carbon pellets were washed thoroughly with deionized water and then dried at 110°C under nitrogen atmosphere. Then 40 mL of chloride solutions bearing metal ions (single, binary, and ternary) were contacted with 0.2–0.3 g of dry adsorbent in sealed 50 mL vessels and placed in a shaker thermostat at 298 K. The mixture was mildly and continuously agitated for 48 hours to attain equilibrium conditions. A solution (1 M) of either NaOH or HCl was used to adjust the feed solution pH. After attaining equilibrium conditions, the carbon pellets and metal-depleted solution were separated by decantation. The suspended microparticles in the decanted solution were filtered through micromembranes (Millipores, 0.2 μm). The clear solution samples obtained after microfiltration were analyzed for residual metal ions by means of a Sequential Plasma Spectrometer (ICPS-5000 Shimadzu, Kyoto). The solution pH was determined by using an HM-60S pH meter, with an accuracy of 0.001 ± pH units. The parameters which affect adsorption were investigated, e.g., effect of feed pH and initial metal concentrations. By varying the initial metal concentrations we were able to determine the loading capacity of carbon pellets as well as the Langmuir isotherms.

In desorption tests, loaded activated carbon pellets (0.2 g) were contacted with several electrolyte samples (20 mL of HCl solution) having different acid concentrations. These samples were gently and continuously agitated in a shaker thermostat at 298 K. At selected intervals the samples were drawn out of the shaker thermostat, followed by separation of solids from the solution. The analyses of solution metals were conducted by using the method outlined above.

The definitions of adsorption and adsorption capacity are given in Eqs. (1) and (2), where M_i, M_{ad}, and M_c stand for initial mass of metal in solution, mass of metal adsorbed onto carbon, and mass of carbon pellets, respectively. The characteristics of activated carbon pellets are shown in Table 1.

$$\%\ \text{Adsorption} = \frac{M_{ad}}{M_i} \times 100 \tag{1}$$

$$\text{Adsorption capacity at equilibrium, } q_e = M_{ad}/M_c \tag{2}$$

TABLE 1
Characteristics of Activated Carbon, Norit 0.8 SUPRA

Apparent density (g/L)	380
Porosity (%)	13
Slurry pH	9.5–9.9
Iodine adsorption (mg/g)	1100
Phenol adsorption (%)	6
Sieved particle size (mm)	0.7–1.0

In this study the adsorption behavior of metal species on the carbon surface was tested on Langmuir isotherms. It is known that the Langmuir isotherms support the monolayer adsorption model. From Langmuir's equation (12, 13),

$$\frac{1}{q_e} = \frac{1}{Q_0 b C_e} + \frac{1}{Q_0} \tag{3}$$

where q_e (mg/g) and c_e (mg/L) are the adsorption capacity and concentration of metal ions at equilibrium, respectively. The Langmuir constants Q_0 (mg/g, related to adsorption capacity) and b (L/mg, dependent on temperature) were determined from single-component adsorption systems. The adsorption factor, β, derived from the Langmuir equation (Eq. 3), indicates whether adsorption is favorable ($\beta \ll 1$) or nonfavorable ($\beta \doteqdot 1$)

$$\beta = \frac{1}{bC_0 + 1} \tag{4}$$

Kinetic Studies

The kinetic measurements were carried out batchwise. Known volumes (40 mL) of single-component solutions containing 200 mg/L of $PdCl_2$, 120 mg/L of $RhCl_3$, and 120 mg/L of $RuCl_3$ were placed in 50 mL vessels. The mixtures were contacted with 0.3 g of dry adsorbent and then agitated mildly at room temperature (278 K) on a continuous basis. At predetermined intervals the vessels were drawn out of the shaker thermostat in stages. The solution samples were filtered through 0.2 μm micromembranes before being analyzed for metal ions using the sequential plasma spectrometer (ICPS). We considered the uptake of Pd(II), Rh(III), and Ru(III) ions from the liquid to the solid phase as a reversible reaction which proceeds to equilibriation of the two phases. Therefore, from a linear graphical relationship between $\log(q_e - q_t)$ and time, we determined the overall adsorption rate constants for single-component systems from the Lagergren first-order rate Eq. (6) which is derived from the rate Eq. (5) (14).

$$dq/dt = -k_{ads}q \tag{5}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_{ads}}{2.303}t \tag{6}$$

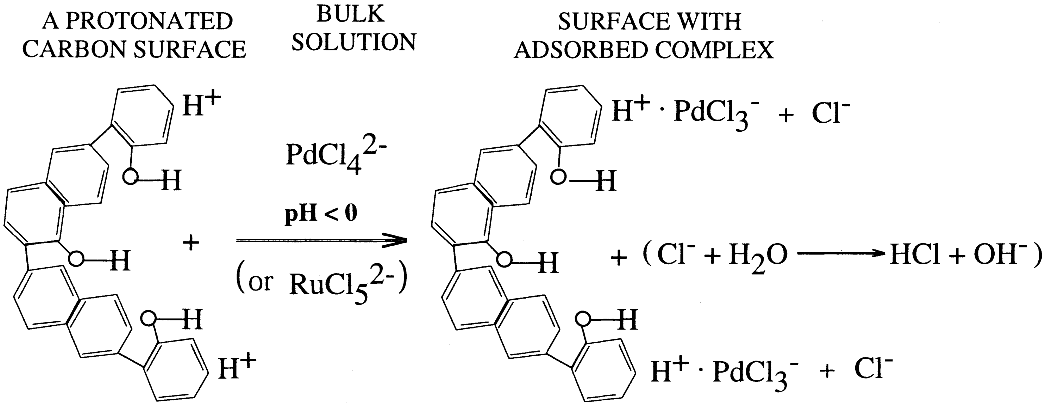

FIG. 1a Diagram illustrating the interaction of $PdCl_4^{2-}$ with a protonated surface. A side reaction in the bulk solution occurs between Cl^- and H_2O to form OH^- ions. The H^+ ion adsorbs competitively.

where q and k_{ads} refer to the adsorption capacity and overall adsorption rate respectively. The subscripts "e" and "t" stand for equilibrium and time, respectively.

RESULTS AND DISCUSSION

Adsorption Schematic Diagrams

The schematic diagrams shown in Figs. 1a and 1b illustrate the adsorption mechanisms of Pd(II) [or Ru(III)] and Rh(III), respectively. According to Fig. 1a, the adsorption of either Pd(II) or Ru(III) follows the ionization and ad-

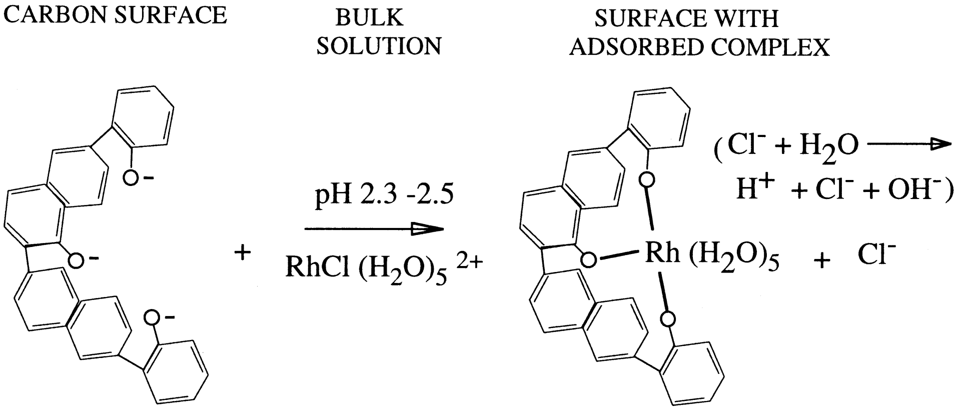

FIG. 1b Diagram illustrating the interaction of $RhCl(H_2O)_5^{2+}$ with oxygen functional groups. A side reaction in the bulk solution occurs between Cl^- and H_2O to form OH^- ions. The H^+ ion adsorbs competitively.

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sorption model discussed extensively by Carrott et al. (15–17). According to this model, the electron donor oxygen-free carbon surface is readily protonated by H^+ (i.e., a coulombic attraction occur between the proton and the carbon electrons) and hence this activated surface behaves like a Lewis-type acid. Subsequently, the protonated carbon surface reacts with the anionic trichloro complex $PdCl(H_2O)_3^-$ (or $PdCl_4^{2-}$ and $RuCl_5^{2-}$) which acts as a Lewis base to form a surface ion complex characterized by a hydrogen bond. This implies that the metal complex become attached to the carbon surface through an electrostatically held proton (18).

Concerning the speciation of palladium complexes, Ma et al. (3) reported that Pd(II) exists in moderate chloride media primarily as the aqua trichloro complex $[PdCl_3(H_2O)^-]$ while Cote et al. (19) showed that Pd(II) exists as the tetrachloro complex ($PdCl_4^{2-}$) in the 0.01–2 M HCl concentration range. Further, Cox et al. (20) also confirmed that the most common Pd(II) chlorocomplex in moderate Cl^- concentrations is $PdCl_3(H_2O)^-$. However, From the speciation diagram (Fig. 10, below), the amounts of $PdCl_3(H_2O)^-$ and $PdCl_4^{2-}$ in 0.01 M HCl solution are 65 and 10%, respectively. Alternatively, in a 2 M HCl solution, the amounts are 1% $PdCl_3(H_2O)^-$ and 99% $PdCl_4^{2-}$. At concentrations above 2 M HCl, palladium exists mainly as the $PdCl_4^{2-}$ complex, the most stable and hydrophilic of palladium chlorospecies in acidic media. In a chloride solution of pH range 2.5–2.8, however, palladium forms the neutral species $PdCl_2$. It is well known that the ruthenium species $RuCl_5^{2-}$ and $RuCl_6^{3-}$ are kinetically inert in chloride media and tend to form complex equilibria at high HCl concentrations.

The schematic diagram of Fig. 1b shows that adsorption of Rh(III) proceeds through the interaction of rhodium species with the chemisorbed oxygen functional groups. In solution, rhodium may exist as hexa-aqua-rhodate $[Rh(H_2O)_6^{3+}]$, or penta-aqua-chloro-rhodate $[RhCl(H_2O)_5^{2+}]$, or tetra-aquo-chloro-rhodate $[RhCl_2(H_2O)_4^+]$ depending on Cl^- concentrations. In our study, adsorption tests for rhodium were carried out in the 0.003–0.005 M HCl range in which case the dominant species are those cited above.

Equilibrium Adsorption in Single-Component Systems

The adsorption behavior of Pd(II), Rh(III), and Ru(III) in single-component systems is shown in Fig. 2. In this case the batch adsorption tests were performed separately, but the graphs are plotted together for comparison purposes. We found that activated carbon pellets showed a strong affinity for Pd(II) ions over a wide range of pH (0–5). We achieved an adsorption capacity of about 26 mg/g for Pd(II). The reason for the decrease in Pd(II) adsorption at higher pH is attributed to the formation of neutral $PdCl_2$ species in solution as well as an increase in OH groups which tend to deprotonate the carbon surface.

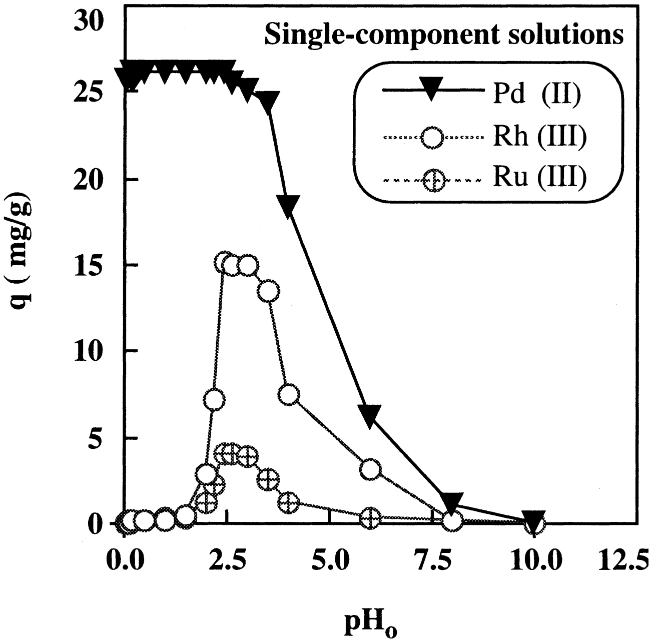

FIG. 2 A plot of adsorption capacity vs. initial pH. Initial concentrations: Pd(II) = 201 mg/L, Rh(III) = Ru(III) = 120 mg/L; mass of carbon = 0.3 g; solution volume = 40 mL; and contact time = 48 hours.

In Fig. 2 it is clear that $Rh(H_2O)_6^{3+}$ and $RuCl_5^{2-}$ species were not adsorbed onto carbon at lower pH conditions (0.0–1.2). In the case of cationic Rh(III) species, the excess amount of protons in the solution hindered rhodium adsorption due to the competitive adsorption of H^+ onto surface oxygen groups. For the anionic Ru(III) species, this is probably due to the fact that ruthenium tends to form complex equilibria (at high HCl concentrations) which are kinetically inert [Cox et al. (20)]. However, sharp adsorption edges for both Rh(III) and Ru(III) were observed within a narrow solution pH range (2.3–2.6). It is not yet clear whether this pH range corresponds to the point of zero charge (pzc) of activated carbon pellets in the presence of metal ions. We have plans to investigate this phenomenon by determining the surface charge density variation on the activated carbon at different pH conditions. However, it is clear that coadsorption of Rh(III) and Ru(III) ions in a binary solution is possible within a pH range of 2.3–2.6. Furthermore, ruthenium showed a strong affinity for OH groups at pH 3.0 and readily formed a precipitate [$Ru(OH)_3$]. This result indicates that coadsorption of ruthenium and rhodium adsorption could be minimized significantly at an initial pH slightly above 3.0 since ruthenium ions would react with OH groups instead of the carbon surface. The decreasing tendency in rhodium adsorption below pH 3.0 is not clearly understood in the absence of the surface charge data. However, the effect of increasing OH groups at the surface interface is that they hinder an interaction of surface oxygen groups with cationic species.

Figure 3 shows the relationship between initial solution pH and equilibrium pH after quantitative adsorption of Pd(II) and Rh(III) at constant metal concentrations. It was found that uptake of either Pd(II) and Rh(III) ions was accompanied by a great change in solution pH. When the initial pH was about 1.0 (less H_2O molecules), there was little change between feed solution pH and equilibrium pH because less of these metals were adsorbed. Generally, we observed that the equilibrium pH increased up to 8.8 when the initial feed pH range was 2.3–2.6 units. However, for an initial feed pH range of 5–6, the adsorption of Pd(II) and Rh(III) was comparatively lower and hence the equilibrium pH was almost equal to the initial feed pH. We attributed the increase in solution pH to the reaction between Cl^- ions and H_2O molecules which yields OH^- anions in solution. (See the schematic diagrams in Figs. 1a and 1b.)

Figures 4a and 4b show the pH dependence of adsorption of Pd(II), Rh(III), and Ru(III) ions at various initial metal concentrations. In all cases the plots form a plateau at higher metal concentrations, indicative of the fact that adsorption has peaked out. The adsorption capacity of carbon pellets with respect to Pd(II), Rh(III), and Ru(III) were determined as 27, 15, and 4 mg/g, respectively. Furthermore, the overall adsorption rates (k_{ads}) of Pd(II), Rh(III),

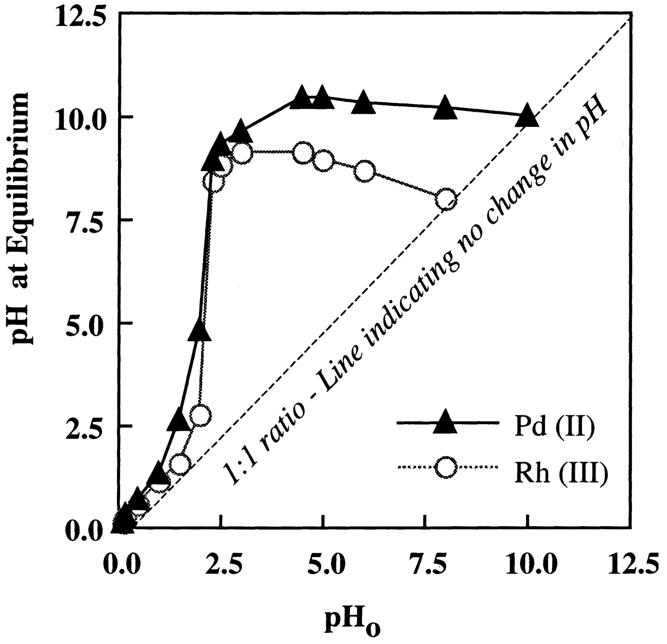

FIG. 3 Change in final solution pH as a result of adsorption at different initial pH values in the presence of cations. Initial metal concentration: Pd(II) = Rh(III) = 90 mg/L; mass of carbon = 0.3 g; and solution volume = 40 mL.

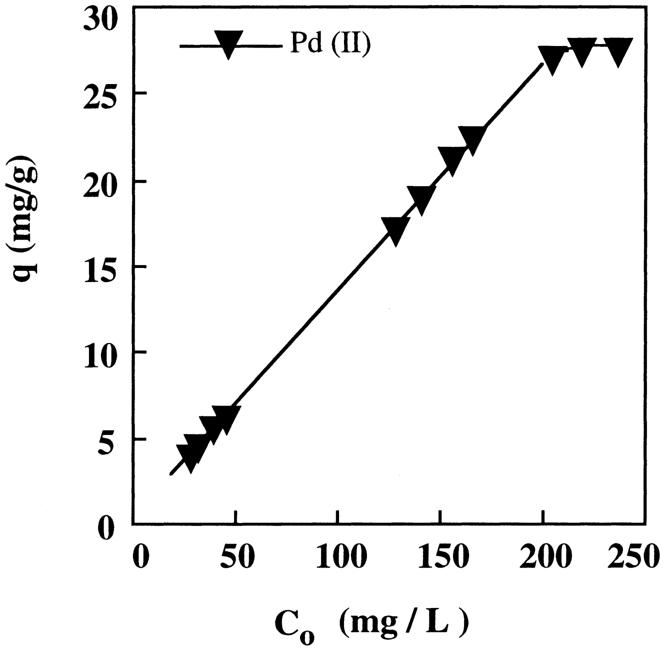

FIG. 4a A plot of adsorption capacity vs initial metal concentration: Single-component solution of Pd(II). Mass of carbon = 0.3 g and solution volume = 40 mL.

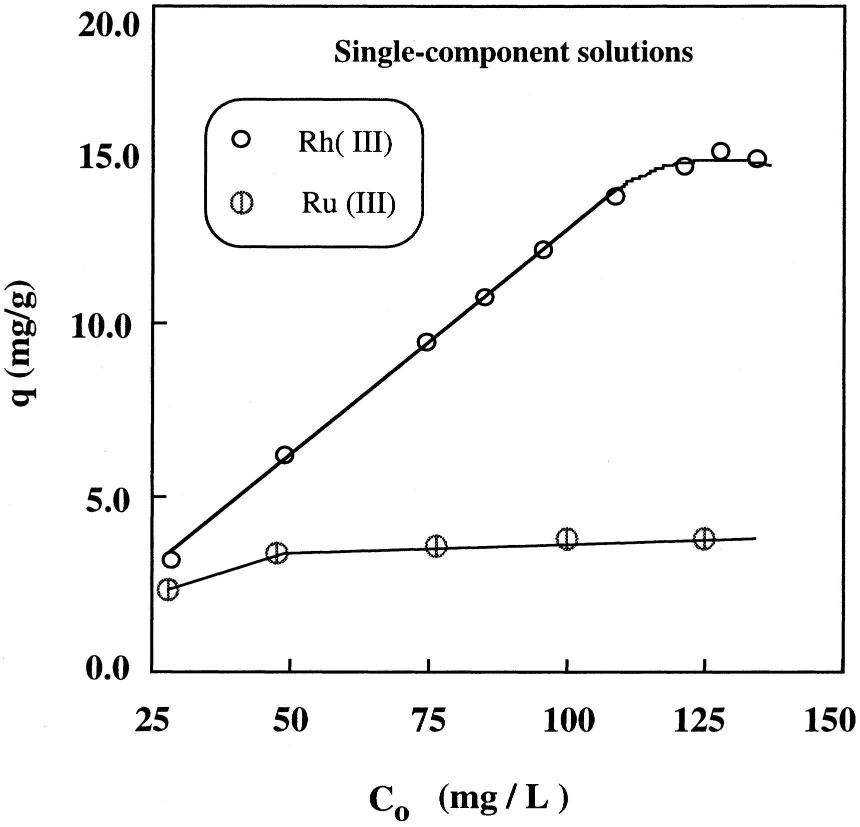

FIG. 4b A plot of adsorption capacity vs initial metal concentration: Single-component solutions of Rh(III) and Ru(III). Mass of carbon = 0.3 g and solution volume = 40 mL.

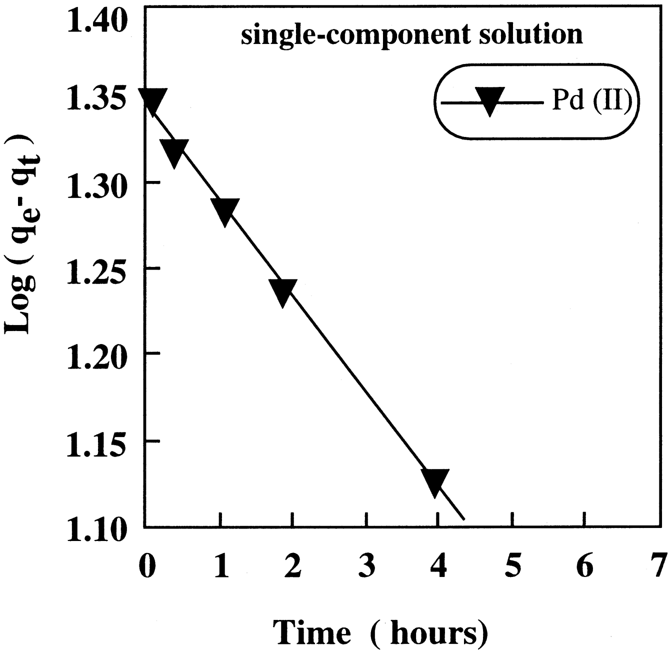

FIG. 5a Log($q_e - q_t$) vs time. A plot illustrating the overall adsorption rate (h^{-1}) of Pd(II) in a single-component system. Initial metal concentration = 180 mg/L, mass of carbon = 0.3 mg/L, and solution volume = 40 mL.

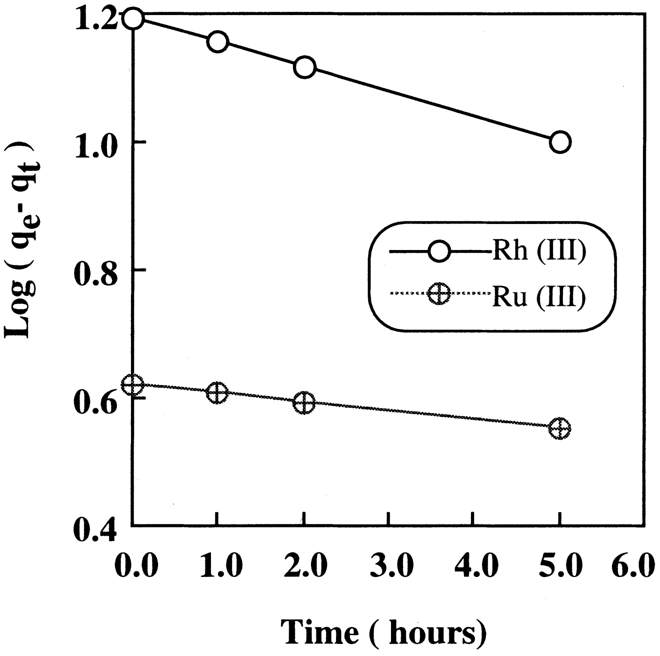

FIG. 5b Log($q_e - q_t$) vs time. A plot illustrating the overall adsorption rate (h^{-1}) of Rh(III) and Ru(III) in single-component solutions. Initial concentration of metals = 120 mg/L, mass of carbon = 0.3 mg/L, solution volume = 40 mL, and feed pH = 2.4.

TABLE 2
Summary of Langmuir Constants and Specific Adsorption Rate Constants, k_{ads}, at 298 K

	Single-component solution[a]				Ternary solution[b]			
Species	k_{ads} (min^{-1})	Q ($mg \cdot L^{-1}$)	b ($L \cdot mg^{-1}$)	β (—)	k_{ads} (min^{-1})	Q ($mg \cdot L^{-1}$)	b ($L \cdot mg^{-1}$)	β (—)
Pd(II)	1.0×10^{-3}	27	7.1	7.0×10^{-4}	6.9×10^{-4}	12	6.5	7.7×10^{-4}
Rh(III)	7.2×10^{-4}	15	0.05	9.1×10^{-2}	3.7×10^{-4}	7.6	0.02	2.0×10^{-1}
Ru(III)	2.9×10^{-4}	[c]	[c]	[c]	1.4×10^{-4}	[c]	[c]	[c]

[a] Pd(II) adsorption batch tests were conducted at 2 M HCl; Rh(III) and Ru(III) adsorption batch tests were conducted at 0.005 M HCl.

[b] All adsorption batch tests in ternary solution were performed at an acid strength of 0.005 M HCl.

[c] Ru(III) adsorption results did not fit the Langmuir isotherms. Thus Q, b, and β constants were not determined.

and Ru(III) are illustrated in Figs. 5a and 5b while the comparative data showing the values of k_{ads} for the metals in single-component systems are given in Table 2. In general, the adsorption of palladium exhibited a value of k_{ads} which is 1.5 times higher than that of Rh(III) and almost four times that of ruthenium. These data refer to adsorption in single-component systems.

Figures 6a and 6b show the adsorption isotherms of palladium and rhodium, respectively, derived from Figs. 4a and 4b. Ruthenium adsorption did not fit

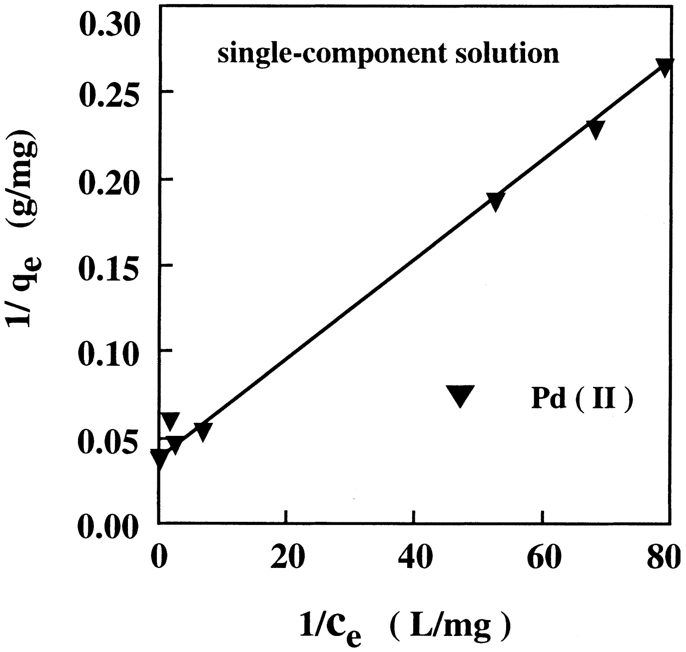

FIG. 6a A plot of $1/q_e$ vs $1/c_e$. Langmuir isotherm for Pd(II) in single-component solution reconstructed from Fig. 4a.

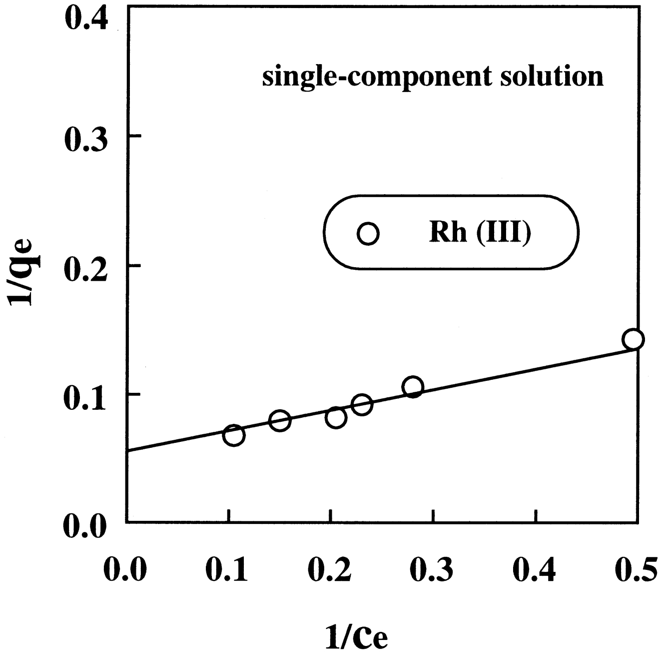

FIG. 6b A plot of $1/q_e$ vs. $1/c_e$. Langmuir isotherm for Rh(III) in single-component system reconstructed from Fig. 4b.

Langmuir isotherms, probably because it readily forms a precipitate at moderately low pH. It is clear that the adsorption behaviors of Pd(II) and Rh(III) in single-component systems fit the Langmuir isotherms. The constant values of *Q*, *b*, and β are summarized in Table 2. By comparison, the determined factor β for Pd(II) was found to be much smaller than unity ($\beta \ll 1$), indicative of a highly favorable adsorption state. The β value of Rh(III) also shows that adsorption is favorable, although the extent of adsorption is limited. The constant value of *b* was found to be different in single and ternary systems for Pd(II) and Rh(III).

Competitive Adsorption: Ternary Systems

Figures 7a, 7b, and 7c illustrate the adsorption profiles of Pd(II), Rh(III), and Ru(III) in a ternary mixture (equal concentration, 120 mg/L) at three HCl concentrations: 2 M, 1 M, and 0.005 M. It is clearly demonstrated that activated carbon pellets have a strong affinity for $PdCl_4^{2-}$ complex ions at high HCl concentration. About 96% of Pd(II) ions were adsorbed onto carbon in the HCl concentration range 1–2 M within 3 hours of contact time, leaving behind Rh(III) and Ru(III) in solution. Further, carbon pellets still showed a stronger affinity for Pd(II) even at 0.005 M HCl concentration, although the coadsorption of 27% Ru(III) and 88% Rh(III) within 6.7 hours of contact time

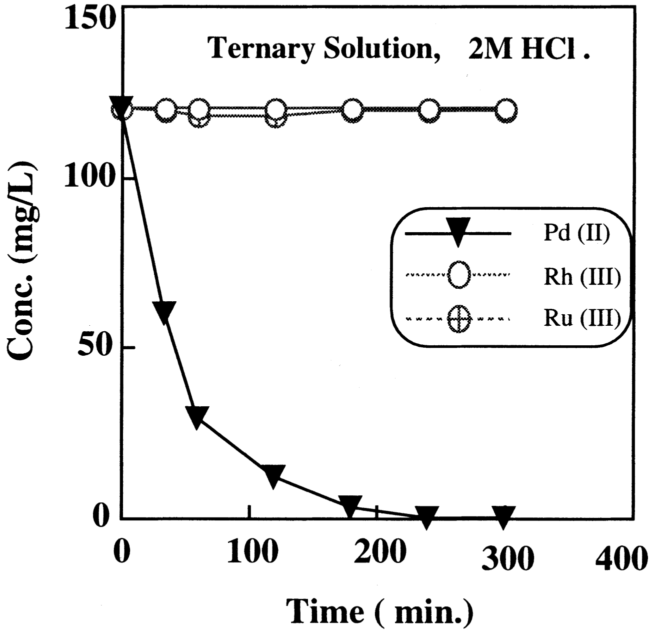

FIG. 7a A change in the concentration profiles of Pd(II), Rh(III), and Ru(III) in a ternary solution of 2 M HCl. Mass of carbon = 0.3 g and solution volume = 40 mL.

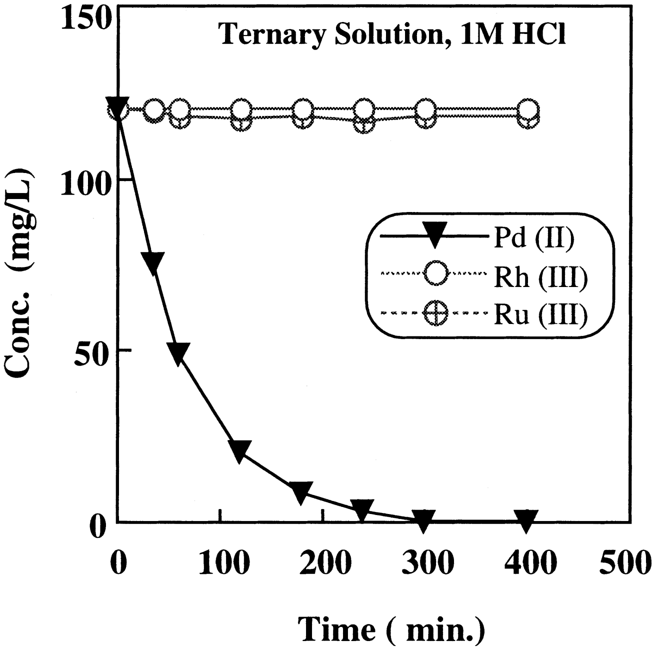

FIG. 7b A change in the concentration profiles of Pd(II), Rh(III), and Ru(III) in a ternary solution of 1 M HCl. Mass of carbon = 0.3 g and solution volume = 40 mL.

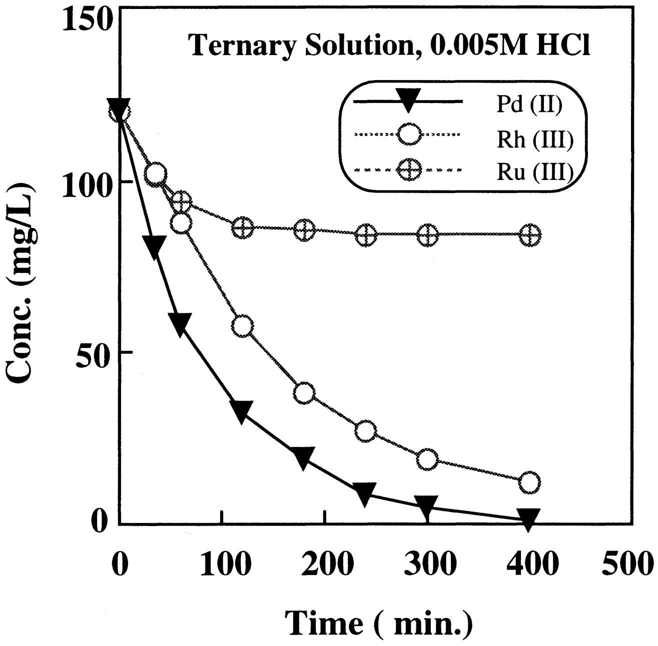

FIG. 7c A change in concentration profiles of Pd(II), Rh(III), and Ru(III) in a ternary solution of 0.005 M HCl. Mass of carbon = 0.3 g and solution volume = 40 mL.

greatly retarded the rate of Pd(II) adsorption. On the basis of this result we concluded that selective adsorption of Pd(II) from a ternary mixture is proton dependent. The overall adsorption rate constants and the adsorption capacities of metals in the ternary system are included in Table 2.

Competitive Adsorption: Binary Systems

Based on the adsorption results from the ternary system, we found that the selective adsorption of palladium was easier and hence we decided to investigate in greater detail the adsorption behavior of rhodium and ruthenium in the binary system. As indicated before, $RhCl(H_2O)_5^{2+}$ and $RuCl_5^{2-}$ are adsorbed differently on the activated carbon surface. However, both of them share a sharp adsorption edge in a narrow pH range (2.3–2.6). From Fig. 8 it was found that Rh(III) adsorption capacity was reduced to 8 mg/g (in binary solution) from 15mg/g (in single-component solution) due to the presence of Ru(III). Apart from the coadsorption effects of Ru(III), this remarkable reduction in the uptake of Rh(III) was partly attributed to an overlayer of $Ru(OH)_3$ precipitate at the reaction interface (pH above 3.0). Since the adsorption of Rh(III) is also accompanied by an increase in OH groups, the Ru(III) ions were rapidly converted to $Ru(OH)_3$ precipitate within a few hours. Furthermore, according to Fig. 8, adsorption of Ru(III) in a binary so-

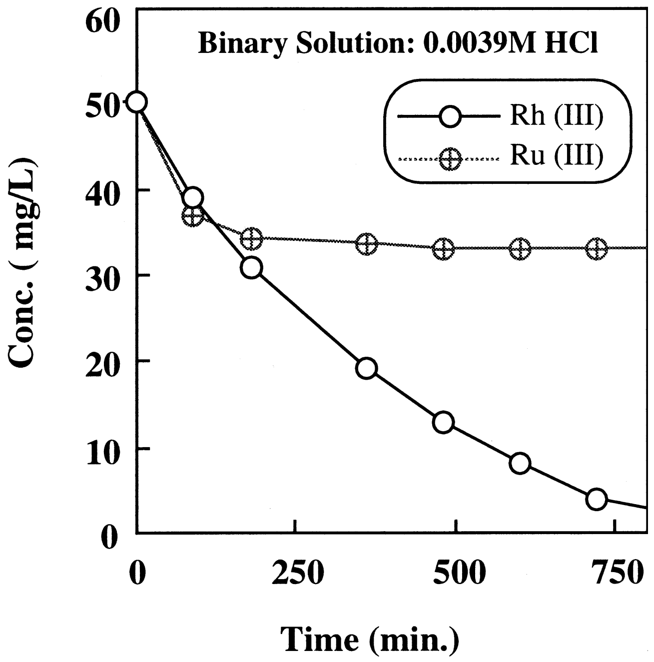

FIG. 8 A change in concentration profiles of Rh(III) and Ru(III) in a binary solution of 0.0039 M HCl. Mass of carbon = 0.2 g and solution volume = 20 mL.

lution ceased within 1 hour 30 minutes, indicating that Ru(III) reacted with OH groups in the solution.

Desorption of Metal Ions from Loaded Activated Carbon Pellets

Batch desorption tests were carried out on loaded activated carbons in three separate stages using various HCl concentrations: 1.2 M, 1.5 M, and 3 M. The pellets were loaded in the ternary system. Figures 9a, 9b, and 9c show the desorption results in order of increasing HCl concentrations. We established that Rh(III) and Ru(III) are readily stripped at HCl concentrations of 1.2 and 1.5 M, respectively. In other words, desorption of rhodium is based on a cationic exchange of H^+ and Rh^+ at the active site of oxygen groups. On the other hand, the desorption of anionic species was dependent on the exchange of Cl^- ions with adsorbed $RuCl_5^{2-}$ ions. It is not yet clear whether some adsorbed $RuCl_5^{2-}$ species react with free Cl^- ions at high HCl concentration to form the inert $RuCl_6^{3-}$ species.

In previous adsorption data we have shown that the uptake of $PdCl_3(H_2O)^-$ or $PdCl_4^{2-}$ is favorable at a protonated surface in 0.005–2.0 M HCl solution. However, at 3 M HCl concentration we found that Pd(II) ions gradually desorb away from the carbon surface. We attribute this desorption behavior to an-

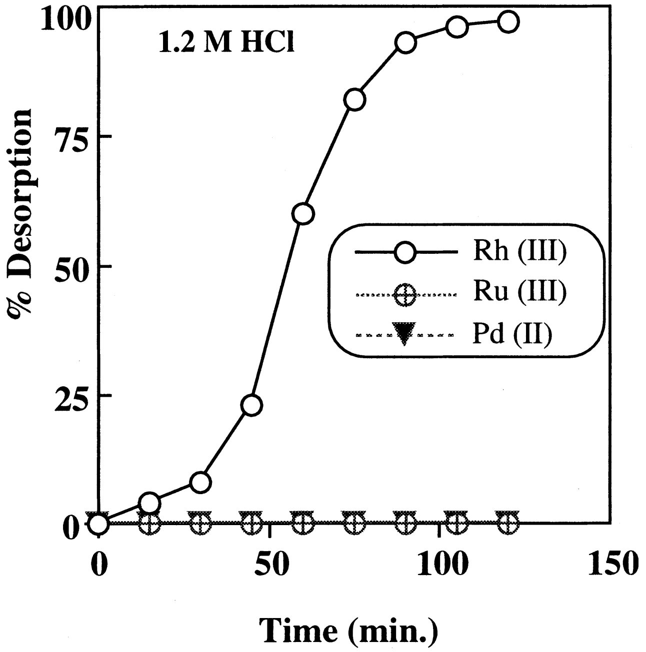

FIG. 9a % Desorption vs time. Competitive desorption of Rh(III) from a carbon surface. Acid strength of strip solution = 1.2 M HCl. Mass of carbon = 0.2 g and solution volume = 20 mL.

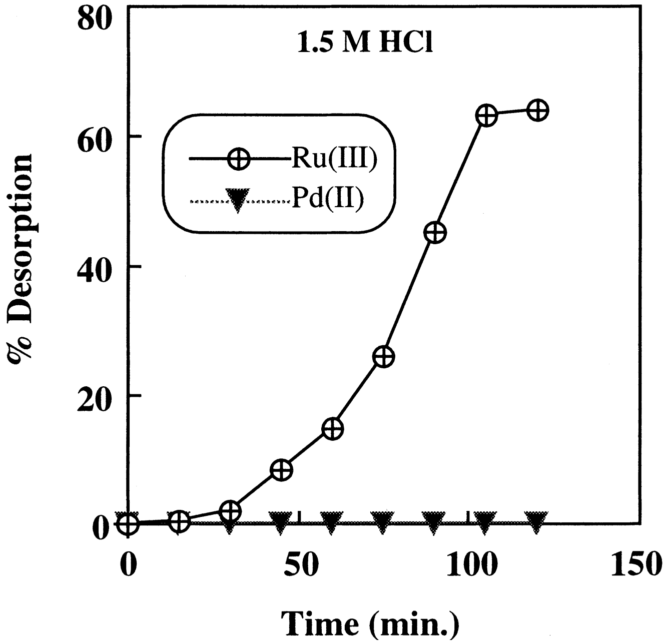

FIG. 9b % Desorption vs time. Competitive desorption of Ru(III) from a carbon surface. Acid strength of strip solution = 1.5 M HCl. Mass of carbon = 0.2 g and solution volume = 20 mL.

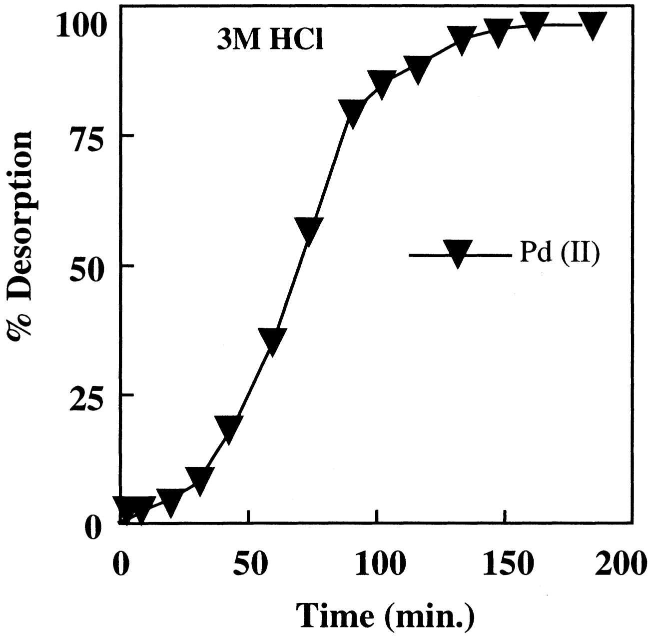

FIG. 9c % Desorption vs time. Acid strength of strip solution = 3 M HCl. Mass of carbon = 0.2 g and solution volume = 20 mL.

ionic exchange between the excess Cl^- groups and the adsorbed $PdCl_4^{2-}$ complex ions at the surface/solution interface. In general, desorption of palladium complexes was also found to be dependent on Cl^- concentration. In other words, excess Cl^- ions (approximately 3 M) adsorb prefentially on the protonated surface, displacing the $PdCl_3(H_2O)^-$ ions which are attached to the carbon surface through a proton. This is a relatively slow process. In Fig. 9a, 95% of rhodium (1.2 M HCl) is desorbed within 1.5 hours, while in Fig. 9c it took 2.2 hours to desorb 95% of palladium (3 M HCl).

COMPARISON OF ADSORPTION CAPACITIES

In this study we achieved adsorption capacities of 27, 15, and 4 mg/g for Pd(II), Rh(III), and Ru(III), respectively. The mass of activated carbon pellets used was in the 0.2–0.3 g range while the solution volume treated was 40 mL. The initial concentrations were 120 mg/L for Ru (III) and Rh(III) and 200 mg/L for Pd(II). Palladium was recovered at 2 M HCl concentration while rhodium and ruthenium were removed at pH 2.3. The contact time was 48 hours in most of the adsorption experiments.

We compared our results on adsorption capacities of PGMs to those for base metals and gold reported by other authors. We observed the following: Yavuz et al. (22) used granular Merck activated carbon (no. 2514) to remove the toxic Fe(III) from industrial effluents at pH 1.15. They achieved an adsorption capacity of 1.13 mg/g after employing a solid/liquid ratio of 1 g/50 mL. Lalvani et al. (23) conducted comparative adsorption tests on chromium (III or IV) using a novel activated carbon (product of soot from graphite) and a commercial activated carbon (RC) from Norit Company. At an initial Cr(III) concentration of 34.2 mg/L and pH 4.5, they achieved a better adsorption capacity of 24 mg/g for a commercial carbon. In the case of gold recovery using coconut shell activated carbon (ACIX), Teirlinck et al. (24) achieved an adsorption capacity of 150 mg/g after equilibriating (for 1 week) 0.2 g of activated carbon and a 1-L solution containing 50 ppm gold at pH 6.5. Finally, Carrott et al. (25) carried out adsorption tests to remove zinc from aqueous solution using at least three commercial activated carbons from Norit Company (Axo, SX+, and S51). They found that zinc adsorption on basic carbons like Axo and SX+ can be explained on the basis of $Zn(OH)_3^-$ interaction with a protonated carbon surface. Their report clearly showed that adsorption capacity was greater on basic carbons.

CONCLUSION

Because platinum group metals (Pd, Rh, Ru) exist as chlorocomplexes in chloride media whose charge or stability depends on Cl^- concentration, we concluded that adsorption of palladium and ruthenium at moderately high HCl concentration is a result of interaction between anionic species ($PdCl_4^{2-}$ or $RuCl_6^{2-}$) and the protonated delocalized zones of the carbon surface. Furthermore, the adsorption of $Rh(H_2O)_6^{3+}$ is favored by low HCl concentration since its interaction with oxygen functional groups is subject to competitive adsorption with protons. The above adsorption characteristics of PGMs make selective adsorption possible depending on proton concentration in the bulk solution. In this study we achieved high adsorption capacities for Pd (27 mg/g), Rh (15 mg/g), and Ru (4 mg/g) using 0.2–0.3 g dry activated carbon pellets. Adsorption of palladium [or Ru(III)] and rhodium was reversible at high Cl^- and proton concentrations, respectively. Thus, activated carbon with base properties was found suitable for the selective adsorption of palladium, rhodium, and ruthenium in chloride solutions.

APPENDIX

Speciation Diagram for Palladium Species in Chloride Media

Palladium ion forms several chloro complexes in chloride media. The stability constants of the complexes, α_i, were evaluated by Elding et al. (26)

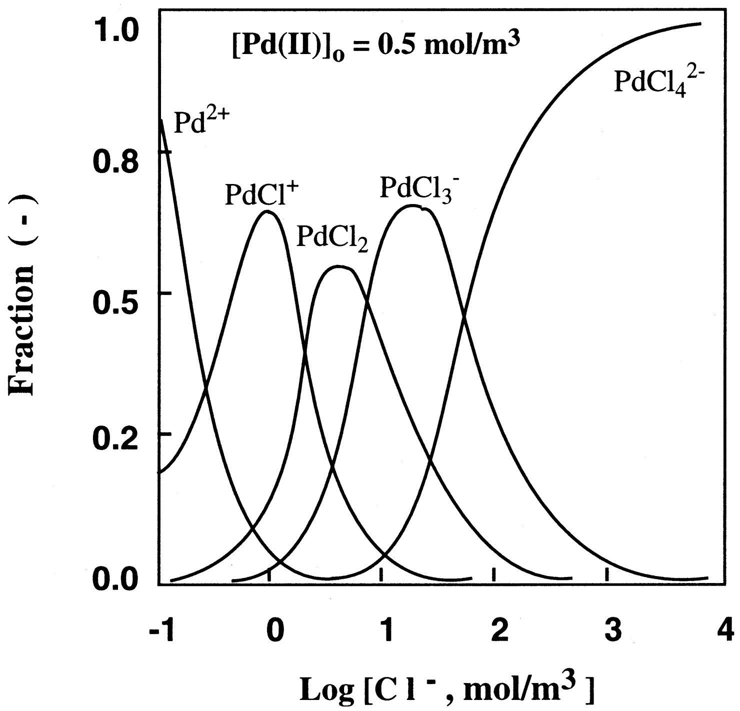

FIG. 10 Speciation diagram for Pd(II) in chloride media.

as follows:

$$\mathrm{Pd}^{2+} + i\mathrm{Cl}^- \leftrightarrows \mathrm{PdCl}_i^{2-i} \qquad (i = 4) \tag{A1}$$

$$[\mathrm{PdCl}_i^{2-i}]/([\mathrm{Pd}^{2+}][\mathrm{Cl}^-]^i) \tag{A2}$$

where $\alpha_1 = 10^{1.147}$, $\alpha_2 = 10^{1.76}$, $\alpha_3 = 10^{1.17}$, and $\alpha_4 = 10^{-0.46}$.

By using the values of α, the fraction of each complex in the chloride solution was evaluated, and the speciation diagram for the palladium species was derived as shown in Fig. 10.

NOMENCLATURE

b	Langmuir constant associated with temperature (L/kg)
C_i	concentration of species i (mol/m^3)
q	adsorption capacity (kg/kg)
K	adsorption equilibrium constant (kg/kg)
M	mass of carbon (kg)
Q	Langmuir constant associated with adsorption capacity (kg/kg)
t	time (minutes)
α_i	stability constant of chloro-complexes [$i = 4$, (m^3/mol)^i]
β	dimensionless adsorption factor (—)

Subscripts

ad	adsorption
Cl	chloride ion
e	equilibrium
f	final
0	initial
Pd	palladium ion
Rh	rhodium
Ru	ruthenium
t	time

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