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Selective Adsorption of Platinum from Mixed Solutions Containing Base Metals Using Chemically Modified Activated Carbons

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Abstract: Bituminous coal was activated by using steam at 750°C in a furnace. The activated carbon (AC) particles were chemically treated with thiophosphoric and amine type extractants, then characterized and tested for precious metal selectivity in chloride media. The adsorption of anions [$PtCl_4^{3-}$, $PdCl_4^{2-}$] or cations [$PtCl^+$, $PdCl(H_2O)^{3+}$, $Ni(H_2O)^+$, Cu^{2+}] on the carbon surface was elucidated by means of complexation and physical adsorption models. Owing to electrostatic repulsion in acidic media (>1 M HCl), the thio- and amine-treated bituminous ACs did not react with copper and nickel cations. The adsorption rate constant for platinum showed a dependence on solution pH and extractant dosage on the surface of the carbon and was of the order $10^{-2}\,min^{-1}$. A three-parameter Toth isotherm best described the adsorption data for single component solutions. Furthermore, platinum adsorption was described by pseudo first order kinetics neglecting the intra-particle diffusivity.

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INTRODUCTION

In the platinum industry, a converter matte containing sulphidic platinum group minerals is leached in two stages: atmospheric acid leaching to recover soluble nickel metal and high-temperature oxidative pressure leaching to recover copper and selenium metals. The final leach residue contains mostly platinum group metals (PGMs) with significant impurities of base metals. PGMs are soluble in halide salts at elevated temperatures and pressure (1, 2). In industrial practice, the PGMs from leach solutions are recovered by means of precipitation with NaHS (3) or by means of highly selective resins. Usually, selenium, copper, and nickel metal ions are removed from the leach solution by precipitation and electrowinning, while volatile metals are distilled off from the mixture prior to the recovery of PGMs. There are few published reports on the recovery of PGMs from solutions using activated carbons (4–6). In this paper, we made an attempt to illustrate that platinum could be recovered selectively from dilute solutions containing base metals using chemically modified activated carbons.

Activated carbons possess complex porous structures and various surface functional groups, which are dependent on activation methods (7–9). Activated carbons are cheaper than commercial resins and are nontoxic, making them environmentally friendly and profitable to use as adsorbents in the hydrometallurgical plants or as support material for metal catalysts (10). A few researchers have reported that pretreatment of carbon surface with azo and amino groups improves the adsorption of polymers or enhances the bonding strength between carbon surface and an epoxy matrix (11). In a similar work, but with different support material, researchers reported that organophosphorus-treated ferromagnetic microparticles enhance the adsorption of Zn and Cd (12).

The concept of grafting organic functional molecules on AC surface to specifically bind precious metal ions from dilute leach solutions is a new approach in adsorption research. Recently, we established that peat-based activated carbons could be used as carriers of metal extractants (5). The thio-treated ACs showed selective properties toward palladium, while amine-treated ACs interacted strongly with platinum in chloride solutions. Nevertheless, the selective ability of thio- and amine-treated carbons was not tested on mixed solutions containing precious and base metals.

In the current research, we focused our investigations on the following: (a) applicability of bituminous-based ACs as active carriers of amine and thio type of extractants and (b) selective binding properties of chemically treated bituminous ACs.

Adsorption of anions [$PtCl_4^{3-}$, $PdCl_4^{2-}$] or cations [$PtCl^+$, $PdCl(H_2O)^{3+}$, $Ni(H_2O)^+$, Cu^{2+}] on the carbon surface can be explained by means of physical adsorption and complexation models. The physical adsorption model involves the electrostatic interaction of metal species with the charged carbon surface while the complexation model involves covalent bonding. The speciation diagrams of PGMs or base metals provide information on the chemical nature and amount of metal species present in the feed solution at a given chloride concentration. Regarding the complexation of thio and amino groups with carbon surface, Buttry et al. (13) elucidated a mechanism in which nucleophilic amines [RN(R')H] react with electrophilic double bonds on the carbon surface to form covalent bonds. The nucleophilic alkyl–sulfur group, R–SH, readily releases a proton to the ketone (or carbonyl group) to form loose ensembles of thioacetyl groups on a carbon surface, which are reversible in highly acidic media (14). In our previous report, we made an attempt to characterize the nature of these covalent bonds, and binding energies of the amino ($\lambda = 195\,\mathrm{cm}^{-1}$) and thio ($\lambda = 215\,\mathrm{cm}^{-1}$) groups on the surface of activated carbons using a Kratos (AXIS − 65, SAC) X-ray photoelectron spectrometer (mono Al Kα, pass 80 eV, 7 mA, 15 kV) (5).

According to the speciation diagrams of Pt(II) and Pd(II) in chloride media (15–17), the most abundant Pt(II) and Pd(II) species are chloro-complex anions (HCl conc. $>$0.01 M) [e.g., in 0.01 M HCl solution, the percent ratio of $PdCl_3(H_2O)^-$ to $PdCl_4^{2-}$ is 65%:10%]. In this case, $PdCl_2$ and $PdCl^+$ species together account for the remaining 25%. Metal speciation of platinum and palladium in the bulk solution is dependent on chloride ion concentration. For solution pH values ranging from 2.7–2.9, palladium exists in the form of neutral species [$PdCl_2$, $PdCl_2.(H_2O)_2$], while in the same pH region platinum exists as $PtCl_3^-$ (15%), $PtCl_2$ (65%), and $PtCl^+$ (20%) complexes.

Adsorption Isotherms

The Langmuir isotherm model (18) assumes that there is a monolayer of adsorbed species on a homogeneous surface. The linearlized form of Langmuir isotherm is shown in Eq. (1)

$$\frac{1}{q_e} = \frac{1}{KQ_{sat}C_e} + \frac{1}{Q_{sat}} \tag{1}$$

where K is the adsorption constant (L/mg) and C_e is the concentration of species in the bulk solution at equilibrium, q_e is the mass of adsorbate per unit mass of adsorbent (mg/g) at equilibrium, and Q_{sat} is the maximum mass of adsorbate (mg/g) at saturation point, which is approached at large concentrations.

For a heterogeneous flat surface, the Freundlich isotherm fits adsorption data accurately over a wide range of concentrations. The Freundlich isotherm is described by Eq. (2) and expressed in logarithmic terms by Eq. (3).

$$q_e = KC_e^{1/n} \tag{2}$$

$$\log q_e = \log K \cdot + \cdot \frac{1}{n} \log C_e \tag{3}$$

where K is a constant of adsorption, and n is positive, q_e is the sequestered quantity of adsorbate at equilibrium. The Toth isotherm combines the Langmuir and Freundlich equations to produce an effective three-parameter (Q_{sat}, K, and n) equation that describes adsorption data on a heterogeneous surface.

$$q_e = \frac{C_e Q_{sat}}{\left[(1/K) \cdot + \cdot C_e^n\right]^{1/n}} \tag{4}$$

Mass Transfer and Adsorption Kinetics

Adsorption kinetics on microporous carbon surface appear to occur in two phases. The first phase consists of a rapid adsorption of metal ions, and the second phase shows a slow adsorption process. Usually, a pseudo first order adsorption rate is observed in the first stage of adsorption (19). The reaction- and diffusion-controlled models have been proposed to describe the kinetics of metal adsorption on porous adsorbents. With regard to the reaction model, researchers have reported that the surface reaction rate is often slower than the external mass-transfer rate (20–22). In other studies, researchers showed that the adsorption rate constant depended on feed pH, initial metal ion concentration, and temperature but was weakly dependent on agitation speed.

At equilibrium, the concentration of the fluid inside the particle pore and in the bulk solution are equal, $C_p = C$. Therefore, apparent diffusivity, D_e, can be estimated from Eq. (5) and subsequently used to determine the diffusivities in the pores (D_p) and solid (D_s) on condition that the adsorption isotherm is linear in the range of collected adsorption data.

$$D_e = \varepsilon_p D_p + \rho_p K D_s \tag{5}$$

where, ρ_p is the particle density, ε_p is the particle porosity, and K is adsorption constant. In the case of external mass transfer, the flux at the particle surface is expressed by Eq. (6)

$$J_e = k_f\left(C^b - C^s\right) \tag{6}$$

where, C^b and C^s are concentrations of components in the bulk solution and particle surface, respectively, and k_f is the mass-transfer rate constant. At steady state, flux at the particle surface [Eq. (6)] and rate of diffusion in the pores [Eq. (5)] are equal, thus

$$-D_e \frac{\partial C_p}{\partial r} = k_m(C^b - C^s) \tag{7}$$

However, if the diffusion of metal ions in solid carbon is negligibly smaller compared to intraparticle diffusion, then the apparent diffusivity consists mainly of diffusion in intraparticle pores.

$$\varepsilon_p D_p \frac{\partial C_p}{\partial r} = k_m(C^b - C^s) \tag{8}$$

Determination of intraparticle concentration gradient, $\partial C_p/dr$, in the pores requires a robust model in which a finite difference method is used to solve all differential equation using a computer software (23). The rate of adsorption can be assumed to be mass-transfer-controlled if the surface reaction is fast and spontaneous where $C^b - C^s$ is the driving force relationship

$$\frac{\partial q}{\partial t} = k_m \cdot f(q, C) \tag{9}$$

Further, if external mass transfer predominates adsorption, the rate constant, k_{ads}, is comparatively larger, and can be estimated from Eq. (10)

$$k_{ads} = \frac{k_m a}{\rho_b} = \frac{3(1 - \varepsilon)k_m}{\rho_b r_p} \tag{10}$$

where ε, ρ_b, a, and r_p are porosity, fluid density, unit surface area, and particle radius, respectively. Since ε, ρ_b, and r_p are constants, the rate constant increases with the external mass transfer. However, it is important to assess the effect of particle size on adsorption rate constant.

EXPERIMENTAL

Reagents

Low ash (7%) bituminous coal was supplied by Kleinkopje mine from Mpumalanga Province, South Africa. High-grade standard solution for analytical use of PtCl, $PdCl_2$, were purchased from Set Point Instrumentation, Johannesburg, South Africa. The standard solutions of $NiCl_2$ and $CuCl_2$ were supplied by Labchem (Pty) Ltd, Johannesburg, South Africa. The commercial suppliers of MSP-8 and 2-amino-2-hydroxymethyl-1,3-propanediol are Cyanamid Co, Cleveland, OH, USA, and Wako Chemical Co, Tokyo, Japan, respectively.

Preparation of Chemically Treated Activated Carbons

Bituminous coal was pulverized and crushed to different particle sizes ($d_{80} = 325-850\,\mu m$). Physical activation experiments were carried out in an activation furnace using steam at 750°C. Activated carbons were allowed to cool in the furnace, washed thoroughly with deionized water, and placed in an oven to dry at 110°C under nitrogen atmosphere. Finally, activated carbons were taken out of the oven and stored in a dessicator. Characterization of inherent porosity was completed by means of N_2 adsorption isotherms at 77 K using the ASAP 2000 micropore analyzer (Micrometrics, USA). Particle sizing (d_{80}) was achieved by using a set of standard ASTM screens. Except where stated, all adsorption experiments were conducted with bituminous ACs having a particle size of 325 μm.

Predetermined masses of ACs were placed into two bulk solutions of known concentrations [i.e., tris(hydroxymethyl)aminomethane (hydrophilic) and thiophosphoric acid (amphiphilic), a commercial extractant with a single donor sulphur atom known as MSP-8]. The amino and thio compounds were initially dissolved in distilled water and *n*-heptane solutions, respectively. The granular ACs were left to equilibriate with the chemical solutions for 24 h. The amine-treated ACs were filtered off and washed with distilled water to remove unreacted amino groups while the thio-treated ACs were washed with *n*-heptane to remove excess organic molecules. The AC samples were then dried in a vacuum (10^{-1} mm Hg) at 298 K for 24 h. All the pretreated carbon samples were stored in air-tight dessicators away from sunlight.

The surface properties of granular native and activated bituminous particles are shown in Table 1. For the purpose of comparison, the surface properties of commercial peat-based ACs are shown in Table 2. According to the pore diameter data in Table 1, bituminous ACs can be classified as microporous adsorbents ($10^{-3}-10^{-1}\,\mu m$) and the pore volume is sufficiently large to allow adsorption to take place in intraparticle pores. However, the total pore volume tends to decrease appreciably with MSP-8-treated ACs compared to that of amine-treated ACs mainly due to the fact that MSP-8

Table 1. Characteristics of chemically treated bituminous-based ACs (extractant dosage applied: 0.1 g/g, carbon)

Adsorbent (bituminous-AC)	Micropore area (m^2/g)	Micropore volume (cc/g)	Pore diameter (nm)
Native AC	530 ± 1.0	0.24 ± 0.01	2.12 ± 0.01
Amine- AC	518 ± 1.0	0.21 ± 0.01	2.07 ± 0.01
MSP-8 treated	497 ± 1.0	0.20 ± 0.01	2.02 ± 0.01

Table 2. Characteristics of chemically treated peat-based ACs (extractant dosage applied: 0.1 g/g, carbon)

Adsorbent (bituminous-AC)	Micropore area (m^2/g)	Micropore volume (cc/g)	Pore diameter (nm)
Native AC	637 ± 1.0	0.35 ± 0.01	2.51 ± 0.01
Amine AC	635 ± 1.0	0.33 ± 0.01	2.49 ± 0.01
MSP-8 treated	619 ± 1.0	0.28 ± 0.01	2.37 ± 0.01

has two long alkyl chains connected to a polar phosphoric group which covers the AC surface (5).

The procedure for quantifying the amounts of adsorbed amino and thio groups onto the surface of ACs involved a thorough analysis of initial and residual solutions using the UV/VIS Spectrophotometer (JASCO V-560) as discussed previously (9). First of all, a calibration exercise was carried out by correlating concentration and absorbance of the extractant solutions. A linear relationship was recorded. Then, known masses of carbon were placed in 50 mL flasks containing known concentrations of extractants. The mixtures in the flasks were air-tight sealed and placed in a thermostated mechanical shaker for 12–24 h. After attaining equilibrium, the carbon particles were decanted off and the microparticles in the decanted solution were filtered through 0.2 μm micromembranes (Advantech Millipores). The clear solution samples were then analyzed for absorbance and subsequently the concentration was read off from the calibrated graph. The characteristic wavelengths for MSP-8 and the amino group are 215 and 195 cm^{-1}, respectively. To control dosage on the AC surface, we contacted several different masses of AC particles with extractant solutions of fixed concentration and volume placed in several 50 mL flasks. The UV/VIS gives ± % uncertainty in the absorbance values. Other techniques such as gravimetry, TPD, or DRIFTS could be used (8) to give a direct measure of dosage, but these were not applied in this study due to lack of equipment.

Batch Adsorption Tests

In all batch experiments, 0.2 g ($d_{80} = 325$ μm) of chemically treated carbons were contacted with 50 mL (in 100 mL air-tight bottles) of chloride solution containing single or multiple metal species. For the equilibrium study, the sample bottles were placed in a thermostated mechanical shaker for 12–24 h. After achieving equilibrium state, solids were separated from the solution using a filter paper. A clear residual solution was analyzed for metal ions using the atomic absorption spectroscopy (Seiko, model SAS

760). The experimental variables were feed pH, temperature, chemical dosage, and metal composition in the feed.

RESULTS AND DISCUSSION

Separation of Platinum from Copper and Nickel Ions

The loading of platinum on the surface of amine- and thio-treated ACs was recorded for binary feed solutions containing palladium and platinum as shown in Figs. 1 and 2, respectively. In both cases, adsorption scaled with surface dosage of amino and thio groups. It is clear that amine- and thio-treated activated carbons showed affinity for platinum and palladium anions, respectively. We observed that at zero dosage (i.e.,untreated ACs), metal selectivity was poor mainly because both metals were adsorbed on the positively charged surface. Therefore, we attributed the selectivity and enhanced adsorption of precious metals due to the presence of amino and sulphur groups on the carbon surface. The rejection of palladium anions was proportional to the amine dosage on the AC surface and vice versa.

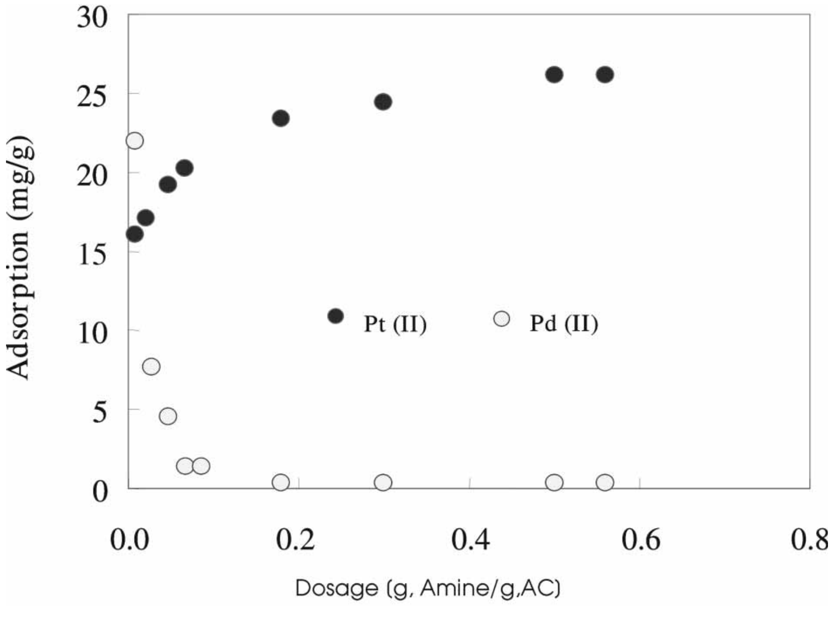

Figure 1. Adsorption of Pt (II) on amine-treated bituminous ACs vs. dosage [Pd (II), Pt (II)]$_o$ = 110 mg/L, mass of AC = 0.2 g, [HCl] = 0.1 M, contact time = 12 h.

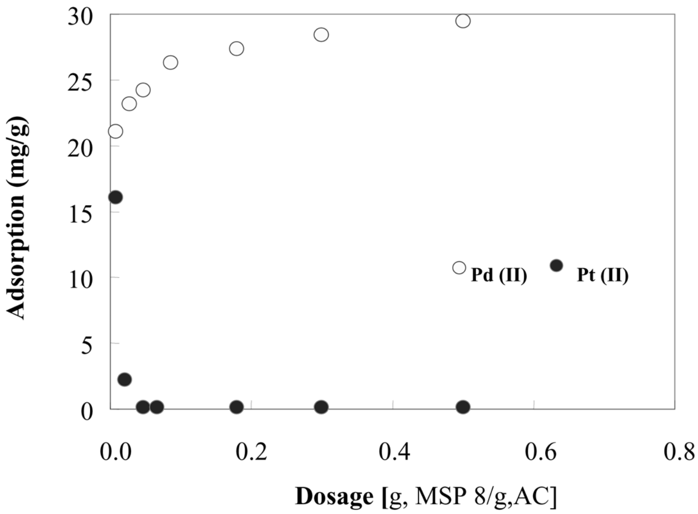

Figure 2. Adsorption of Pd (II) on MSP 8 -treated bituminous ACs vs. dosage [Pd (II), Pt (II)]$_o$ = 115 mg/L, mass of AC = 0.2 g, [HCl] = 0.1 M, contact time = 12 h.

Other researchers have observed a similar phenomenon in liquid-liquid separation systems. According to published data by Kakoi et al. (24, 25) and Baba et al. (26), extractants that contain sulphur as a donor atom exhibit affinity toward palladium anions, while extractants possessing amino groups react with platinum anions selectively.

The adsorption of palladium ions on the thio-treated ACs was attributed to the covalent interaction between palladium complex anions ($PdCl_4^{2-}$, $PdCl_3^-$) and both sulphur atoms and OH groups. However, at low dosage of MSP-8 (<0.03 g/g, AC), a small amount of platinum ions were co-adsorbed with palladium (Fig. 2) mainly due to insufficient MSP-8 molecules on the carbon surface. Platinum adsorption was not favored by a carbon surface covered with thio groups.

Uptake of platinum ions was enhanced on the surface of amine-treated ACs. The amino groups ($-NH_2$) were readily protonated at low pH (0.1 M HCl) and therefore physical attraction occured between platinum ($PtCl_6^{2-}$) anions and the positively charged ($-NH_4^+$) sites (Fig. 1). At 0.1 M HCl, the palladium speciation diagram shows that the amount of $PdCl_3^-$ anions in the feed is comparably smaller (5%) than that of $PdCl_2$ (75%), $PdCl^+$ (17%), and Pd^+ (3%), implying that palladium exists essentially as a neutral species at this pH. Therefore, selective adsorption of platinum ions at 0.1 M HCl was mainly because palladium existed mainly as a cationic or neutral species which was either repelled by the highly protonated surface or remained inert in solution. However, in the absence of amino groups at the carbon surface, appreciable amounts of $PdCl_2$ were adsorbed by covalent bonding on electron deficient carbonyl and OH sites. However, at higher HCl acid concentration (>1 M), palladium ions were co-extracted with platinum ions since under this condition palladium exists mainly as anionic species ($PdCl_3^-$). Data showing the adsorption profiles of palladium and platinum on untreated ACs at various acid strengths can be found in our previous article (4).

According to Fig. 3, co-adsorption $Ni(H_2O)^+$ (3mg/g) and Cu^{2+} (3,4 mg/g) ions with platinum anions (7.5 mg/g) on untreated bituminous ACs was found to be favorable at pH 3.0 implying that the surface condition was negatively charged. Platinum ions did not adsorb on the surface of carbon at pH higher than 3. Conversely, adsorption of base metal cations (Cu^{2+} and Ni^{2+}) decreased at lower pH (<2.9) due to formation of a positively charged carbon surface. The acid strength of the mixed solutions was adjusted with hydrochloric acid.

Figure 4 shows that amine-treated ACs did not adsorb Ni $(H_2O)^+$ and Cu^{2+} ions at a chloride concentration of 0.1 M and a dosage above 0.1 g/g due to repulsion between the protonated amino groups on the carbon surface and the cations in the solution. The positive charge on carbon surface was enhanced by the presence of protonated $-NH_4^+$ groups. At a chloride concentration of 0.1 M, the separation factor between base metals and platinum

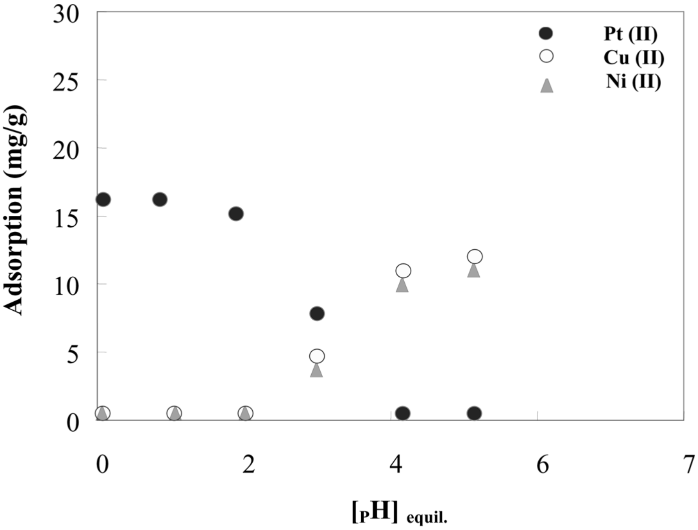

Figure 3. Adsorption of platinum, copper and nickel on native bituminous ACs at different feed pH. [Pt (II) = 71 mg/L, Cu (II) = 47 mg/L, Ni (II)]$_o$ = 51 mg/L, mass of AC = 0.2 g, contact time = 12 h.

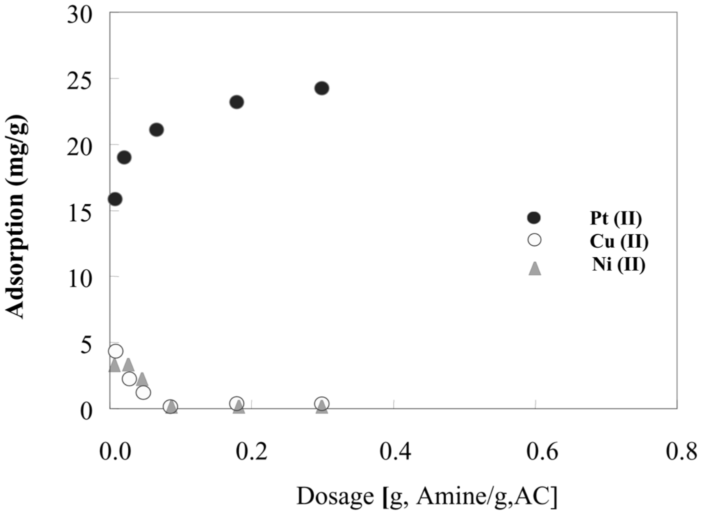

Figure 4. Adsorption of Pt (II) on amine-treated bituminous ACs vs. dosage. Mixed feed: [Pt (II)]$_o$ = 108 mg/L,Cu (II), Ni (II)]$_o$ = 50 mg/L mass of AC = 0.2 g, [HCl] = 0.1 M, contact time = 12 h.

increased from 4 (on untreated ACs) to infinity (on amine-treated ACs). The active sites that were responsible for adsorbing base metals in untreated ACs are mainly ketone (R–C=O) and ester (CH_2–O) groups. After chemical treatment the amino groups were bonded to the electrophilic sites containing ketone and ester groups. In our previous report, we confirmed the presence of amino groups on the carbon sites that were previously occupied by these chemical groups through X-ray spectra (5).

Adsorption Isotherms

The adsorption equilibrium of Pt(II) on treated bituminous ACs was characterized by using the Langmuir, Freundlich, and Toth isotherms. Figure 5 compares the platinum loading as predicted by each model isotherm. The adsorption data was fitted with the three parameter Toth isotherm fairly accurately using non-linear regression (Statistica program 6.0). The derived model parameters are listed in Table 3. It is clear from this result that Frieundlich isotherm overestimated adsorption of Pt(II) on the porous AC surface by assuming an exponential distribution of heats of adsorption while the Langmuir isotherm underestimated adsorption by assuming a flat and homogeneous surface.

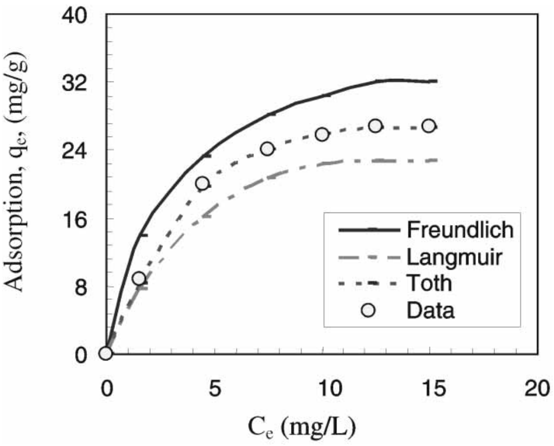

Figure 5. Predictive isotherm models describing adsorption data for platinum at T = 298 K.

Kinetics

Figure 6 illustrates the two types of adsorption profiles which we observed on amine-treated bituminous ACs; namely, a rapid adsorption of Pt(II) in the first 30 min followed by a slow adsorption process leading to equilibrium state. We assumed a mass-transfer-controlled rate in the initial adsorption stage and attributed the slow adsorption stage to pore diffusion. In the first stage of adsorption, Lagergren's pseudo first-order rate equation was applied to obtain the overall adsorption rate constants (Fig. 7). We established that the rate constant was of the order 10^{-2} $\min^{-1}$ for the acid concentration range 0.1–2.0 M HCl. The rate constants were then plotted against temperature (1/T) in the range 298–333 K and the enthalpy of adsorption was found to be approximately 0.7 J/mol.

As shown in Fig. 8, a reduction in particle size from 850 μm–425 μm improved the adsorption rate slightly by 20%, probably due to an appreciable increase in micropore area and volume of carbon particles, indicating that pore

Table 3. Predictive constants for Langmuir, Freundlich, and Toth isotherms at 298.15 K

Model	Q_{sat}	K (L/mg)	n
Langmuir	46.9	0.22	–
Freundlich	32.4	10.20	2.0
Toth	26.8	1.21	0.5

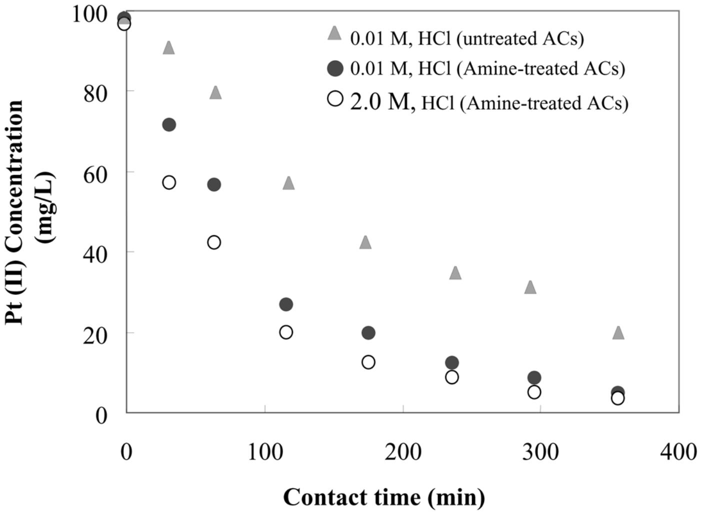

Figure 6. Adsorption of platinum on untreated and amine-treated bituminous ACs vs. time. The figure highlights the effects of acid strength and chemical treatment (0.08 g, amine/g, AC).

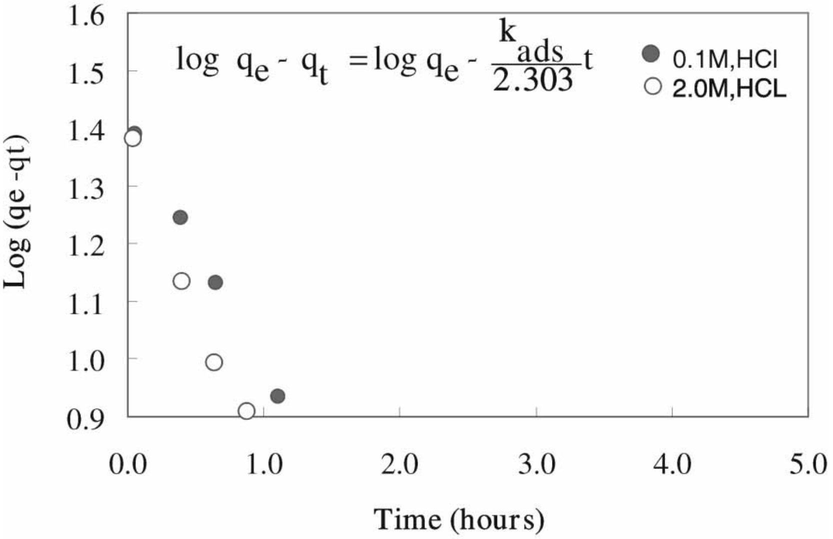

Figure 7. Logarithmic plot of Log (qe − qt) vs. time. Pseudo first order kinetics. Temperature = 298 K.

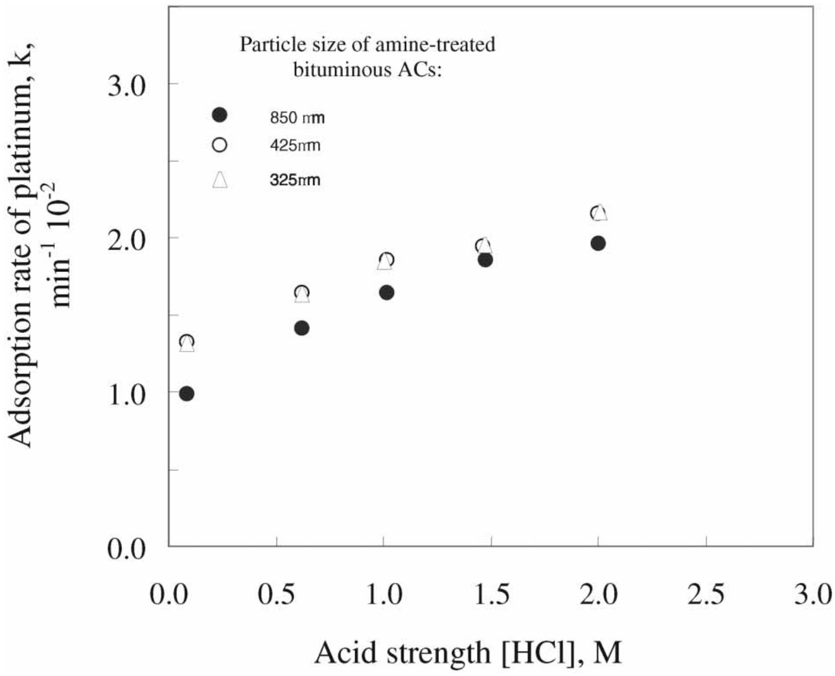

Figure 8. A plot of first order rate constant vs. acid strength of feed solution. Effect of particle size is highlighted in the figure. Temperature = 298 K.

diffusion effects were scaled down slightly by decreasing the particle size. Nevertherless, a further reduction in particle size to 325 μm did not appreciably increase the rate of adsorption.

The mass-transfer coefficient, k_m, was evaluated according to Eq. (10), where particle size at 325 μm and bulk density were kept constant. Mass-transfer coefficient was in the order of 10^{-1} cm/s for platinum adsorption on amine-treated ACs and in the acid strength region of 0.1–2 M HCl. Since the adsorption of copper and nickel on treated bituminous AC was extremely low, we did not investigate the effects of competitive adsorption on platinum uptake. In the next study, we will measure the surface potential of native and chemically treated carbons and correlate the surface charge to carbon performance. Also, we will study the desorption mechanism of PGM complex anions from the surface of carbon into a mixed solution.

Figure 9 compares the adsorption performance of commercial peat-based carbon and bituminous ACs. The result showed that the two adsorbents can be used as carriers of extractants effectively.

Activated carbons were successfully prepared from bituminous coal and subsequently used as active solid supports for phosphoric and amine

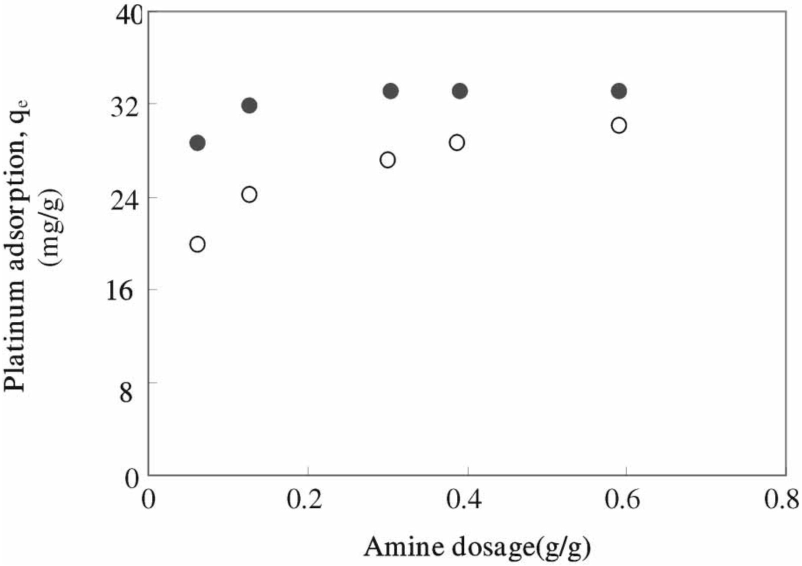

Figure 9. A comparison of platinum adsorption on amine-treated peat and bituminous ACs. HCl acid strength = 0.1 M, contact time = 12 h. $[\mathrm{Pt}]_o = 129\,\mathrm{mg/L}$, mass of AC = 0.2 g, solution volume = 0.05 L. • Commercial, Norit 0.8 AC pellets ○ Bituminous AC granules.

type of extractants. Chemically modified bituminous AC showed affinity for precious metals [Pt(II), Pd(II)] but did not adsorb base metals [Cu(II), Ni(II)] at high HCl acid concentrations. The adsorption kinetics was sufficiently fast with an adsorption rate in the order of $10^{-2}\,\mathrm{min}^{-1}$. It is hoped that chemically modified carbons will find wide applications in precious metal separation industry and compete well with commercial adsorbents or resins.

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