Equilibrium and Kinetic Studies of Platinum Adsorption from Acidic Chloride Solutions on Anionic Exchange Resin AG1-x8

Pan-Pan Sun, Tae-Young Kim, Byoung-Jun Min, Thi-Hong-Hue Dinh, Sung-Yong Cho

Abstract— **The adsorption properties of platinum from hydrochloric acid solutions on an anionic exchange resin (AG1-x8) were investigated. Adsorption of Pt increased with increasing temperature and decreasing acid concentration in the stock solution. The adsorption equilibrium isotherm of platinum on AG1-x8 resin could be described by the Langmuir adsorption model. Thermodynamic parameters indicated that adsorption of Pt on AG1-x8 resin was spontaneous and endothermic. Kinetic studies showed that adsorption of Pt onto AG1-x8 resin in this system followed pseudo-second-order kinetics.**

Index Terms— **Pt, adsorption, HCl, temperature, AG1-x8 resin**

I. INTRODUCTION

Platinum, together with other platinum group metals (PGMs), is extensively used in catalysts, electronic devices, space materials, and other applications. [1] The used/discarded products from such materials, especially spent catalysts, are an important secondary source of platinum. The concentration of platinum in the spent catalysts is generally higher than those in ore bodies. [2] In hydrometallurgical treatment of the spent catalysts, the valuable metals are first dissolved by leaching with chloride-based solutions. Solvent extraction and ion exchange methods are typically employed to separate platinum from the leaching liquors. [3–9]

Ion exchange technology is widely used in water treatment, hydrometallurgical separation and purification, chemical plants, pharmaceuticals and medicines, biotechnology, and drug delivery owing to its simplicity, selectivity, and efficiency. [10], [11] Further, compared with the solvent extraction method, it is a powerful method of recovering platinum from a feed solution with a low concentration, and it can produce platinum with high purity. [12], [13] Although many commercial ion exchangers for recovering PGMs from hydrochloric acid solution have been studied, features of interest, such as the effect of temperature on the equilibrium loading, are not covered well in the available literature. [3]

In this study, to determine the adsorption properties of platinum on AG1-x8 resin, batch adsorption experiments were conducted. The effects of the acidity of the feed solution and the temperature on adsorption were investigated. Adsorption equilibrium data were correlated with the Langmuir isotherm, Freundlich isotherm, and Sips isotherm models. The thermodynamic and kinetic parameters were studied under various experimental conditions.

Manuscript received March 22, 2016

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II. EXPERIMENTAL

A. Materials

The feed solution was prepared by dissolving $PtCl_4$ (Aldrich, 98%) in distilled water. The concentration of Pt was 1 × 10−3 mol/dm^3. The acidity was adjusted by adding HCl (Daejung, 35%).

Commercial resin AG1-x8 was purchased from Bio-Rad Laboratories; its properties are shown in Table 1. AG1-x8 resin is a strong basic anion exchanger with quaternary ammonium functional groups attached to the styrene divinylbenzene copolymer lattice. In this study, the resin was used as received, without any pretreatment.

B. Adsorption process

Batch experiments were performed in a shaker (VS-8480SF, Vision Scientific Co., Ltd.) in 100 cm^3 screw-top bottles. The temperature was adjusted in a range of 15 to 35 °C. Bottles containing feed solution (20 cm^3) and resin in the concentration range of 0.2–5 g/dm^3 were shaken for 24 h to obtain the adsorption equilibrium. In kinetics study experiments, the samples were shaken for predetermined time intervals. After separation by filtration, the concentration of metal ions in the solution was analyzed using ICPS-7500 (Shimadzu). The concentration of metal ion loaded onto the resin was obtained by mass balance.

III. RESULTS AND DISCUSSIONS

A. Adsorption equilibrium

Adsorption equilibrium information is important for understanding adsorption processes. In this study, the Langmuir, Freundlich, and Sips adsorption isotherms were used to correlate the experimental equilibrium data of adsorption of Pt on AG1-x8 resin. These isotherms are frequently used for analyzing experimental adsorption equilibrium data of metal ions during ion exchange. [14] The equation parameters of these models often provide insights into the adsorption mechanism and the surface properties and affinity of the adsorbent. These isotherm equations are as follows:

Langmuir isotherm, $q = q_m\, b\, c_e /(1 + b\, c_e)$ (1)

where c_e is the supernatant concentration at equilibrium (mol/m^3), b is the Langmuir affinity constant (m^3/mol), and q_m is the maximum adsorption capacity of the material (mol/kg), assuming a monolayer of adsorbate was taken up by the adsorbent.

Freundlich isotherm, $q = k\, c_e^{\,1/n}$ (2)

where k is the Freundlich constant related to the adsorption capacity (mol/kg)(mol/m^3)−1/n, and n is the Freundlich exponent (dimensionless).

Sips isotherm, $q = (q_m\, b C_e^{\,1/n})/(1 + b C_e^{\,1/n})$ (3)

where b is the Sips constant related to the affinity constant (mol/m^3) −1/n, and q_m is the Sips maximum adsorption capacity (mol/kg).

To obtain the isotherm parameters for each adsorption isotherm, the linear least squares method and a pattern search algorithm were used. The value of the mean percentage error was used as a test criterion for the fit of the correlations. The mean percentage deviation between the experimental and predicted values was obtained as follows:

$$error(\%) = (100/N)\sum_{k=1}^{N}\left[\left|q_{\exp,k} - q_{cal.k}\right| / q_{\exp,k}\right] \quad (4)$$

where $q_{cal,k}$ is each value of q predicted by the fitted model, $q_{exp,k}$ represents each value of q measured experimentally, and N is the number of experiments performed.

To investigate the effect of acid concentration on the adsorption behavior of Pt on AG1-x8 resin, adsorption experiments were conducted using a synthetic $PtCl_4$ solution at 25 °C. The concentration of HCl in the feed solution and the concentration of resin were varied from 1 to 5 mol/dm^3 and 0.1 to 10 g/dm^3, respectively. The results are shown in Fig. 1. According to Fig. 1, the amount of Pt adsorbed onto the resin decreased with increasing concentration of HCl in the feed solution. Because the predominant species of Pt is $PtCl_6^{2-}$ in 1–5 mol/dm^3 HCl solution, the adsorption of Pt onto AG1-x8 resin can be represented as follows:

Table 1. Properties of AG1-x8 resin.

Property	Value
Mesh	200–400
Total capacity (meq/cm^3 resin bed)	1.2
Density (g/cm^3)	0.75
Moisture	48%
Ionic forms	Chloride
Surface area (m^2/dry gram)	23

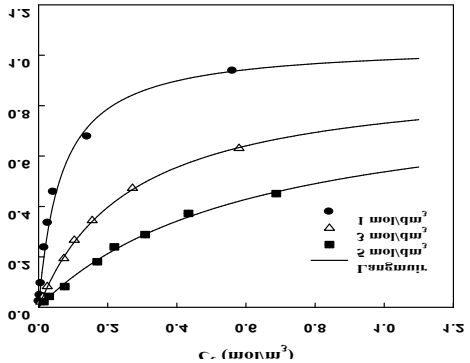

Figure 1. Adsorption equilibrium isotherm of Pt on AG1-x8 resin at different HCl concentrations (298 K)

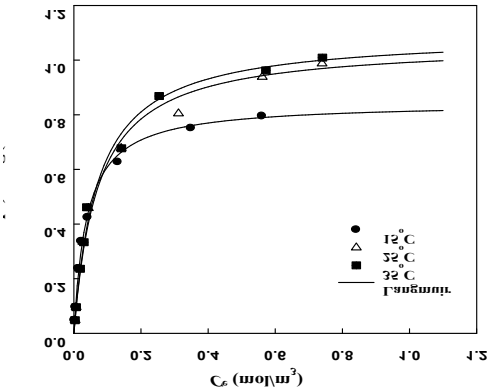

Figure 2. Adsorption equilibrium isotherm of Pt on AG1-x8 resin at different temperatures ([HCl] = 1 mol/dm^3).

Table 2. Adsorption equilibrium constants of Pt on AG1-x8 at different temperatures and acid concentrations

Isotherm type	Parameters	Temperature (HCl, 1 mol/dm^3)			HCl concentration (298 K)		
		288 K	298 K	308 K	1 M	3 M	5 M
Langmuir	q_m	0.84	1.06	1.09	1.05	0.92	0.87
	B	25.92	14.11	14.25	15.20	3.76	1.62
	Error (%)	3.56	8.15	4.42	7.98	1.95	5.27
Freundlich	K	1.48	1.56	1.65	2.36	1.29	0.72
	n	2.04	1.90	1.86	1.54	1.29	1.23
	Error (%)	28.24	29.19	27.89	31.81	13.91	7.30
Sips	q_m	0.84	1.01	1.09	1.05	0.92	0.87
	B	25.03	27.98	14.37	15.91	3.81	1.59
	n	1.01	0.88	1.00	0.99	0.995	1.01
	Error (%)	3.46	6.28	4.43	7.90	1.71	4.88

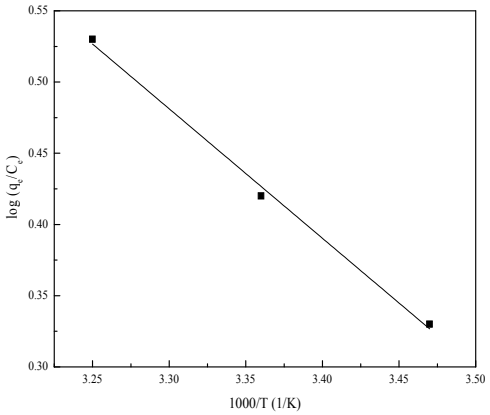

Figure 3. Plot of log qe/Ce vs. 1/T for adsorption of Pt on AG1-x8 resin at different temperatures ([HCl] = 1 mol/dm^3).

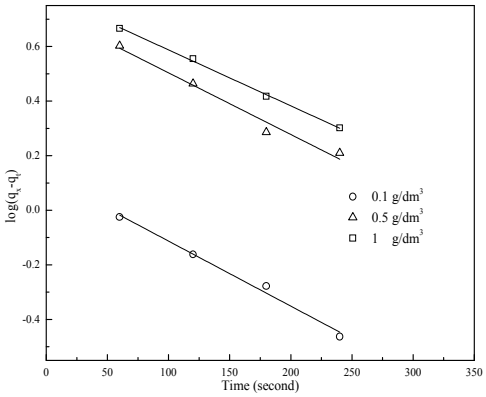

Figure 4. Linearized pseudo-first-order kinetic model at different AG1-x8 resin concentrations

$$2[RCH_2N^+(CH_3)_3Cl^-] + PtCl_6^{2-} = [RCH_2N^+(CH_3)_3]_2PtCl_6 + 2Cl^- \quad (5)$$

The above equation implies that adsorption of platinum decreases at higher concentrations of HCl because of the mass action effect of chloride ions. [1], [15]

To examine the effect of temperature on adsorption of Pt on AG1-x8 resin, the temperature was varied from 15 to 35 °C while the concentration of HCl in the feed solution was kept at 1 mol/dm^3.

Fig. 2 shows the effect of temperature on adsorption of Pt on AG1-x8 resin from a 1 mol/dm3 HCl solution. Adsorption increased slightly with increasing temperature, although the effect was not significant when thetemperature was increased beyond 25 °C. The reason may be explained as follows. With increasing temperature, the diffusion rate of complexes of molecules increases, and at higher temperature, more functional groups of ion exchangers are available owing to their surface activation. [14]

The obtained parameters and average percentage difference between the measured and calculated values for adsorption of Pt on AG1-x8 resin at different HCl concentrations and temperatures are listed in Table 2.

Table 3. Thermodynamic parameters of Pt on AG1-x8 at different temperatures ([HCl] = 1 mol/dm^3).

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	R^2
288	−1.74	16.984	0.065	0.997
298	−2.39			
308	−3.04			

Table 4. Kinetic parameters for adsorption of Pt onto AG1-x8 resin

Resin(g/dm^3)	Pseudo-first order			Pseudo-second order			Measured q_e (mol/kg)
	k_1 (min)	q_e (mol/kg)	R^2	k_2 (min)	q_e (mol/kg)	R^2	
0.1	0.0024	0.13	0.99	0.12	1.11	0.99	0.95
0.5	0.0023	0.73	0.97	0.10	6.53	0.99	6.51
1	0.0021	0.79	0.99	0.13	9.44	0.99	9.43

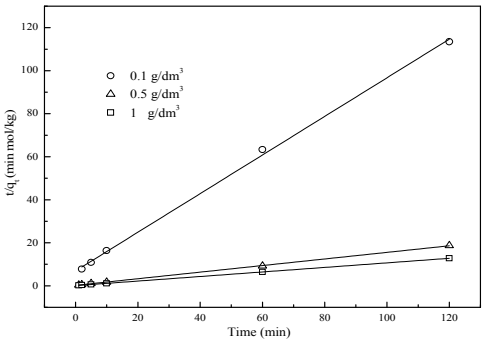

Figure 5. Linearized pseudo-second-order kinetic model at different AG1-x8 resin concentrations.

According to these results, for both cases, the Langmuir and Sips model fit the adsorption data well with little difference. Because the Sips model has one more adjustable parameter, the error value is smaller than that of the Langmuir model. Thus, the Langmuir model is sufficient to describe the adsorption of Pt on AG1-x8 resin under the present conditions.

A comparison of Fig. 1 and 2 reveals that the HCl concentration had a greater effect on the adsorption than the temperature did. Thus, efficient adsorption could be obtained by adjusting the acid concentration in the feed solution. The maximum amount of Pt adsorbed on AG1-x8 resin from 1 mol/dm^3 HCl was 1.06 mol/kg at 298 K. This value suggests that AG1-x8 resin is a good adsorbent for Pt uptake from aqueous solutions.

B. Thermodynamic study

According to the results shown in Fig. 2, increasing the temperature favored adsorption of Pt on AG1-x8 resin slightly. This observation indicates that adsorption of Pt on AG1-x8 is an endothermic process. Therefore, the free energy change ΔGo was calculated using the Van't Hoff equation:

$$\log \frac{q_e}{c_e} = -\frac{\Delta H^o}{2.303RT} + \frac{\Delta S^o}{2.303R} \quad (6)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (7)$$

where ΔGo is the change in the Gibbs free energy (J/mol), ΔHo is the change in the enthalpy (J/mol), ΔSo is the change in the entropy (J/mol K), R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K). The change in the Gibbs free energy of adsorption (ΔGo) calculated using Eq. (6) for different temperatures is presented in Table 3. The values of ΔHo and ΔSo were calculated from the slope and intercept of linear regression of log qe/Ce versus 1/T, as shown in Fig. 3. In this temperature range, the obtained ΔGo values are negative, suggesting that adsorption of Pt on AG1-x8 resin is spontaneous. [16], [17] The absolute value of ΔGo is directly proportional to the driving force of the adsorption process. Additionally, the positive value of ΔHo indicates that the process is endothermic, which is consistent with the observation in Fig. 2. The positive value of ΔSo suggests its increased randomness and can be associated with the affinity of the studied complexes toward ion exchangers. [18]

C. Kinetic study

In this study, the kinetics of adsorption of Pt onto AG1-x8 resin was analyzed using pseudo-first- and pseudo-second-order models. The pseudo-first-order rate expression of Lagergren can be expressed as [19], [20].

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303} t \quad (8)$$

where qe and qt are the amounts (mol/kg) of Pt adsorbed onto AG1-x8 resin at equilibrium and at time t, respectively, and k1 is the rate constant (1/min). Fig. 4 shows the Lagergren pseudo-first-order kinetic plot for adsorption of Pt onto AG1-x8 resin. The k1 and theoretical qe values were calculated from the slope and intercept, respectively (Table 4). The values of R2 are reasonably high in these cases; however, the calculated qe values obtained from this kinetic model (Table 4), which were too low compared with those obtained experimentally, were unreasonable. This phenomenon suggested that adsorption of Pt onto AG1-x8 resin does not follow Lagergren pseudo-first-order adsorption. A similar phenomenon was previously reported. [21]

The second-order kinetic model can be expressed as [22]

$$\frac{t}{q_t} = \frac{1}{k_{2,ad} q_{eq}^2} + \frac{1}{q_{eq}} t \quad (9)$$

where k_2 is the rate constant of the pseudo-second-order kinetic model (kg/mol min). The rate parameters k_2 and qe can be obtained directly from the intercept and slope of a plot of t/qt versus t, as shown in Fig. 5. The results in Table 4 show that the correlation coefficients for the second-order kinetic model were close to 1.0 for all cases, and the theoretical values of qe agreed well with the experimental data. The values of k_2 increased with increasing Pt concentration, presumably because of enhanced mass transfer of Pt ions to the surface of the AG1-x8 resin.

CONCLUSIONS

Adsorption of Pt on AG1-x8 resin increased with decreasing acid concentration in the feed solution and increasing temperature. The acid concentration in the feed solution had a greater effect on adsorption of Pt than the temperature did. The equilibrium data could be described well using the Langmuir model. A thermodynamic study suggested that adsorption of Pt on AG1-x8 resin occurred through endothermic interactions, accompanied by thermodynamically favorable entropy and Gibbs energy changes. Batch kinetic studies indicated that the kinetics data tended to fit the second-order kinetics.

ACKNOWLEDGMENTS

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (No. 2014R1A1A2007063). The authors are grateful for the financial support. The Gwangju Green Environment Center (No. 06-2-70-73) is also gratefully acknowledged.

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