

ADSORPTION OF Pb(II) ON METAL OXIDE PARTICLES CONTAINING ALUMINUM AND TITANIUM IN AQUEOUS SOLUTIONS

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Abstract : Metal oxide particles with mole ratio of aluminum: titanium of 1:1 were synthesized by a sol-gel method. Langmuir (a) and Freundlich (b) adsorption isotherms of dissolved lead [Pb(II)] ion on the metal oxide particles containing aluminum and titanium were determined as follows, respectively,

$$(a) q_e = \frac{1.326C_e}{1+6.678C_e}, (b) q_e = 0.687C_e^{(1/1.147)} \text{ at pH } 6$$

where, correlation coefficients (R^2) of Langmuir and Freundlich adsorption isotherms were 0.95 and 0.96, respectively.

The overall adsorption rate of Pb(II) on the metal oxide particles containing aluminum and titanium was determined by a differential bed reactor. The overall adsorption rate at pH 6 was as a following equation.

$$r = 0.016C_e^{2.264} - 30.060q_e^{4.270} \text{ at pH } 6$$

Key Words : adsorption, removal of lead [Pb(II)], metal oxide particle containing aluminum and titanium, sol-gel method, aqueous solutions

INTRODUCTION

With industrial advances, current interests in the study of water pollution problems have stimulated the removal of heavy metal ions from aqueous solutions. Heavy metal ions dissolved in aqueous solutions from the mine field and plating plant were considered as hazardous pollutants due to their toxicity even at a low concentration. The removal of heavy metals from industrial wastewater has become a very important environmental issue.¹⁾

Lead is a heavy metal used extensively in our industry. Since its high toxicity even at a

low concentration was reported²⁾, the removal method of Pb(II) from a wastewater has been the subject of studies in recent years. Zhan and Zhao³⁾ studied the mechanism of Pb(II) adsorption on a new adsorbent synthesized from natural condensed tannin. Barbier et al.⁴⁾ investigated the adsorption phenomena of Pb(II) and Cd(II) on montmorillonite, where the adsorption increased with pH and the adsorption rate of Pb(II) increased more rapidly than that of Cd(II). Sublet et al.⁵⁾ reported that the removal of lead from drinking water was investigated to develop a point-of-use water filter, where the measurement of equilibrium isotherms is not sufficient to predict the effectiveness of an adsorbent and must be coupled with dynamic experiments.

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A number of conventional methods for the removal of heavy metals from aqueous solutions have been reported such as ion exchange, electrochemical reduction, reverse osmosis, chemical precipitation, and membrane filtration.^{6,7)} However, since they have a few problems such as their operational demerits and high cost, modified technical processes have been studied recently. The adsorption process is shown to be an economically feasible alternative way for the removal of heavy metals from aqueous solutions.⁸⁾ The adsorption of heavy metals by inorganic materials such as silica, mica, kaolin, calcium carbonate, titanium dioxide, and alumina has received much attention owing to the latest development of more advanced skills and sophisticated equipment.^{9,10)}

The synthesis of a metal oxide containing titanium and aluminum and the study of adsorption characteristics was reasonable in considering its economic aspect and effective adsorptivity. Jiang and Gao¹¹⁾ found that the colloidal stabilization of nano-sized alumina in suspensions containing 1,2-dihydroxy-3,5-benzenedisulfonic acid disodium salt (Triron) with a varying pH was examined systematically. Nagashima and Blum¹²⁾ investigated proton adsorption onto alumina. Adsorption and precipitation processes of aqueous Zn(II) on alumina powders were reported by Trainor et al.¹³⁾ Fahmi and Minot¹⁴⁾ have proposed a model of water adsorption on the titanium dioxide surface. Ashida et al.¹⁵⁾ have studied charge movements on the interface between water and the titanium dioxide surface. However, since the expectation for high adsorption efficiency by using simply titanium dioxide or alumina as the adsorbent was limited,⁸⁾ the synthesis of inorganic materials with more enhanced adsorption efficiency than those of titanium dioxide and alumina, and so on was requested. Therefore, a metal oxide particle with aluminum and titanium was synthesized by a sol-gel method and the adsorption characteristics of Pb(II) was investigated.

Most adsorption studies on Pb(II) with an inorganic adsorbent in aqueous solutions laid

mainly stress on the influence of parameters such as adsorbent concentration, crystal structure of surface, pH, and temperature in a static system. Information obtained from the adsorption study was limited to applying for the industry. Therefore, this paper attempted to determine adsorption characteristics of dissolved Pb(II) with metal oxide particles containing aluminum and titanium, which was synthesized by a sol-gel method. Overall adsorption rate by a differential bed reactor was investigated in addition.

EXPERIMENTAL MATERIALS AND METHOD

The metal oxide particle containing aluminum and titanium was synthesized by a sol-gel method¹⁰⁾, where TTIP (titanium tetraisopropoxide, Junsei Co., Japan) and AIP (aluminum isopropoxide, Aldrich, U. S. A.) were used as chemicals. Ethylalcohol (Carlo Erba Co., France) was selected as an anti-gelatin agent in this experiment.

The metal oxide containing aluminum and titanium was synthesized with pH, mole ratio of TTIP/AIP, temperature for calcinations. Figure 1 is the synthesis process for metal oxide particles by a sol-gel method.¹⁶⁾

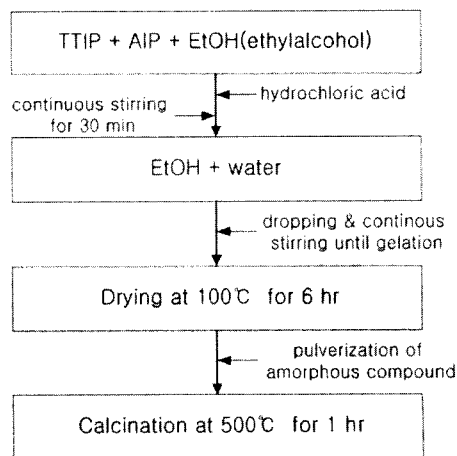


Figure 1. Synthesis procedure for metal oxide particle containing aluminum and titanium by a sol-gel method.

The metal oxide particle was synthesized by sol-gel method, where mole ratio of AIP: TTIP was 1:1, 2:1, 3:1, and 4:1, respectively, since the reaction was not done normally at mole ratio of AIP: TTIP with 1:2, 1:3, and 1:4. Average diameter of particles was controlled within 200~300 μm with the mill, which its specific area was 115~175 m^2/g , where was measured by using BET adsorption method with hydrogen gas.

The preparation method of solutions containing Pb(II) was as follows. Lead powder was dissolved in a 6 N HNO_3 solution and dried at 120°C. Adding 1 N HNO_3 solution to the dried lead-nitrogen-oxide compounds, the solution of 1,000 $\text{mg-Pb}^{2+}/\text{L}$ was prepared. The prepared solution was stored at pH 2 and diluted to 10 $\text{mg-Pb}^{2+}/\text{L}$ in the subsequent adsorption experiments.¹⁰⁾

The experiments for adsorption isotherms and effects of pH and adsorbent composition were performed with a 500 mL beaker in a static method. Overall adsorption rate in a dynamic state was determined by a differential bed reactor packed with metal oxide particles.^{17,18)}

The schematic diagram of a differential bed reactor is shown in Figure 2.

To determine overall adsorption rate, the differential bed reactor consisted of an acryl cylindrical reactor, a series of teflon rings, and

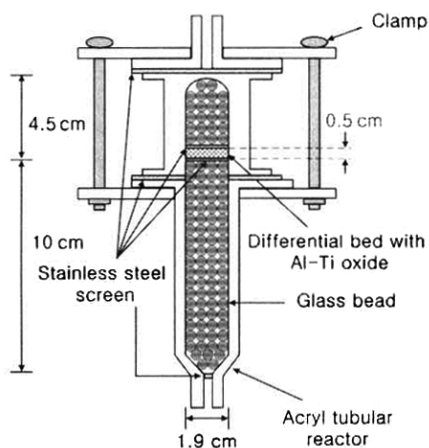


Figure 2. Schematic diagram of a differential bed reactor with dimensions.

stainless steel mesh screens. The total height of a reactor and the height of a bed with a clamp are 14.5 and 0.5 cm, respectively. The bed consisted of metal oxide particles containing aluminum and titanium. The 800 mesh steel screen was used to support the particles and glass beads.

A diagram of the apparatus with a differential bed reactor is shown as in Figure 3.

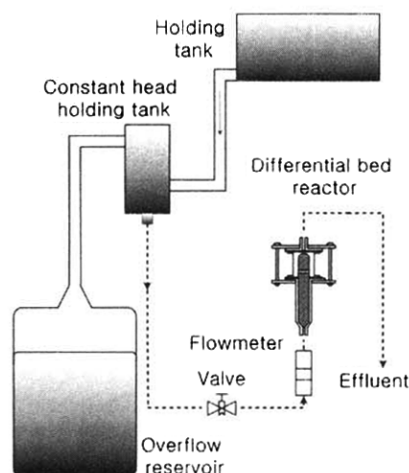


Figure 3. Schematic diagram of an experimental unit.

In order to maintain a constant head for the system, the feed solution of Pb(II) was placed to a constant head holding tank, which had an overflow port. The overflow from holding tank was recycled to the overflow reservoir. This mode of operation provided a constant liquid head to the system and insured continuous mixing of the feed solution. The flow rate of the solution leaving from the bottom of the constant head holding tank was regulated with a valve at the inlet of the rotameter located between the constant head holding tank and the differential bed. To minimize channeling, the space was filled with spherical glass beads between stainless steel screen immediately below the differential bed and an inlet at the bottom of acryl tubular reactor. Also the domed space above the differential bed was filled with glass beads of similar size. Samples leaving the re-

actor were collected and analyzed for Pb(II) concentration.

The adsorbed amount of Pb(II) was calculated indirectly by the difference between Pb(II) concentration remained in solutions before and after the adsorption,¹⁹⁾ where concentration of Pb(II) was measured at 217 nm wavelength with an atomic absorption spectrophotometer (AA, Model Z-6100, Hitachi Co., Ltd., Japan).

RESULTS AND DISCUSSION

Effects of pH and Composition of Metal Oxide Particle on Adsorbed Amount of Pb(II)

pH is one of very important parameters in controlling the adsorbed amount since hydroxyl concentration on the surface is affected by pH of solutions.¹⁰⁾ The variation of Pb(II) amount adsorbed on metal oxide particles with varying mole ratio of aluminum/titanium at pH 2, 6, and 9, respectively, is shown as in (a), (b), and (c) of Figure 4.

The adsorbed amount increased rapidly from the initial time to 10 h and slowly increased or remained constant over 10 hr. The amount adsorbed on metal oxide particle with 1:1 mole ratio of aluminum/titanium was larger than that with particles with any other mole ratio. At pH

2, the amount adsorbed on metal oxide with 1:1 mole ratio was 6.0, 6.8, and 7.0 mg-Pb²⁺/L in 5, 10, and 15 hr, respectively. At pH 6, the Pb(II) amount adsorbed on metal oxide with 1:1 mole ratio was 7.0, 7.9, and 8.0 mg-Pb²⁺/L in 5, 10, and 15 h, respectively. At pH 9, the amount adsorbed on metal oxide with 1:1 mole ratio of aluminum : titanium was 5.5, 6.8, and 6.8 mg-Pb²⁺/L in 5, 10, and 15 hr, respectively.

The varying adsorbed amounts at pH 2, 6, and 9, respectively, as shown in (a), (b), and (c) of Figure 4 is summarized as in Figure 5 and the adsorbed amount at maximum is shown at pH 6.

The adsorbed amount increased rapidly with increasing pH from 2 to 6 and decreasing pH from 6 to 9. Below pH 6, the adsorbed amount increased with an increasing pH, however, above pH 6 the adsorbed amount decreased with an increasing pH. The effect of pH on the adsorbed Pb(II) amount can be explained by the hydrogen concentration and the counter-ion activity in aqueous solutions.²⁰⁻²¹⁾

On metal oxide particles with 1:1 mole ratio of aluminum: titanium, the adsorbed amount at pH 2, 6, and 9 was 7.0, 8.0, and 6.8 mg-Pb²⁺/L, respectively. The amount adsorbed on the metal oxide with 2:1 mole ratio of aluminum: titanium pH 2, 6, and 9 was 5.8, 7.1,

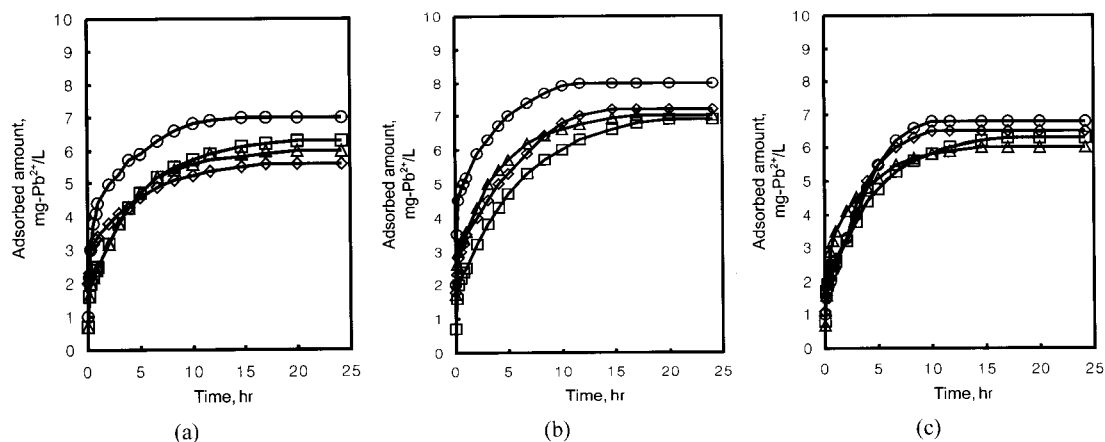


Figure 4. Relationship between time and Pb(II) amount adsorbed on metal oxide particles with mole ratio of aluminum: titanium (○ 1:1, △ 2:1, ◇ 3:1, and □ 4:1, initial concentration: 10 Pb²⁺ mg/L, particle concentration: 5 g/L, temperature: 23°C, (a) pH 2, (b) pH 6, and (c) pH 9.

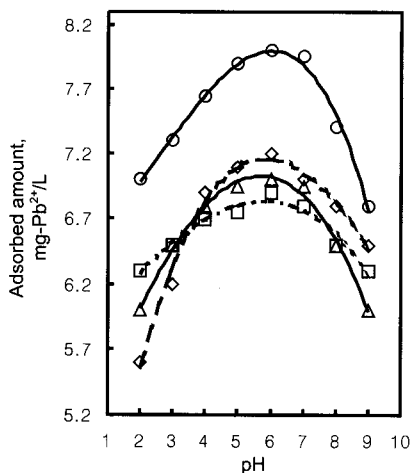


Figure 5. Relationship between pH and adsorbed amount with varying mole ratio of aluminum: titanium (\circ 1:1, \triangle 2:1, \diamond 3:1, and \square 4:1, temperature : 23°C for 25 hr).

and 6.0 mg-Pb²⁺/L. That with 3:1 mole ratio at pH 2, 6, and 9 was 5.6, 7.2, and 6.5 mg-Pb²⁺/L and that on the metal oxide with 4:1 mole ratio at pH 2, 6, and 9 was 6.3, 6.9, and 6.3 mg-Pb²⁺/L. Adsorptivity on the metal oxide particles with 1:1 mole ratio increased more by about 1.1% than that on the metal oxide particles with any other mole ratio. The adsorbed amount was the largest at pH 6. The specific surface area was 175, 132, 128, and 115 m²/g with 1:1, 2:1, 3:1, and 4:1 mole ratio of aluminum: titanium respectively, where it decreased with an increasing aluminum mole.

The fact that adsorptivity varied with pH was explained by the behavior of hydrogen ion (H⁺) and counter-ion activity in aqueous solutions.⁸⁾ Since hydrogen ion and Pb(II) activity increase simultaneously at pH 6, adsorptivity at pH 6 was higher than at any other pH. Since Pb(II) activity is lower at lower value than pH 6, adsorptivity decreased. At higher value than pH 6, adsorptivity decreased, too, since concentration of hydrogen ion decreased. Over pH 8, since concentration of hydrogen ion was too low, adsorption was not performed but precipitation was readily in strong basic region.

Mole ratio of aluminum/titanium was consi-

dered to affect on total surface energy and specific surface area of metal oxide. In case that mole fraction of titanium was higher than mole fraction of aluminum, the metal oxide containing both aluminum and titanium could not be obtained. At mole ratio of 1:1, the specific surface area was larger than any other mole ratio. The specific surface area decreased with an increasing of mole fraction of aluminum. Aluminum was considered to play a role to prevent titanium from being titanium dioxide.

Determination of Langmuir and Freundlich Adsorption Isotherms

Initial concentration of solution containing Pb (II) was changed from 0.05 to 0.16 mg-Pb²⁺/L and adsorption time was kept constant in 25 hr. Values of C_e and q_e with an increasing C_i were obtained as shown in Table 1 and adsorption isotherms in Langmuir and Freundlich forms^{22,23)} were determined as in Figure 6.

Table 1. Values of C_e and q_e with an increasing C_i on metal oxide particles with 1:1 mole ratio of aluminum: titanium (particle concentration: 1 g/L, pH 6, temperature: 23°C, calcination at 500°C)

(N=10)

C _i (Pb ²⁺ mg/L)	C _e (Pb ²⁺ mg/L)	q _e (Pb ²⁺ mg/g)
0.05	0.021	0.029
0.05	0.022	0.028
0.06	0.031	0.029
0.06	0.033	0.028
0.08	0.04	0.04
0.09	0.051	0.039
0.09	0.052	0.038
0.1	0.05	0.05
0.11	0.06	0.05
0.15	0.07	0.08
0.16	0.08	0.08

Figure 6 shows Langmuir and Freundlich adsorption isotherms on the metal oxide particles with 1:1 mole ratio of aluminum: titanium at pH 6.

From Figure 6, Langmuir adsorption isotherm was given as Equation (1). Langmuir isotherm coefficient (KL) was 6.678 and standard deviation

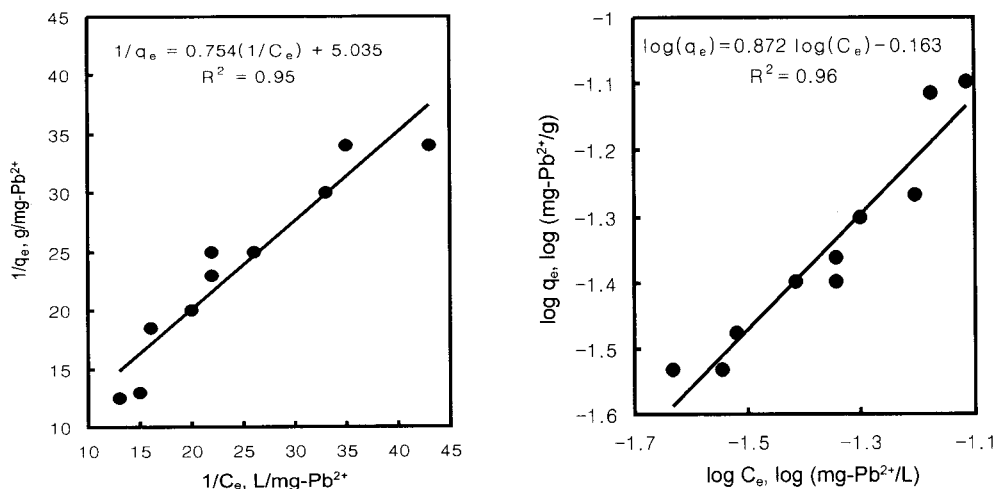


Figure 6. Langmuir and Freundlich adsorption isotherms of Pb(II) on metal oxide particles with 1:1 mole ratio of aluminum: titanium (particle concentration: 5 g/L, pH 6, temperature: 23°C, calcination at 500°C); (a) Langmuir adsorption isotherm and (b) Freundlich adsorption isotherm.

was 0.021.

$$q_e = \frac{1.326C_e}{1+6.678C_e} \tag{1}$$

And Freundlich adsorption isotherm at pH 6 was calculated as Equation (2).

$$q_e = 0.687C_e^{(1/1.147)} \tag{2}$$

where q_e is the amount of Pb(II) adsorbed on the metal oxide of unit weight and C_e is the residual concentration of Pb(II) in solutions which have been removed partially at equilibrium state. Freundlich isotherm coefficient (K_F) was calculated as 0.687 and standard deviation was 0.027. In previous works on Pb(II) adsorption on calcite-type calcium carbonate¹⁰⁾, rutile-type titanium dioxide¹⁷⁾, alpha-type alumina¹⁷⁾, Freundlich isotherm coefficient (K_F) was 0.345, 0.558, and 0.692, respectively. Coefficient (K_F) of metal oxide particles containing aluminum and titanium is higher than calcium carbonate and titanium dioxide but lower than alumina. Aluminum (Al) was considered as an

important role to enhance adsorptivity of an adsorbent.

Values of correlation coefficient (R^2) of Langmuir and Freundlich adsorption isotherms were 0.95 and 0.96, respectively. Adsorption characteristics on the surface of metal oxide particles was partially heterogeneous in its composition with aluminum and titanium as correlation coefficient of Langmuir adsorption isotherm was low.⁷⁾ Although the remarkable difference between values of correlation of Langmuir and Freundlich adsorption isotherms could not be observed, if recommend to be used, it is reasonable to select Freundlich adsorption isotherm.

Determination of Overall Adsorption Rate

The experiment for the overall adsorption rate was performed with constant flow rate at 200 mL/min to minimize film diffusion resistance as shown in Figure 7.

Initial adsorption rate increased rapidly with an increasing flow rate from 10 to 126 mL/min and it was constant over 126 mL/min. Since film diffusion resistance decreases with an increasing initial adsorption rate,²⁴⁾ film diffusion

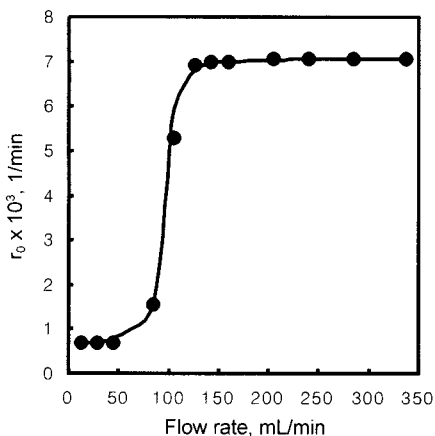


Figure 7. Relationship between flow rate and initial adsorption rate of Pb(II) for film diffusion resistance (metal oxide particles: 1 g, pH 6, temperature: 23 °C, calcination at 500°C).

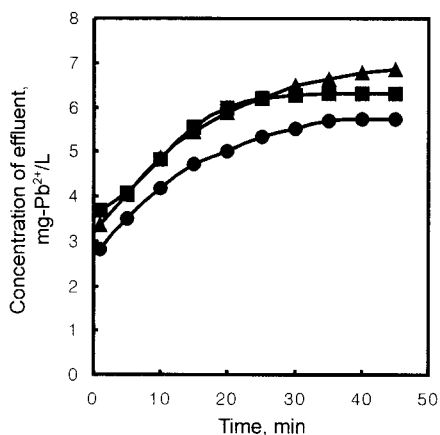


Figure 8. Relationship between time and Pb(II) concentration of effluent from bed (\blacktriangle : pH 2, \bullet : pH 6, and \blacksquare : pH 9, particle: 1 g, temperature: 23°C, flow rate: 126 mL/min, calcination at 500 °C, initial concentration: 10 mg-Pb²⁺/L).

resistance was assumed to be minimized over 126 mL/min. The effluent concentration from the end of differential bed with time is shown as in Figure 8.

Concentration of the effluent at pH 6 was 2.8, 3.5, and 4.2 mg-Pb²⁺/L in 1, 5, and 10 min, respectively. Concentration of the effluent at pH 2 was 3.3, 4.1, and 4.8 mg-Pb²⁺/L in 1, 5, and 10 min, respectively. At pH 9, Concentration of the effluent was 3.7, 4.1, and 4.8 mg-Pb²⁺/L in

1, 5, and 10 min, respectively. The initial concentration was 10 mg-Pb²⁺/L in this experiment. The adsorbed amount of Pb(II) on the metal oxide particles at pH 6 was larger than those of pH 2 and 9 in the range from initial time to 45 min.

The solid-liquid interface adsorption is usually complicated by the presence of a film diffusion across the external solid surface and a particle diffusion through the pores of the solid. It is necessary to establish the operating conditions to minimize the influence of film and particle diffusions. With the elimination of these diffusion effects, the net rate of the adsorption may be expressed in a general form as an overall adsorption rate.¹⁰⁾

The overall adsorption rate can be expressed as shown in Equation (3).

$$r = k_1 C_e^{a_1} - k_2 q_e^{a_2} = \text{forward adsorption rate} - \text{reverse adsorption rate} \quad (3)$$

The overall adsorption rate could be obtained from experimental data as shown in Figure 9(a) and Figure 9(b).

Values of a_1 and k_1 of a forward adsorption rate were determined by a straight line in Figure 9(a).

From the relationship between $\log q_e$ and $\log (k_1 C_e^{a_1} - r)$ shown in Figure 9(b), a_2 and k_2 were obtained. The overall adsorption rate of Pb(II) on the metal oxide particles containing aluminum and titanium at pH 6 was shown as a following Equation (4), where k_1 , k_2 , a_1 , and a_2 was 0.016, 30.060, 7.264, 4.270, respectively, and standard deviations were 0.0005, 1.021, 0.211, 0.164, respectively.

$$r = 0.016 C_e^{7.264} - 30.060 q_e^{4.270} \quad (4)$$

CONCLUSIONS

In this experiment, metal oxide particles used as the adsorbent were contained aluminum and titanium, which were synthesized by a sol-gel

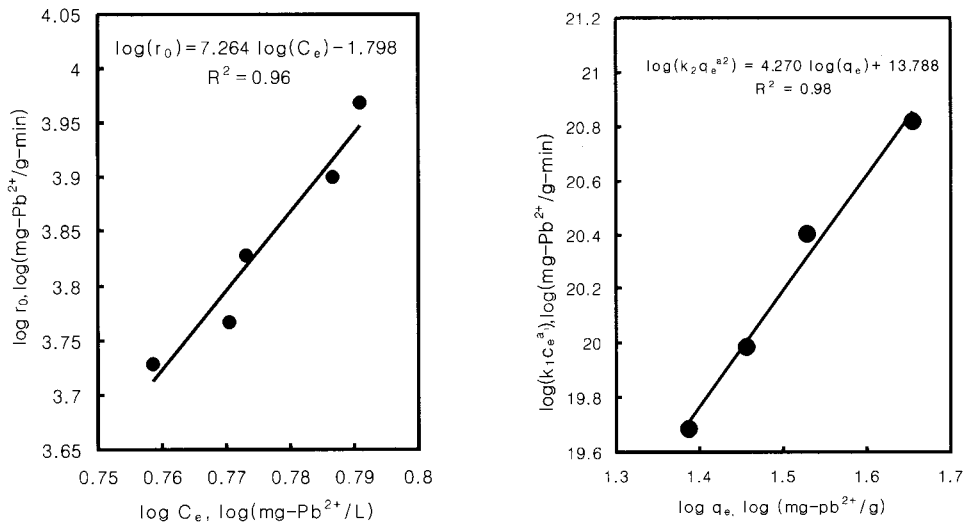


Figure 9. Relationships (a) between $\log C_e$ and $\log r_0$ and (b) between $\log q_e$ and $\log(k_1 C_e^{a_1} - r)$ for metal oxide particles containing aluminum and titanium (mole ratio of aluminum: titanium=1:1, pH 6, temperature: 23°C, calcination at 500°C, flow rate: 126 mL/min).

method. In case mole ratio of Al:Ti was 1:1, adsorptivity on metal oxide was higher than that with any other mole ratio.

The adsorption isotherms of Pb(II) on metal oxide in a batch reactor was obtained. Langmuir (a) and Freundlich (b) adsorption isotherms were obtained as following equations, respectively,

$$(a) \quad q_e = \frac{1.326C_e}{1 + 6.678C_e},$$

$$(b) \quad q_e = 0.687C_e^{(1/1.147)} \quad \text{at pH 6}$$

where, the correlation coefficients (R^2) of Langmuir and Freundlich adsorption isotherms were 0.95 and 0.96, respectively. The adsorption amount increased rapidly from pH 2 to pH 6 and decreased over pH 6, where the adsorbed amount was 8 mg/L at pH 6. The adsorptivity on the metal oxide particles, which the ratio of aluminum: titanium was 1:1, was more higher by about 1.1% than that with other mole ratio at pH 6.

The overall adsorption rate of Pb(II) on the

metal oxide particles containing aluminum and titanium by a differential bed at a flow rate of 126 mL/min at pH 6 was determined as a following equation.

$$r = 0.016C_e^{7.264} - 30.060q_e^{4.270}$$

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