REMOVAL OF COPPER(II) ION BY KAOLIN IN AQUEOUS SOLUTIONS

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Abstract : This study concerns the removal of copper ion (Cu^{2+}), which is a highly toxic element, from wastewater by using kaolin in a adsorption process. Experiments were performed at kaolin concentration of $50 \ g \cdot L^{-1}$ in a static system with a batch type. The adsorptivity increased rapidly with an increasing pH value from pH 3 to pH 5 and more slowly with an increasing pH value from pH 5 to pH 8. The pH value of the solutions decreased from pH 5.5 to pH 4.2 with time owing to the ion-exchange mechanism between the hydrogen ion and the Cu^{2+} ion. The isoelectric point of solutions containing $50 \ g \cdot L^{-1}$ kaolin was 4.3 at 28°C. The adsorptivity increased with an increasing pH value, whereas the zeta potential decreased. Adsorption rate constants at pH 4 and 7 at 28°C were 5.43×10^{-2} and $4.63 \times 10^{-2} \ min^{-1}$, respectively. The adsorption of Cu^{2+} on kaolin did not make CO_2 of a by-product.

Key Words : adsorption, copper ion, kaolin, pH dependence

INTRODUCTION

Current interest in the study of water pollution problems has stimulated interest for the removal of heavy metal ions from aqueous solutions by various methods. The removal of metal ions with a method such as neutralization or precipitation is ineffective owing to the high solubility of these metal ions.[1] Studies on the adsorption of heavy metal ions by inorganic material have received much attention due to the recent development of more advanced skills and sophisticated equipment.[1~4]

As copper ion (Cu^{2+}) is a highly toxic element, the removal of Cu^{2+} from wastewater has been the subject of many studies. Shim and Ryu[1] found that the adsorptivity of Cu^{2+} on the activated carbon fiber was not affected by physical properties but rather by chemical properties. Spark et al.[2] studied the adsorption characteristics of Cu^{2+} on goethite, alumina, and silica and showed that the adsorption efficiency of Cu^{2+} on goethite was the best and that of silica is the worst. Zaporozhets et al.[4] studied the interaction phenomena between adsorbed Cu^{2+} and silica gel, where Cu^{2+} was adsorbed effectively on the surface of silica gel immobilized with the ratio of Cu^{2+} : 1,10-phenanthroline = 1:1. Korngold et al.[5] found that Cu^{2+} from tap water could be effectively adsorbed using a cation exchange resin with an imino-di-acetic acid group. Lee and Davis[6] and Jung et al.[7] studied the removal of Cu^{2+} by the seafood gained from waste sludge, where Cu^{2+} was strongly adsorbed at pH 6 and the efficiency of a metal removal was affected by the initial metal concnetration. Vengris et al.[8] found that the clay treated with a 20% HCl

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solution was effective on the Cu^{2+} removal from wastewater.

Kaolin is an inorganic material which so far cannot be synthesized and yet has advantages in its cost and productivity. Kaolin has three types of crystalline surfaces onto which adsorption can take place: a flat oxygen plane associated with a silica (tetrahedral) sheet, a hydroxyl plane associated with an alumina (octahedral) sheet, and particle edges formed from an incomplete or irregular lattice structure in the silica-alumina layers.

In this study the adsorption by using kaolin was carried out to investigate various aspects of an adsorption process. Spark et al.[9] showed that the adsorption process of heavy metals on kaolinite was dependent on the pH value. Chen et al.[10] studied the kinetics of phosphate adsorption with kaolinite in aqueous solutions, where the first-order rate constant at 50°C was 0.022 day^{-1} and the activation energy at rate of 2.4 Kcal·mol^{-1} increased with an increasing temperature. Dalang et al.[11] reported that the adsorbed fulvic material led to an increase in the total amount of adsorbed Cu^{2+} on kaolinite, when systems containing free Cu^{2+} concentrations were compared. Blokhus and Ersland[12] reported that the adsorption of sodium dodecyl sulfate on kaolin increased with an increasing chain length of the alcohol in the alcohol-water solvent by using parameters such as the dielectric constant of solvent and other aggregation properties. Husband[13] reported that the widely differing adsorption behavior occurred onto kaolin depending on the source of the starch and its derivation and Hussein et al.[14] studied the removal efficiency of a carotene by a kaolin-carbon adsorbent, where the optimum carotene adsorption was at 20 wt% kaolin of the adsorbent.

This study was performed to examine the removal of Cu^{2+} on kaolin at the optimum condition in an adsorption process and to investigate the pH dependence of Cu^{2+} adsorption in aqueous solutions.

EXPERIMENTAL

Materials

The kaolin employed in this study was obtained from natural soil in Hadong, Gyungnam, Korea. Its density, BET specific area, and hardness are 2.6 g/cm^3, 14.2 m^2/g, and 2~2.5. Kaolin has two major components; silica and alumina. The minor components are inorganic oxides such as iron, calcium, titanium, and magnesium.[15]

The adsorptivity is affected by surface pollutants. The purification condition of kaolin is very important when investigating the adsorption behavior on the surface. Kaolin was placed in aqueous solutions of pH 2~4 for 4~6 h to remove pollutants on the surface. It was then cleaned in aqueous solutions at pH 9~10 for 4~6 h and washed in distilled water for at least one day. Finally, it was dried in an oven at 100~110°C for 2 days.[10,15] The dried kaolin was ground to particles of 25 μm of average diameter as shown in Figure 1.

If the kaolin particle size is too fine, the resulting flocculation would inhibit the Cu^{2+} adsorption as the surface site area available for adsorption decreases.[9]

The copper sulphate(CuSO$_4$·5H$_2$O, Wako Pure Chemical Co., Japan) was used to make the copper solution and the initial concentration of the copper solution was at the concentration of 5 Cu^{2+} mg/L.
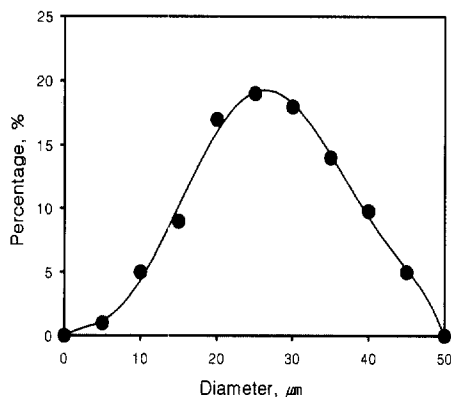

Figure 1. Particle size distribution of kaolin particles.

Methods

The adsorption experiments were performed with a 200 mL beaker to determine the optimum conditions; adsorption time and kaolin weight to investigate the adsorption behavior with a varying pH value. The reactor employed was a cylinder type (diameter: 300 mm, height: 420 mm) with a stirrer. The kaolin particle solution of 10 L was placed in the reactor and stirred at 10,000 rpm by using an agitator (model: 4554-00, Cole-Parmer Instrument Co., U.S.A.).

The concentration of Cu^{2+} in the solution was measured using an inductively coupled plasma mass spectrometer (model: PS 1000, Leeman Labs. Inc., U.S.A.) and the amount of adsorbed Cu^{2+} on the kaolin was indirectly evaluated by calculating the difference between the initial and final concentrations. The solution pH was measured by a pH meter (model: 720A, Orion Research Inc., U.S.A.) and the zeta potential was measured using a zeta potential analyzer (model: 3000HS, Malvern Co., U.S.A.). The by-product, CO_2, the gas from the adsorption of Cu^{2+} on kaolin was detected by the gas chromatography(model: M-600D, Younglin Co., Korea, column; carboxen-1004, carrier gas: He).

RESULTS AND DISCUSSION

The change of a Cu^{2+} concentration in aqueous solutions with time at pH 5.8 and kaolin concentration of 50 g/L was shown in Figure 2. Up to 10 h the Cu^{2+} concentration decreased rapidly to 0.8 Cu^{2+}mg/L with time, through 0.35 Cu^{2+}mg/L at 15 h and leveled off in 0.2 Cu^{2+}mg/L after 20 h. It is reasonable that the period of about 20 h is enough to reach the adsorption-equilibrium state.

Figure 3 shows the relationship between kaolin concentration and adsorptivity at pH 5.8. The adsorptivity (τ) of Cu^{2+} on the kaolin was then calculated by the following Equation (1).[16,17]

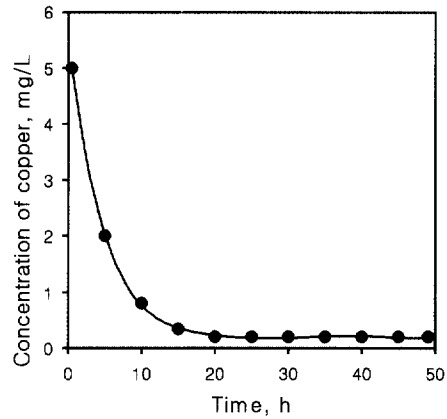$$\tau = (C_o - C_e) \times V/W_s \qquad (1)$$

Figure 2. Relationship between time and copper concentration in aqueous solutions (C_o : 5 Cu^{2+}mg/L, temperature: 28℃, kaolin concentration: 50 g/L, pH: 5.8).
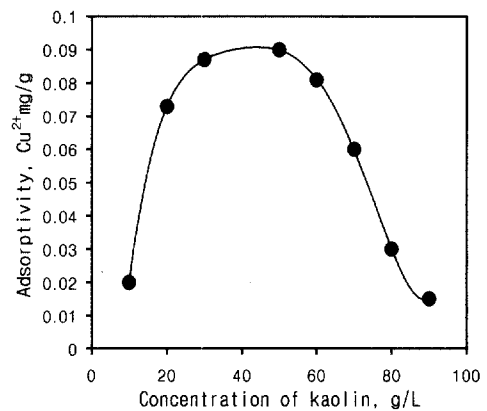

Figure 3. Relationship between kaolin concentration and adsorptivity (C_o : 5 Cu^{2+} mg/L, temperature: 28℃, pH: 5.8).

where τ is the adsorptivity and C_o and C_e are the initial and equilibrium Cu^{2+} concentrations in the aqueous solutions, respectively. V is the total volume of the aqueous solution and W_s is the weight of the kaolin as the adsorbent. The adsorption effect of a kaolin concentration cannot be expressed reasonably in terms of a total adsorbed amount but an adsorptivity. Adsorptivities for the kaolin concentration from 10 to 90 kaolin-g/L were from 0.015 to 0.09 Cu^{2+}mg/g, where the highest adsorptivity was 0.09 Cu^{2+}mg/g at kaolin concentration of 50 g/L. The adsorptivity increased with an increasing kaolin concentration below concentration of
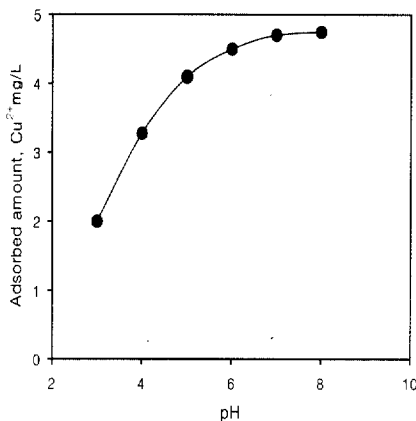
Figure 4. Effect of pH on adsorbed amount of copper ion on kaolin (C_o: 5 Cu^{2+} mg/L, temperature: 28 ℃, kaolin concentration: 50 g/L).

Figure 5. Amounts of the adsorbed Cu^{2+} relative to adsorption time at pH 4 and 7 (C_o: 5 Cu^{2+} mg/L, temperature: 28 ℃, kaolin concentration: 50 g/L, ◆: pH 4 and ■: pH 7).

50 g/L, whereas above 50 g/L, the adsorptivity decreased with an increasing kaolin concentration.

Experiments were performed at the conditions of a kaolin concentration of 50 g/L and time of 20 h to investigate the adsorption characteristics of Cu^{2+} relative to a varying pH value. The relationship between amount of adsorbed Cu^{2+} and pH value at 28 ℃ for 20 h is shown in Figure 4.

The adsorption of Cu^{2+} displayed two pH dependence. The adsorption amount increased rapidly with pH at 3 ~ 5 and then more slowly with pH at 5 ~ 8. The fact that the adsorption amount varies with varying pH can be explained by the hydrogen ion concentration effect and the counter-ion activity in aqueous solutions. As the hydrogen concentration and Cu^{2+} activity increased simultaneously in the region of pH 3 ~ 5, the adsorption amount is highest. Over pH 8, Cu^{2+} ions showed a trend to change $Cu(OH)_2$ easily than to adsorb on the adsorbent with an increasing pH value. Total adsorbed amounts of pH 3 and 4 were 2 and 3.28 Cu^{2+}mg/L, through 3.95 and 4.5 Cu^{2+}mg/L at pH 5 and 6, respectively, to 4.7 ~ 4.78 Cu^{2+} mg/L at pH 7 ~ 8.

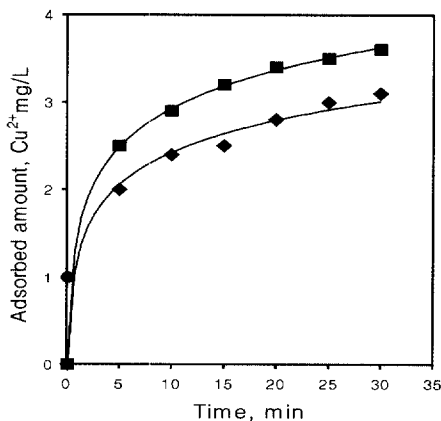Figure 5 shows the variation of the adsorption amount of Cu^{2+} with time at pH 4 and 7,

respectively. The adsorption amount increased with time at pH 4 and 7 and the adsorption rate at pH 7 was higher than at pH 4. These results showed that pH was the important parameter on the adsorption in aqueous solutions and the hydroxyl concentration on the kaolin surface was affected by a pH value.

The adsorption on kaolin is related to the inorganic compound content of kaolin and this can give a good insight into the contribution of contents to the adsorption kinetics with kaolin.[18] The solubility of silica and alumina, which are the main chemical components of kaolin, may affect its surface characteristics and adsorption in two ways. The first is that dissolved Si(Ⅳ) or Al(Ⅲ) can reprecipitate, thereby causing a change in the nature of the adsorbent surface, and the second is that these species may compete with the divalent metals for adsorption sites. Adsorption experiments of Cu^{2+} on the silica and alumina, respectively, to compare the adsorptivity of silica and alumina were performed and Figure 6 shows the adsorption differences with pH.

Silica (Silysia K-88, Fuji Silysia Chem. Co., Ltd., Japan) and alumina (Sunjun Chem. Co., Ltd., Korea) as adsorbents were used and BET specific areas were 6.8 and 5.1 m^2/g, respec-
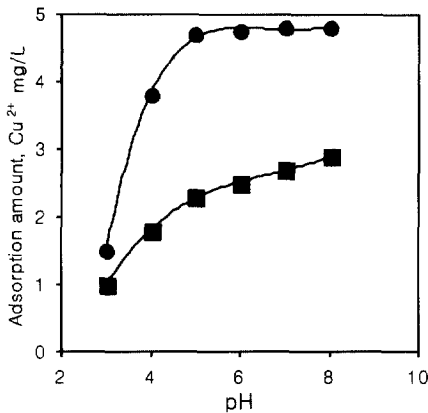
Figure 6. Amounts of the adsorbed Cu^{2+} on silica and alumina with pH change, respectively (C_o: 5 Cu^{2+} mg/L, temperature: 28℃, adsorbent concentration: 50 mg/L, time: 5 h, ■: silica and ●: alumina).

Figure 7. Relationship between pH and adsorptivity depending on kaolin concentration in aqueous solutions (C_o: 5 Cu^{2+} mg/L, temperature: 28℃, time: 20 h, ◇: 30, □: 50, ○: 70, and ●: 100 kaolin-g/L, respectively).

Figure 8. Change of the pH value of aqueous solutions with adsorption time (C_o: 5 Cu^{2+} mg/L, temperature: 28℃, kaolin concentration: 50 g/L).

tively. As shown in Figure 6, the adsorbed Cu^{2+} amount on alumina was higher than silica. The adsorption on alumina increased rapidly at pH 3~5 but on silica increased slowly. The adsorption amount on alumina was 4.5 Cu^{2+} mg/L at pH 5, whereas that on silica was 2.3 Cu^{2+} mg/L. At pH 8, the adsorption amount on alumina (4.8 Cu^{2+} mg/L) was higher than that on silica (3.0 Cu^{2+} mg/L). These results indicate that the adsorptivity of kaolin is not dependent on Si(IV) but Al(III) content of a kaolin surface. The adsorptivity on kaoline can be explained by both solvation energy and surface energy of silica or alumina.[19]

The relationship between adsorptivity and pH on the kaolin concentration was as shown in Figure 7. The trend of adsorptiviy was similar to the kaolin concentration. Below 50 g/L, the adsorptivity increased with the concentration of kaolin and over 50 g/L, decreased with the concentration. It would appear that the highest adsorptivity was at the kaolin concentration of 50 g/L and an initial concentration of 5 Cu^{2+}mg/L. It was found that the kaolin concentration was one of important parameters dominating the adsorptivity in the aqueous solutions, where the kaolin concentration of 50 g/L was the optimal condition at
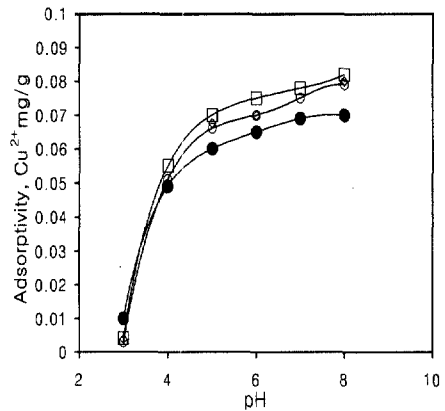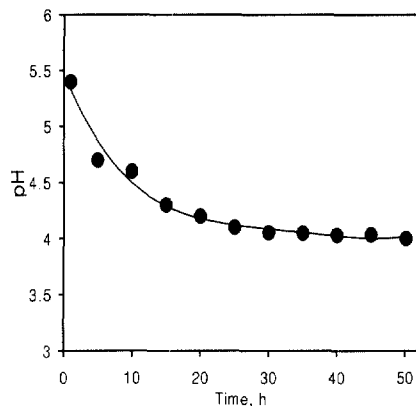
the initial aqueous concentration of 5 Cu^{2+}mg/L.

Figure 8 shows the change of the pH value in aqueous solutions with time. Due to the adsorption mechanism, the pH of the solutions changed from pH 5.4 to pH 4.2 at 50 h as shown in Figure 8. These can be explained using the ion-exchange mechanism between the hydrogen ion on the kaolin surface and the Cu^{2+} ion in the solution. It would be noted that the concentration of the hydrogen ion in the

solutions increased with time and consequently with an increasing adsorption amount of a Cu^{2+} ion adsorbed on the surface.

Adsorption has an association with the reaction on the oxide or oxyhydroxide of surface and Al-OH groups on the surface normally tend to adsorb more Cu^{2+} than Si-OH groups. The surface energy of inorganic powders is influenced by the pH value and the level of the surface energy can be expressed using a zeta potential.[20] Therefore, it is reasonable to evaluate the adsorptivity of adsorbents based on the zeta potential because the surface reaction, such as the chemisorption, is related to the surface energy; the electrostatic interaction energy.[21] The variation of zeta potential with pH was as shown in Figure 9.

At pH 3, the value of the zeta potential was 28 mV. The zeta potential decreased rapidly with an increasing pH value of pH 3~7 and more slowly with an increasing pH value from pH 7 to pH 8. The zeta potential was -30 mV at pH 8. The stability of the kaolin particle in a colloid system or an emulsion is dependent upon the adsorption of ions. The stability of a particle in solutions increases with an increasing absolute value of a zeta potential and the absolute value of a zeta potential increased with an increasing adsorption amount of ions. With proper techniques and interpretation of the curve, the zeta potential can be employed accurately to measure the adsorption.[20] It was shown that the zeta potential decreased with an increasing amount of adsorbed Cu^{2+} on the kaolin, plus the surface energy of the kaolin decreased with a decreasing zeta potential. The isoelectric point of 50 g/L kaolin solution at 28 ℃ was 4.3 as shown in Figure 9, where the isoelectric point means the pH value at the zeta potential of zero. The fact that the zeta potential varies with pH can be explained by the adsorption with ions such as H^+, OH^-, and Cu^{2+} on kaolin surface in aqueous solutions.[22] As H^+ and Cu^{2+} activity increases below pH 4.3, the charge of a particle is positive. At pH 4.3, as the charge amount of H^+ and Cu^{2+} on kaolin is equal to that of OH^-, the charge of a particle
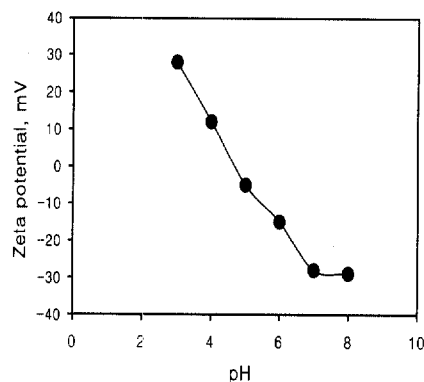

Figure 9. Relationship between pH value and zeta potential in aqueous solutions (C_0: 5 Cu^{2+} mg/L, temperature: 28℃, kaolin concentration: 50 g/L).

is neutral and zeta potential is zero. Over pH 4.3, the OH^- activity is higher than H^+ and Cu^{2+} activity on kaolin and the charge of a particle is negative.

The kaolin weight and Cu^{2+} concentration were found to be important parameters in determining the adsorption behavior because the ratio of the adsorbent weight and the concentration of the adsorbate had a strong influence on the adsorption characteristics. The adsorption capacity relative to the kaolin weight and Cu^{2+} concentration was shown in Figure 10.

Below 30 g/L, the zeta potential decreased with an increasing concentration of kaolin, whereas above 30 g/L, the zeta potential increased with an increasing concentration of kaolin. At 30 g/L, the zeta potential was at a minimum, which was related to the amount of Cu^{2+} adsorbed on the kaolin at pH 5.6. The electric charge with pH dependence is one of the important characteristics to understand the interfacial properties of metal oxide/ electrolyte solutions. The pH value of solutions affects the alkali-acid character of the surface with hydroxyl groups and its surface charge and the magnitude of the charge depend on the pH value. Therefore, the adsorption of ions on a kaolin surface depends on pH value.[18]

The adsorption of heavy metals on kaolin has been shown to be significantly different
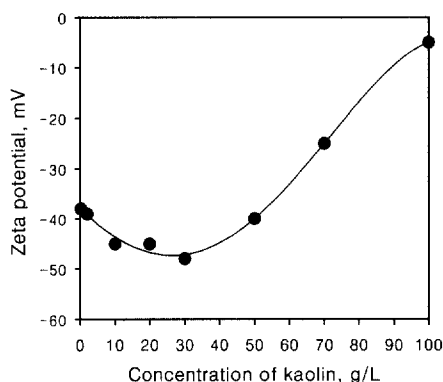
Figure 10. Effect of kaolin concentration on zeta potential under condition of aqueous solutions(C_o: 5 Cu^{2+} mg/L, temperature: 28℃, pH: 5.6).

from that on oxides. Kaolin surfaces in aqueous solutions with a basic or neutral pH would appear to have a negative charge and those in an acid solution tend to have a positive charge yet this decreases in magnitude with an increasing pH value. The magnitude of the positive charge is dominated by the ratio of the surface sites occupied by hydrogen and hydroxyl ions.[9]

Kinetic modeling of the Cu^{2+} adsorption on kaolin was carried out and various parameters were determined. The removal of Cu^{2+} by adsorption on kaolin was found to be of the first order and the rate of Cu^{2+} removal at different temperatures was determined using Lagergren's rate equation as shown in Equation (2).[23]

$$Log\ (q_e - q) = Log\ q_e - k_{ad}\ /2.303 \times t \quad (2)$$

where q_e and q are the adsorbed amount at equilibrium state and at any time (t), respectively, and k_{ad} is the coefficient of adsorption rate. Figure 11 shows the variation of the difference between adsorption amount of Cu^{2+} at equilibrium state and adsorption time at pH 4 and 7 and the slope means the adsorption rate constant, k_{ad}.

Adsorption rate constants at pH 4 and 7 at 28℃ were 5.43×10^{-2}, 4.63×10^{-2}, respectively, where the adsorption rate constant at pH
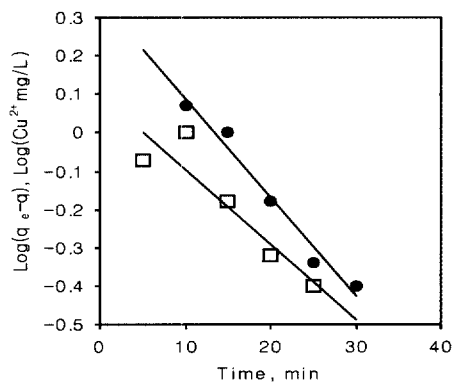

Figure 11. Variation of the difference between adsorption amount of Cu^{2+} at equilibrium state with adsorption time at pH 4 and 7(C_o: 5 Cu^{2+} mg/L, temperature: 28℃, kaolin concentration: 50 g/L, ●: pH 4, □: pH 7).
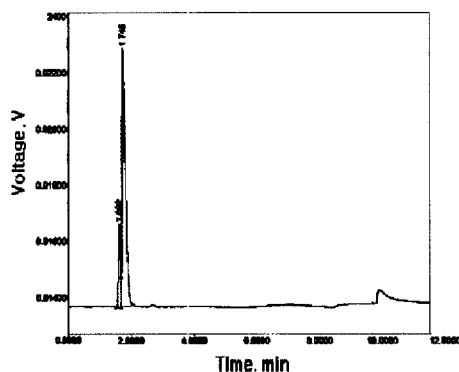

Figure 12. Analysis of gas generated from the adsorption of Cu^{2+} on kaolin (C_o: 5 Cu^{2+}mg/L, temperature: 28℃, kaolin concentration: 50 g/L, pH: 5.6).

4 was higher than that at pH 7.

Current interest in by-products with the adsorption has been increasing and the study on that was considered to be important. To investigate the by-product, CO_2, the gas from the adsorption of Cu^{2+} on kaolin for 20 h was detected and the result was as shown in Figure 12.

Peaks at 1.587, 1.707, and 9.131 min describe the presence of N_2, O_2, and CO_2, respectively and Figure 12 displayed only the occurrence of N_2 and O_2 except CO_2. The adsorption of Cu^{2+} on kaolin means that any

organic compound is not degraded judging from the absence of CO_2. However, CO_2 can be occurrent from the adsorption of a metal ion on kaolin in a contaminated water.

CONCLUSIONS

The following results were obtained through this study for the removal of copper(II) ion by a kaolin in aqueous solutions. The adsorption amount is highest in the region of pH 3~5 because the hydrogen concentration and Cu^{2+} activity increased simultaneously in the region of pH 3~5 and over pH 8, Cu^{2+} ions showed a trend to change $Cu(OH)_2$ easily than to adsorb on the adsorbent with an increasing value of pH. The adsorptivity increased with an increasing pH value, whereas the zeta potential decreased. Adsorption rate constants at pH 4 and 7 at 28℃ were 5.43×10^{-2} and 4.63×10^{-2}/min, respectively. The adsorption of Cu^{2+} on kaolin did not make CO_2 of a by-product.

NOMENCLATURE

C_e = equilibrium concentration [Cu^{2+} mg/L]
C_o = initial concentration of Cu^{2+} [Cu^{2+} mg/L]
k_{ad} = coefficient of adsorption rate [1/min]
q_e, q = adsorbed amount at equilibrium state and at any time, respectively [Cu^{2+} mg/L]
t = time [min]
V = total volume of aqueous solutions [L]
W_s = weight of kaolin [g]

Greek letter

τ = Adsorptivity of Cu^{2+} on kaolin [Cu^{2+} mg/g-kaolin]

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