수세 제강 슬라그의 중금속 폐수 흡착 처리 특성
Adsorption Features of Heavy Metal Ion on Water-Cooling Steel Slag

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1. Introduction

In the present study, we sought to apply water-cooling slag as an adsorbent for treatment of wastewater containing lead ion.   Lead is introduced to the environment in large amount mainly by battery or paint industry and mining processes.   The toxicity of lead includes damages to kidney, reproductive organs, liver, brain, and the central nervous system.   Lead ion exists mostly as a bivalent form in an aqueous phase, and once absorbed into human body, it exerts the long-term effects.

We evaluated the adsorbability of lead ion in specific conditions on steel slag, which were separated based on its size class.   The adsorbability was kinetically assessed based on the changes of adsorption with time for different concentrations of adsorbate.   The effect of pH on the adsorbability of lead ion was also investigated.   Then, adsorption isotherm was derived from equilibrium adsorptions, and thermodynamic parameters were calculated using the effects of temperature and thermodynamic relationships.   Finally, desorption experiment was conducted to check the feasibility of reuse of the slag as adsorbent.   Our aim was to provide basic informations on the adsorption and desorption characteristics of steel slag and feasibility of application to wastewater treatment using it.

2. Materials and Methods

Preliminary leaching experiment in the POSCO revealed that the slag is stable and leaches little metals even when exposed to strong acidic conditions.   Steel slag was sieved (-100/+200 mesh) and washed with triple distilled water followed by oven drying at 105℃.   The sample was maintained in a desiccator flushed with N_2 until the experiment.   Wastewater containing lead was prepared by dissolving $Pb(NO_3)_2$ (Fisher Co.) in triple distilled water and ionic strength was controlled by adding 0.01 M of $NaNO_3$ as swamping electrolyte.

An adsorption experiment was conducted in batch test using mechanical shaker which provided temperature and velocity gradients.   pH was maintained at 3.0 because Pb^{2+} precipitates as a hydroxide form under higher pH which may affect the adsorption reaction.   Basic conditions were 200 rpm, 25℃, and 200 ppm for the shaking speed, temperature, and Pb^{2+} concentration, respectively.

One hundred mL of wastewater with a certain concentration of lead and pH was amended with 1 g of steel slag in a 200 mL flask.   The flask was sealed with a rubber lid and stirred on a automatic shaker. We prepared samples for each reaction time instead of subsampling from a single flask, because such

subsampling could change the concentration of adsorbent remained. After the reaction, adsorbent was removed by centrifugation and lead concentration in the supernatant was determined by Atomic Absorption Spectrophotometry (Perkin Elmer, AAnlyst 100).

For a desorption experiment, steel slag, previously exposed to 200 ppm of lead solution, was added to 100 mL of $NaNO_3$ solution (0.01 M; pH 7.0). Similar to the adsorption experiment, the concentrations of lead released to the aqueous phase were determined according to the reaction time. In particular, a certain concentration of EDTA was added to examine effects of complexing agents on the desorption process.
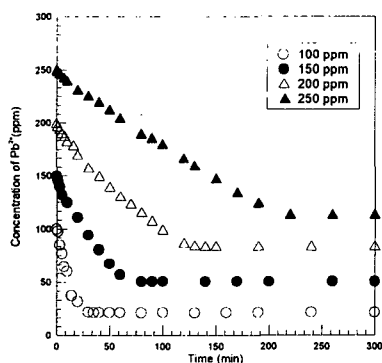
3. Results and Discussion

Fig. 1. Changes in the remaining concentration of Pb^{2+} according to adsorption time for various initial adsorbate concentrations (pH 3.0, 0.01 M $NaNO_3$, 25 ℃).

Changes in the amount of Pb^{2+} adsorbed to steel slag along the reaction time were determined to investigate the kinetics of the adsorption. Figure 1 shows the Pb^{2+} concentrations remained in the aqueous phase along the reaction times. When initial concentration was 100 ppm, adsorption proceeded rapidly and reached equilibrium state in 35 minutes. In general, higher initial conditions in lead concentration exhibited longer time to reach the equilibrium. For example, equilibrium was observed in 80 minutes when the initial concentration was 150 ppm, while 140 minutes and 220 minutes required for the solutions to reach equilibriums with initial concentrations of 200 ppm and 250 ppm, respectively.

When comparing the absolute amount of adsorbate reacted at equilibrium conditions, the initial concentration of adsorbate exhibited a positive correlation with equilibrium adsorption. This was considered to be due to that higher adsorbate concentration increased the amount of adsorbent diffuses into micropores on the surface of adsorbent.

A kinetic analysis was attempted using the time series data of the adsorption before they reached equilibrium. Assuming that the concentration of Pb^{2+} at a certain time is c and that reaction order is m, then following relationship is given.

$$-dc/dt = kc^m \qquad (1)$$

where k is a rate constant. A least square fitting indicated that the result follows the 1st order reaction, and hence the solution of equation (1) can be expressed as follows.

$$\ln(c_t/c_o) = -kt + I \tag{2}$$

where c_t and co are concentrations of Pb^{2+} at time t and time 0, respectively, and I is integration constant. Using this equation, changes in $\ln(c_t/c_o)$ over the reaction time can be linearly regressed and initial rate constants can be withdrawn from the slope of the regression lines. In all initial concentrations of Pb^{2+}, we considered good linearities were observed. In addition, as the initial concentrations decreased, the rate constants increased.
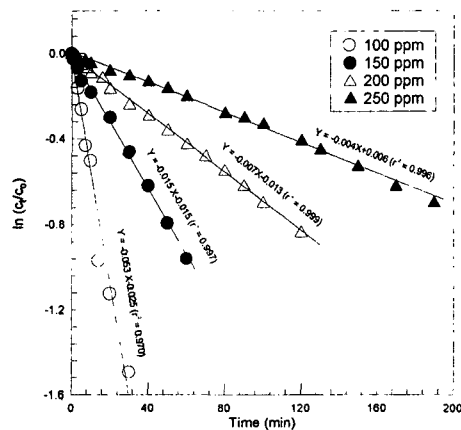

Fig. 2. Plots of ln(ct/co) vs. time for various initial concentrations of Pb^{2+} (pH 3.0, 0.01 M $NaNO_3$, 25 $^\circ$C).

Thermodynamic parameters for the adsorption of Pb^{2+} have been estimated based on the effect of temperature on adsorption. Figure 3 shows the relation between the equilibrium remaining concentrations of Pb^{2+} and temperature under the condition of the initial Pb^{2+} concentration of 200 ppm. The adsorbed amount of Pb^{2+} was 115.8 ppm at 25 $^\circ$C for 1 g of slag and its adsorption capacity showed a positive linear function with the temperature, thereby increased up to 147.2 ppm at 60 $^\circ$C. These observations suggest that the adsorption of Pb^{2+} on steel slag is an endothermic reaction.
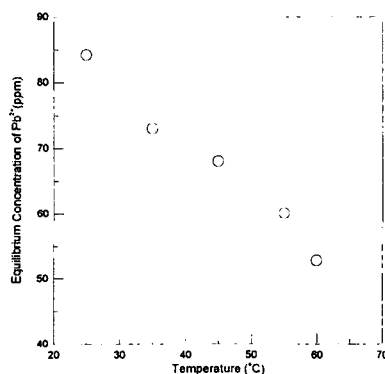

Fig. 3. The effect of temperature on the remaining concentration of Pb^{2+} at the equilibrium after

adsorption (pH 3.0, 0.01 M $NaNO_3$, initial conc. of Pb^{2+}; 200 ppm).

The solubility and desorption of metallic components which existing as a precipitate or an adsorbed state to the surface of adsorbents in solution are known to be influenced by complexing agents. This influence is due to the chemical affinity between complexing agents and metallic components. In this study, we evaluated the variation in the desorption of Pb^{2+} after it had absorbed to the slag according to the concentration of EDTA, which taken as a complexing agents. This investigation has a significant meaning in the separation and recovery of adsorbate and the regeneration of adsorbent.

Figure 4 shows the changes in the desorbed amount of Pb^{2+} with time for different concentrations of complexing agent and it can be seen that the desorption of Pb^{2+} increases in the presence of EDTA than in its absence. Also, the rate and total amount of desorption had a positive functional relation with the concentrations of EDTA. In particular, more than 90% of the total desorption of Pb^{2+} occurred within 10 minutes at the EDTA concentration of 1×10^{-4} M, indicating a direct influence of EDTA on the desorption capacity of Pb^{2+}.
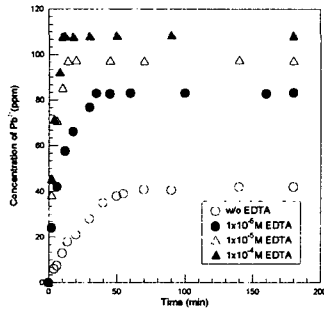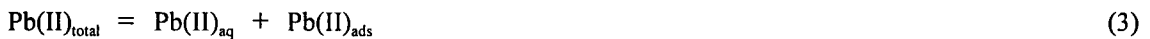

Fig. 4. Changes of the desorbed amount of Pb^{2+} as a function of time for various concentrations of EDTA (pH 7.0, 0.01 M $NaNO_3$).

As mentioned above, the reason on the relation between the existence of EDTA in solution and the desorption of Pb^{2+} is due to the complex formation between these two species. A series of equations on the absorption, desorption, and complexation of Pb^{2+} ions with EDTA in solution can be suggested as follows;

$$Pb(II)_{total} = Pb(II)_{aq} + Pb(II)_{ads} \tag{3}$$

$$Pb(II)_{aq} = Pb\text{-}EDTA^{2-}{}_{aq} + Pb^{2+}{}_{aq} + PbY_{aq} \tag{4}$$

$$Pb(II)_{ads} = Pb\text{-}EDTA^{2-}{}_{ads} + Pb^{2+}{}_{ads} + PbY_{ads} \tag{5}$$

As shown in the equations, all Pb^{2+} in solution can be classified as dissolved and adsorbed state and these are classified again as combined and not combined with EDTA, respectively. When Pb^{2+} reacts with EDTA in neutral pH conditions, the formation constant is very high (1.1×10^{18}), therefore, it is expected that the desorption of Pb^{2+}, which already adsorbed on the slag surface, will be promoted by the presence of EDTA in solution.

The desorbed amount of Pb^{2+} was attempted to be expressed as a functional equation of the initial

concentrations of EDTA when the desorption reaction reached to the equilibrium state. The amount of Pb^{2+} desorbed from the adsorbent was observed to increase almost in a constant ratio with the exponential increase in the concentration of EDTA. Therefore, by taking the log-transformed value of EDTA concentration and its relation with the desorbed amount of Pb^{2+} (Y) has been derived as follows.

$$Y = -33.5 \times \log_{10}[EDTA] + 244.8 \tag{6}$$

Equation (6) presents the relationship between the amount of desorbed Pb^{2+} and the initial concentration of EDTA, which in the range of $1 \times 10^{-6} \sim 1 \times 10^{-4}$ M. Regression analysis showed that the variation in the concentration of EDTA accounted 97.9 % of the variation in the desorbed amount of Pb^{2+}. Therefore, the suggested equation may be an useful empirical linear model for the prediction of the desorption of Pb^{2+} within the experimental range of the EDTA concentration.

4. Conclusion

The applicability of the water-cooling steel slag which produced in a steel making process as an adsorbent for the treatment of heavy metal components in wastewater was evaluated for the purpose of wastes reuse. Absorbed amount of Pb^{2+} on slag was proportional to its initial concentration and the adsorption reached an equilibrium state within 220 minutes in the investigated range of Pb^{2+} concentration. It was found that the adsorption rate was accelerated with smaller initial concentrations of Pb^{2+} and was fitted well to first order reaction over all concentration ranges of Pb^{2+}. The adsorption of Pb^{2+} was closely related with the variation of the electrokinetic potential of steel slag according to the pH. The adsorbed amount of Pb^{2+} increased with temperature, which indicating an endothermic property of the adsorption reaction and increase in the concentration of swamping electrolyte resulted in the decrease in Pb^{2+} adsorption. We found that the desorption reactions of adsorbed Pb^{2+} reached the equilibrium state generally faster compared with the adsorption reactions and that the desorption of Pb^{2+} had a positive increase with concentrations of the complex agents.

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