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A STUDY ON REMOVAL OF Pb^{2+} ION USING PELLET-TYPE RED MUD ADSORBENTS

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Abstract : The two kinds of pellet-type red-mud adsorbents (bead-type, crushed-type) were made from red mud, which is generated as a by-product during the production of aluminum hydroxide from bauxite ore. The adsorption experiments of Pb^{2+} ion in the aqueous solution by these red-mud adsorbents were studied with a continuous adsorption column. As a result, the crushed-type adsorbent shows better performance in adsorption of Pb^{2+} than the bead-type adsorbent between the two types of the pellet-type adsorbents. The continuous adsorption experiment shows that the pellet-type adsorbents made from red mud have good performance for removal of Pb^{2+}. The breakthrough curves of the red-mud adsorbents were compared with that of activated carbon.

Key Words : adsorption, Pb^{2+} ion, recycling of waste materials, red mud

INTRODUCTION

It is an important technique to remove heavy metal ions in the industrial wastewater since toxic heavy metals are major causes of environmental problems. Recently, the problem of solid-wastes disposal has taken an increasing interest. In this work, removal of heavy metal ions by utilizing waste materials such as red mud had been studied.

Red mud is generated as a by-product during the production of aluminum hydroxide from bauxite ore. Red mud is composed of oxides of iron, aluminum, silicon, calcium, and titanium. In most of countries, red mud is currently dumped in holding ponds or into the sea. Because of its high alkalinity, salinity and sodicity, red mud is toxic and poses a serious pollution problem around its disposal site. There have been many studies of red mud for recovery of iron, aluminum, and titanium, and for utilization as building materials.[1~4] Owing to its high content of aluminum, iron and calcium, red mud has been suggested as a cheap adsorbent for wastewater treatment.[5~9]

Kim and Bae[10] tested red mud with its powder-type form as adsorbents for removal of heavy metal ions in the wastewater. They reported that red mud treated with simple washing and drying operation showed good performance in adsorption of heavy metal ions. However, it is difficult for the powder-type red mud to be utilized in the industrial field because of inconvenience of its handling. Kim et al.[11] synthesized the pellet-type adsorbents through sintering red mud with various additives, such as polypropylene, sodium metasilicate, and fly ash. Their results show that the removal efficiency of Pb^{2+} by the pellet-type

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adsorbents was higher than the removal efficiency of Cu^{2+} and Cd^{2+}. In this study, the pellet-type adsorbents were tested for their adsorption capacities of Pb^{2+} ion in the aqueous solution in a standard jar tester and in a continuous packed-column facility, and the adsorption performance of the pellet-type adsorbents was compared with that of the commercial activated carbon.

EXPERIMENTAL

Materials and Preparation Methods of Adsorbents

The red mud used in this work was obtained from an alumina production company in Australia, which is using the same bauxite ore as a raw material and employing the same manufacturing process that Korea General Chemical Corporation, located in Daebul Industrial Park in Korea, is empolying. It was found that the red mud is composed of 36.3 wt% Fe_2O_3, 18.3 wt% Al_2O_3, 16.4 wt% SiO_2, 9.1 wt% Na_2O, 9.1 wt% CaO, 7.5 wt% TiO_2, and 10.3 wt% loss of ignition, as analyzed by x-ray fluorescence spectrometry.[10] The activated carbon (Hanil Green Tech. Co.) used in the present experiment is granular-type and made from coconut-shell char. The activated carbon have Iodine No. 1,100 mg/g, specific gravity 0.48, and particle size -8/10+ mesh.

The synthetic method of the pellet-type adsorbents is presented schematically in Figure 1. The pellet-type adsorbents were made from a mixture of 96.0 wt% red mud, 0.5 wt% fly ash, 2.5 wt% polypropylene, and 1.0 wt% sodium metasilicate. These compositions were found to be the optimum ones for adsorption capacity of heavy metal ions through many experiments. Details of the experiments are elsewhere.[11] After molding it, the pellets were sintered at various temperatures for 30 min in a muffle furnace. In the present study, the red-mud adsorbents were developed into two types of adsorbents (bead-type, crushed-type). The bead-type adsorbent was made from spherical

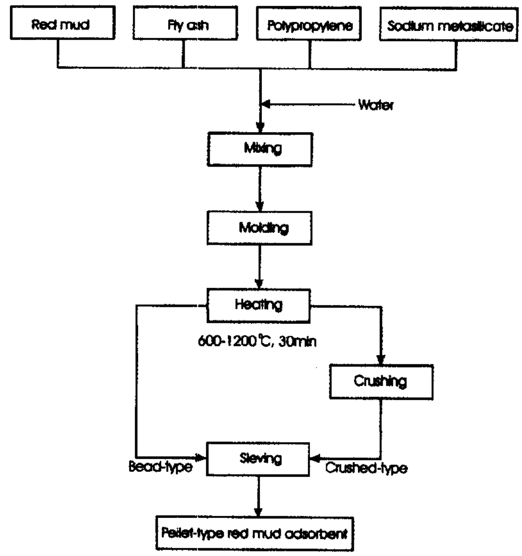


Figure 1. Schematic diagram of manufacturing of pellet-type adsorbents.

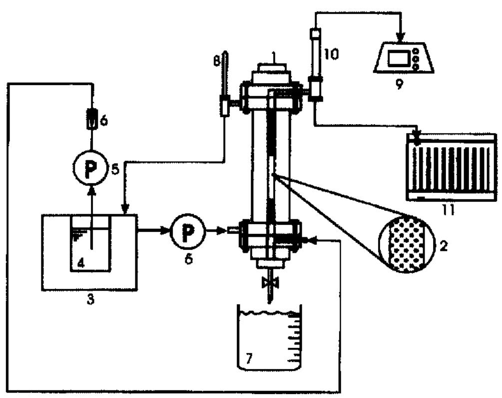
molds with various sizes. The crushed-type adsorbent was made by crushing the sintered adsorbent having a diameter of 3 cm. These adsorbents were sieved in -6/10+ mesh size, i.e. 2.00～3.35 mm in diameter. Kim et al.[11] found that as the sintering temperature decreases, removal capacity of Pb^{2+} increases while the hardness of the pellet decreases. It was also found that sintering the pellet below 1,200℃ caused brittleness and sintering it above 1,250℃ reduced its adsorption capacity. Thus, the optimum sintering temperature for the red mud adsorbent was determined to be 1,200℃ in this work.

A stock solution of lead (Pb^{2+}) with a concentration of 20 ppm (20 mg/L) was prepared by dissolving reagent grade chemicals of lead nitrate ($Pb(NO_3)_2$) in the ultrapure water. The concentration of metal ions was measured by AAS (atomic absorption spectrophotometry, GBC 932 AA) and by a voltameter (Chemtronics PDV2000). The pH of the solution was measured by a pH meter (Dongwoo medical DMP400). The specific surface area and the density of the pellet-type adsorbent were measured by using a BET surface area analyzer (Minometrics Gemini III 23D5) and a pycnometer (Minometrics Gemini III 2375), respectively.

Adsorption Experiment

The removal capacity of the pellet-type adsorbents was measured by using a standard jar testing procedure. 50 mL of stock solution of Pb^{2+} with a concentration of 20 ppm was prepared in 300 mL flasks, and 0.2 g of the adsorbent was added. The solution was shaked at 100 cycles/min using a thermostatic shaker/water bath at 25℃. It took about 24 h to reach equilibrium.

The continuous adsorption experiments of Pb^{2+} was carried out in a packed bed charged with the pellet-type adsorbents, as shown in Figure 2. The adsorption column was made of a double tube, and the constant temperature water at 25℃ was circulated through the outer tube. The inner diameter of the column is 1 cm. A stock solution of Pb^{2+} with a concentration of 20 ppm was prepared, and 10 g of the pellet-type adsorbent was packed in the column. The flow rate of the solution was controlled by a peristaltic pump. The exit concentration of Pb^{2+} was measured with time by AAS.



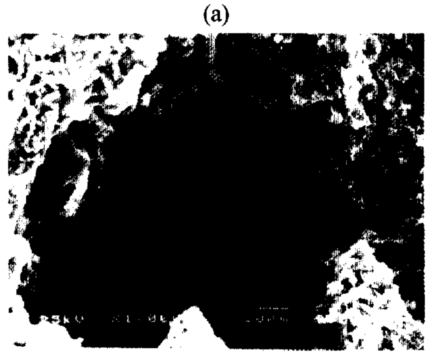
1. Adsorption column
2. Red mud adsorbents
3. Water bath
4. Vessel
5. Peristaltic pump
6. Flow meter
7. Reservoir
8. Thermometer
9. pH meter
10. pH cell
11. Fraction collector

Figure 2. Schematic diagram of continuous adsorption column apparatus.

RESULTS AND DISCUSSION

The specific surface area is known to be an important property for characterizing adsorptivity of adsorbents.[12] The specific surface area of the bead-type and the crushed-type adsorbents was measured as 0.181 m^2/g and 0.187 m^2/g, respectively. The absolute density of the bead-type adsorbent was measured as 3.417 g/cm^3, and that of the crushed-type adsorbent as 3.404 g/cm^3. The absolute density of the pellet-type adsorbent made in this work is greater than that of powder-type red mud adsorbent (3.043 g/cm^3) prepared by Kim and Bae.[10] It is observed that the density of the red mud adsorbent increases a little due to sintering. The structure of the pellet-type adsorbents was investigated by the SEM (scanning electron microscopy) micrograph as shown in Figure 3. It shows that there are many pores on the surface of the pellet-type adsorbents.

(a)



(b)

Figure 3. (a) SEM micrograph of bead-type adsorbent (×1,000), (b) SEM micrograph of crushed-type adsorbent (×1,000).

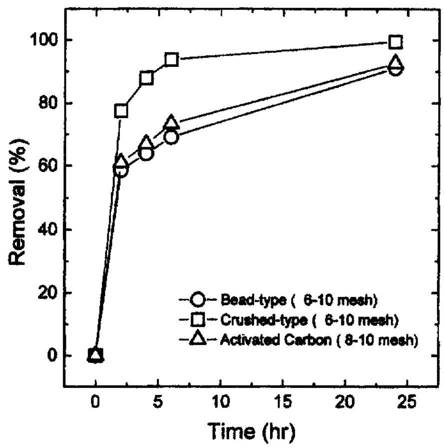


Figure 4. Percentage removal of Pb^{2+} by pellet-type adsorbents as a function of time.

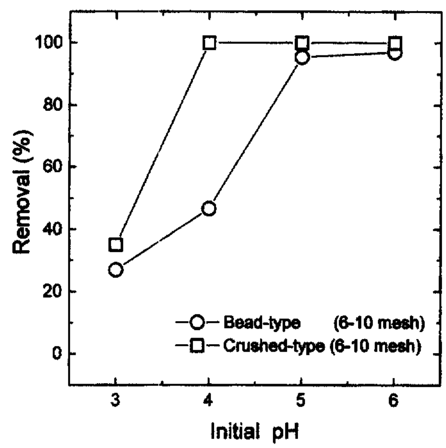


Figure 5. Percentage removal of Pb^{2+} by pellet-type adsorbents.

The percentage removal of Pb^{2+} in the aqueous solution by the two types adsorbents and the activated carbon is shown as a function of time in Figure 4. The initial pH of the stock solution was 5.14. The crushed-type adsorbents show higher removal efficiency of Pb^{2+} and reaches equilibrium faster than the bead-type adsorbent and the granular activated carbon. It seems that the adsorptivity of the crushed-type adsorbent is better than that of the bead-type adsorbent because the specific surface area of the former is higher than that of the latter. After 24 h the percentage removal of Pb^{2+} by the crushed- type adsorbent is more than 99%, which is similar to the case of the powder-type adsorbents.[10)]

Adsorption capacity of heavy metal ions is generally affected by the pH of wastewater. The percentage removal of Pb^{2+} by two types of pellet-type red mud adsorbents with various initial pHs of the stock solution is shown in Figure 5. The percentage removal of Pb^{2+} by the pellet-type red mud adsorbents increases with increasing the initial pH, which is similar to that of the powder-type red mud adsorbents.[11)] At the pH range of 5~6 the percentage removal of Pb^{2+} by both the pellet-type adsorbents is more than 95%.

The experimental facility of the continuous Pb^{2+} adsorption by the adsorbents is shown in Figure 2. The stock solution of Pb^{2+} was

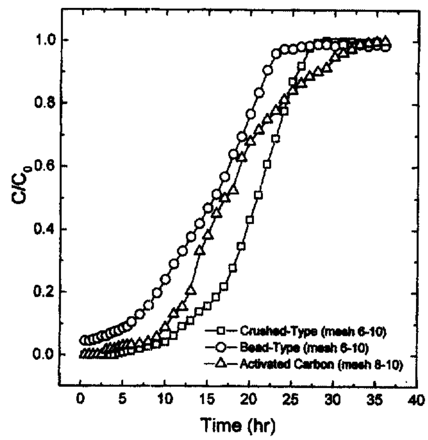


Figure 6. Breakthrough curves for removal of Pb^{2+} by fixed bed of pellet-type adsorbents (flow rate=5 mL/min).

passed upward through the fixed bed of the adsorbents. The inlet concentration, C_0, was 20 ppm, and the pH of the solution was 5.12. In the present experiment the breakthrough curves for Pb^{2+} adsorption by the pellet-type adsorbents were evaluated at different flow rates. At a flow rate of 5 mL/min the breakthrough curves for removal of Pb^{2+} are shown in Figure 6. The breakthrough curves exhibit simple S-shaped behavior. The break point was 10.4 hr for the crushed-type adsorbent, 2.2 h for the bead-type adsorbent, and 8.5 h for the activated carbon. It is found that the break point of the crushed-type adsorbent was much longer than that of the bead-type adsorbent and the activated carbon.

CONCLUSIONS

In the present study Pb^{2+} ion was successfully removed by the pellet-type adsorbents made from red mud. The crushed-type adsorbent shows better performance in adsorption of Pb^{2+} than the bead-type adsorbent. The present results of the continuous adsorption experiment show that the crushed-type adsorbents made from red mud have a good potential for removal of Pb^{2+} from wastewater in the industrial application.

ACKNOWLEDGMENT

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NOMENCLATURE

C = outlet concentration [mg/L]
C_0 = inlet concentration [mg/L]

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