# A study on removal characteristics of heavy metals from aqueous solution by fly ash

Heechan Cho [*], Dalyoung Oh, Kwanho Kim

*School of Civil, Urban & Geosystem Engineering, Seoul National University, San 56-1, Shinrim-Dong, Kwanak-Ku, Seoul 151-742, Republic of Korea*

## Abstract

The purpose of this study was to investigate the possibility of the utilization of coal fly ash as a low cost adsorbent. Batch experiments were conducted to evaluate the removal of heavy metals from aqueous solutions by fly ash under various conditions of metal concentration, pH and fly ash dosage. The heavy metals used in this study were zinc, lead, cadmium and copper. Adsorption studies were done at various pH values (3–10) at 25 °C and at heavy metal concentrations of 10–400 mg/L using fly ash concentrations of 10, 20 and 40 g/L, respectively. Experiments were also conducted without fly ash to determine the extent of heavy metal removal by precipitation. Kinetic experiments were also performed and the zeta-potentials of the fly ash particles were measured at various pH's. The adsorption data was described by the Freundlich adsorption model. The test results using real wastewater indicated that fly ash could be used as a cheap adsorbent for the removal of heavy metals in aqueous solutions if not strongly acidic.
© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Fly ash; Adsorption; Heavy metals; Freundlich isotherm; Waste water

## 1. Introduction

Fly ash is particulate material produced from the combustion of coal in thermoelectric power plants. The amount of fly ash generated in Korea was 4.43 million tonnes in 2000, of which 54.62% (2.42 million tonnes) was recycled while the rest was land-filled [1]. It is well known that because of its spherical shape and pozzolanic properties, fly ash is a valuable and desirable additive to cement concrete. It has also been used effectively in many other areas such as ALC manufacturing, building materials, soil amendment and fillers [2–4]. However, the rate of increase in demand in these applications is far less than the rate of increase in production. Therefore, there are growing concerns about fly ash disposal problems. In particular, fly ash with high unburned carbon content cannot be used as a cement additive because of the adverse effects it has on the quality of concrete. Thus, there is

a research need to develop an alternative technology that can further exploit fly ash. In the present study, efforts have been made to investigate the use of fly ash as a low-cost adsorbent in the treatment of waste water bearing heavy metals (Zn, Pb, Cd and Cu).

Fly ash is strong alkali material, which exhibits pH of 10–13 when added to water, and its surface is negatively charged at high pH's. Hence, it can be expected that metal ions can be removed from aqueous solutions by precipitation or electrostatic adsorption. In fact, a number of studies were conducted to show the effectiveness of fly ash in the removal of heavy metal ions [5–12] and organic materials [13–16] from aqueous solutions. However, the results appeared to not be comprehensive since the test conditions were limited. Also, the effectiveness of fly ash has not been tested when various metal ions are present together.

In the present study, the adsorption of heavy metal ions on fly ash particles was evaluated under various conditions such as pH, heavy metal concentrations and fly ash dosages through both kinetic and isotherm studies. The optimum

* Corresponding author. Tel.: +82 2 880 8271; fax: +82 2 871 8938.
*E-mail address:* hccho@snu.ac.kr (H. Cho).

removal condition was also identified for each metal ion. In addition, a series of tests were conducted to investigate how the presence of other metal ions affected the removal of one metal ion. Finally, the effectiveness of fly ash in the removal of heavy metals was evaluated using real wastewater.

## 2. Experimental

### 2.1. Materials and equipment

The fly ash used in this study was obtained from a bituminous coal-burning power plant of Korea Electric Power Corporation, Boryung, Korea. Scanning electron micrographs (model X-650, Hitachi, Japan) and Inductively Coupled Plasma-Atomic Emission Spectrometer, model SPECTRO.P (ICP-AES) were used to characterize the fly ash and its morphology. The surface area of the sample was measured by light diffractometry using the Mastersizer (model MSS, Malvern Instruments, Worcestershire, UK). The zeta potential of fly ash particles was determined by a zeta meter (model Zetasizer 3000HS, Malvern Instruments, Worcestershire, UK). All heavy metal solutions were prepared in stock solutions up to 400 mg/L of metal from the corresponding chloride salts purchased from Junsei Chemical, Japan. A pH meter (model SP-701, SUNTEX, Taipei, Taiwan) was used to measure the pH of the solutions. The concentrations of heavy metal ions were measured by an atomic absorption spectrometer (Perkin-Elmer model 3100, Norwalk, CT, USA).

### 2.2. Adsorption experiments

Batch adsorption experiments were carried out by shaking a series of bottles containing various amounts of fly ash and heavy metal ions at different pH's. Fly ash particles were dried at 110 °C for 2 h before tests. A predetermined amount of the fly ash sample was mixed with 50 mL of distilled water in polyethylene bottles to obtain fly ash slurries of 10, 20 and 40 g/L. The pH of the slurry was adjusted to a desired value in the range of 3–10 with 1 M HNO$_3$ and was agitated in a shaking bath at 25 °C for 2 h until the pH was stabilized. Then, the zinc, lead, cadmium and copper ions in the form

of chloride salts were added to the bottles to make initial concentrations of 10–400 mg/L and the bottles were further agitated for 2 or 3 h until equilibrium was obtained. At the end of mixing, the fly ash particles were separated from suspensions by filtration through a 0.45 μm membrane filter. The residual concentration of heavy metals was determined by an atomic absorption spectrometer. In addition to adsorption tests, a set of blank tests with fly ash was conducted in order to evaluate the removal by metal hydroxide precipitation at various pH's.

### 2.3. Kinetic studies

The kinetics of the adsorption of the heavy metal ions on fly ash were evaluated using a procedure similar to that used in the adsorption experiments. A series of bottles containing 20 g/L fly ash slurries and heavy metals of concentration 50 mg/L were kept in a thermostatic shaking water bath. After shaking for different time intervals, the samples were collected and analyzed for residual concentrations as mentioned before.

## 3. Results and discussion

### 3.1. Characterization of fly ash

Fly ash is a heterogeneous material consisting largely of small spheres, formed by the condensation of aluminous and siliceous glass droplets in the air. Also found in fly ash samples are irregular, porous, coke-like particles of unburned carbon material, which are often concentrated in the larger size fractions. The SEM (Fig. 1) image clearly shows that finer fly ash particles (smaller than 200 mesh) are primarily spherical, whereas the coarser particles (larger than 200 mesh) are mainly composed of irregular and porous particles.

Table 1 shows the distribution of the fly ash sample and LOI by size. It can be seen that the sample is generally less than 70 mesh, but the majority (72.75%) is in the size range of less than 400 mesh. It is common in fly ash that the carbon tends to predominate in larger sizes. As indicated by the SEM image, this was also true for the fly ash sample used in this
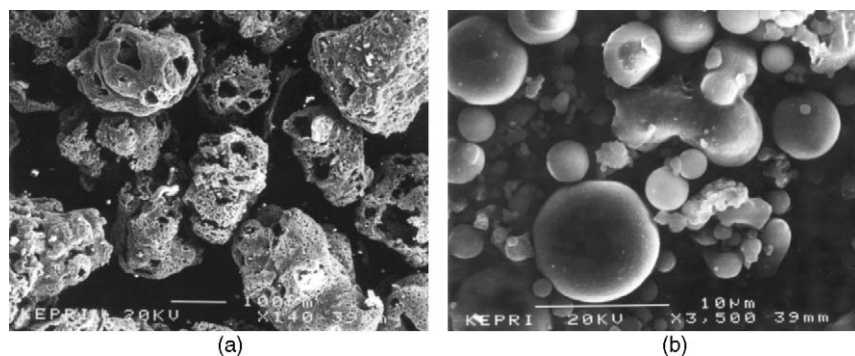


(a)

(b)

Fig. 1. SEM pictures: (a) +200 mesh particles of the fly ash and (b) −200 mesh particles of the fly ash.

Table 1
Size fraction and LOI of the fly ash

| Size (mesh) | wt. (%) | LOI (%) |
|---|---|---|
| <70 | 1.58 | 58.33 |
| 70–100 | 3.19 | 28.51 |
| 100–140 | 2.23 | 25.19 |
| 140–200 | 6.53 | 10.56 |
| 200–270 | 7.47 | 5.49 |
| 270–400 | 6.25 | 4.77 |
| >400 | 72.75 | 2.99 |
| Total | 100 | 5.7 |

study. The carbon concentration determined by loss on igni-
tion (LOI) was less than 3% for the fly ash particles smaller
than 400 mesh and significantly increased up to 58.3% as the
particle size increased.

All fly ash contain the same basic chemical elements but
in different proportions. The main constituents of fly ash are
silicon, aluminum, iron and calcium with smaller amounts
of sulfur, magnesium, alkalies and tracers of many other ele-
ments. Table 2 shows the chemical composition of the fly ash
samples used in this study. $SiO_2$ and $Al_2O_3$ contents make up
about 80% of the fly ash. $Fe_2O_3$ and CaO contents compose
about 11%. According to the ASTM C618, this fly ash can be
classified as class F for having a less than 10% CaO content
with a greater than 70% content of three components—$SiO_2$,
$Al_2O_3$ and $Fe_2O_3$.

Fig. 2 shows the zeta-potentials of the fly ash particles in
water measured at various pH's. It can be seen that the fly ash
particles are positively charged at low pH's and negatively
charged at high pH's, having a point of zero charge (PZC)
at a pH of 2.8. Therefore, it can be expected that positively
charged metal ions are likely to adsorb onto the negatively
charged fly ash particles at a pH above 2.8.

### 3.2. Effect of pH

The pH of the solution has a significant impact on the
uptake of heavy metals, since it determines the surface charge
of the adsorbent, and the degree of ionization and speciation
of the adsorbate. Fig. 3 shows the percent removal of the four
heavy metals as a function of pH at a heavy metal concen-
tration of 100 mg/L and a fly ash concentration of 20 g/L. In

Table 2
Chemical composition of the fly ash

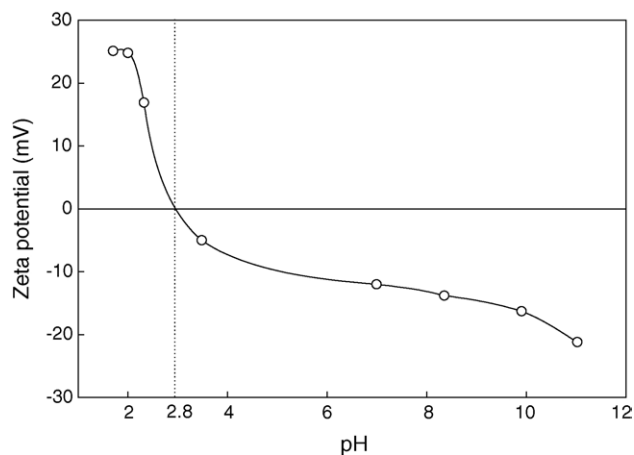| Constituent | wt. (%) |
|---|---|
| $SiO_2$ | 57.82 |
| $Al_2O_3$ | 22.10 |
| $Fe_2O_3$ | 8.33 |
| CaO | 2.57 |
| MgO | 0.91 |
| $SO_3$ | 0.73 |
| $TiO_2$ | 0.64 |
| $K_2O$ | 0.45 |
| Others | 6.47 |



Fig. 2. Zeta-potential of the fly ash at various pH's.

general, the amount of heavy metal removed increased as pH
increased, and sharply reached over 90% removal at a specific
pH value.

As shown, the precipitation of the heavy metal ions except
copper was less than 20% at pH's below 8, indicating that
the removal of the metals except copper was mainly accom-
plished by adsorption. Since the fly ash has a low PZC (pH
2.8), the surface of the fly ash was negatively charged under
the pH investigated. As pH increased from 4 to 8, it can be
expected that the fly ash surface becomes more negatively
charged. Thus, more favorable electrostatic attraction forces
enhanced cationic metal ion adsorption as pH increased.

However, the dependence of heavy metal adsorption on
pH was different for each metal. The removal of zinc was
about 70% at pH 6 and it increased to 95% at pH 8. For
lead, 90% was removed at pH 4.5 and it increased to 99% at
pH 6. For cadmium, removal increased proportionally with
increasing pH from 0% at pH 3–95% at pH 8. In all cases,
over 95% of all the four metals were removed at pH 8. It is
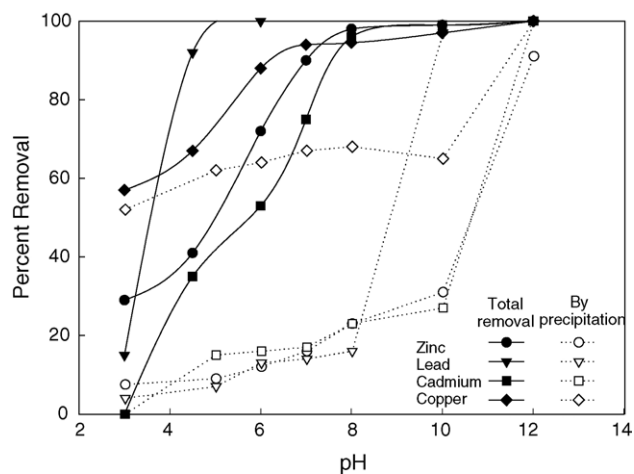often suggested that the tendency of metal cations to adsorb



Fig. 3. Effect of pH on the percent removal of zinc, lead, cadmium and
copper: initial metal concentration of 100 mg/L and fly ash dosage of 20 g/L.

to oxide surfaces is highly correlated with their tendency to undergo hydrolysis reactions in solution [5]. Metal cations in aqueous solutions hydrolyze according to the generalized expression for divalent metals.

$$M^{2+}(aq.) + nH_2O = M(OH)^{2-n} + nH^+$$
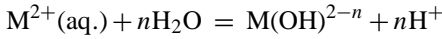
The distribution of various hydroxo complexes depends on pH of the solution and the respective stability constants. The stability constants ($^*K_1$) for the first hydrolysis reaction are 10.08 for Cd, 8 for Cu, 7.71 for Pb, and 8.96 for Zn [17]. The order of the pH for abrupt increase in heavy metal uptake by fly ash follows the same order of the p$^*K_1$. Hydroxyl–metal complexes are known to adsorb with a higher affinity than the completely hydrated metals because the formation of an OH group on the metal reduced the free energy requirement for adsorption [18]. Therefore, it seems that the adsorption of metal ions can be related to the change in availability of MOH$^+$, since the first hydrolysis product starts to appear at a lower pH with decreasing p$^*K_1$, as shown in the speciation diagrams given by Panday et al. [5] for Cu, Weng and Huang [8] for Zn, and Ellott and Denney [17] for Cd. Similar results were reported in several studies on adsorption of heavy metals on oxide particles [12,19,20].

### 3.3. Effect of heavy metal concentration and fly ash dosage

The adsorption experiments were carried out in the heavy metal concentration range of 10–400 mg/L, and two different dosages of fly ash at various pH's. The results are presented in Figs. 4–7. Generally, the curves shifted toward higher pH's with increasing heavy metal concentration or decreasing fly ash dosage. Particularly for zinc, the pH–adsorption curves were approximately parallel. At the medium pH value (pH 6), percent removal ranged from 19 to 76, and 38 to 87 with the 10 and 20 g/L fly ash dosage, respectively, for the 50, 100, 200 and 400 mg/L zinc concentrations.
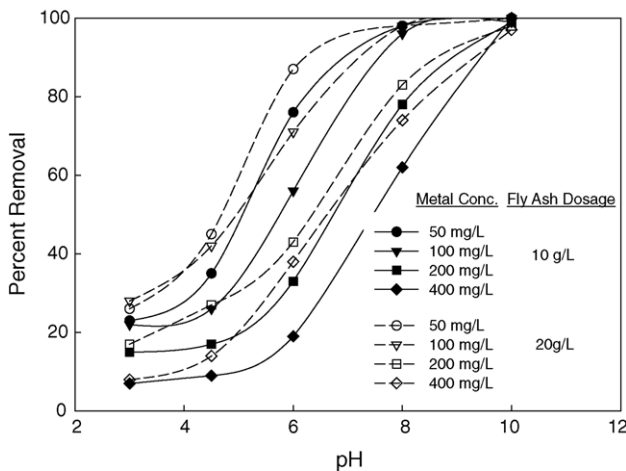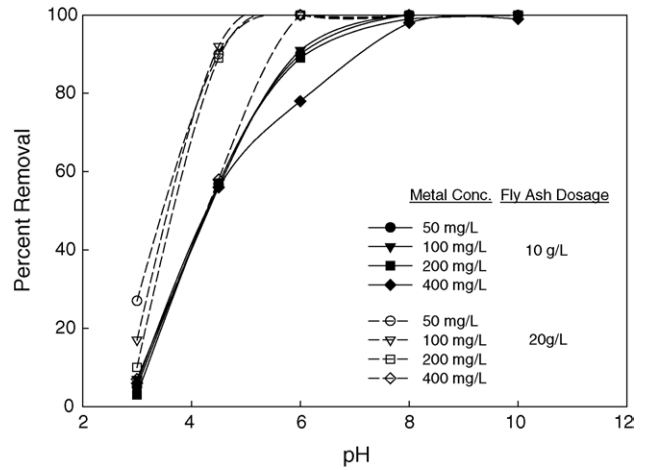


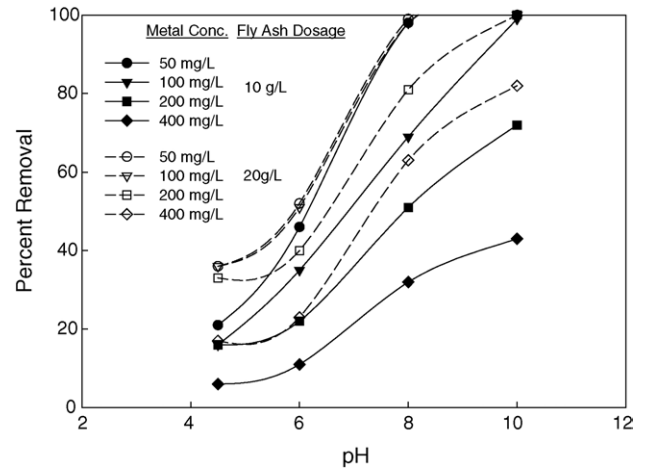Fig. 5. Effect of pH on the lead removal at various metal concentrations fly ash dosages.



Fig. 6. Effect of pH on the cadmium removal at various metal concentrations fly ash dosages.



Fig. 4. Effect of pH on the zinc removal at various metal concentrations fly ash dosages.
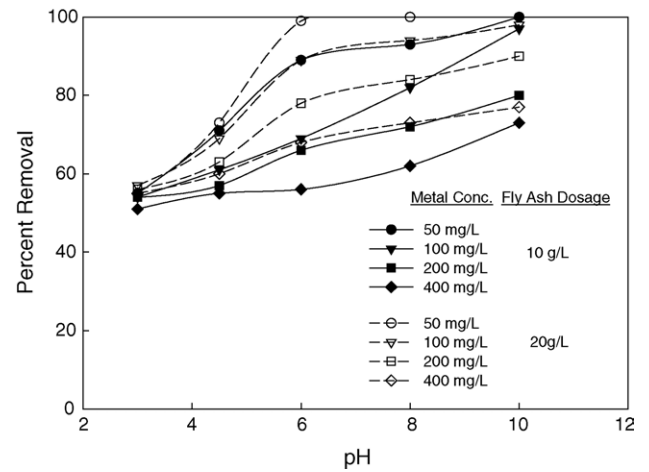


Fig. 7. Effect of pH on the copper removal at various metal concentrations fly ash dosages.

The removal of lead was more effective than that of zinc. Even at the highest lead concentration (400 mg/L), almost all of the lead was removed at pH 6 or greater. The reason for this tendency was that the precipitation of lead was higher than that of zinc when they were under the same conditions. At lead concentrations lower than 400 g/L, the pH–adsorption curves were similar. On the other hand, the removal of cadmium was the lowest. At acidic conditions, removal was under 50% even for the lowest cadmium concentration. At pH values above 6, the removal of cadmium increased up to 90–99% at the initial concentration below 100 mg/L.

Compared to other metal ions, copper was well removed even at a low pH likely due to precipitation (Fig. 3). At pH 3, the copper removal owing to precipitation was over 90% of the total removal. But as the pH was increased, its contribution decreased and a considerable amount of copper ions was removed by adsorption as well. At pH 6, the copper removal was almost 100% with the use of 20 g/L fly ash at a concentration of 50 mg/L. Consequently, of the four heavy metal ions, the total removal of lead was the highest and decreased in sequence of copper, zinc and cadmium.

### 3.4. Multi-ion adsorption studies

Industrial wastewater can contain several heavy metal ions, which may mutually enhance adsorption, may act relatively independent or may interfere with one another. Therefore, tests were conducted to investigate the effect of other ions on the adsorption of each metal. The results at initial concentrations of 50 and 200 mg/L at pH 6 are shown in Table 3. It can be seen that the presence of one metal affected the removal of the other metal ions. The removal of zinc was reduced in the presence of lead and copper, but was enhanced when with cadmium. On the other hand, the removal of lead increased from 90% to 99.9% when in the presence of all the other heavy metal ions.

The effect of other metals on the removal of cadmium varied; when the concentration was low, the removal increased, and when the concentration was high, the removal decreased.
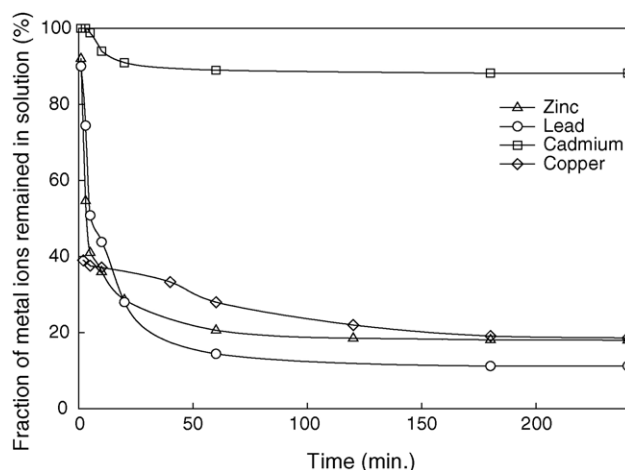


Fig. 8. Kinetics of heavy metal adsorption onto fly ash at pH 6: initial metal concentrations of 50 mg/L and fly ash dosage of 20 g/L.

But when with lead, the removal of cadmium increased greatly. Considering that the cadmium removal rate is lowest, we can expect that a much higher removal rate of cadmium can be achieved by mixing cadmium wastewater and lead wastewater.

Like lead, the removal of copper was enhanced when all four metals were present at the lower concentration. However, the removal decreased when the concentration of other metal ions was high, especially of zinc and lead. When all four metals were present together, the removal of lead and copper was enhanced, while the removal of zinc and cadmium was reduced. From this, it can be concluded that adsorption of heavy metals is favorable in the order Pb > Cu > Cd > Zn.

### 3.5. Kinetics

Fig. 8 shows the adsorption characteristics as a function of time. The kinetic experiments were performed by agitating the fly ash slurry bottles in a shaking bath for 4 h at 25 °C. In these tests, 10 g of fly ash in 1 L of aqueous solution containing 50 mg/L of metals were used. The pH was 6.0 where

Table 3
Effect of interfering ions on the uptake of heavy metals

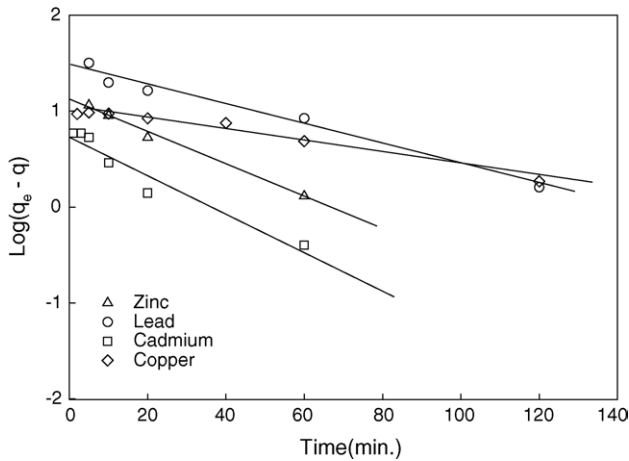| Interfering ions | Concentration (mg/L) | Percent increase or reduction in the uptake of | | | |
|---|---|---|---|---|---|
| | | Zn | Pb | Cd | Cu |
| Zn | 50 | | +11 | +29 | +20 |
| | 200 | | +11 | −47 | −17 |
| Pb | 50 | −100 | | +87 | +24 |
| | 200 | −100 | | +36 | −26 |
| Cd | 50 | +22 | +12 | | +25 |
| | 200 | −23 | +15 | | 0 |
| C | 50 | −74 | +12 | +53 | |
| | 200 | −97 | +15 | −64 | |
| With other three heavy metal | 50 | −3 | +12 | +13 | +25 |
| | 200 | −100 | +15 | −100 | 0 |

(+), Increase; (−), reduction.

Fig. 9. Lagergren plots for the heavy metals at pH 6: initial metal concentrations of 50 mg/L and fly ash concentration of 20 g/L.



Fig. 10. Freundlich isotherm plot for zinc, lead and cadmium and copper at pH 4.5.

precipitations were relatively low. The metal concentrations were determined at varying time intervals. As shown, the rate of uptake of metal ions by the fly ash was quite rapid. The metal removal in the first 20 min was 87% and 80% of the maximum removal in the case of zinc and copper, respectively, while it was 63% and 50% for lead and cadmium, respectively. Equilibriums were reached within 2 h for zinc and 3 h for lead, cadmium and copper. At equilibrium, 82% of the zinc, 88.8% of the lead and 81% of the copper were removed from the solution. However, only 15.2% of the cadmium was removed at equilibrium, indicating that more fly ash was needed to remove cadmium ions.

The rate constants for adsorption of metal ions on fly ash were determined using the Lagergren equation [8]:

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303}t \tag{1}$$

where $q_e$ is the amount of metal ions adsorbed at equilibrium, $q$ the amount of metal ions adsorbed (both in mg/L) at time $t$ (min) and $K_{ad}$ is the rate constant (min$^{-1}$). Fig. 9 shows that the data is well described by the Lagergren equation. $K_{ad}$ values obtained by regression were 0.0389 for zinc, 0.0239 for lead, 0.0465 for cadmium and 0.0140 for copper, indicating that the adsorption of cadmium was the most rapid, although the ultimate removal was the lowest.

### 3.6. Adsorption isotherm

In order to successfully represent the dynamic adsorptive behavior, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Various kinds of adsorption isotherms, especially Langmuir and Freundlich were tested to fit the experimental data. The best fit was achieved using a Freundlich isotherm. The Freundlich isotherm model is given by the equation:
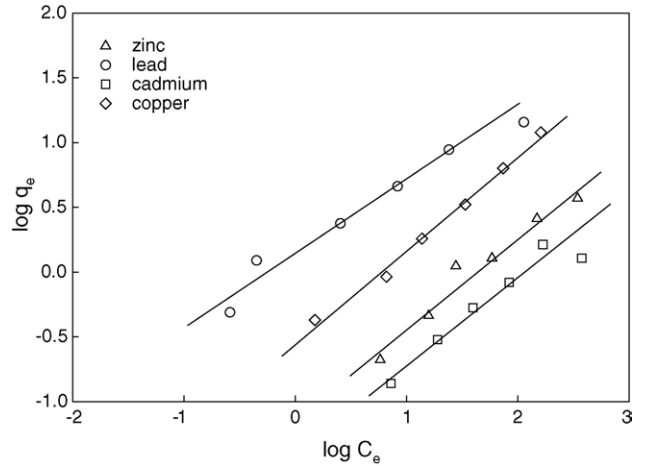
$$q_e = K_F C_e^{1/n} \tag{2}$$

where $C_e$ (mg/L) is the concentration of metal ions in solution at equilibrium, and $K_F$ (mg/g) and $n$ are constants related to adsorption capacity and adsorption intensity.

Figs. 10–12 show the Freundlich isotherm plots for the four metal ions at various pH's. All four heavy metals tended to form a precipitate to some extent even at acidic conditions and therefore adsorption by fly ash was difficult to quantify especially at higher pH values. Furthermore, the copper exhibited an unusually high precipitation even at acidic conditions. Consequently, only the data of the adsorption tests conducted at a pH up to 8 was analyzed to determine the isotherm constants, and the isotherm curves of the copper were included for a comparison purpose. At pH 4.5, the isotherm was linear over the entire range of concentrations studied (Fig. 10). However, at higher pH's, the isotherm exhibited two distinct linear regions (Figs. 11 and 12). Similar results were reported by Benjamin and Leckie [19], who studied adsorption of Cu and Zn onto amorphous iron oxyhy-
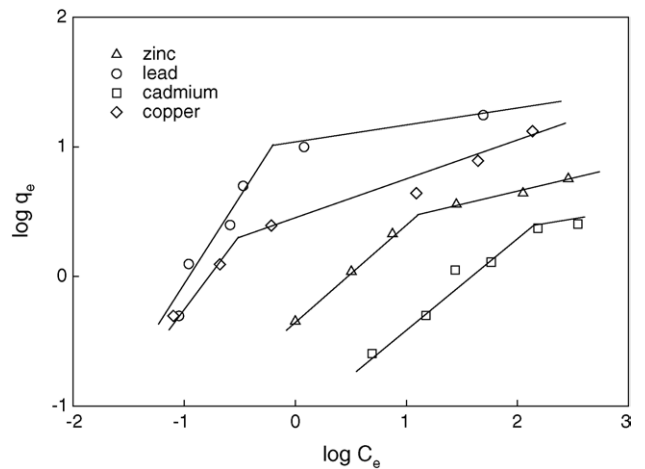


Fig. 11. Freundlich isotherm plot for zinc, lead and cadmium and copper at pH 6.
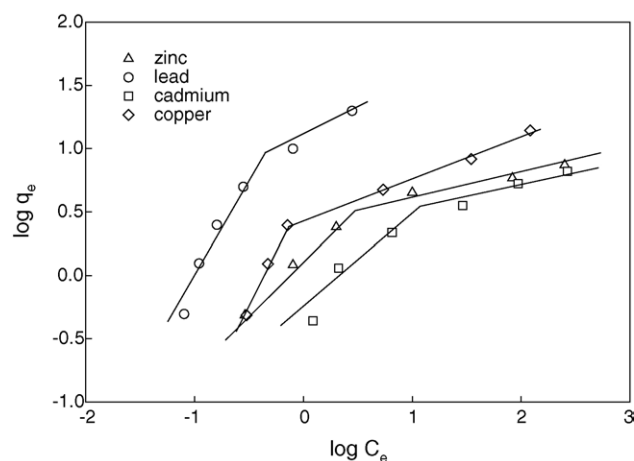
Fig. 12. Freundlich isotherm plot for zinc, lead and cadmium and copper at pH 8.

Table 5
The distribution coefficient of the metals

| pH | Zn | Pb | Cd | Cu |
|----|------|-------|------|------|
| 6  | 0.24 | 15.84 | 0.02 | 3.98 |
| 8  | 1.12 | 19.95 | 0.35 | 3.55 |

droxide. An explanation for the results given by them was that the surface consisted of different sites with varying affinities for adsorbate ions. When the adsorption density was low, the metal ions bound preferentially to sites where the binding strength was maximal and the adsorption intensity was high. As the surface coverage increased, adsorption to the highest energy sites became limited and only sites of lower interaction energy were available for adsorbing ions, leading to a decrease in the adsorption intensity.

As mentioned previously, the removal of the heavy metal ions was low at pH 4.5, but it increased considerably as the pH increased. Therefore, it can be assumed that the adsorption of the heavy metal ions onto the fly ash particles was not intense at pH 4.5, and hence, a considerable amount of active sites of the fly ash surfaces was available even at the high metal concentrations in the solution phase. However, at higher pH's, the adsorption was intense resulting in the depletion of high-energy sites as the heavy metal concentration increased.

Table 4 shows the values of $1/n$ and $K_f$ of the two linear regions for various pH values. At pH 4.5, the slope of the lead isotherm (0.6) was less than those of other three metals, which ranged from 0.7 to 0.74. At higher pH's (pH 6 and 8), the slope of the first linear region was significantly higher than that of the second linear region for the four metals. In the first linear region, the slope of the lead isotherm was about 1.1 at pH 6 and 8. The slope of the copper isotherm seems to

increase with increasing pH, but the trend was not clear due to too few data points. The slopes of the zinc and cadmium isotherm curve in the first linear region were very similar and were very close to those at pH 4.5. In the second linear part, the slope of the isotherms for the four metals was very low ranging from 0.15 to 0.3. Therefore, in this region, the heavy metal removal per weight of fly ash was nearly equal at all equilibrium concentrations along the isotherm curve. This may indicate a condition of increased occupation of active surface sites with metal loading.

Interestingly, the $q_e$ values of the critical point at which the adsorption intensity changed were similar regardless of the pH values for each heavy metal. It was 3.2 mg/g for Zn, 10.0 mg/g for Pb, 5.0 mg/g for Cd and 2.8 mg/g for Cu. When converted to a mole basis, these values were all about the same, ranging from $4.8 \times 10^{-5}$ to $4.4 \times 10^{-5}$ mol/g. However, it does not mean that the four metals show the same affinity for fly ash. Table 5 shows the solid/water distribution ratios, $K_d = q_e/C_e$, determined at the critical point for pH 6 and 8. At both pH's, the order of the distribution coefficient increased Cd < Zn < Cu < Pb. Therefore, it can be said that the relative tendency for different metals to bind to them increased in the same order. Also, the distribution coefficient increased as the pH increased. As shown in Fig. 3, the tendency for the precipitation of the four metals followed in the same order, which again indicates the close relationship between heavy metal hydrolysis and adsorption characteristics of metals on fly ash.

### 3.7. Treatment of metal industrial wastewater

Based on the promising results of heavy metal removal from aqueous solutions, tests were conducted to evaluate these results using real wastewater. The wastewater used was taken from a local metal plating factory. It had a pH of 3.25 and contained Cd of 12.18 mg/L, Pb of 1.82 mg/L, Zn of 11.70 m/L and Cu of 1.89 mg/L. Tests were conducted over a range of pH values (4–8) with varying fly ash concentra-

Table 4
Freundlich constants

|  | pH | Zn | | Pb | | Cd | | Cu | |
|---|---|---|---|---|---|---|---|---|---|
|  |  | $1/n$ | $K_f$ | $1/n$ | $K_f$ | $1/n$ | $K_f$ | $1/n$ | $K_f$ |
| First region | 4.5 | 0.70 | 0.07 | 0.70 | 1.66 | 0.74 | 0.05 | 0.72 | 0.28 |
|  | 6.0 | 0.76 | 0.45 | 1.07 | 10.43 | 0.71 | 0.12 | 0.95 | 5.45 |
|  | 8.0 | 0.74 | 2.75 | 1.12 | 47.67 | 0.75 | 1.06 | 1.95 | 173.06 |
| Second region | 6.0 | 0.19 | 1.85 | 0.15 | 9.67 | 0.28 | 1.40 | 0.30 | 2.58 |
|  | 8.0 | 0.28 | 19.08 | 0.30 | 15.08 | 0.29 | 1.27 | 0.26 | 3.68 |

tions. The samples were shaken at 25 °C for 24 h. At the end of the period, the solutions were separated by filtration and the residual metal concentration in the supernatant was determined by atomic absorption spectrophotometry.

As observed in the tests with artificial solutions of heavy metals, the heavy metal removal increased with increasing fly ash concentrations, as well as increasing pH. It was noted that Cd removal increased from 45% to 70%, and 95% as the pH was increased from 4 to 6 and 8, respectively, at a fly ash dosage of 10 g/L. When the fly ash dosage was increased to 20 g/L, Cd removal increased to 70%, 85% and 98% at pH 4, 6 and 8, respectively. Removal of zinc was much higher than that of cadmium under the same conditions, ranging from 55% to 100% at a fly ash dosage of 10 g/L, and from 84% to 100% at a fly ash dosage of 20 g/L. Also, fly ash was effective in removing Cu and Pb. Even at a low pH of 4, the percentage removal for both metals was over 90% at a 10 g/L fly ash dosage.

## 4. Conclusions

In this study, tests were performed to evaluate the use of coal fly ash particles as an adsorbent for heavy metal ions. It was found that that zinc, lead, cadmium and copper were adsorbed onto the fly ash very rapidly (within the first 20 min), while equilibrium was reached in 2 h for the zinc and 3 h for the other heavy metals.

When the fly ash was hydrated, its pH reached 10–13, where a high degree of the precipitation of metal ions can be expected. Furthermore, the surface of the fly ash was negatively charged when the pH was above 2.8. The precipitation of zinc and cadmium increased rapidly around pH 10 and 90% of the two metals were precipitated when the pH was over 11. For lead, precipitation occurred around pH 8 and 99% was precipitated over pH 9. On the other hand, copper precipitated even at a low pH.

Between pH 5 and 8, where the influence of precipitation is negligible, the removal for zinc was 86–98%, 96–99% for lead, 51–95% for cadmium, and 60–99% for copper when concentrations were below 100 mg/L. The percent removal of the heavy metal ions increased as the pH increased. Most of the metal ions had a 95% removal when the pH was above 8.

The adsorption data corresponded with the Freundlich isotherm well. However, the adsorption isotherm data appeared as two distinct linear regions at higher pH's. It was postulated that when the adsorption was intense, the surface of the fly ash was covered with heavy metal ions, resulting in the decreased adsorption rate.

When various heavy metals coexist, the adsorption of a particular heavy metal ion was influenced by the other ions. The removal of lead was always enhanced by the presence of other ions. On the other hand, the removal of copper was enhanced when a smaller amount (50 mg/L) of other ions were present, but decreased moderately when the amount of other ions increased to 200 mg/L. The removal of zinc generally decreased when in the presence of other ions. Finally, the removal of cadmium was enhanced especially by the presence of lead ions. Therefore, it would be beneficial for the wastewater containing lead to be mixed with the water containing cadmium for the synergetic removal of both lead and cadmium.

The results of the tests using real wastewater showed that fly ash was effective in the simultaneous removal of various heavy metals in metal industrial wastewater. It was found that the percentage removal of heavy metals was dependent on the pH of the solution. However, at neutral pH conditions (pH 6–8), the removal was high even when small amounts of fly ash were used.

## References

[1] An Annual Report, Korea Electric Power Corporation, Seoul, Korea, 2001. 7–10.

[2] T. Beaver, Adding coal ash to the composting mix, BioCycle 36 (1995) 88–89.

[3] P.L. Pratt, The use of fly ash in concrete—a European view, in: R. Day, F. Glasser (Eds.), Fly Ash and Coal Conversion By-products: Characterization, Utilization and Disposal VI, Material Research Society, Pittsburgh, PA, USA, 1990, pp. 177–188.

[4] G.F. Brendel, Development of an ASTM standard guide for the use of coal combustion fly ash in structural fills, in: Proceedings of the 11th International Symposium on Use and Management of Coal Combustion By-products, Orlando FL, USA, January 15–19, 1995.

[5] K.K. Panday, G. Prasad, V.N. Singh, Copper(II) removal from aqueous solutions by fly ash, Water Res. 19 (1985) 869–873.

[6] T. Viraraghavan, G.A.K. Rao, Adsorption of cadmium and chromium from wastewater, J. Environ. Sci. Health A26 (5) (1991) 721–753.

[7] C.H. Weng, C.P. Huang, Treatment of metal industrial water by fly ash and cement fixation, J. Environ. Eng. Div. ASCE 120 (1994) 1470–1487.

[8] C.H. Weng, C.P. Huang, Adsorption characteristics of Zn(II) from dilute aqueous solution by fly ash," Colloids and Surfaces A: Physicochem, Eng. Aspects 247 (2004) 137–143.

[9] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes –I. The case of nickel (II), copper (II) and zinc (II), J. Hazard. Mater. B95 (2002) 251–273.

[10] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes –II. The case of chromium (VI) and cadmium (II), J. Hazard. Mater. B95 (2002) 275–290.

[11] J. Ayala, F. Bianco, P. Garcia, P. Rodriguez, J. Sancho, Asturian fly ash as a heavy metals removal material, Fuel 77 (1998) 1147–1154.

[12] R. Apak, E. Tutem, M. Hugul, J. Hizal, Heavy metal cation retention by unconventional sorbents (red muds and fly ashes), Water Res. 32 (1998) 430–440.

[13] H. Nollet, M. Roels, P. Lutgen, P. Meeren, W. Verstraete, Removal of PCBs from wastewater by fly ash, Chemosphere 53 (2003) 655–665.

[14] S. Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu, Removal of dyes from aqueous solution using fly ash and red mud, Water Res. 39 (2005) 129–138.

[15] K.V. Kumar, V. Ramamurthi, S. Sivanesan, Modeling the mechanism involved during the sorption of methylne blue onto fly ash, J. Colloid Interface Sci. 284 (2005) 14–21.

[16] G.S. Gupta, G. Prasad, V.N. Singh, Removal of chrome dye from aqueous solutions by mixed absorbents, Water Res. 24 (1990) 45–50.

[17] M.M. Benjamin, Water Chemistry, McGraw-Hill, New York, 2002, p. 368.

[18] H.A. Elliott, C.M. Denneny, Soil adsorption of cadmium from solutions containing organic ligands, J. Environ. Qual. 11 (1982) 658–663.

[19] M.M. Benjamin, J.O. Leckie, Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide, J. Colloid Interface Sci. 79 (1981) 209–221.

[20] R.O. James, T.H. Healy, Adsorption of hydrolysable metal ions at the oxide–water interface, J. Colloid Interface Sci. 40 (1972) 42–52.