

Removal of Heavy Metals from Aqueous Solution by Fly Ash

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The present work investigates the possible use of fly ash for the removal of heavy metal ions from aqueous solutions. Batch experiments were conducted and the influences of metal concentration, pH, and fly ash concentration were investigated. Heavy metals used in these studies were zinc, lead and cadmium. Adsorption studies were done over a range of pH values (3-10) at 25 °C and heavy metal concentrations of 10-400 mg/L using fly ash concentrations of 10, 20 and 40 g/L. Experiments were also conducted without fly ash to determine the extent of heavy metal removal by precipitation. Kinetic and equilibrium experiments were performed and adsorption data were correlated with both Langmuir and Freundlich adsorption models. The results indicate that fly ash can be used as an adsorbent for heavy metals in the aqueous solutions, yet the degree of removal depends on the pH.

Keywords: Fly ash, Adsorption, Zinc, Lead, Cadmium, Langmuir isotherm

Introduction

Discharge of heavy metal into the aquatic environment can be hazardous not only to the aqueous systems but also to humans. Up till this point, majority of heavy metals in industrial wastewater have been removed through precipitation using limestone or adsorption using activated carbon. Recently, however, due to the high-cost of activated carbon, studies on applying relatively cheap adsorbents have been conducted.^{1,2,3,4,5,6)}

Fly ash is particulate material that is collected through electrostatic precipitator from the ash produced from combustion of coal at thermoelectric power plants. The production of fly ash generated in Korea is increasing and in year 2000, 4.43 million tons were produced where 54.62 percent (2.42 million tons) were recycled and the rest land-filled.⁷⁾

Fly ash particles have specific surface area of about 3,000 cm²/g with major constituents of SiO₂ and Al₂O₃. 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 also be shown to be effectively used in many other areas such as ALC manufacturing, building materials, soil amendment and fillers.^{8,9,10)} But the demand increase in these applications is far less than the increase in production. Therefore, the necessity of developing a new demand is increasing. Especially, fly ash with high unburned carbon content can not be used as cement additives because of the adverse effects on the quality of concrete.

Fly ash is a strong alkali material which exhibits pH 10-13 when added to water, and its surface is charged negatively at high pH. Hence, it can be expected that metal ions can be removed from the aqueous solution by precipitation or electrostatic adsorption.

In this study, adsorption of heavy metal ions in fly ash under various conditions was investigated through both kinetic study and isotherm study and the optimum removal condition was identified for each metal.

Materials and methods

Material and Equipment

Fly ash used in this study was obtained from Korea Electric Power Corporation and was generated from the combustion of bituminous coal. Heavy metal ions were in the form of chloride salts. pH was measured by a pH meter (SUNTEX), zeta-potential was determined by a zeta meter (Delsa 440SX, Coulter), and heavy metal content after adsorption were measured by atomic adsorption spectrometer (Perkin Elmer 3100).

Experiments

Adsorption experiments were performed using batch technique and the procedure is illustrated in Fig. 1. At first, fly ash, dried at 110 °C for 2 hours, was mixed with 50 ml of distilled water in polyethylene bottles to make ash concentrations 10 g/L, 20 and 40 g/L. The fly ash were hydrated for 2 hours in shaking bath at 25 °C to make pH stable. pH was adjusted to 3-10 by adding 1M HNO₃. Zinc, lead and cadmium ions in the form of chloride salts were added to the bottles to make initial concentrations 10-400 mg/L and then the bottles were agitated until equilibrium was obtained. The equilibrium times were predetermined from kinetic experiments using a procedure similar to the adsorption experiments. The concentrations of metal ions in the kinetic study were 50 mg/L each. For various time intervals (2-240 min.), the solutions were filtered and the remaining concentrations were measured.

Experiments without fly ash were also performed to investigate the effect of precipitation. pH was controlled to be 3-10 using 1M HNO₃ and 0.1M NaOH in distilled water. The precipitation rate was determined at various pH's by measuring the concentrations of metal ions remaining in the solution of the initial concentration of 100 mg/L. Zeta-potentials were measured for the pH range of 3-12.

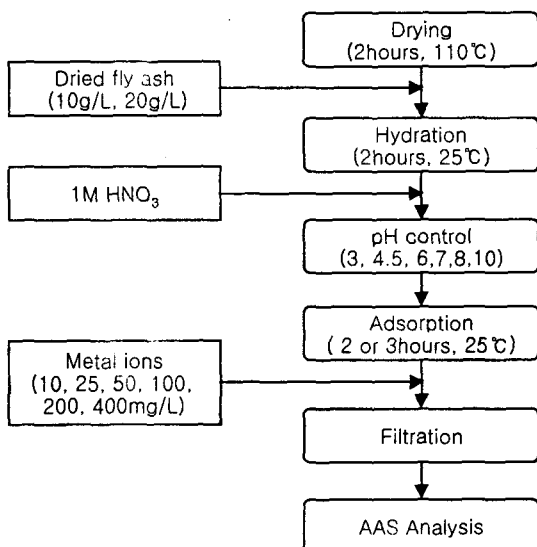


Fig. 1. Flow chart of Adsorption experiment.

Results and discussions

Characterization of Fly Ash

Table 1 shows the chemical composition of the fly ash samples used in this study. SiO_2 and Al_2O_3 contents are about 80 percent of the fly ash and Fe_2O_3 and CaO contents are about 11 percent and LOI (Loss of Ignition) was 5.7 percent.

Table 1. Chemical composition of the fly ash

| Constituent | Percent by weight |
|-------------------------|-------------------|
| 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 |

Table 2 shows the distribution of the fly ash sample and LOI by size. It can be seen that the sample is generally less than 70mesh, but majority (72.75 %) is in the size range of -400mesh. The total LOI content of the sample is 5.7 percent, but a significant variation in the LOI of the size fractions can be seen. As observed in many other studies, the unburned carbon is preferentially concentrated in the large sizes. The LOI of the +200mesh fractions is 10.56–58.33 percent, whereas that of the -200mesh fractions is less than 6 percent. SEM pictures are shown in Fig. 2 for the +200 mesh fractions and the -200mesh fractions of the fly ash. It can be seen that the +200mesh fractions are mainly composed of irregular and porous particles, whereas the -200mesh particles are spherical without any noticeable pores.

Kinetic studies

Fig. 3 shows the adsorption characteristics as a function of time. The kinetic experiments were performed by agitating in shaking bath for 4 hours at 25°C and pH 6. The concentration of the fly ash was 10 g/L (20 g/L for cadmium) and concentration of metal ions was 50 mg/L. It can be seen that the rate of uptake of metal ions was quite rapid; 87 percent of zinc, 63 percent of lead and 45 percent of cadmium of the total precipitation occurred in the first 20 minutes. The equilibriums were reached in 2 hours for zinc and 3 hours for lead and cadmium, respectively. At equilibrium, 82 percent of the zinc, 88.8 percent of the lead and 32.2 percent of cadmium were adsorbed on fly ash.

Table 2. Size fraction and LOI of the fly ash

| Size (mesh) | Mass percentage | LOI (%) |
|-------------|-----------------|---------|
| +70 | 1.58 | 58.33 |
| 70x100 | 3.19 | 28.51 |
| 100x140 | 2.23 | 25.19 |
| 140x200 | 6.53 | 10.56 |
| 200x270 | 7.47 | 5.49 |
| 270x400 | 6.25 | 4.77 |
| -400 | 72.75 | 2.99 |
| Total | 100 | 5.7 |



Fig. 2. SEM picture of a) +200mesh particles of the fly ash, b) -200mesh particles of the fly ash

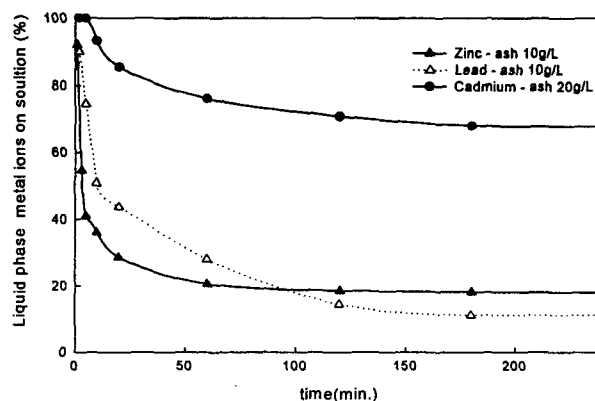


Fig. 3. Effect of contact time of zinc, lead and cadmium adsorption on fly ash at pH 6 and of initial concentration of 50 mg/L.

The rate constants for adsorption of zinc, lead and cadmium on fly ash were determined using Lagergren equation :

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

where, q_e and q (both in mg/L) are the amounts of metal ions adsorbed at equilibrium, t (min.) is time and K_{ad} (min^{-1}) is the rate constant.⁵⁾ Fig. 4 shows good fitness. K_{ad} values were 0.0307 for zinc, 0.0237 for lead and 0.0263 for cadmium, indicating that adsorption of zinc is more intensive than lead and cadmium.

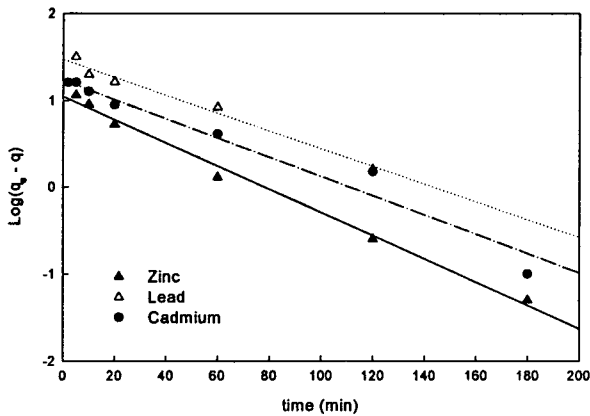


Fig. 4. Lagergren plot for the removal of zinc, lead and cadmium at pH 6 and of initial concentration of 50 mg/L.

Total Removal

Removal of metal ions from aqueous solution by fly ash can occur via adsorption and precipitation. Total removal of heavy metals at various pH's is presented in Table 3 , 4 and 5. Removal rate of zinc was 90-99 percent for low initial concentrations and 20-90 percent for the higher concentration over pH 6. For lead, it was 97-99.9 percent for low initial concentration and 50-99 percent for the higher concentration over pH 4.5. And for cadmium, it was 45-99 percent for low initial concentration and 12-98

percent for the higher concentration over pH 6. Therefore, total removal rate could be over 99 percent for low initial concentrations below 100 mg/L in neutral and alkaline environment. To increase the removal rate for higher initial concentration, more fly ash was required. Fig. 6 shows that removal rate of 400 mg/L lead ions at pH 6 is increased from 60 percent to 88 percent and 95 percent at fly ash concentration of 10 g/L, 20 g/L and 40 g/L, respectively.

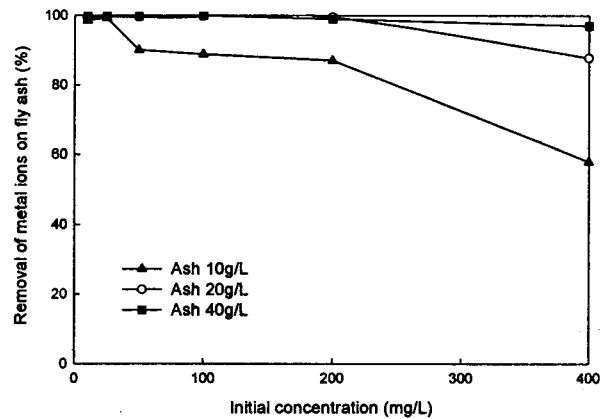


Fig. 5. Effect of fly ash dosage on adsorption of lead on fly ash

Effect of precipitation

The precipitation rate of zinc, lead and cadmium for various pH's is illustrated in Fig. 6. As pH increase, zinc, lead and cadmium precipitation gradually increases but when the pH reaches to a certain values, precipitation starts to increase rapidly. The pH values for the sudden jump for zinc was 10 and 90 percent of zinc was precipitated at pH 11. On the other hand precipitation of lead suddenly increases at pH 8 and 99 percent of lead was precipitated at pH 9.

Table 3. Removal after adsorption of zinc on fly ash (unit: %)

| Adsorbent dosage | Ini. Conc. (mg/L) | pH | | | | | |
|------------------|-------------------|-------|-------|-------|-------|-------|-------|
| | | 3 | 4.5 | 6 | 7 | 8 | 10 |
| Ash 10g/L | 10 | 27.00 | 34.20 | 85.79 | 91.40 | 98.20 | 99.10 |
| | 25 | 25.90 | 34.10 | 85.04 | 91.20 | 98.08 | 99.12 |
| | 50 | 23.30 | 33.02 | 76.00 | 90.32 | 97.76 | 98.92 |
| | 100 | 22.62 | 25.67 | 55.02 | 75.00 | 93.00 | 97.90 |
| | 200 | 14.03 | 17.34 | 34.39 | 53.88 | 77.32 | 92.17 |
| | 400 | 7.12 | 9.34 | 19.00 | 34.51 | 63.49 | 87.41 |
| Ash 20g/L | 10 | 30.60 | 42.00 | 90.00 | 97.10 | 99.00 | 99.70 |
| | 25 | 30.04 | 36.76 | 87.20 | 96.80 | 98.68 | 99.44 |
| | 50 | 27.94 | 44.44 | 85.00 | 96.00 | 98.26 | 99.58 |
| | 100 | 28.33 | 41.43 | 71.80 | 90.00 | 97.46 | 99.18 |
| | 200 | 17.18 | 25.84 | 43.84 | 58.33 | 83.84 | 94.84 |
| | 400 | 9.13 | 14.09 | 28.33 | 37.08 | 72.84 | 90.59 |

Table 4. Removal after adsorption of lead on fly ash (unit: %).

| Adsorbent dosage | Ini. Conc. (mg/L) | pH | | | | | |
|------------------|-------------------|-------|-------|-------|-------|-------|-------|
| | | 3 | 4.5 | 6 | 7 | 8 | 10 |
| Ash 10g/L | 10 | 15.00 | 96.90 | 98.50 | 99.10 | 99.80 | 99.60 |
| | 25 | 7.08 | 70.76 | 99.16 | 99.44 | 99.76 | 99.76 |
| | 50 | 4.30 | 56.36 | 88.80 | 99.58 | 99.68 | 99.84 |
| | 100 | 7.15 | 56.09 | 90.00 | 99.67 | 99.83 | 99.87 |
| | 200 | 2.80 | 40.70 | 86.95 | 97.63 | 98.90 | 99.81 |
| | 400 | 4.80 | 54.93 | 57.88 | 92.95 | 96.95 | 99.50 |
| Ash 20g/L | 10 | 25.90 | 97.40 | 99.10 | 99.20 | 99.80 | 99.80 |
| | 25 | 35.68 | 98.20 | 99.56 | 99.56 | 99.80 | 99.88 |
| | 50 | 28.12 | 94.90 | 99.48 | 99.68 | 99.82 | 99.86 |
| | 100 | 15.40 | 91.70 | 99.66 | 99.72 | 99.85 | 99.90 |
| | 200 | 8.90 | 88.00 | 99.40 | 99.60 | 99.88 | 99.92 |
| | 400 | 6.33 | 71.73 | 87.68 | 99.30 | 99.73 | 99.88 |

Table 5. Removal after adsorption of cadmium on fly ash (unit: %).

| Adsorbent dosage | Ini. Conc. (mg/L) | pH | | | | | |
|------------------|-------------------|------|-------|-------|-------|-------|-------|
| | | 3 | 4.5 | 6 | 7 | 8 | 10 |
| Ash 10g/L | 10 | 0.00 | 27.50 | 50.70 | 87.80 | 94.70 | 97.70 |
| | 25 | 0.00 | 24.00 | 40.00 | 91.60 | 94.76 | 98.96 |
| | 50 | 0.00 | 21.20 | 44.80 | 86.94 | 96.82 | 99.24 |
| | 100 | 0.00 | 16.60 | 41.80 | 70.90 | 69.10 | 98.61 |
| | 200 | 0.00 | 16.30 | 23.50 | 52.90 | 52.00 | 72.10 |
| | 400 | 0.28 | 6.40 | 12.70 | 33.10 | 32.80 | 43.68 |
| Ash 20g/L | 10 | 0.00 | 35.50 | 72.10 | 90.30 | 95.50 | 98.70 |
| | 25 | 0.00 | 36.00 | 54.12 | 93.44 | 96.56 | 99.08 |
| | 50 | 0.40 | 34.60 | 53.20 | 91.38 | 97.82 | 99.52 |
| | 100 | 0.20 | 34.60 | 52.60 | 75.10 | 95.73 | 99.65 |
| | 200 | 0.55 | 32.65 | 35.05 | 73.15 | 81.40 | 99.15 |
| | 400 | 0.47 | 17.80 | 24.70 | 49.98 | 63.70 | 82.23 |

And the tendency of the precipitation of cadmium is very similar to that of zinc. Because pH of aqueous solution by fly ash exhibits 10–13, metal ions as zinc, lead and cadmium could be removed to a great extent by precipitation. If wastewater is strongly acidic, fly ash solution is neutralized somewhat and precipitation may not be so predominant.

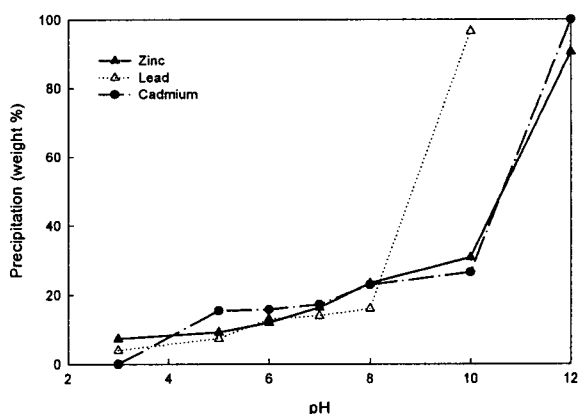
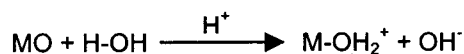


Fig. 6. Precipitation of zinc, lead and cadmium at various pH

Effect of pH

The effect of pH on the adsorption of zinc, lead and cadmium on fly ash was studied in the range of pH 3 to 10. Fig. 7 shows results at the initial concentration of 200mg/L. The removal rate of zinc was about 50 percent at pH 6 and it increased to 90 percent at pH 8. For lead, 55 percent was removed at pH 4.5 and 90 percent at pH 6. The removal of metal ions at acidic conditions can be explained on the basis of aqua-complex formation of the oxides present in the fly ash. Positive charge develops on the surface of the oxides of fly ash in acidic solution as follows.⁶⁾



Therefore, adsorption of metal ions is not suitable at low pH. On the other hand, at higher pH's, the surface of the fly ash becomes negatively charged so that metal ions can be easily adsorbed. Fig. 8 shows that the zeta-potentials of the fly ash particles measured at various pH's. It can be seen that the fly ash particles are charged negatively at the pH's over 5. Therefore, positively charged metal ions can be adsorbed to the negatively charged fly ash particles above pH 5. Consequently in alkaline environment, both

adsorption and precipitation take place for the efficient removal of metal ions for aqueous solution.

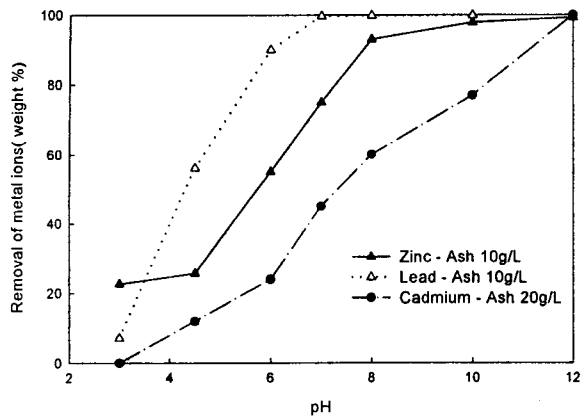


Fig. 7. Removal of zinc, lead and cadmium on fly ash at various pH and of initial concentration of 200 mg/L.

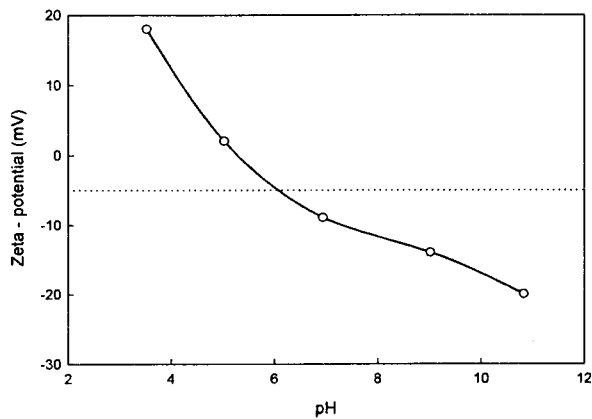


Fig. 8. Zeta-potential of the fly ash at various pH

Adsorption isotherm

The adsorption data was analyzed by Langmuir isotherm and Freundlich isotherm. Langmuir isotherm model is as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0}$$

where, C_e (mg/L) is the equilibrium concentration of metal ions, q_e (mg/g) is the amount of adsorbed metal ions on fly ash, and Q^0 (mg/g), the quantity makes mono layer on the surface and b (L/mg) is Langmuir constant related to the capacity and energy of adsorption.⁵⁾

Freundlich isotherm model is as follows:

$$q_e = K_F C_e^{\frac{1}{n}}$$

where, C_e (mg/L) and q_e (mg/g) are the same as previous one, K_F (mg/g) is the constant to indicate the relative amount of adsorbed on adsorbent and n is related to the intensity of adsorbent. Freundlich isotherm usually

represents double layer adsorption model but at low concentration adsorbate forms mono layer on adsorbent and may show the similar results to Langmuir isotherm.

Fig. 9 and 10 show the results of analysis by two isotherms. Fig. 9 is the linear plot of C_e/q_e vs. C_e , indicating that Langmuir isotherm model is very applicable to this experiment. On the other hand Freundlich isotherm plot (Fig. 10) is not linear but below the concentration of 100mg/L it shows the linearity.

Langmuir constants, Q^0 and b is shown in Table 6. For zinc, constant b increases by pH, 0.02 at pH 4.5, 0.07 at pH 6 and 0.66 at pH 10. For lead, the tendency is the same, it is 0.01, 0.07 and 0.66 and for cadmium, it is 0.01, 0.02 and 0.28 by turns. Q^0 also increases by pH. For zinc, Q^0 constant is 4.49 at pH 4.5, 7.87 at pH 6 and 36.76 at pH 10. For lead, it is 17.85, 23.15 and 72.46 and for cadmium, it is 1.61, 2.94 and 8.29 at pH 4.5, 6 and 10 respectively. At pH 4.5 and 6 where there is minimal precipitation, constant b of zinc, lead and cadmium are similar. When Q^0 at pH 6 is converted to the unit of mmole/g, it becomes 0.121 (mmole/g) for zinc and 0.112 (mmole/g) for lead. Therefore, on a mole base, the adsorption capacity of fly ash for the two metal ions is similar. But for cadmium it is 0.026 (mmole/g), which indicates that higher dosage of fly ash is required to remove cadmium ion efficiently from the aqueous solution.

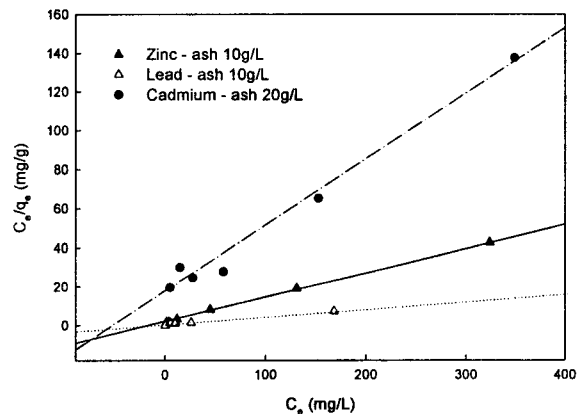


Fig. 9. Langmuir plot for zinc, lead and cadmium at pH. 6

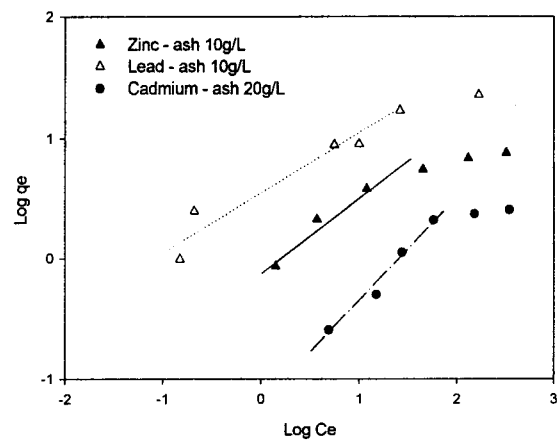


Fig. 10. Freundlich plot for zinc, lead and cadmium at pH 6.

Table 6. Langmuir constants of zinc, lead and cadmium adsorption on fly ash.

| pH | Zinc | | Lead | | Cadmium | |
|-----|---------|--------------------------|---------|--------------------------|---------|--------------------------|
| | b(L/mg) | Q ⁰ (mg/g) | b(L/mg) | Q ⁰ (mg/g) | b(L/mg) | Q ⁰ (mg/g) |
| 4.5 | 0.02 | 4.49 | 0.01 | 17.85 | 0.01 | 1.61 |
| 6 | 0.07 | 7.87 | 0.07 | 23.15 | 0.02 | 2.94 |
| 10 | 0.18 | 36.76 | 0.66 | 72.46 | 0.28 | 8.79 |

Conclusions

The following conclusions can be drawn from this investigation.

1. The kinetic studies indicated that zinc, lead and cadmium were adsorbed on fly ash very rapidly in first 20 minutes and equilibrium was reached in two hours for zinc and three hours for lead and cadmium.

2. When the fly ash hydrated, its pH reached to 10–13, where a high degree of precipitation of metal ions can be expected. Furthermore the surface of the fly ash was negatively charged in neutral and alkaline environment.

3. Precipitation of zinc and cadmium increased rapidly around pH 10 and 90 percent was precipitated over pH 11. For lead, precipitation occurred around pH 8 and 99 percent was precipitated over pH 9.

4. Between pH 5 and 8, where the influence of precipitation is negligible, removal rate of low initial concentration metals is mainly resulted from adsorption and it showed 86-98 percent of removal for zinc, 96 - 99 percent for lead and 51-95 percent for cadmium.

5. Total removal of zinc was 90-99 percent for low initial concentration and 20-90 percent for the higher initial concentration over pH 6 and that of lead was 97-99.9 percent for low initial concentration and 50-99 percent for the higher initial concentration over pH 4.5 with 10 g/L ash concentration. And for cadmium, it was 72-99 percent for low initial concentration and 18-82 percent for the higher initial concentration over pH 6 with 40g/L ash concentration. Therefore it can be expected that 99 percent removal rate will be obtained in neutral and alkaline environment under 100 mg/L initial metal concentration.

6. The adsorption data was described by isotherm models, and well fitted to the Langmuir isotherm but Freundlich isotherm correlated well only for low initial concentrations.

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