Potential of Treated Fly Ash for Removal of Lead from Wastewater

Suwan Chaiyasith and Chutima Septhum
Department of Chemistry, Faculty of Science,
King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand.

Abstract

In this work we examined the possible use of fly ash by reflux with alkali solution as a means of removing lead from wastewater. Treated fly ash is an effective adsorbent because of its high cation exchange capacity. The adsorption of lead onto treated fly ash has been found to depend on suspension density, pH and concentration of lead solution. Under optimised operating conditions at a suspension density of 0.5 g l^{-1} of treated fly ash, a concentration of 40 mg l^{-1} of lead and pH>3, the adsorption was almost completed within 30 minutes. Experimental results showed that Pb^{2+} and $Pb(OH)^{+}$ were adsorbed and the adsorption followed the Langmuir adsorption isotherm. The removal efficiency was lower at higher anion concentrations and when nickel or cadmium were added to the solutions. Desorption of adsorbed lead from the treated fly ash was very low and the concentration of lead in the leachate was less than 0.25 mg l^{-1}.

Keywords: adsorption, anion, cation exchange capacity (CEC), desorption, fly ash, heavy metals, lead

1. Introduction

Environmental pollution by toxic metals occurs globally through agricultural and industrial processes and also through waste disposal. Metals, discharged into the environment often not only cause large environmental impact but also economic and health problems [1]. Environmental regulations require the removal of heavy metals from wastewater. Today there are many technologies available to reduce the concentration of heavy metals to levels that comply with the regulatory standards.

Lead is one of the heavy metal elements with significant levels that are being removed from industrial waste. It is a toxic element mainly found in industrial waste from batteries, gasoline, plating, pigment industry, etc. It is toxic resulting from the binding to haemoglobin [2]. When absorbed by the human body, lead accumulates in the bone tissue.

Aside from Pb(II), heavy metals such as As, Cd, Cr, Cu, Hg, Ni, Pb, Se and Zn are being removed from wastewater. Standard techniques used for removal of heavy metals are e.g., precipitation, filtration, ion exchange, reverse osmosis, oxidation-reduction, solvent extraction and electrolysis [3]. While these methods are efficient at high concentration levels, they are usually not efficient at low concentration levels.

Another method to remove heavy metals is the adsorption to an adsorbent. In recent works, fly ash has been proven to be a suitable adsorbent for various heavy metals [4] such as copper [5]. Similar research was reported for adsorption of cadmium [6], lead [7], iron [8], chromium [9-11], arsenic [12], nickel [13] and zinc [14].

Fly ash is widely available as a waste product from electric power plants. In previous works, it has been shown that the CEC of untreated fly ash can be improved by undergoing a treatment process [15], improving its suitability to adsorb heavy metals. In this work we will examine the adsorption of lead on treated fly ash.

2. Materials and Methods

Fly ash was collected from the Mea-Moh electric power plant in Lampang province in the North of Thailand. Treated fly ash was prepared by refluxing the fly ash in 1.0 M NaOH for 24 hr at a fly ash to alkali ratio of 1:8. The refluxed fly ash was then separated from alkali solution, cleaned with deionized water and dried at 50 °C for 48 hr.

Batch adsorption experiments were carried out in a solution of lead nitrate in various concentrations(10-40 mg l^{-1}). A range of between 0.5-10 mg l^{-1} of treated fly ash with a particle size of less than 63 μm was added to 50 ml of Pb(II) solution. For pH adjustment with a pH between 2-5, a preliminary test volume of HNO_3 or NaOH solution was pipetted into the solution. The solution was then shaken at 25 °C and a constant speed of 100 rpm. After the 10-240 min reaction time, the solution was centrifuged, filtered through a 0.45 μm membrane filter and collected in a polyethylene bottle. The final pH of the solution was measured again with a pH meter (Metrohm 713 pH meter). For the determination of adsorption equilibrium, the effect of suspension density of treated fly ash, concentration of Pb(II), reaction time, pH of the solution, desorption of adsorbed lead from treated fly ash and interference of anions of 0-80 mg l^{-1} of SO_4^{2-}, Cl^-, PO_4^{3-}, NO_3^- and F^- and cations of 0-30 mg l^{-1} of Ni(II) and 0-10 mg l^{-1} of Cd(II) were investigated. All samples were analyzed for Pb(II) using a Shimadzu Model AA-680 atomic absorption spectrophotometer

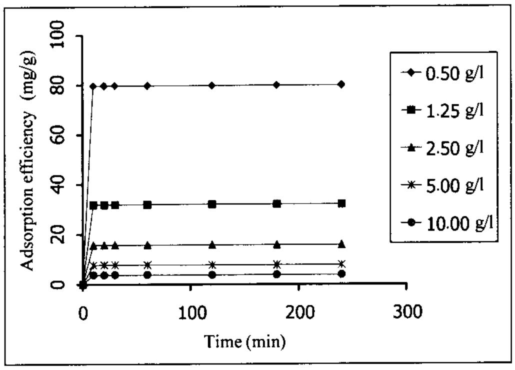

Figure 1. Effect of time and solid suspension density of the treated fly ash on adsorption efficiency of Pb(II) solution at 40 mg l^{-1} and pH 5.

according to Standard Methods for the Examination of Water and Wastewater [16]. Each experiment was repeated three times and the average result of the three repetitions was reported.

All chemicals used in this experiment were of analytical grade. For anion interference, Na_2SO_4, NaCl, Na_3PO_4, $NaNO_3$ and NaF were used, $Ni(NO_3)_2$ and $Cd(NO_3)_2$ were used for cation interference.

3. Results and Discussion

3.1 Effect of solid suspension density of treated fly ash and reaction time

Figure 1 shows the adsorption curves for various solid densities of treated fly ash. At a given Pb(II) concentration of 40 mg l^{-1}, the highest absorption of lead (79.49 mg g^{-1}) was acquired at a solid density of 0.5 g l^{-1} and a pH of 5. At higher solid densities (1.25 to 10.0 g l^{-1}) the adsorption efficiency decreased from 31.94 to 3.99 mg g^{-1}. The adsorption equilibrium was reached within 30 min. This shows that an excess of adsorbent does not improve the lead removal from aqueous solution.

3.2 Effect of pH and reaction time

Treated fly ash consists of a high amount of silica, alumina, iron oxide and sodium oxide [15]. With these components, it can be expected that treated fly ash may be a good adsorbent for metals. These oxides show a high affinity towards heavy metals and possess a highly specific

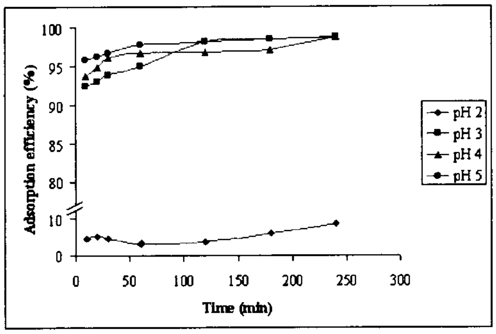

Figure 2. Effect of pH and time on the adsorption efficiency of Pb(II) solution at 10 mg l^{-1} of Pb(II) and 0.5 g l^{-1} of the treated fly ash.

surface area [17]. As can be seen in Figure 2, the adsorption process is highly pH dependent. The ANOVA-test for 95% confidence level shows a significant difference in adsorption efficiency. While at a pH of 2 the adsorption of a 10 mg l^{-1} solution of Pb(II) is less than 10%, at a pH of 3 or higher the adsorption rate is almost 100%.

This observation corresponds with the results of Yavada et al. [7] that at a pH of 6.4 and a Pb(II) concentration of 2-6 mg l^{-1} at 30°C, the adsorption efficiency of Pb(II) onto untreated fly ash was 88.10% lower than treated fly ash. This effect can be explained with the help of charge effects on the adsorbent surface as follows:

The speciation of Pb(II) is pH dependent as shown in Figure 3 [18]. While at a pH of 2-5 lead always exclusively exists as Pb(II), above pH 8 it is hydrolysed to $PbOH^+$ and $Pb(OH)_2$ (eq. 1-2).

$$Pb^{2+} + H_2O \rightarrow PbOH^+ + H^+ \quad (1)$$
$$PbOH^+ + H_2O \rightarrow Pb(OH)_2 + H^+ \quad (2)$$

At a pH of 2, Pb^{2+} is the prevailing species. At the same time, due to reaction (eq. 3) the adsorbed surface is positively charged. As the two positive charges repel each other the adsorption efficiency is low (M is Si or Al).

$$\equiv MOH + H^+ \rightarrow \equiv MOH_2^+ \quad (3)$$

At higher pH the surface of the adsorbent is negatively charged due to dissociation (eq. 4) so

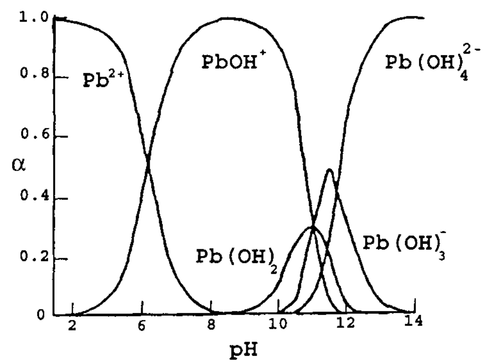

Figure 3. Speciation of Pb(II) [18].

Pb^{2+} and also $Pb(OH)^+$ can be adsorbed (eq. 5)

$$\equiv MOH + OH^- \rightarrow \equiv MO^- + H_2O \quad (4)$$
$$2(\equiv MO^-) + Pb^{2+} \rightarrow (\equiv MO)_2Pb \quad (5)$$

For fly ash, the affinity of Pb(II) to the surface can therefore be described by eq. 6 and eq. 7.

$$2(\equiv SiO^-) + Pb^{2+} \rightarrow (\equiv Si\text{-}O)_2Pb \quad (6)$$
$$2(\equiv AlO^-) + Pb^{2+} \rightarrow (\equiv Al\text{-}O)_2Pb \quad (7)$$

The removal of Pb(II) from the water increases with time (Figure 2) and concentration (Figure 4). The adsorption equilibrium was thereby attained within 120 min at 10 mg l^{-1} at a pH of 3. The time to reach the equilibrium depends on the pH of the lead solution and the Pb(II)-concentration. At an initial Pb(II)-concentration of 20 mg l^{-1} the equilibration is reached within 60 min. At 40 mg l^{-1} the time is shortened to only 30 min at a pH of 3. This observation corresponds with the results of Yadava et al. [7] that at a pH of 6.4 and a Pb(II)-concentration of 2-6 mg l^{-1} at 30 °C, the adsorption efficiency of Pb(II) onto untreated fly ash was 88.10 % lower than treated fly ash.

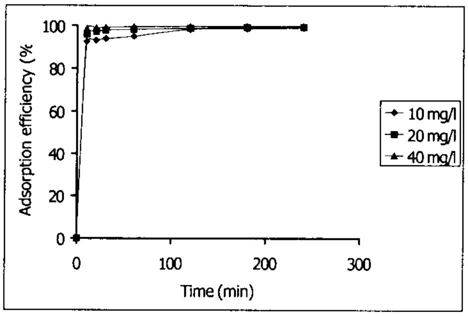

Figure 4. Effect of concentration of Pb(II) on the adsorption efficiency at 0.5 g l^{-1} of the treated fly ash and pH 3.

3.3 Adsorption isotherm

The adsorption mechanism of Pb(II) was determined in a solution of 40 mg l^{-1} Pb(II)at pH 5 and 25 °C and evaluated following the Langmuir equation (eq. 8)

$$\frac{C_e}{X} = \frac{1}{bX_m} + \frac{C_e}{X_m} \quad (8)$$

where C_e is the equilibrium concentration (mg l^{-1}) of Pb(II), X is the amount of Pb(II) (mg g^{-1}) adsorbed at the equilibrium, X_m and b are the adsorption capacity and the energy of adsorption, respectively. The linear plot of C_e/X vs. C_e (Figure 5) confirms that Pb(II) is adsorbed on the surface of the treated fly ash in a monolayer which can be described by the Langmuir isotherm [9]. Linear regression of the experimental data lead to an X_m of 89.28 mg g^{-1} and a b of 0.264 l mg^{-1}(eq 9).

$$C_e/X = 0.011C_e + 0.039 \quad (9)$$

3.4 Effect of anions on the adsorption efficiency

In Figure 6 the adsorption efficiency of Pb(II) which is dependent on increasing concentrations of various anions such as F^-, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}, was investigated. The results showed that for NO_3^- only a very small decrease of 0.3 % in the adsorption efficiency can be observed, whereas the other anions clearly decrease the adsorption efficiency. The sharpest decrease can be found for SO_4^{2-} when the efficiency is reduced by 4% when the concentration is increased from 0 – 80 mg l^{-1}. F^- also shows a strong negative effect on the adsorption efficiency. From 0 – 80 mg l^{-1} the efficiency decreases by 5%. For PO_4^{3-} and Cl^- the results show a similar effect of less than 1% between 0 and 80 mg l^{-1}.

The reason for the effect of anions on the adsorption efficiency may lie in the fraction of negatively charged Pb(II) complexes that dispelled for the also negatively charged surface of the adsorbent.

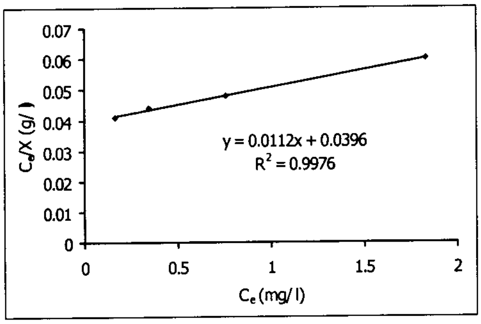

Figure 5. Linear plot of C_e/X versus C_e.

3.5 Effect of cations on the adsorption efficiency

Industrial wastewater usually contains a mixture of various metals. Because of the high CEC of fly ash for Ni(II) and Cd(II) [6][19-20], mixture cations such as Ni(II) and Cd(II) can compete with Pb(II) for adsorption positions on the surface of the adsorbent, thereby reducing the adsorption efficiency for Pb(II) itself. The effect of increasing concentrations of Ni(II) and Cd(II) on the adsorption efficiency of Pb(II) is shown in Figure 7. In the experiments, only a very small decrease of less than 1 % efficiency can be observed.

3.6 Desorption of metal from treated fly ash

For the study of desorption rate of Pb(II) from treated fly ash, samples of treated fly ash from the adsorption process with 10, 20 and 40 mg l^{-1} Pb(II) solution were leached for 6 hr with diluted HCl solution (ratio 1:100 w/v) at a pH of 5.8-6.3. The analysis of the leachate showed (Table 1) that the desorption of Pb(II) from the treated fly ash is rather low (26.04, 14.45 and 12.39 %). With final concentrations of 0.13, 0.14 and 0.25 mg l^{-1} the concentration of Pb(II) in the leachate after treatment are clearly below the legal limit of 5 mg l^{-1} Pb(II) of Thai Wastewater Industrial Effluent Standard [21].

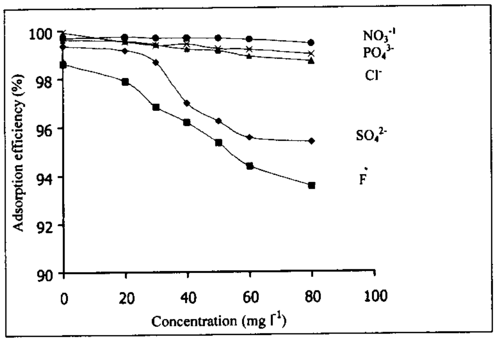

Figure 6. Effect of anions on the adsorption efficiency of Pb(II) solution of 40 mg l^{-1} at 0.5 g l^{-1} of the treated fly ash for 30 min.

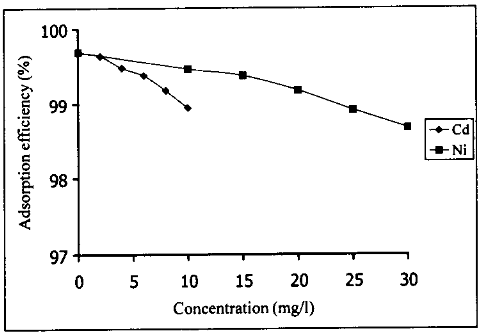

Figure 7. Effect of Cd(II) and Ni(II) on the adsorption efficiency of 40 mg l^{-1} Pb(II) at 0.5 g l^{-1} of the treated fly ash at pH 5 for 30 min.

Table 1. Adsorption and desorption efficiency of Pb(II) from the treated fly ash.

Pb (mg l^{-1})	Adsorption (%)	Desorption (%)
10	96.77	26.04
20	98.26	14.45
40	99.28	12.39

4. Conclusions

The adsorption efficiency of Pb(II) on treated fly ash depends on pH, time, concentration of treated fly ash, anions and concentration of Pb(II). The efficiency was high until the adsorption equilibrium was reached within 30 min. The efficiency increases at high pH due to the fraction of Pb(II) and $Pb(OH)^+$. While there is a strong effect of anion on the adsorption efficiency of Pb(II), cations as Ni(II) and Cd(II) only have a minimal effect. Although the desorption of adsorbed lead from the treated fly ash was very low, in the case of an environmental application the possible leaching of Pb(II) into the ground water should be considered [22].

Acknowledgement

The authors acknowledge the Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang for providing the facility for this study. We would like to thank Dr. Jochen Amrehn for much help.

5. References

[1] Gadd, G. M. and White, C., Microbial Treatment of Metal Pollution. *TIBTech.*, Vol. 11, pp.353-359, 1993.

[2] Barltrop, D. and Smith, A., Lead Binding to Human Haemoglobin. *Experientia,* Vol. 28, pp.76-77, 1972.

[3] Wilkins, E. and Yang, Q., Comparison of Heavy Metal Removal Efficiency of Biosorbents and Granular Activated Carbons. J. *Environ. Sci. Health.,* A31, pp.2111-2128, 1996.

[4] Theis, T. L. and Wirth, J. L., Sorptive Behavior of Trace Metals on Fly Ash in Aqueous System. *Environ. Sci. Technol.* Vol.11, pp.1096-1100, 1977.

[5] Panday, K. K., Prasad, G. and Singh, V. N., Copper (II) Removal from Solutions by Fly Ash. *Water Res.,* Vol.19, pp.869-873, 1985.

[6] Yadava, K. P., Tyagi, B. S., Panday, K. K. and Singh, V. N., Fly Ash for the Treatment of Cd(II) Rich Effluents. *Environ. Technol. Lett.,* Vol.8, pp.225-234, 1987.

[7] Yadava, K. P., Tyagi, B. S. and Singh, V. N., Fly Ash for Treatment of Water Enriched in Lead(II). *J. Environ. Sci. Health.,* 24A, pp.783-808, 1989.

[8] De, A. K. and Lal, M. M., Removal of Iron from Water by Coal Fly Ash. *J. Environ. Sci. Health.,* A25, pp.665-677, 1990.

[9] Panday, K. K., Prasad, G., and Singh, V. N., Removal of Chromium(VI) from Aqueous Solution by Adsorption on Fly Ash-Wollastonite. *J. Chem. Tech. Biotechnol.* 34A, pp.367-374, 1984.

[10] Gupta, G. S., Prasad, G., Panday, K. K. and Singh, V.N., Removal of Chrome Dye from Aqueous Solutions by Fly Ash. *Water Air Soil Pollut.,* Vol.37, pp.13-24, 1988.

[11] Rai, D. and Szelemczka, R. W., Aqueous Behavior of Chromium in Coal Fly Ash. *J. Environ. Qual.*, Vol.19, pp.378-382, 1990.

[12] Diamadopoulos, E., Loannidis, S. and Sakellaropoulos, G. P., As (V) Removal from Aqueous Solutions by Fly Ash. *Water Res.,* Vol.12, pp.1773-1777, 1993.

[13] Ricou-Hoeffer, P., Héquet, V., Lécuyer, I. and Le Cloirec, P., Adsorption and Stabilization of Nickel Ions on Fly Ash/Lime Mixing. *Water Sci. Technol.*, Vol.42, pp.79-85, 2000.

[14] Weng, C. H. and Huang, C. P., Treatment of Metal Industrial Wastewater by Fly Ash and Cement Fixation. *J. Environ. Eng.,* Vol.120, pp.1470-1487, 1994.

[15] Chaiyasith, S. and Septhum, C., Treatment of Coal Fly Ash for Cation Exchange Capacity Improvement. *KMITL Science J.*, Vol.3, pp.38-44,2003

[16] Eton, D. A., Clesari, L. S. and Greenberg, E., Standard Metstewater, Washington. APHA pp.3-1-3-7, 1995

[17] Huang, C. P. and Rhoads, E. A., Adsorption of Zn(II) onto Hydrous Aluminosilicates. *J. Colloid and Interface Sci.,* Vol.131, pp.289-306, 1989.

[18] Fergusson, J. E., The Heavy Elements Chemistry, Environmental Impact and Health Effect, 1st ed., Pergamon Press, Inc. N.Y. pp. 57-63, 1990.

[19] Apak, R., Tuetem, E., Hueguel, M. and Hizal, J., Heavy Metal Cation Retention by

Unconventional Sorbents (red muds and fly ashes) *Water Res*, Vol.32, pp. 430-440, 1998.

[20] Viraraghavan, T. and Dronamraju, M. M., Use of Fly Ash in the Removal of Copper, Nickel and Zinc from Wastewater. *Water Poll. Res. J. Canada,* Vol.28, pp.369-384, 1993.

[21] Thai Wastewater Effluent Standard, Notification of Ministry of Industry, No. 2, B.E. 2539 (1996), issued under the Factory Act B.E. 2535 (1992) published in the Royal Government Gazette Vol. 113, part 52D, June 27, B.E. 2539(1996).

[22] Evangelou, V. P. and Neathely, J. K., Bituminous Fly Ash Release Potential Modeling and Remediation of Arsenic, Boron and Heavy Metals, Agronomy and Center for Applied Energy Research University of Kentucky, November, 1998.