

Influence of Operating Conditions on Heavy Metal Cation Removal By Fly Ash in Aqueous Solutions

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ABSTRACT

Disposal of a growing amount of fly ash creates environmental problems and utilizations of the material has to be developed in industrial fields. Ash is known to remove metal ion from water. However, the best operating conditions have to be found and a better mechanism knowledge has to be approached.

Coal fly ash was used to study adsorption of several cations (Cu^{2+} , Ni^{2+} , Zn^{2+} and Pb^{2+}) within various experimental conditions : dry or wet fly ash, pH, metallic ion/fly ash ratio. Adsorption isotherms were carried out at room temperature for different pH. It has been shown that alkalinity of fly ash is an important factor and pH control is required. At high pH, precipitation is performed with a complete removal of the ion but a dissolution of alumina sites has been shown. At a pH range between 3 and 6, depending of the hydrolysis properties of the metallic ion, adsorption is the main mechanism. The removal order is $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$. For a pH < 3 a smaller adsorption capacity is found due to a competition between metal cations and hydronium ions.

INTRODUCTION

The awareness of increasing water and soil pollution implies permanent studies concerning water treatment. Elsewhere control and reduction of waste volume in landfills are being taken into account. Consequently, wastes or naturally occurring materials like biopolymers or clays, are tested for depollution of waters¹⁻⁴. Coal fly ash is a cheap adsorbent since they are widely available. Moreover, fly ash is an efficient adsorbant for water treatment concerning removal of DOC (Dissolved Organic Carbon)^{5,6} and a useful additive in cement industry due to the pozzolanic and cementitious properties of fly ash⁸. As a matter of fact, although fly ash are considered as a waste, several studies have pointed out their efficiency in the removal of heavy metallic ions in aqueous phase⁹⁻¹³. Their alkaline property makes them interesting for use in water treatment to precipitate metallic ions, by analogy with lime treatment, as it was already shown^{8,9,14-16}.

Considering a wide range of pH, and by comparison with phenomena occurring at oxide/water interface¹⁷, ion exchange, adsorption, surface precipitation and bulk solution precipitation could be responsible for the removal of heavy metals in aqueous solution by fly ash, which seems to be experimentally pointed out¹³. In fact ion exchange probably does not occur in the case of fly ash, and competition for adsorption between hydronium ions and metallic ions would better explain removal in low pH medium. The three other phenomena, are predominant in different pH range. Precipitation lead to complete removal of heavy metals by formation of hydroxides ions, but sorption, i.e. adsorption and surface precipitation, could be

more effective to immobilize metallic ions on the fly ash. Less information on mechanisms is available concerning adsorption on the complex mixing of oxides making up the fly ash. The main goal of this study was to use coal fly ash as an adsorbent of several cations (Cu^{2+} , Ni^{2+} , Zn^{2+} and Pb^{2+}) within various experimental conditions : dry or wet fly ash, pH, metallic ion/fly ash ratio.

MATERIALS AND METHODS

Coal fly ash used in these experiments results from the combustion of South African coal in a 600 MW pulverized-coal power plant. Its chemical composition and main characteristics are presented in table 1. The surface area of fly ash was determined by measuring nitrogen gas adsorption using a Coulter SA3100 (BET method). Stock solutions of Cu^{2+} , Ni^{2+} , Zn^{2+} (10 g.L^{-1}) and Pb^{2+} (1 g.L^{-1}) were prepared from their chloride form (Aldrich). The metallic ions solution (0.5 L) was obtained by diluting mother solutions with permuted water to the following concentrations : 150 mg.L^{-1} for Cu^{2+} , Ni^{2+} , Zn^{2+} , 25 mg.L^{-1} for Pb^{2+} . Suspensions of sorbent were stirred at 200 rpm for 48 hours. pH was fixed initially at 5 by adding HCl 36%, and maintained at this value by HCl 1 M additions when necessary. Metallic ion concentrations were measured with a flame atomic absorption spectrophotometer Perkin Elmer model 2280.

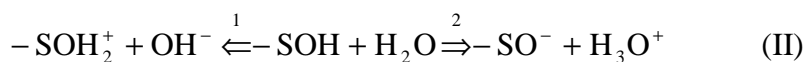
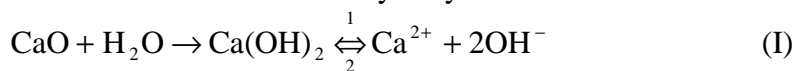
Table 1. Chemical composition and characteristics of fly ash used.

Constituent	% by weight
Si as SiO_2	50.9
Al as Al_2O_3	35.4
Fe as Fe_2O_3	4.1
Ca as CaO	1.9
Loss on ignition (550°C)	2.6
Humidity	0.13
S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	< 2
pH_{pzc}	3.1

RESULTS AND DISCUSSION

Initial reactions of ash in aqueous solution

Fly ash has an alkaline reaction. The determination of calcium oxide dissolution indicates that the alkalizing ability of 1 g of fly ash is equal to 0.15 meq.L^{-1} . Alkalinity resulting from calcium oxide dissolution is sufficient to cause variation of pH as observed. Final pH results from dissolution of calcium oxide and from hydrolysis of surface -SOH sites :



In acidic medium more than in basic medium, equilibrium (I) is favored in sense 1, which explains the stronger variation of pH, when initial pH is acidic.

Since pH at the point of zero charge (pH_{pzc}) is equal to 3.1 (see Table 1), equilibrium (II) is preferentially establish in sense 2 for systems where pH is above 3.1. Consequently, a

negative charge appears on surface of fly ash.

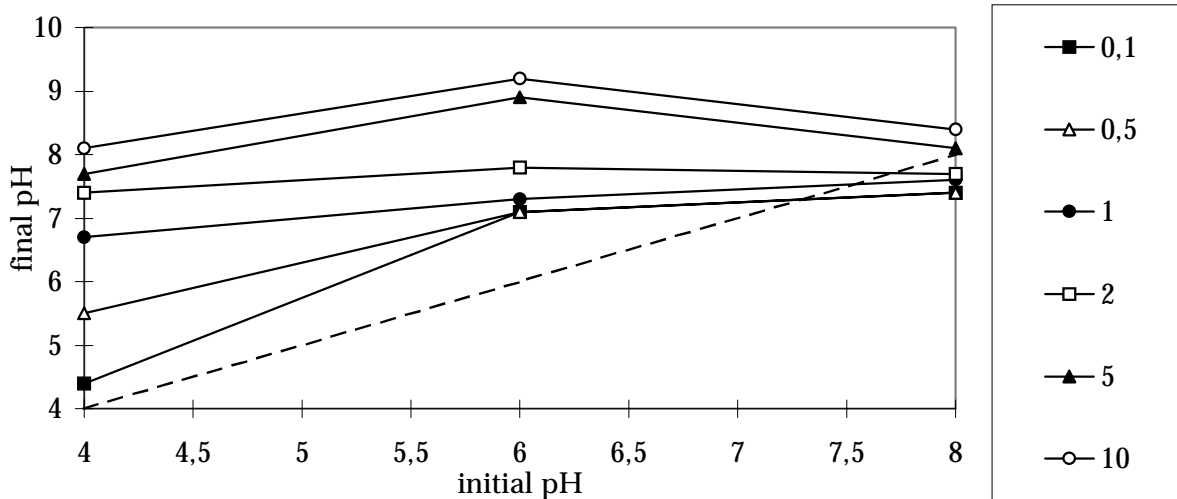


Figure 1 : Alkalinity of fly ash in distilled water (100 ml) for different concentrations. The dashed line corresponds to the equality of initial and final pH. Fly ash concentration are expressed in g.L^{-1} .

Ash preparation and resulting pH influences

Figure 2 presents results from removal of Cu^{2+} (initial concentration 500 mg.L^{-1}) in four different types of experimental conditions. The shape of the isotherms seems to be of type II or III in the BET classification. It is clear that the best removal of copper is reached when pH is not kept constant and using dry fly ash, i.e. fly ash with its total alkalinizing ability. In these conditions removal varies from 34% to 96% when fly ash concentration increases from 20 to 100 g.L^{-1} . On the contrary, the lowest equilibrium capacities are observed by using wet fly ash at constant pH, i.e. pH equal to 5. In this case, removal ranges between 16% and 33% as fly ash concentrations increase from 20 to 100 g.L^{-1} . Experiments carried out with dry fly ash at constant pH or with wet fly ash at non-constant pH give similar and intermediate results between the two previous conditions. For these tests, removal varies from 11% to 44% with dry fly ash at constant pH, and between 7% and 44% with wet fly ash at non-constant pH, as fly ash concentrations increase from 20 to 100 g.L^{-1} .

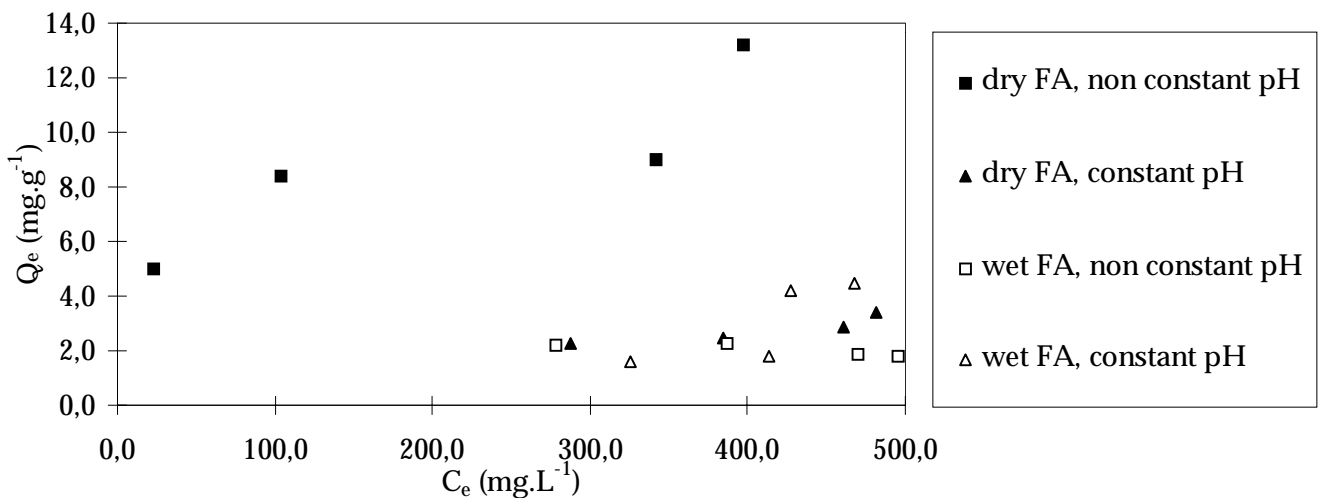


Figure 2 : Equilibrium capacity Q_e (mg.g^{-1}) vs equilibrium concentration C_e (mg.L^{-1}). FA : Fly Ash. $\text{pH}_{\text{initial}} = 5$; $[\text{Cu}^{2+}]_{\text{initial}} = 500 \text{ mg.L}^{-1}$. Experiment durations : 8 to 16 days.

pH influence

Figure 3 presents removal of Pb^{2+} for different pH. From the shape of the curve and using previous works^{13,19}, three different mechanisms are proposed :

- pH > 6 precipitation
- $6 < pH < 5$ adsorption and surface precipitation
- pH < 5 competitive adsorption with H_3O^+

Similar results were obtained with other metal ions Cu^{2+} , Ni^{2+} and Zn^{2+} .

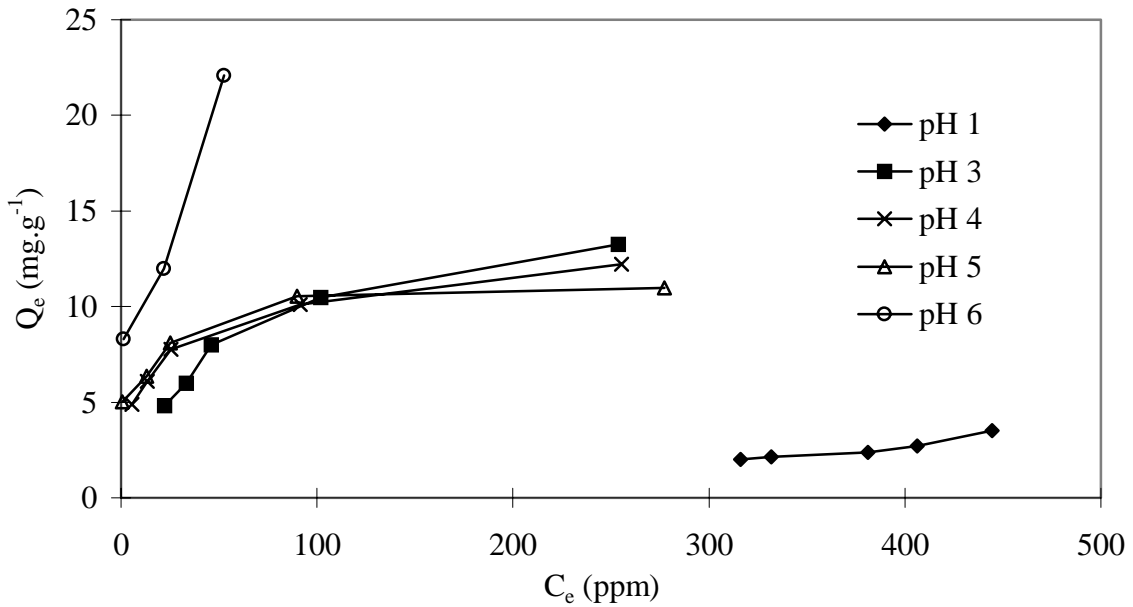


Figure 3 : Isotherm removal of Pb^{2+} as a function of constant pH in the aqueous solution

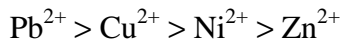
Adsorption capacity

From isotherm curves and using Langmuir classical equation, maximal adsorption capacity are calculated. Results are given in Table 2.

Table 2 : Maximal adsorption capacity for different metal cations. $pH_{initial} = 5$.

		Non-constant pH	Constant pH = 5
Nickel	Q_m (mg.g ⁻¹)	3.9	2.6
	$(C_0)_{experimental}$ (mg.L ⁻¹)	497.7	478.1
Zinc	Q_m (mg.g ⁻¹)	3.4	1.2
	$(C_0)_{experimental}$ (mg.L ⁻¹)	528.6	519.3
Lead	Q_m (mg.g ⁻¹)	18.8	9.4
	$(C_0)_{experimental}$ (mg.L ⁻¹)	482.6	508.5
Copper	Q_m (mg.g ⁻¹)	7.5	2.2
	$(C_0)_{experimental}$ (mg.L ⁻¹)	500	500

Removal of the different metallic ions can be ranked from the results at non-constant pH. The following order was either established by comparison of percentage removal at a given fly ash concentration or using maximum removal capacity (Table 2) :



This order remains valid considering any fly ash concentration from 10 to 100 g.L⁻¹. Similar classification were already observed with fly ash or soils^{12, 20}, but often removal capacity observed are stronger for zinc than for nickel. The hypothesis was made that adsorption affinities of metallic ions could correspond to the order of the first hydrolysis products^{12, 20}. But, this assumption does not fit with the order observed above, and data already published indicate that metallic ions could be adsorbed in their free form^{17,18,20}.

CONCLUSION

The results obtained in this study indicate the importance of pH control. The alkalizing ability of fly ash not only leads to higher removal capacities for Cu²⁺, Ni²⁺, Zn²⁺ and Pb²⁺. For experiments at non-constant pH, nickel and zinc are sorbed (adsorption and surface precipitation) under their free ionic form. On the contrary, copper and lead are sorbed under hydroxide species. For experiments at constant pH, nickel, zinc, lead and cadmium are sorbed under their free ionic form, whereas copper and chromium may be sorbed in their hydroxide species, with respect to pH and hydrolysis products. Bulk solution precipitation occurs for all the metallic ions at pH 10. The affinity of metallic ions for fly ash at non constant and constant pH is : Pb²⁺ > Cu²⁺ > Ni²⁺ > Zn²⁺.

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REFERENCES

- 1 Weng C.H., Huang C.P. Treatment of metal industrial wastewater by fly ash and cement fixation. *J. Environ. Eng.*, **120**, 1470-1487, 1994.
- 2 Jansson-Charrier M., Guibal E., Roussy J., Surjous R., Le Cloirec P. Dynamic removal of uranium by chitosan : influence of operating parameters. *Wat. Sci. Tech.*, **34**, 169-177, 1996.
- 3 Desauziers V., Castre N., Le Cloirec P. Sorption of methylmercury by clays and mineral oxides. *Env. Technol.*, **18**, 1009-1018, 1997.
- 4 Bosinco S., Roussy J., Guibal E., Le Cloirec P. Interactions mechanisms between hexavalent chromium and corncob. *Env. Technol.*, **17**, 55-62, 1996.
- 5 Banerjee K., Cheremisinoff P.N., Cheng S.L. Sorption of organic contaminants by fly ash in a single solute system. *Environ. Sci. Technol.*, **29**, 2243-2251, 1995.
- 6 Vandenbusch M.B., Sell N.J. Fly ash as a sorbent for the removal of biologically resistant organic matter. *Res. Conserv. Recycl.*, **6**, 95-116, 1992.
- 7 Beeghly J.H. Roller compacted base course construction using lime stabilized fly ash and flue gas desulfurization sludge by-product. *Proc., American Chemical Society, Division of fuel chemistry*, **41**, New Orleans, 1996.

- 8 Roy W.R., Thiery R.G., Schuller R.M., Suloway J.J. Coal fly ash : a review of the literature and proposed classification system with emphasis on environmental impacts. *Environ. Geol. Notes*, **96**, 1981.
- 9 Gangoli N., Markey D.C., Thodos G. Removal of heavy metal ions from aqueous solutions with fly ash. *Proc. of the Natl. Conf. on Complete Watereuse (2nd)*, Publ. by A.I.Ch.E, New York, NY, p.270, 1975.
- 10 Panday K.K., Gur Prasad, Singh V.N. Copper (II) removal from aqueous solutions by fly ash. *Wat. Res.*, **19**, 869-873, 1985.
- 11 Dasmahapatra G.P., Pal T.K., Bhadra A.K., Bhattacharya B. Studies on separation characteristics of hexavalent chromium from aqueous solution by fly ash. *Sep. Sci. Technol.*, **31**, 2001-2009, 1996.
- 12 Dimitrova S.V. Metal sorption on blast-furnace slag. *Wat. Res.*, **30**, 228-232, 1996.
- 13 Ricou P., Lecuyer I., Le Cloirec P., Influence of pH on removal of heavy metallic cations by fly ash in aqueous solution, *Env. Technol.*, **19**, 10, 1005-1016, 1998.
- 14 Van Der Hoek E.E., Comans R.N.J. Modeling arsenic and selenium leaching from acidic fly ash by sorption on iron (hydr)oxide in the fly ash matrix. *Environ. Sci. Technol.*, **30**, 517-523, 1996.
- 15 Albanis T.A., Danis T.G., Kourgia M.G. Adsorption-Desorption studies of selected chlorophenols and herbicides and metal release in soil mixtures with fly ash. *Environ. Technol.*, **19**, 25-34, 1998.
- 16 Hammermeister H.A., Naeth M.A., Chanasyk D.S. Implications of fly ash application to soil for plant growth and feed quality. *Environ. Technol.*, **19**, 143-152, 1998.
- 17 Stumm W. *Chemistry of the Solid-Water Interface - Processes at the Mineral-Water and Particle-Water Interface in Natural Systems*. John Wiley & Sons, Inc., 428 p., 1992.
- 18 Sigg L., Stumm W., Behra P. *Chimie des Milieux Aquatiques - Chimie des eaux naturelles et des interfaces dans l'environnement*. Masson, 2^e éd., 391 p., 1994.
- 19 Pourbaix M. *Atlas d'équilibres électrochimiques*. Gauthier-Villars, 644 p., 1963.
- 20 Elliott H.A., Liberati M.R., Huang C.P. Competitive adsorption of heavy metals by soils. *J. Environ. Qual.*, **15**, 214-219, 1986.
- 21 Ricou P., Lecuyer I., Le Cloirec P., Removal of Cu²⁺, Zn²⁺ and Pb²⁺ by adsorption on fly ash and fly ash/lime mixing, *Wat. Sci. Technol.*, **39**, 10, 239-247, 1999.