

# Removal of Cu<sup>2+</sup> and Zn<sup>2+</sup> in Aqueous Solutions by Sorption onto Fly Ash and Fly Ash Mixtures

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## ABSTRACT

Several studies have pointed out ash efficiency in the removal of heavy metal ions present in aqueous solutions. Contact time, pH and ash origin seem to be the major operating parameters in the metal concentration control. The mechanisms of interactions between metal and solid are a function of pH and are found to be precipitation, adsorption or ion exchange as discussed in previous papers. The objectives of this work were to study the removal of Cu<sup>2+</sup> and Zn<sup>2+</sup> in water by sorption onto fly ash and fly ash mixtures. The stability of the resulting cake was also approached in term of leaching capability. Experimental design methodology was used in order to identify influential parameters and to evaluate their interactions. Temperature, fly ash to ion concentration ratio, and ash quality were particularly studied. Different ashes and a mixture were investigated. Fly ash and fly ashes mixture investigated in this study, have alkaline reaction in water, especially one of them, and allow to control the pH of the solution without lime addition. Final metal ion concentration in solution, sorption capacity and ion leaching were determined. The results are discussed in order to get the optimal operating parameters in terms of ion control and industrial developments to remove and stabilize heavy metal ions present in wastewater.

## INTRODUCTION

Because of the widespread pollution of water and soil by industrial activities, water treatments have been the subject of numerous investigations. Elsewhere control and reduction of waste volume in landfills are being taken into account. As a matter of fact, fly ash is considered as a waste. Nevertheless, so far fly ash has been the more often used as an additive in cement industry<sup>1</sup> due to the pozzolanic and cementitious properties<sup>2,3</sup>. Moreover, fly ash is an efficient adsorbent for water treatment concerning removal of DOC (Dissolved Organic Carbon)<sup>4,5</sup> and suspended solids<sup>6,7</sup>. Several studies have also pointed out its efficiency in the removal of heavy metallic ions in aqueous phase<sup>8-11</sup>. Coal fly ash is a cheap adsorbent since they are widely available. Their alkaline property makes them interesting for use in water treatment for the precipitation of metallic ions, by analogy with lime treatment, as it was already shown<sup>8</sup>. The aim of this study was to assess the influence of three parameters on the removal of Cu<sup>2+</sup> and Zn<sup>2+</sup>: temperature, metal ion/adsorbent ratio and ash quality. Two fly ashes and a mixture of them were investigated. The pH of the solution was controlled without lime addition. Experimental design

methodology was used to identify influential parameters and to assess their interactions. The stability of the resulting cake was also approached in term of leaching capability.

## MATERIAL AND METHODS

### Adsorbent

Coal fly ash used in these experiments result from different pulverised-coal power plants in France. The fly ashes were used without pre-treatment. Table 1 shows the chemical composition of the fly ashes.

Table 1. Chemical composition of three different fly ashes (% by weight)

Constituent	A fly ash	B fly ash	C Fly ash
Lime	16.7 %	0.6 %	0.1 %
CaO	23.6 %	6.8 %	2 %
SiO <sub>2</sub>	16.2 %	48 %	52.3 %
Al <sub>2</sub> O <sub>3</sub>	7.2 %	22.8 %	36.4 %
Fe <sub>2</sub> O <sub>3</sub>	5.5 %	9.6 %	4.2 %
Unburned particles	1.2 %	9.6 %	2.7 %

The mixture has been prepared with the A fly ash and C fly ash in ratio providing a final lime composition of 5%. In this case, fly ashes were mixed in water, and then dried at 105°C.

### Adsorption experiments

Experiments were carried out in 1 L glass flashes tightly closed at two temperatures, 30°C and 60°C, introducing sorbent in 0.5 L of ZnCl<sub>2</sub> or CuCl<sub>2</sub> ion solution (500 mg.L<sup>-1</sup> of Zn<sup>2+</sup> or Cu<sup>2+</sup>). The pH was set at the desired value with HCl 36% and 1M and NaOH 1M. The pH was maintained at 5 ± 0.5. For each experiment, control and regulation of pH were made every day. The salinity of the solution was adjusted to 5 g.L<sup>-1</sup> with NaCl. Solutions were stirred continuously. 7 days were necessary to reach equilibrium conditions of experiments. Every day, samples were filtered through 0.45 µm membrane, and metallic ion concentrations were determined by a flame atomic absorption spectrometer (Perkin Elmer model 2280).

### Leaching experiments

Leaching experiments were carried out on contaminated sorbents after a drying period of one week, using a procedure derived from French standard<sup>15</sup>. A liquid / solid mass ratio of 10 (5 g of solid for 50 mL of solution) was observed and solutions were stirred for 24 hours at 150 rpm in a rotating movement. Three leaching solutions were used, either characterized by their resistivity (permuted water with a resistivity at least equal to 0.2 MΩ.cm) or their pH (pH 2, pH 4.6) set by adding HCl 1 M, NaOH 1 M and acetic / acetate buffer solution.

## RESULTS AND DISCUSSION

### Factorial design for adsorption experiments

The influence of the parameters, temperature, metal/adsorbent ratio and fly ash composition, on the removal of ions onto fly ash, were studied through a screening design<sup>16</sup>.

The adsorption experimental conditions are presented in table 2, as well as the parameters and their two levels (-1; +1).

Table 2. Screening design for adsorption experiments

Exp.	Temperature (°C)	Metal/adsorbent mass ratio
# 1	30	0.005
# 2	60	0.005
# 3	30	0.01
# 4	60	0.01
Level -1	30	0.005
Level +1	60	0.01

The results were interpreted by computation of the parameter weights. The influence of the parameters on adsorption is screened on table 3. The information reported is the importance of the factor (weight) and the eventual interaction between the factors. Responses considered for the adsorption are the equilibrium concentration  $C_e$  and the equilibrium adsorption capacity  $Q_e$  accounting the initial concentration and the adsorbent mass involved.

Table 3. Experimental results given in  $\text{mg.L}^{-1}$  for adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ; A : average, T : temperature, R : metal/adsorbent ratio, T.R : interaction between the two factor

	A fly ash		A/C fly ash		B fly ash	
Copper						
Parameter	$C_e$ ( $\text{mg.L}^{-1}$ )	$Q_e$ ( $\text{mg.g}^{-1}$ )	$C_e$ ( $\text{mg.L}^{-1}$ )	$Q_e$ ( $\text{mg.g}^{-1}$ )	$C_e$ ( $\text{mg.L}^{-1}$ )	$Q_e$ ( $\text{mg.g}^{-1}$ )
A	71	6	76,2	5,8	88,1	5,7
T	-25,5	0,4	-31,6	0,5	-53,9	0,9
R	16,5	1,6	17,2	1,7	26,4	1,6
T.R	-15,8	0,4	-5,9	0,2	-18,0	0,5
Zinc						
Parameter	$C_e$ ( $\text{mg.L}^{-1}$ )	$Q_e$ ( $\text{mg.g}^{-1}$ )	$C_e$ ( $\text{mg.L}^{-1}$ )	$Q_e$ ( $\text{mg.g}^{-1}$ )	$C_e$ ( $\text{mg.L}^{-1}$ )	$Q_e$ ( $\text{mg.g}^{-1}$ )
A	338,9	1,6	317,4	1,9	293,7	2,2
T	-32,26	0,4	-60,9	0,8	-91,4	1,4
R	39,99	-0,1	34,7	0,2	59,3	-0,1
T.R	-1,61	0,1	11,0	0,1	31,2	0

Table 4. Experimental results given in percentage for adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ; A : average, T : temperature, R : metal/adsorbent ratio, T.R : interaction between the two factor

	A fly ash		A/C fly ash		B fly ash	
Copper						
Parameter	$C_e$	$Q_e$	$C_e$	$Q_e$	$C_e$	$Q_e$
A	55,1%	71,4%	58,2%	70,7%	47,3%	65,5%
T	<b>19,8%</b>	4,8%	<b>24,1%</b>	6,1%	<b>28,9%</b>	10,3%
R	12,8%	<b>19%</b>	13,1%	<b>20,7%</b>	14,2%	<b>18,4%</b>
T.R	12,3%	4,8%	4,5%	2,4%	9,6%	5,8%

Parameter	Zinc					
	C <sub>e</sub>	Q <sub>e</sub>	C <sub>e</sub>	Q <sub>e</sub>	C <sub>e</sub>	Q <sub>e</sub>
A	82,1%	72,8%	74,8%	63,3%	61,7%	59,5%
T	7,8%	<b>18,2%</b>	<b>14,4%</b>	<b>26,7%</b>	<b>19,2%</b>	<b>37,8%</b>
R	<b>9,7%</b>	4,5%	8,2%	6,7%	12,5%	2,7%
T.R	0,4%	4,5%	2,6%	3,3%	6,6%	0%

According to these results, globally the greatest removal is achieved for copper. In term of C<sub>e</sub> results, adsorption is optimized with an increasing temperature. Temperature is the most influential parameter for adsorption of Cu<sup>2+</sup> and Zn<sup>2+</sup>. In term of Q<sub>e</sub>, addition of fly ash decreased the adsorption capacity. The ratio parameter has a lowest influence on zinc removal. Zinc is less adsorbed than copper and an addition of fly ash would change the equilibrium less efficiently. The quality of fly ash has a low influence on zinc removal. However, differences are shown between fly ashes. A fly ash (high lime composition) is the most efficient for the removal of copper. The fly ash mixture is slightly more efficient than B fly ash.

### Leaching experiments

The solutions used for leaching tests had either a pH of 4.6 and 7, or a strong resistivity. The results obtained are reported in the tables 4, 5 and 6. The responses considered for the leaching tests, are the leached concentration of Cu<sup>2+</sup> and Zn<sup>2+</sup> ions (C<sub>leached</sub>) and the leached percentage (P<sub>leached</sub>).

Table 5 : Leachability of Cu<sup>2+</sup> and Zn<sup>2+</sup> for B fly ash

		final	[Cu <sup>2+</sup> ] <sub>leached</sub>	P <sub>leached</sub> %	final	[Zn <sup>2+</sup> ] <sub>leached</sub>	P <sub>leached</sub> %
		pH	(mg.L <sup>-1</sup> )	[Cu <sup>2+</sup> ]	pH	(mg.L <sup>-1</sup> )	[Zn <sup>2+</sup> ]
# 1	Acetate buffer	4,8	288,2	77,3	4,6	74,6	76,1
	pH 2	4,8	170,5	45,7	4,2	61,0	62,2
	Permuted water	7,9	0,1	0	7,2	2,1	2,1
# 2	Acetate buffer	4,8	288,9	64,6	4,7	223,5	59,4
	pH 2	4,6	150,3	33,6	4,6	124,8	33,2
	Permuted water	7,3	0,2	0	7,3	1,6	0,4
# 3	Acetate buffer	4,7	236,4	80,1	4,6	42,3	124,4
	pH 2	4,5	165,4	56,1	4,0	37,1	109,1
	Permuted water	6,9	0,1	0	6,5	5,4	15,9
# 4	Acetate buffer	4,7	319,6	74,7	4,6	124,1	70,9
	pH 2	4,7	139,7	32,6	4,4	93,4	53,4
	Permuted water	6,8	0,2	0	6,8	6,4	3,6

Table 6 : Leachability of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  for A/C fly ash mixture

		pH final	$[\text{Cu}^{2+}]$ leached ( $\text{mg.L}^{-1}$ )	$P_{\text{leached}} \%$ [ $\text{Cu}^{2+}$ ]	final pH	$[\text{Zn}^{2+}]$ leached ( $\text{mg.L}^{-1}$ )	$P_{\text{leached}} \%$ [ $\text{Zn}^{2+}$ ]
# 1	Acetate buffer	4,7	381,8	99,2	4,7	88,3	94,9
	pH 2	5,1	89,7	23,3	5,3	62,2	66,9
	Permuted water	6,3	1,0	0,25	6,2	14,8	15,9
# 2	Acetate buffer	4,3	379,4	87	4,6	196,3	81,4
	pH 2	4,9	72,1	16,5	5,3	79,9	33,1
	Permuted water	6,5	0,2	0	6,6	9,4	3,9
# 3	Acetate buffer	4,7	354,6	104	4,6	53,9	98
	pH 2	5,0	75,7	22,2	5,0	35,6	64,7
	Permuted water	6,2	1,1	0,3	5,9	10,9	19,8
# 4	Acetate buffer	4,5	418,8	101	4,7	138,2	93,4
	pH 2	5,0	56,5	13,7	5,5	56,3	38
	Permuted water	6,8	0,15	0	6,7	7,7	5,2

The leaching test for the A fly ash has been realized on a metallic ions solution issued from an industrial effluent. In this case, pH has not been controlled during the adsorption phase. Metal ions were entirely removed by fly ash during adsorption. The leaching experiments are summarised in table 6.

Table 7 : Leachability of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  for A fly ash

		pH final	$[\text{Cu}^{2+}]$ leached ( $\text{mg.L}^{-1}$ )	$P_{\text{leached}} \%$ [ $\text{Cu}^{2+}$ ]	final pH	$[\text{Zn}^{2+}]$ leached ( $\text{mg.L}^{-1}$ )	$P_{\text{leached}} \%$ [ $\text{Zn}^{2+}$ ]
# 1	Acetate buffer	5,2	5,8	62,4	5,2	119,9	56,8
	pH 2	12,3	0,1	1,1	12,3	0	0
	Permuted water	12,4	0,1	1,1	12,4	0	0
# 2	Acetate buffer	5,0	4,7	50,5	5,0	83,2	39,4
	pH 2	11,9	0,1	1,1	11,9	0	0
	Permuted water	12,3	0,1	1,1	12,3	0,1	0
# 3	Acetate buffer	5,2	24,3	66,4	5,2	503,0	55,1
	pH 2	12,4	0,1	0,3	12,4	1,2	0,1
	Permuted water	12,5	0,1	0,3	12,5	1,5	0,2
# 4	Acetate buffer	5,1	19,9	54,4	5,1	404,2	44,3
	pH 2	12,2	0,2	0,5	12,2	0,8	0,1
	Permuted water	12,5	0,2	0,5	12,5	0,7	0,1

According to the leaching experiments, pH is a major parameter. The leached percentage decreases as soon as pH exceeds a value around 5. Precipitation as well as adsorption is then supposed to occur between metal and solid.

## CONCLUSION

The results obtained for adsorption of copper, and zinc ions onto fly ash show an increasing removal capacity with increasing temperature. Considering the isotherms  $Q_e$  versus  $C_e$ , three mechanisms, competition, adsorption, and precipitation, are observed. Removal efficiency of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  is a function of fly ash quality, lime and silica composition. The effect of lime addition by mixing fly ash provides an equilibrium between the influence of lime on adsorption and the pH value on precipitation. In the case of fly ashes mixture, the stability of cake in term of leaching capability is obtained with permuted water leaching solution. Nevertheless, other formulations of the fly ashes mixture are needed to be realized in order to increase the removal of metal ions from industrial effluent and stability the resulting cakes.

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