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Removal of Cadmium and Nickel From Aqueous Solution by Adsorption Onto Treated Fly Ash From Thailand

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Abstract

Feasibility studies of using treated fly ash in the removal of cadmium and nickel from aqueous solutions were performed. Batch adsorption determinations were used to investigate the adsorption efficiency of treated fly ash for the removal of cadmium and nickel. Concentrations of cadmium and nickel varied in the range of 1-10 mg l^{-1} and 10-40 mg l^{-1}, respectively. The adsorption efficiency was found to increase with increasing treated fly ash concentration. At treated fly ash concentrations above 1.25 g l^{-1} the removal was almost instantaneous. Adsorption equilibration was usually attained within 30 min at a pH of 3-5. Results suggest that the kinetics follow a monolayer adsorption according to Langmuir. Interference of anions in the removal of cadmium and nickel was not significant. Interference by cations such as lead reduced the adsorption efficiency for cadmium and nickel. Leaching experiments of adsorbed cadmium and nickel show that the concentration in the resulting leachate do not exceed limit concentrations of the Thai Wastewater Effluent Standard.

Keywords : adsorption, cadmium, desorption, fly ash, heavy metals, Langmuir isotherm, nickel

1. Introduction

Heavy metals in wastewater are mainly from industrial sources [1]. Nickel is an important metal in many industries such as electroplating, nickel-base alloys and nickel-cadmium battery manufacture. In the blood circulation, it is transported bound to albumin. It is then distributed to the kidney and further into other tissues. Cadmium is used in electroplating and in the manufacturing of alloys, pigments, plastic stabilizers and automotive tires. Cadmium causes an acute and chronic disorder which is called, itai-itai disease. Half of the cadmium is stored in the liver and kidney [2].

Many conventional techniques such as precipitation, electrolysis and ion exchange are used for the removal of heavy metals in wastewater treatment, but they are suitable for high concentrations of metals. At low concentrations, these techniques fail in certain cases. Also they are not cost-effective. For this reason, low cost adsorbents have been evaluated for the removal of heavy metals from aqueous solutions. Examples for such low-cost adsorbents are clay [3], cotton [4], wool fiber [5], activated carbon [6], tea leaves [7], agricultural waste [8], [9] and cellulose [4]. Previous work has shown that the cation exchange capacity of treated fly ash is higher than untreated fly ash and that treated fly ash is effective for the removal of lead [10]. Therefore, in the present work, treated fly ash was used as an adsorbent to improve the removal of cadmium and nickel. In the study, the dependent parameters such as amount of treated fly ash, time, pH, concentration of heavy metals, anions and cations interference on removal and desorption of adsorbed heavy metals were investigated.

2. Materials and Methods

Fly ash was obtained from Mae Moh electric power plant in the north of Thailand. Only the fraction of fly ash, with a particle size smaller than 63 μm was used. The fly ash was refluxed with 1.0 M NaOH solution at a ratio of 1:8 for 24 hr. It was then cooled down to room temperature, separated from the basic solution by centrifugation, decantation and washed four times with deionized water. After the washing process the sample was dried at 60 °C for 48 hr and analysed for the constituents by an X-ray fluorescence spectrophotometer (Fison model ARL 8410, Switzerland).

Batch adsorption experiments were carried out by shaking various amounts of treated fly ash (0.5 –10.0 g l^{-1}) with 50 ml of aqueous solution of cadmium nitrate and nickel nitrate with initial concentrations of 1-10 mg l^{-1} and 10-40 mg l^{-1}, respectively at a constant speed of 100 rpm and various times at 25 °C. The pH of the solution was adjusted between 2-5 with the help of NaOH or HNO_3. The pH was controlled with a pH meter (Metrohm model 713, Switzerland). The sample solutions were shaken at 100 rpm with a shaker (Heto model Hetofrig CB60VS, Germany) and then centrifuged. After decantation, the solutions were filtered through a 0.45 μm membrane filter, and collected in polyethylene bottles. The concentration of cadmium and nickel in each sample was determined spectrophotometrically by an atomic absorption spectrophotometer (Shimadzu model AA-680, Japan). Chemicals used to investigate the effect of anions on adsorption of cadmium and nickel to treated fly ash were NaF, NaCl, $NaNO_3$, Na_2SO_4 and Na_3PO_4; lead nitrate was used in a binary system. Leaching experiments of cadmium and nickel were carried out by shaking 0.1 g l^{-1} of preadsorbed fly ash with acid at a pH of 5.8 - 6.3 for 6 hr. Each experiment was conducted in triplicate.

After investigation of the adsorption efficiency of treated fly ash under laboratory conditions, the method was tested with real industrial wastewater samples. Industrial wastewater from two metal plating factories were used in these studies.

All chemicals were analytical reagent grade purchased from Carlo ERBA, Italy.

3. Results and Discussion

The composition of treated fly ash was 38.12 % SiO_2, 23.08 % Al_2O_3, 13.92 % CaO 2.09 % MgO and 8.72 % Fe_2O_3.

3.1 Effect of amount of treated fly ash

Removal of Ni(II) increased with increasing contact time for each treated fly ash con-centration (Figure 1a). The amount of Ni(II) adsorbed onto the treated fly ash increased from 29.60 to 99.73 % while the concentration of treated fly ash was increased from 0.5 to 10 g l^{-1}. At a pH of 5, similar results were observed for the removal of Cd(II), which increased from 45.65 to 99.87 % (Figure 1b). These results are in good agreement with the results obtained in the removal of Pb(II) onto the treated fly ash under similar experimental conditions i.e. 99.36 to 99.64 % [10]. The adsorption equilibrium was reached within 30 min at treated fly ash concentrations above 1.25 g l^{-1}. Almost all Ni(II) and Cd(II) was removed. At low treated fly ash concentrations, it took more than 2 hr to reach the adsorption equilibrium. Similar results have been shown in previous work [11] for Cd(II) removal onto untreated fly ash at 20 g l^{-1} with an adsorption efficiency of 84.80 to 89.82 % at a pH of 8.5.

3.2 Effect of pH

Removal of Ni(II) and Cd(II) onto treated fly ash was pH dependent (Figure 2); the smallest adsorption was found at pH 2 [6]. It then rapidly increased in the range of pH 2-3. At higher pH, adsorption of Ni(II) and Cd(II) did not increase further. The highest efficiency was 99 % at a pH of 5.

The increase in adsorption with increasing pH can be explained by the hydrolysis of heavy metals [12](eq 1-2) and the charge at an active site on the surface of the treated fly ash (eq 3-4) which allows metals (M^{+2}) to be complexed at the surface (eq 5-6).

$$M^{2+} + H_2O \rightarrow MOH^{+} + H^{+} \qquad (1)$$
$$MOH^{+} + H_2O \rightarrow M(OH)_2 + H^{-} \qquad (2)$$
$$\equiv SiOH + OH^{-} \rightarrow \equiv SiO^{-} + H_2O \qquad (3)$$
$$\equiv AlOH + OH^{-} \rightarrow \equiv AlO^{-} + H_2O \qquad (4)$$
$$2(\equiv SiO^{-}) + M^{2+} \rightarrow (\equiv Si\text{-}O)_2M \qquad (5)$$
$$2(\equiv AlO^{-}) + M^{2+} \rightarrow (\equiv Al\text{-}O)_2M \qquad (6)$$

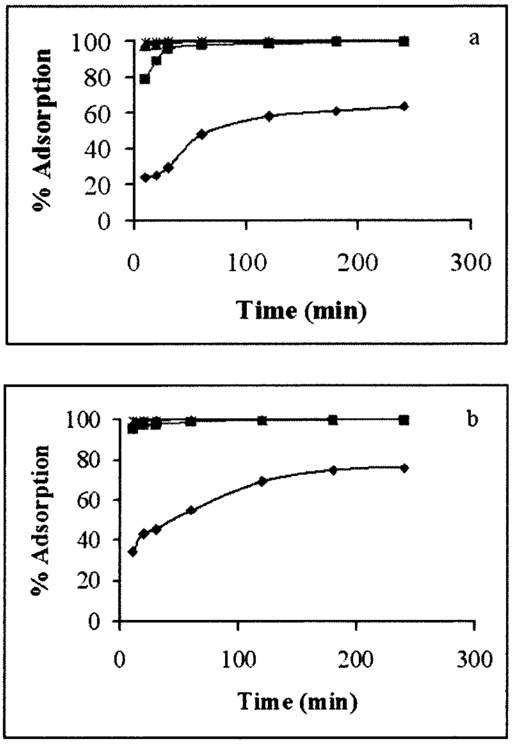

Figure 1. Effect of time and solid suspension density of treated fly ash on the adsorption (a) 40 mg l^{-1}Ni(II) and (b) 10 mg l^{-1}Cd(II) at pH 5: (◆) 0.5 g l^{-1}, (■) 1.25 g l^{-1}, (▲) 2.50 g l^{-1}, (x) 5 g l^{-1} and (∗) 10 g l^{-1} of treated fly ash.

In solutions at pH 2-5, both metals exist in their double positively charged form (Ni(II) and Cd(II)) (Figure 3). At increasing pH they are hydrolysed to their hydroxide form[13]. At a low pH (pH 2), the adsorption is very low [14], [15]. This effect is caused by a positive charge at the surface of the treated fly ash (eq 7) that leads to a repulsion between the surface charge and metal ion [16-19].

$$\equiv SiOH + H^+ \rightarrow \equiv SiOH_2^+ \qquad (7)$$

3.3 Effect of concentration of heavy metals and contact time

Removal of Ni(II) and Cd(II) from aqueous solutions was very rapid at pH 5 (Figure 4). For all studied concentrations in the range of 10 – 40 mg l^{-1} for Ni(II) and 1 - 10 mg l^{-1} for Cd(II), an efficiency of more than 96 % was reached within 10 min compared with untreated fly ash [16]. The adsorption equilibrium of treated fly ash was reached within a very short time (30 min). The percentage of removal depends on the concentration of heavy metals with the highest efficiency of 99 % for both Ni(II) and Cd(II).

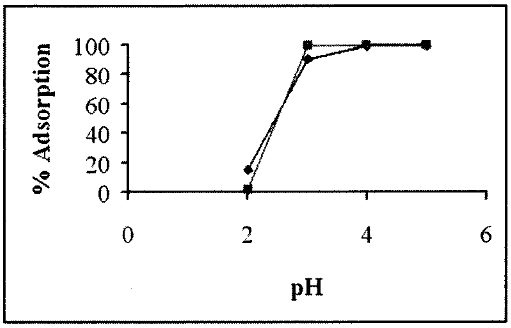

Figure 2. Effect of pH on the removal of heavy metals from aqueous solution at treated fly ash of 1.25 g l^{-1} for 30 min: (◆) 40 mg l^{-1} Ni(II) and (■) 10 mg l^{-1} Cd(II).

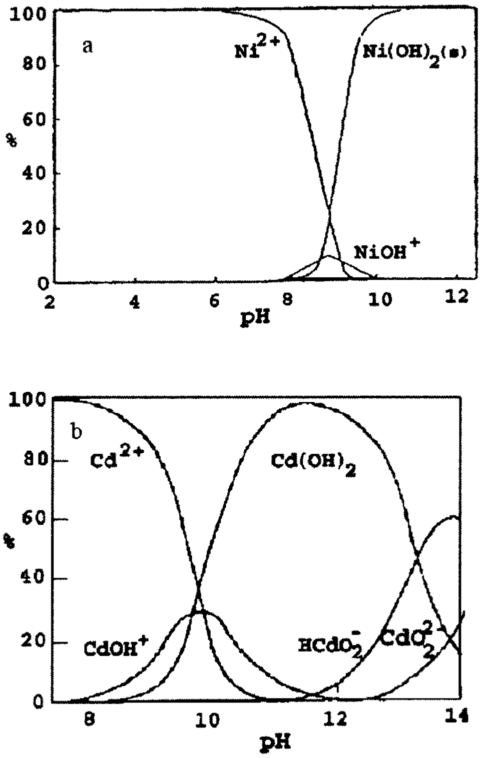

Figure 3. Hydrolysis of (a) Ni(II) and (b) Cd(II)[13].

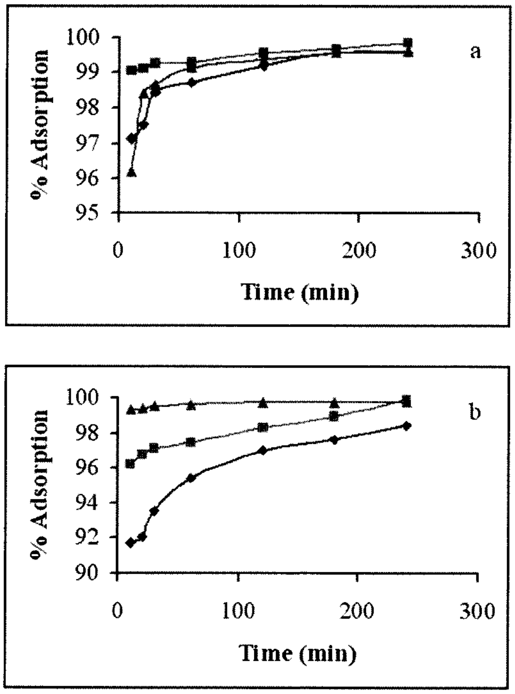

Figure 4. Effect of concentration of metal ions and time at 1.25 g l^{-1} of treated fly ash and pH 5: (a) (◆) 10 mg l^{-1}, (■) 20 mg l^{-1} and (▲) 40 mg l^{-1} Ni(II) and (b) (◆) 1 mg l^{-1}, (■) 5 mg l^{-1} and (▲) 10 mg l^{-1} Cd(II).

3.4 Effect of concentration of heavy metals and pH

The adsorption of both heavy metals onto the treated fly ash increased with increasing pH, i.e., to lower than 15 % at a pH of 2 and higher than 95 % at a pH of 5 (Figure 5). The effect of the metal concentrations on the adsorption efficiency is only marginal with the exception of the 1 mg l^{-1} Cd solution which showed a slightly lower adsorption.

3.5 Adsorption isotherm

The uptake of 40 mg l^{-1} Ni(II) and 10 mg l^{-1} Cd(II) by treated fly ash at 25 °C is correlated following the Langmuir adsorption isotherm and can be expressed as (eq 8):

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

where C_e is the equilibrium adsorption (mg l^{-1}) of metals, X is the amount (mg g^{-1}) of metal adsorbed, X_m and b are the adsorption capacity and energy of adsorption, respectively. The linear regression of C_e/X vs C_e (Figure 6) for Ni(II) and Cd(II) show a good correlation (r^2) (Table 1). The resulting values for X_m and b are given in Table 1.

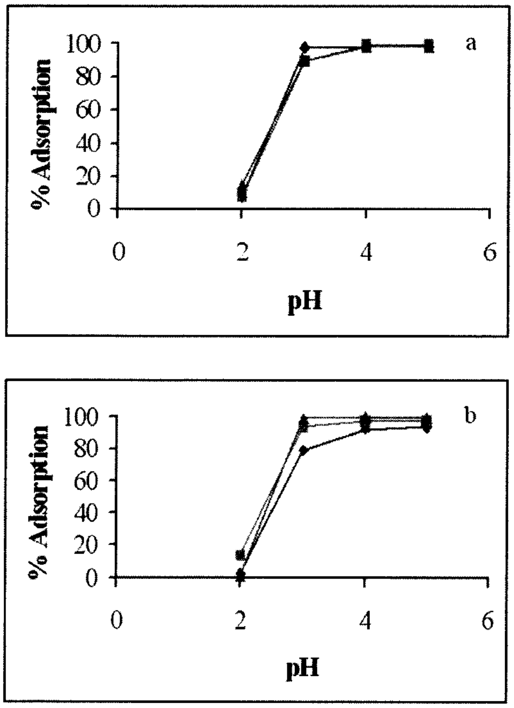

Figure 5. Effect of concentration of metal ions and pH on adsorption at 1.25 g l^{-1} of treated fly ash for 30 min: (a) (◆) 10 mg l^{-1}, (■) 20 mg l^{-1} and (▲) 40 mg l^{-1} Ni(II) and (b) (◆) 1 mg l^{-1}, (■) 5 mg l^{-1} and (▲) 10 mg l^{-1} Cd(II).

Table 1. Langmuir constants at 25 °C

	X_m (mg g^{-1})	b (l mg^{-1})	r^2
Ni	55.55	0.704	0.9996
Cd	14.33	0.585	0.9965

The good correlation confirms the formation of a monolayer of Ni(II) and Cd(II) on the surface of the treated fly ash. Similar results were reported in the adsorption of other metal ions on fly ash [15-16], [21].

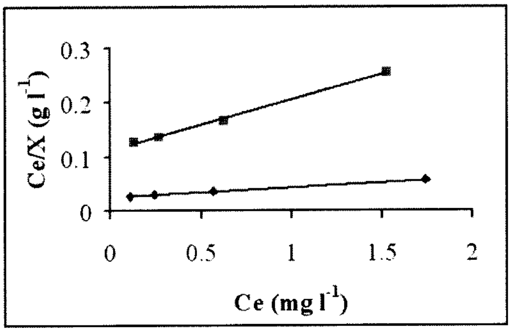

Figure 6. Linear plot of C_e/X vs C_e for (◆) Ni(II) and (■) Cd(II).

3.6 Effect of interfering cations on adsorption

With the introduction of other cations such as Pb(II) (0-30 mg l^{-1}) and Cd(II) (0-10 mg l^{-1}) into the system, the adsorption efficiency for Ni(II)(40 mg l^{-1}) should be reduced due to competition of the different cations for active positions on the surface. In the experiment, only an insignificant reduction in the adsorption efficiency for Ni(II) (40 mg l^{-1})i.e., 2 % for Pb(II) and below 1 % for Cd(II) was recorded. Also for Cd(II)(10 mg l^{-1}) the effect of competing cations, (Pb(II)(0-30 mg l^{-1}) and Ni(II) (0-30 mg l^{-1}), is below 1% (Figure 7).

3.7 Effect of anions on adsorption

Figure 8 shows the effect of anions such as F^-, Cl^-, NO_3^- , SO_4^{2-} and PO_4^{3-} on the adsorption efficiency of Ni(II) and Cd(II) with treated fly ash. While for F^-, Cl^-, NO_3^- and $SO_4^{2-}$the effect on the adsorption efficiency for Ni(II) and Cd(II) can be neglected (<2%), adding PO_4^{3-} to the solution results in a drop in efficiency of approximately 20 % for Ni(II), due to precipitation, and 2 % for Cd(II) when the PO_4^{3-} concentration is increased from 0 to 80 mg l^{-1}.

3.8 Leaching of heavy metals from preadsorbed fly ash

The leaching experiments for adsorbed Ni(II) and Cd(II) from the treated fly ash were carried out with an aqueous solution at a pH of 5.8 - 6.3, a concentration of treated fly ash of 0.1 g l^{-1} and a temperature of 25 °C. The results are shown in Figures 9. It was found that for the adsorbed Ni(II), between 6 % and 2 % leached into the solvent with the amount of leached Ni(II) decreasing with the original Ni(II)-concentration. At an original of 5 mg l^{-1}, the highest Cd(II)-concentration in the leachate was less than 1 %. Both at higher and lower original concentrations, the Cd(II) concentration in the leachate was lower (0.1 to 0.2%). The concentrations of both Ni(II) and Cd(II) in the leachate were less than 0.8 mg l^{-1} and 0.02 mg l^{-1}, respectively. These are less than the limits of concentration of the Thai Wastewater Effluent Standard [20].

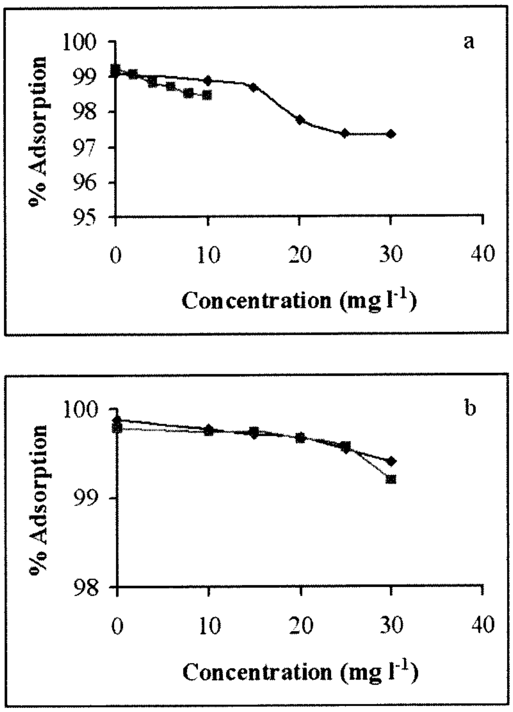

Figure 7. Effect of interfering cations on adsorption at 1.25 g l^{-1} of treated fly ash for 30 min of (a) 40 mg l^{-1} Ni(II), interfering ions: (◆) Pb(II), (■) Cd(II) and (b) 10 mg l^{-1} Cd(II), interfering ions: (◆) Pb(II), (■) Ni(II).

The result can be explained by cation exchange between hydrogen ions and adsorbed metal ions at the active site of treated fly ash. The exchangeability depends on the types of adsorbed ion and on their ionic radius. The positively double charged metal ions and the low concentration of hydrogen ion in the solution result in a stronger binding of the metals to the surface of the treated fly ash. Therefore Ni(II) and Cd(II) can only be desorbed with difficulty.

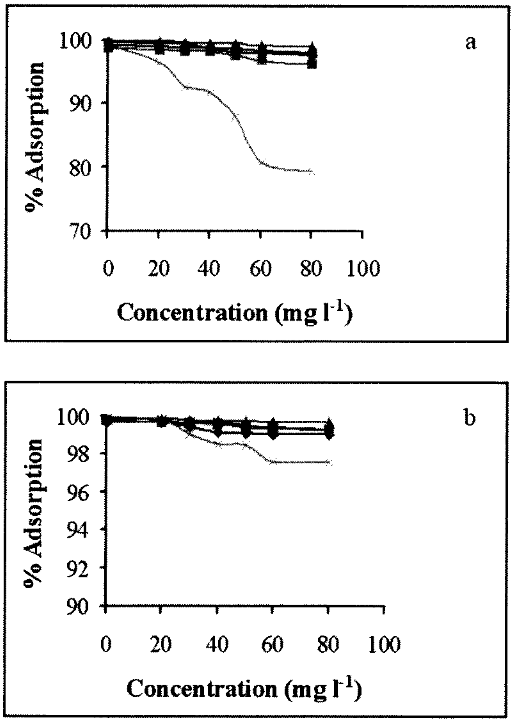

Figure 8. Effect of anions on adsorption at 1.25 g l^{-1} of treated fly ash for 30 min of (a) 40 mg l^{-1} Ni(II) and (b) 10 mg l^{-1} Cd(II), interfering anions: (■) F^-, (▲) Cl^-, (∗) NO_3^-, (◆) SO_4^{2-}, (x) PO_4^{3-}.

3.9 Removal of heavy metals from industrial wastewaters

To study the efficiency of Ni(II) and Cd(II) removal from industrial wastewaters by treated fly ash, samples of wastewater from a plating manufactory were treated with treated fly ash. Table 2 shows the removal efficiency of treated fly ash for Ni(II) was higher in sample 1 than in sample 2. In general, the removal efficiency for Ni(II) was higher for synthetic wastewater (>98 %) than for industrial wastewater (92 % and 86 %). In industrial wastewater, in contrast to synthetic wastewater, other cations are competing with Ni(II) for active sites on the treated fly ash and at the same time a large number of different anions are reacting with Ni(II). Both effects lead to the observed reduced adsorption efficiency in the industrial wastewater. Nevertheless the efficiency of Ni(II) removal from the industrial wastewater still lies between 86 % to 92 %.

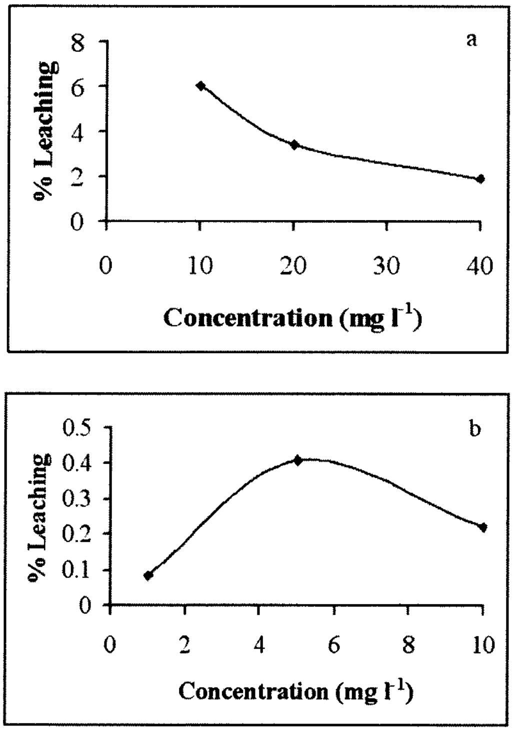

Figure 9. Leaching of (a) Ni(II) and (b) Cd(II) from 0.1 g l^{-1} of preadsorbed fly ash at pH 5 for 30 min.

Table 2. Efficiency of treated fly ash for heavy metal removal from industrial waste

Sample	Metal	Concentration (mg l^{-1})		%Removal
		Before	After	
1	Ni(II)	37.33	2.98	92.01
	Cd(II)[a]	-	-	-
	Pb(II)[a]	-	-	-
2	Ni(II)	41.53	5.63	86.45
	Cd(II)[a]	-	-	-
	Pb(II)	8.56	0.20	97.62

[a] not found

4. Conclusion

As the results presented above, the conclusions can be summarized as follows:

- Treated fly ash is a good adsorbent for both Cd(II) and Ni(II) fixation. The adsorption of Cd(II) and Ni(II) onto treated fly ash leads to a monolayer according to Langmuir. It can be used for removal of both metals from wastewater.
- Adsorption equilibrium for both metals is reached in a short time and environmental factors such as concentration of treated fly ash, concentration of heavy metal, pH, interfering anion and coexistence of different heavy metal ions will affect the adsorption efficiency of treated fly ash.
- Adsorption efficiency of treated fly ash for Ni(II) and Cd(II) increased with pH.
- Leaching of adsorbed heavy metal from treated fly ash with moderate acid solution results only in very low concentrations in the leachate.

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5. References

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