USE OF FLY ASH FOR THE REMOVAL OF NICKEL IONS FROM WASTEWATERS

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ABSTRACT

The use of Greek fly ash as a means of removal of heavy metal ions from waste waters has been investigated for the case of artificial Ni ion wastewaters. The addition of a high CaO content fly ash resulted in the raising of the pH of the solution to values where Ni precipitates as a hydroxide on the fly ash particles. These may then be removed by some solid/liquid separation method, e.g. filtration, flotation, centrifugation etc. The range of Ni content studied varied from 10 to 500 mg/l and of fly ash from 0.1 to 5 g/l. Nickel removals of nearly 100% were easily achieved in a very short time.

Keywords: Fly ash, wastewater treatment, Nickel ion, removal, sorption, adsorption.

INTRODUCTION

Small industrial plants are often located near or even inside urban areas; this results in their wastewaters, often containing toxic metals and other unwanted species, being mixed with urban wastewaters, which are then somehow treated before being discharged into the sea or a local stream or lake.

Since it is becoming accepted that these should be sufficiently stripped of all harmful matter before being discharged, a lot of work has been done to devise systems for the removal of these unwanted species from the wastewaters. The usual way of treating them with up to three cleaning stages results in a thick "toxic" sludge, which must be disposed of; this is often done by dumping it into the sea, as is the case of the UK [1] or in a landfill.

Another way of cleaning these effluents is the use of an adsorbing material. Activated carbon is one such material, widely used (see for example refs. [2-4]) but quite expensive. Work is being done to find alternative substances, which could be used as adsorbents. Peat [5], lignite [5-8], magnesium [9] and manganese solid waste [10] have been investigated as a means of stripping effluents from toxic metals and colouring matter from solutions.

Fly ash has been investigated as an adsorbent [8,11-17] for the removal of anions, cations and colouring matter; it seems that its adsorbing capabilities may be attributed mainly to its SiO₂, Al₂O₃ and CaO content. However, the percentage of these constituents varies from ash to ash [18]. A high CaO content results in a high alkalinity of the ash; this means that these ashes may be beneficial for the removal of toxic metal ions from wastewaters. This capability has already been demonstrated for lead ions [17] and chrome and manganese ions [19]. In the present work, fly ash from both these plants has been used to remove Ni ions from artificial wastewaters. An effort has also been made to study the fundamentals of the process, i.e. to investigate the mechanism responsible for the ion removal.

MATERIALS AND METHODS

The fly ash used in these experiments was obtained from the power plants of Kardia (near Ptolemais) and Megalopolis (in the Peloponnesse); they were kept in tightly closed containers. They differed mainly in their content in SiO₂ (28.7% and 38.9% for Kardia and Ptolemais ash, respectively) and CaO (44.0% and 22.3% for Kardia and Ptolemais ash, respectively), both lying in the usual ranges [18].

Stock solutions of Ni were prepared using NiSO₄ (Fluka, purum p.a.), using deionised water.
All experiments were performed in one-litre beakers, in which one litre of solution with the required Ni concentration was poured. Fly ash was added and the dispersion mixed with a mechanical agitator at 300 RPM for the required time period (10 min for all experiments, found to be sufficient in preliminary tests). Temperature for all experiments was 20±1 °C.

Samples of the dispersion were collected, fly ash was removed by filtration and the solution was analysed for Ni by AAS (Perkin Elmer 2360). The Ni removal was calculated using the formula

$$R_{Ni} = 100 \times \left(1 - \frac{C}{C_0}\right) \; [\%]$$

where $C_0$ is the initial and $C$ the final Ni concentration.

Except where stated, all experiments were performed at specified pH values; the pH was controlled by adding adequate amounts of 0.1 M or 1 M H$_2$SO$_4$.

RESULTS AND DISCUSSION

The addition of fly ash in Ni solutions resulted, as expected, in the removal of the Ni ions. The extent of this removal varied, depending upon the amount of flyash added and the pH, at which the dispersion was maintained. Figure 1 illustrates the results for 0.1, 0.5, 1 and 5 g of Kardia flyash. When the amount of added flyash is increased up to a certain quantity, this generally leads to higher removals of Ni ions from more acidic pH values. The Megalopolis fly ash gave similar results; however, because of its lower alkalinity, it required more fly ash to achieve a similar removal level (Figure 2): 10 g/l of Megalopolis fly ash were required to achieve similar results to 5 g of Kardia ash.

![Figure 1](image)

**FIGURE 1.** Effect of pH on the removal of Ni ions from a solution. Kardia fly ash, initial Ni concentration 50 ppm.

Once it was confirmed that fly ash effectively removed the Ni ions from solution, the mechanism of this process was investigated. First of all, the effect of the addition of fly ash in water was studied. Figure 3 shows that the
FIGURE 2. Comparison of the effectiveness of the Kardia vs. the Megalopolis fly ash for the removal of Ni ions.

FIGURE 3. Effect of the addition of Kardia fly ash amounts to the water pH.

equilibrium pH is reached extremely fast, in the first or so minute. The equilibrium value itself depends upon both the amount of fly ash added to the water and the species dissolved in it; when ash is added in a 50 ppm Ni solution instead of just water, the equilibrium pH reached is lowered for small amounts of fly ash added (Figure 4), due partly to consumption of initial flyash alkalinity, caused by the addition of Ni ions.

The Megalopolis fly ash had a similar effect on equilibrium pH, as seen in Figure 5, for 1 and 2 g/l of fly ash in water and Ni solution; however, the pH reached was lower than for the Kardia fly ash.

The influence of the Ni concentration was investigated next; solutions of up to 500 ppm were used with 0.5 g of Kardia fly ash (Figure 6). While pH is low (8), the removal of Ni is relatively low and is affected by the Ni
concentration, as soon as the pH of Ni(OH)₂ precipitation is reached, removal increases and from pH 9 upwards removal is almost 100% for all Ni concentrations tested.

**FIGURE 4.** Effect of the addition of Kardia fly ash amounts to the pH of a 50 ppm Ni solution.

**FIGURE 5.** Effect of the addition of Megalopolis fly ash amounts to the pH of water and of a 50 ppm Ni solution.

It is obvious, then, that there is a relation between the removal of Ni ions, the pH and the amount and type of fly ash added. The latter raises the pH of the solution above the point where Ni precipitates, therefore it is not clear whether adsorption alone or some other mechanism is co-responsible for the removal of the metal ions. In order to clarify this point, tests were performed with Ni solutions at various pH values and filtration through sintered-glass Gooch filters having different porosities, i.e. without the addition of fly ash. Figure 7 shows that above pH 7-8, Ni
is removed by filtration, since it has precipitated as Ni(OH)$_2$ particles having size smaller than 40 μm and mainly in the region 10-20 μm. Comparing then with Figure 1, it is obvious that fly ash acts not only as an adsorbent (seen in the lower pH range of 4-8), but also precipitates Ni ions, as well. Fly ash then forms aggregates with the minute Ni(OH)$_2$ particles and thus removal is achieved by a dual mechanism.

**FIGURE 6.** Effect of the initial Ni concentration on its removal, for 0.5 g Kardia fly ash.

![Ni removal vs. Ni concentration](image)

**FIGURE 7.** Influence of pH on the removal by filtration of Ni precipitate using various Gooch filters.

Concluding, experiments were performed with addition of fly ash from two Greek combustion plants, one of them highly alkaline (Kardia), to Ni solutions. Ni ions were removed by a concerted action of adsorption on the fly ash particles and aggregate formation of the ash particles with the Ni(OH)$_2$ formed because of the high alkalinity of the solution caused by the addition of fly ash.
Thus, it is possible to foresee a process of industrial effluent treating with a low-cost industrial by-product (fly ash) which has been considered also as solid waste, achieving a relatively fast and highly efficient stripping of water from undesirable toxic metals and possibly other unwanted species, too. This fly ash may then be removed by some kind of solid-liquid separation process, like flotation, filtration etc.

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REFERENCES


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