

## Copper and cadmium adsorption on pellets made from fired coal fly ash

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### Abstract

Studies on the utilization of low cost adsorbents for removal of heavy metals from wastewaters are gaining attention. Fired coal fly ash, a solid by-product that is produced in power plants worldwide in million of tonnes, has attracted researchers' interest. In this work, fly ash was shaped into pellets that have diameter in-between 3–8 mm, high relative porosity and very good mechanical strength. The pellets were used in adsorption experiments for the removal of copper and cadmium ions from aqueous solutions. The effect of agitation rate, equilibration time, pH of solution and initial metal concentration were studied. The adsorption of both cations follows pseudo-second order kinetics reaching equilibrium after an equilibration time of 72 h. The experimental results for copper and cadmium adsorption fit well to a Langmuirian type isotherm. The calculated adsorption capacities of pellets for copper and cadmium were 20.92 and 18.98 mg/g, respectively. Desorption experiments were performed in several extraction media. The results showed that both metals were desorbed substantially from pellets under acidic solutions. For this reason, metal saturated pellets were encapsulated in concrete blocks synthesized from cement and raw pulverized fly ash in order to avoid metal desorption. The heavy metals immobilization after encapsulation in concrete blocks was tested through desorption tests in several aqueous media. The results showed that after 2 months in acidic media with pH 2.88 and 4.98 neither copper nor cadmium were desorbed thus indicating excellent stabilization of heavy metals in the concrete matrix. As a conclusion, the results showed that fly ash shaped into pellets could be considered as a potential adsorbent for the removal of copper and cadmium from wastewaters. Moreover, the paper proposes an efficient and simple stabilization process of the utilized adsorbents thus guarantying their safe disposal in industrial landfills and eliminating the risk of pollution for groundwater and other natural water receivers.

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### 1. Introduction

Aqueous waste streams arising from many industrial activities such as metal plating, mining, metallurgy, tanneries, painting, etc. are normally contaminated with heavy metals. The effluents from these industrial activities contain dissolved metals such as Cu, Cd, Pb, Zn, Cr, etc. and can pose a serious risk for soil and for groundwater contamination. Heavy metals are not biodegradable and tend to accumulate in living organisms causing various diseases and disorders [1].

The treatment methods of these kind of industrial effluents include precipitation, ion exchange, adsorption and membrane

processes such as ultrafiltration and reverse osmosis. The membrane processes are normally concentration processes which produce an aqueous solution more concentrated in heavy metals that needs subsequent treatment with one of the other above mentioned alternative methods. The major disadvantage of all the above methods is that after the end of treatment a new more toxic waste, solid in most cases, is produced. The management of this new waste rich in toxic heavy metals becomes more and more difficult.

Adsorption is one of the wastewater treatment alternatives that has been widely studied for the removal of toxic compounds. A number of researchers have studied different adsorption means for removal of all kinds of pollutants. The material that has been widely used for more than 3 decades is activated carbon [2]. The high cost of activated carbon has motivated scientists into the search for new low cost adsorption means. In general, a sorbent

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can be characterized as low cost if it requires little processing, is abundant in nature or is a by-product of industrial activities. Industrial by-products are almost zero-cost materials and in the same time their utilization could contribute to the solution of their management problem improving the material efficiency within several industrial activities. Several researchers [3–5] refer to a number of potential low cost adsorbents such as, tannin rich materials, clays, zeolites, red mud, fly ash, agricultural siliceous waste, etc.

Fly ash because of its composition [6] has been widely used in construction [7–11], in manufacturing of ceramic construction products [12,13] and for geopolymers development [14,15]. In addition, fly ash has been studied as a potential adsorption material for the treatment of wastewater containing heavy metals [16–24], arsenic compounds [24,25] as well as organic compounds such as phenols and dyes [26–29] showing very good adsorption properties.

The aim of this study is: (a) the development of cost effective adsorption media from raw pulverized fly ash for the treatment of industrial effluents containing heavy metals and (b) the development of methods for the safe management of saturated adsorption media after the end of their life cycle. In order to achieve both targets the adsorptive and the hydraulic properties of fly ash were exploited. Raw pulverized fly ash was agglomerated into porous pellets which comprise the shaped adsorption media. The adsorption properties of pellets were studied in the cases of copper and cadmium sorption from synthetic aqueous solutions. The metal releasing capacities of pellets saturated in copper and cadmium were studied and the results proved the high mobilization of both metals in aqueous acidic media. In order to face effectively this problem, the stabilization of metal saturated pellets was studied through their encapsulation in different concrete blocks.

## 2. Materials and methods

### 2.1. Raw material

The raw material used for pellets development was fly ash from the Megalopolis power plant in southern Greece. Fly ash is the residue from lignite combustion recovered from cyclones and electrostatic filters of the power plant. The raw material was chemically analyzed through dissolution and determination of metal's content with atomic absorption spectrophotometry. For determination of trace elements, atomic absorption spectrophotometry with graphite furnace was applied. The mineralogical characterization was carried out through X-rays diffractometry with Cu K $\alpha$  radiation. The leachability of heavy and toxic elements from raw material was determined in deionized water with the application of the European standard test EN 12457-2:2002 as well as in CH<sub>3</sub>COOH/NaOH buffer solution (pH 2.88  $\pm$  0.05) with the application of the U.S.EPA TCLP Method 1311. The pulp pH was determined in a suspension of fly ash in deionized water at 25 °C and 2% (w/v) pulp density. The particles size distribution was determined with the low angle laser light scattering method. Finally, the specific surface of raw material was measured with the BET/N<sub>2</sub> method.

### 2.2. Pellets development procedure

#### 2.2.1. Pellets preparation

Before pellet development, raw fly ash was pulverized in an industrial mill. The pulverized material had a mean particle size of 13  $\mu$ m while the whole material was passed through a 90  $\mu$ m sieve. Pulverized fly ash was mixed with water without the addition of any binder and was shaped into pellets in a laboratory scale pelletizing machine [30]. The rotation speed of the drum was kept constant at 24 rpm and the drum angle was varying with 2.5° intervals between 37.5° and 47.5°. At any angle pellets were prepared at low and high fly ash/water ratio (*R*) which normally was varying in-between 2.30 and 3.70 g/mL. After preparation, the green pellets had to be cured for a period of 15 days closed in plastic bags under constant temperature (20 °C) and high relative humidity (>90%), in order for the hydraulic bond to be developed.

#### 2.2.2. Pellets characterization

The cured pellets were characterized with three tests in order to determine the best pellets' preparation conditions. These tests were sieving for the estimation of the pellets' diameter, 2 h self-milling in a rotary mill for checking the abrasion resistance and measurement of relative porosity with Archimedes method in order to evaluate the available surface of the pellet/solution interface. Pellets were mineralogically characterized with X-ray diffraction. The particles size distribution, the specific surface area and the pulp pH were determined with the methods described in Section 2.1. Finally, the average pore diameter was measured with the BJH method [31].

### 2.3. Adsorption experiments

In order to determine the adsorption properties of fly ash pellets, adsorption experiments of copper and cadmium ions from synthetic aqueous solutions were performed. The experiments were taken place in a glass reactor with a useful volume of 500 mL under mechanical stirring and constant temperature of 25 °C. The solutions were prepared by dissolution of the appropriate amount of copper or cadmium sulfate salts in deionized water. The amount of added pellets was kept constant at 5 g/L. Samples were withdrawn from solution at predetermined time intervals and were analyzed for their metal content by atomic absorption spectrophotometry. Four experimental series were performed.

#### 2.3.1. Influence of stirring rate

In order to estimate the effect of stirring rate on the metal removal efficiency, experiments took place under various stirring rates ranging from 60 to 230 rpm. Higher rate destroyed the pellets due to their attrition with the metal propeller. Adsorption experiments had duration of 24 h and were carried out under initial copper concentration of 50 mg/L and solution pH 7.51.

#### 2.3.2. Influence of solution pH

In order to estimate the influence of solution pH on metal adsorption, the pH edges for both metals were measured exper-

imentally. Adsorption experiments were taken place under constant initial metal concentration, which is for copper 50 mg/L and for cadmium 20 mg/L. These are usual copper and cadmium concentrations in wastewater being treated with adsorption technology [16]. The solution pH was varied in the region 1–10 using droplets of concentrated HNO<sub>3</sub> or NaOH solutions to adjust it. The duration of the adsorption experiments was 72 h and the stirring rate was kept constant at 140 rpm.

### 2.3.3. Adsorption kinetics

The effect of the equilibration time on the removal of copper and cadmium was studied up to 3 days. The experiments were performed under the optimum pH values which were pH 9 for copper and pH 10 for cadmium. The stirring rate was kept constant at 140 rpm and the copper as well as the cadmium concentrations were varied from 20 to 80 mg/L.

### 2.3.4. Determination of pellets adsorption capacity

The adsorption capacity of pellets in copper and cadmium was estimated experimentally for each metal under the optimum values of pH 9 and pH 10, respectively. The equilibration time was 72 h and the stirring rate was kept constant at 140 rpm. The initial concentrations of Cu and Cd in solutions were varied in the region 5–200 mg/L.

### 2.4. Desorption experiments

Desorption experiments were performed in order to estimate the metal releasing capacity of pellets loaded with copper and cadmium. Pellets saturated with copper and cadmium were dried at 60 °C and then 5 g of them were added in a glass reactor containing 200 mL of an aqueous solution under constant temperature of 25 °C. The resulting pulp was mechanically agitated with a stirring rate of 140 rpm and several samples were withdrawn at predetermined time intervals and analyzed for their metal content with atomic adsorption spectrophotometry. The desorption experiments were performed with four different solutions. The two acidic ones were prepared from acetic acid with pH values  $2.88 \pm 0.05$  and  $4.98 \pm 0.05$  according to the standard TCLP leaching procedure (USEPA, 1995). The other two solutions were pure deionized water (neutral solution) and an alkaline sodium hydroxide solution with pH 12.

### 2.5. Stabilization of metal saturated pellets

Taking into account the cementitious properties of fly ashes, encapsulation of metal saturated pellets in concrete structures was selected as the most promising stabilization technique. Ten grams of metal saturated pellets were encapsulated within a cubic concrete block of 50 mm edge as is shown in Fig. 1. The concrete block was synthesized with the admixture of 240 g crushed sand, 50 g CEM II type cement, 0.8 g commercial plasticizer and 30 g water. Moreover, encapsulation blocks were prepared with admixtures in which 50 and 75% of CEM II type cement was replaced with pulverized (under 90 μm) fly ash. These encapsulation matrices are called ashcrete-50 and ashcrete-75. Finally, six blank blocks were prepared. The

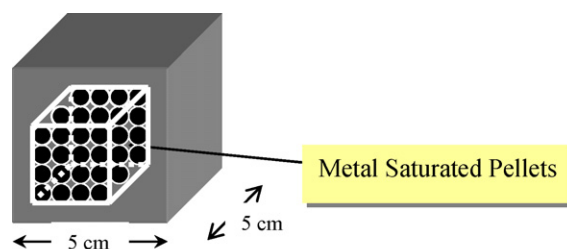


Fig. 1. Encapsulation of metal saturated pellets in concrete blocks.

first three blank blocks were prepared only from concrete, ashcrete-50 and ashcrete-75 matrices without the addition of metal saturated pellets and were called blank-concrete-I, blank-ashcrete-50-I and blank-ashcrete-75-I, respectively. The other three blank blocks were prepared from concrete, ashcrete-50 and ashcrete-75 matrices in which 10 g of “clean” (nonmetal loaded) pellets were encapsulated and were called blank-concrete-II, blank-ashcrete-50-II and blank-ashcrete-75-II, respectively. All blocks remained in a curing chamber under constant temperature of 20 °C and relative humidity higher than 90% in order to develop mechanical strength. After 28 days ageing, the blocks were tested for their porosity with the Archimedes method and compressive strength.

In order to evaluate the degree of Cu and Cd immobilization after the encapsulation of metal saturated pellets in the above blocks, desorption experiments were performed at 25 °C. The blocks containing metal saturated pellets were put in a beaker and totally covered with 400 mL of an aqueous medium that was mechanically agitated at 140 rpm. The aqueous media used in all tests were the same with the solutions used in the case of pellets desorption experiments. The duration of tests was 2 months. Samples were withdrawn from solution every day for the first 2 weeks and then every week till the end of tests. The samples were analyzed for their metal (Cu or Cd) content with atomic absorption spectrophotometry.

## 3. Results and discussion

### 3.1. Characterization of raw fly ash

The chemical analysis of raw fly ash is given in Table 1. The results showed that the most important main components of the material are silicon, aluminum, calcium and iron compounds. The XRD analysis (Fig. 2a) showed that the major crystalline constituents are quartz, gehlenite, anhydrite, maghemite, albite and calcium aluminum oxide. Moreover, fly ash is also constituted of an X-ray amorphous phase indicated by the broad hump registered between  $2\theta = 20^\circ$  and  $2\theta = 30^\circ$ . Cr, Ni and Mo constitute the most important trace elements occurring in raw material (Table 1). The particles of fly ash have spherical, oval or irregular shape as it was found after morphological analysis through scanning electron microscopy and their mean size was 100 μm. Finally, the BET/N<sub>2</sub> specific surface area of fly ash was 10.20 m<sup>2</sup>/g.

The results of the dissolution of heavy and toxic elements from the raw material during the standard leaching tests are

Table 1  
Fly ash characterization

|  |        |
|--|--------|
| BET/N <sub>2</sub> specific surface area (m <sup>2</sup> /g) | 10.20  |
| Pulp pH  | 11.27  |
| Chemical analysis of the main components of fly ash (% w/w)  |        |
| SiO <sub>2</sub>   | 48.22  |
| Al <sub>2</sub> O <sub>3</sub>                               | 18.16  |
| CaO  | 12.87  |
| Fe <sub>2</sub> O <sub>3</sub>                               | 9.40   |
| MgO  | 4.18   |
| TiO <sub>2</sub>   | 1.20   |
| K <sub>2</sub> O   | 1.63   |
| Na <sub>2</sub> O  | 0.65   |
| LOI  | 1.28   |
| Chemical analysis of the trace elements of fly ash (mg/kg)   |        |
| Mn   | 378.24 |
| Zn   | 118.76 |
| Pb   | 7.59   |
| Cu   | 1.52   |
| Cr   | 327.33 |
| Ni   | 297.40 |
| Mo   | <140   |
| As   | 11.98  |
| Cd   | 0.16   |

shown in Table 2. It is obvious that the raw material was not leached in extent higher than the maximum allowed limits imposed by the TCLP standard test as well as the European legislation for solid wastes. According to the results presented in Table 2, fly ash can be characterized as a non-hazardous solid waste as concerns the leachability of contained heavy and toxic elements. In addition, the results showed that there was not any serious leaching of main constituent metals with the exception of calcium. The high CaO dissolution which is responsible for

the high pulp pH value (pH 11.27) of fly ash (Table 1) proves that the free lime content in Megalopolis fly ash is high giving it very good cementitious properties. Therefore, this raw material has the potential to be safely used for production of low cost adsorbents for heavy metals removal from wastewaters.

### 3.2. Pellets preparation and characterization

The scope of the pelletization trials was the determination of the conditions under which the optimum pellet properties are developed. The produced pellets ought to have high porosity, good mechanical strength and pellet diameter in the range of 3–8 mm. The results for each pelletization trial are shown in Table 3. As it is observed after the sieving test the experimental conditions that gave the higher percentage of pellets with the desired diameter was the drum angle 37.5° with a fly ash/water ratio  $R = 3.16$ . Almost all pellets (99%) developed under these conditions had diameter in the range of 3–8 mm. Moreover, these pellets had the highest relative porosity (53.71%) while they showed the highest % mass loss during self-milling among all the other pellets. This was an expected result because there is normally a direct proportional correlation between mass loss and relative porosity of pellets. In general, the pellets prepared under these conditions (37.5°,  $R = 3.16$ ) showed very good stability in water as well as high porosity and in spite of their relative high mass loss they comprise satisfactory structures for utilization in wastewater treatment.

X-ray diffraction analysis of cured pellets (Fig. 2b) showed that quartz, gehlenite, maghemite and albite remain as the main mineralogical phases. Anhydrite and calcium aluminum oxide disappeared and calcium was present with the form of calcium silicate hydrated mineral phases indicating the development of

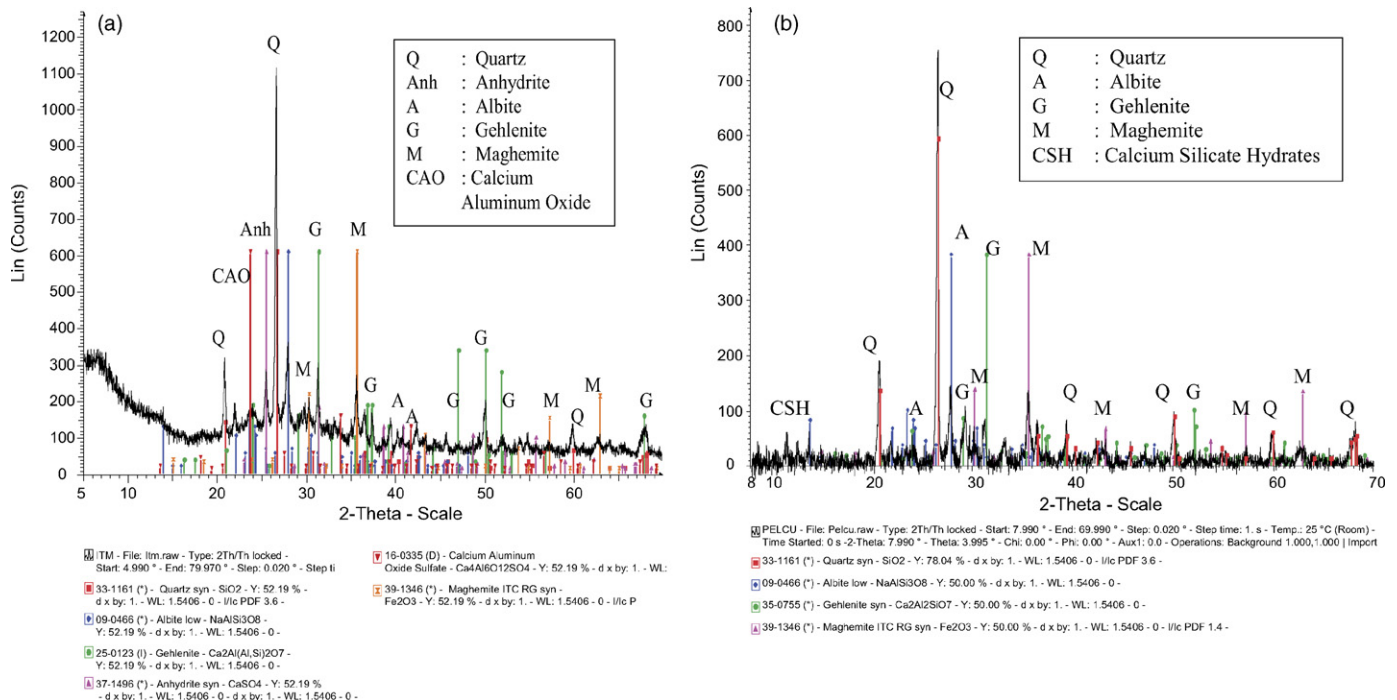


Fig. 2. XRD analysis of: (a) fly ash and (b) cured pellets.

Table 2  
Leachability of heavy and toxic elements from raw fly ash

| TCLP test |                         |                       | EN test |                           |                         |     |     |
|-----------|-------------------------|-----------------------|---------|---------------------------|-------------------------|-----|-----|
| Metal     | Leaching capacity (ppb) | Toxicity limits (ppb) | Metal   | Leaching capacity (mg/kg) | Toxicity limits (mg/kg) |     |     |
|           |                         |                       |         |                           | IW                      | NHW | HW  |
| Pb        | 6                       | 5,000                 | Pb      | 0.06                      | 0.5                     | 10  | 50  |
| Cd        | <0.4                    | 1,000                 | Cd      | <0.004                    | 0.04                    | 1   | 5   |
| As        | 16.5                    | 5,000                 | As      | <0.05                     | 0.5                     | 2   | 25  |
| Cr        | 23.5                    | 5,000                 | Cr      | 0.22                      | 0.5                     | 10  | 70  |
| Cu        | <2                      | 100,000               | Cu      | 0.06                      | 2                       | 50  | 100 |
| Zn        | <40                     | 500,000               | Zn      | 0.36                      | 4                       | 50  | 200 |
| Se        | <5.0                    | 1,000                 | Ni      | 0.05                      | 0.4                     | 10  | 40  |
| Ag        | <0.5                    | 5,000                 | Mo      | <7                        | 0.5                     | 10  | 30  |

IW, inert waste; NHW, non-hazardous waste; HW, hazardous waste.

hydraulic bond and the fixation of free calcium in the formed binding phase of cured pellets. The pulp pH of cured pellets had the value of 7.86 which was substantially lower than the one of the fly ash shown in Table 1 (11.27) strengthening the conclusion mentioned above.

The BET/N<sub>2</sub> specific surface area of pellets was 23.41 m<sup>2</sup>/g and their average pore diameter was 8.04 nm. The pore size distribution is shown in Fig. 3. It is clearly observed that almost the 52% of the pellet pore volume was occupied by pores with a diameter in the range 3.51–4.19 nm. The shape of desorption hysteresis loop attributes the pellets' porosity either to spherical cavities and voids in-between spherical particles or to ink bottle type pores. The point of zero charge (pH<sub>pzc</sub>) for pellets suspensions in deionized water was estimated through  $\zeta$ -potential measurements and found to be at pH value of 5.

The pelletization of fly ash solved two very important drawbacks related to its utilization as adsorptive material. Dusty fly ash cannot be applied for adsorption in columns because after a short period of time it is transformed to solid impermeable concrete. Its application in agitated vessels causes serious problems which are related to the separation of a dusty material from an aqueous solution. The use of fly ash pellets permits the application of adsorption in columns without problems. Wastewater can percolate easily within a column filled with fly ash pellets

without the risk of clogging with time. Additionally, the use of dusty fly ash changes substantially the wastewater pH and creates strong alkaline effluents with pH values higher than 11 after wastewater treatment. The use of fly ash pellets affects slightly the wastewater pH after treatment producing effluents with pH lower than 8 which lies within the allowed limits for discharge in several natural receivers.

### 3.3. Adsorption experiments

#### 3.3.1. Influence of stirring rate

The results showed (Fig. 4) that the copper removal is optimized at an intermediate stirring rate value (140 rpm). As the stirring rate decreased from 140 to 60 rpm, the copper removal decreased drastically from 55% to less than 10%. Increase of stirring rate to values higher than 140 rpm had also as a result the reduction of the copper removal from the solution. The experimental results were expected because under very low agitation rates a thick boundary layer is established around the pellets making the copper removal a slow, diffusion controlled process. As the stirring rate increases, the boundary layer becomes thinner thus improving the copper removal process from the

Table 3  
Pellets characterization

| Experimental conditions |          | Porosity (%) | % Mass loss during self-milling | % Pellets with size 3–8 mm |
|-------------------------|----------|--------------|---------------------------------|----------------------------|
| Angle (°)               | R (g/mL) |              |                                 |                            |
| 37.5                    | 3.26     | 52.20        | 20.74                           | 94.0                       |
|                         | 3.16     | 53.71        | 23.94                           | 99.0                       |
| 40.0                    | 3.26     | 47.50        | 15.10                           | 89.0                       |
|                         | 3.16     | 47.20        | 9.57                            | 94.0                       |
| 42.5                    | 3.70     | 53.83        | 20.74                           | 93.4                       |
|                         | 3.06     | 52.16        | 23.94                           | 90.8                       |
| 45.0                    | 2.70     | 46.74        | 8.64                            | 85.0                       |
|                         | 2.30     | 48.74        | 9.61                            | 90.0                       |
| 47.5                    | 3.13     | 54.47        | 11.57                           | 91.4                       |
|                         | 3.00     | 52.67        | 8.18                            | 96.0                       |

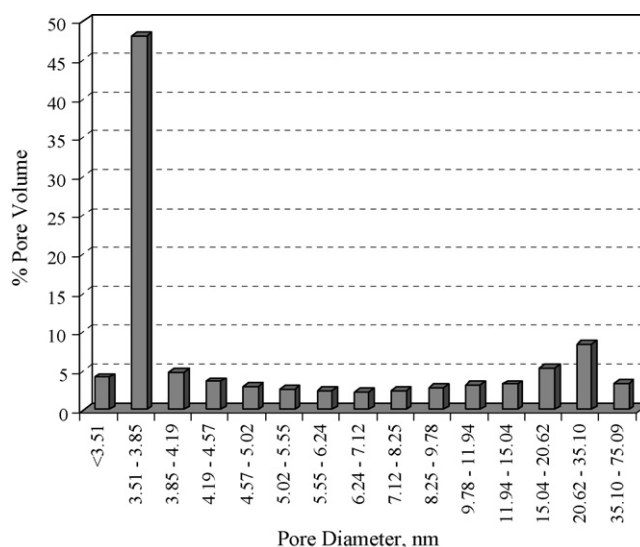


Fig. 3. Pore size distribution in cured pellets.

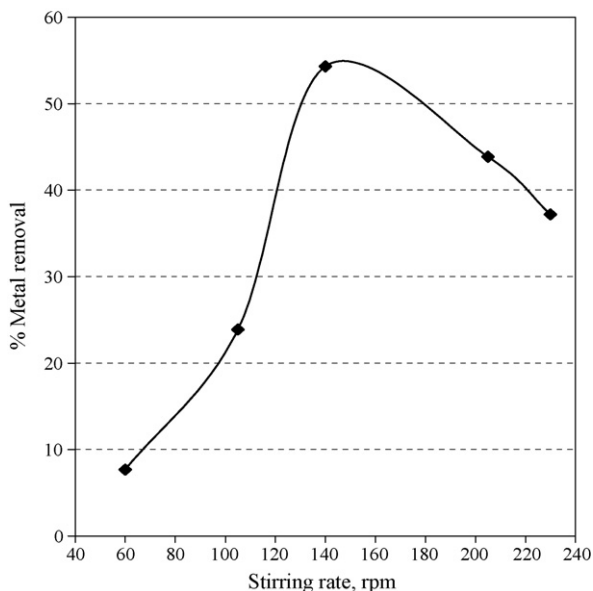


Fig. 4. Effect of stirring rate on copper removal.

solution. Under very high stirring rates, copper ions can reach easily the external pellet surface and be adsorbed on its active sites. At the same time, they are not able to access easily the pore surface of the pellets because the convection from the surface toward bulk solution is faster than the diffusion toward the pores. For this reason an increase of stirring rate from 140 to 230 rpm had as a result the decrease of copper removal from the solution.

### 3.3.2. Influence of solution pH

The results (Fig. 5) showed that the adsorption of both cations is strongly dependent on pH. The adsorption increases with pH and the percent ion sorbed increases sharply over a narrow pH range. The metal adsorption is intensified for both metals in the pH range 6–7 and reaches 100% sorption above pH 9. The results are in good agreement with the  $\zeta$ -potential measurements shown in Fig. 6.  $\zeta$ -potential becomes zero in the pH range 4–6 and takes negative values as pH increases. Above this pH range and till pH 11, the copper and cadmium solutions are composed from positively charged ions ( $\text{Cu}^{2+}$ ,  $\text{CuOH}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{CdOH}^+$ ,

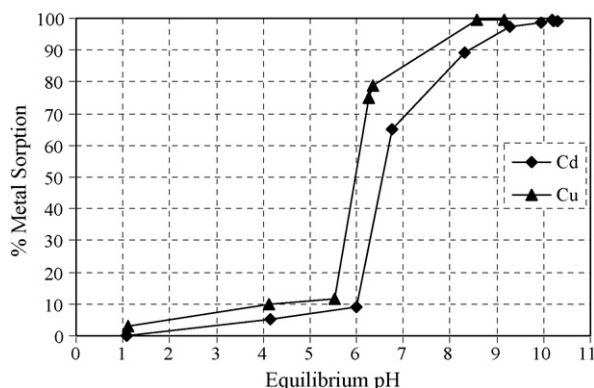


Fig. 5. pH-edges for Cu and Cd adsorption on pellets.

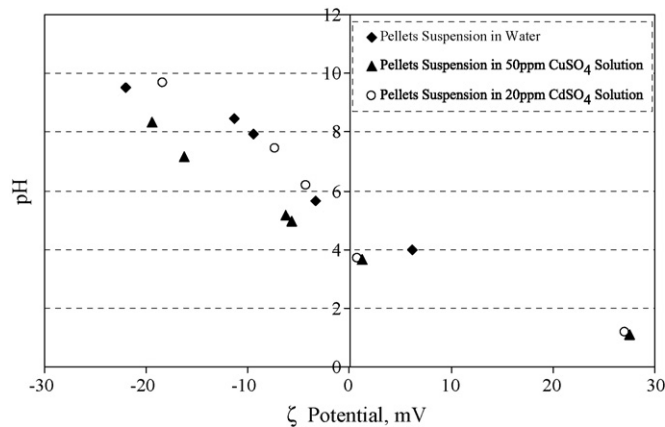


Fig. 6.  $\zeta$ -potential of pellets suspensions with pulp density 5 g/L in water, 50 mg/L  $\text{CuSO}_4$  solution and 20 mg/L  $\text{CdSO}_4$  solution.

$\text{Cd}_2(\text{OH})_3^+$ ) as well as neutral species ( $\text{Cu}(\text{OH})_2^0$ ,  $\text{CuSO}_4^0$ ,  $\text{Cd}(\text{OH})_2^0$ ) while the high acidic solutions are composed from single  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  cations [32]. As a result, the strong repulsive forces between the adsorbent surface and the metal species in solution, which dominate in high acidic solutions and inhibit the metals' adsorption process, are attenuated substantially in the pH range 4–6 and eliminated at higher pH values till pH 11. Therefore, the metal species in solution can easily access the adsorbent surface and the copper and cadmium adsorption are intensified in this pH region.

### 3.3.3. Adsorption kinetics

The kinetic results for both metals are shown in Figs. 7 and 8 where the metal sorbed on fly ash pellets is plotted against the equilibration time. The experimental data were analyzed with the utilization of a pseudo-second order adsorption kinetic model [33]. In accordance to this model, the rate of adsorption has to obey the following rate equation:

$$\frac{dq_t}{dt} = k(q_{eq} - q_t)^2 \quad (1)$$

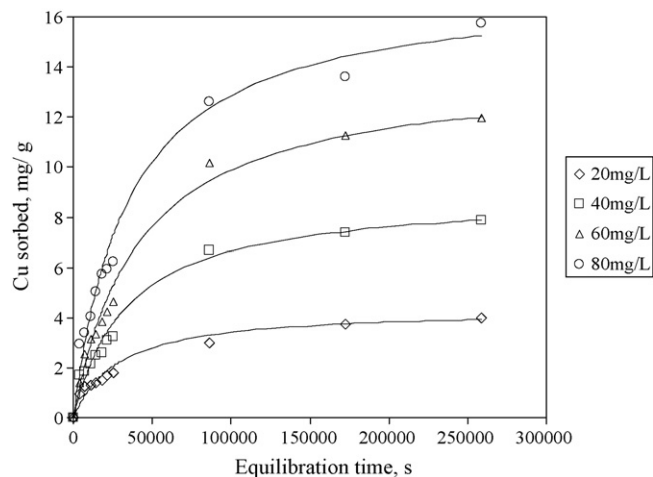


Fig. 7. Kinetics of copper adsorption on fly ash pellets.

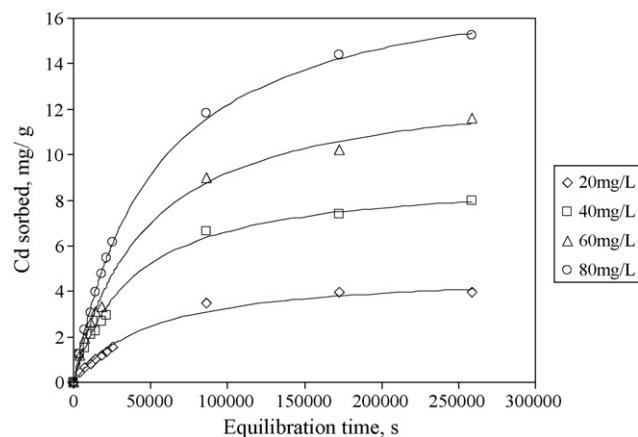


Fig. 8. Kinetics of cadmium adsorption on fly ash pellets.

where  $k$  is the adsorption rate constant (g/mg s),  $q_{eq}$  the amount of metal sorbed at equilibrium (mg/g) and  $q_t$  is the amount of metal sorbed at any time  $t$  (mg/g).

The linear form of the pseudo-second order rate expression that is obtained after the integration of Eq. (1) has as follows:

$$\frac{t}{q_t} = \frac{1}{kq_{eq}^2} + \frac{1}{q_{eq}}t \quad (2)$$

where  $h = kq_{eq}^2$  denotes the initial adsorption rate in mg/g s.

The validity of this model in the case of copper and cadmium adsorption on fly ash pellets was examined by the plots of  $t/q_t$  versus  $t$ . The plots showed the existence of very good linearity in all cases for both metals indicating that the copper and cadmium adsorption on fly ash pellets obeys a pseudo-second order rate expression. The calculated values of the model parameters  $k$  and  $q_{eq}$  for both metals are shown in Table 4. It can be seen that the metal adsorption rate constant decreases and the initial adsorption rate increases as the initial metal concentration increases. Moreover, an almost linear relation exists between the log  $k$  or log  $h$  and the initial metal concentration. The above observations were expected. Since all adsorption experiments were carried out under constant pellet amount of 5 g/L, the number of available active surface sites for adsorption was constant

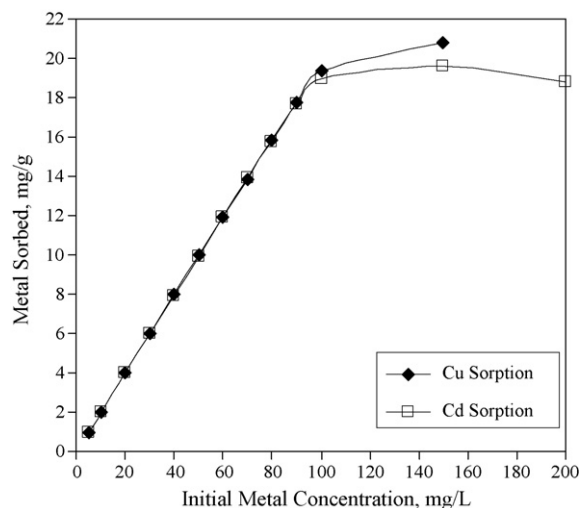


Fig. 9. Estimation of experimental adsorption capacity.

in all experiments. As the initial metal concentration decreased, the excess of the available active surface sites increased and thus the system reached the equilibrium faster. As the rate constant indicates how fast the equilibrium is approached, the decrease of the initial metal concentration caused an increase to the adsorption rate constant. On the other hand, the initial adsorption rate is proportional to the driving force at the beginning of sorption,  $(q_{eq} - q_t)^2 = q_{eq}^2$  as  $q_t = 0$ , which was substantially higher in the cases of higher initial metal concentrations as is it shown in Table 4. Therefore, an increase in the initial metal concentration caused an increase to the initial metal adsorption rate.

Based on the data presented in Table 4, the solid lines of Figs. 7 and 8 were drawn indicating that the copper and cadmium adsorption on fly ash pellets can be described quantitatively with a pseudo-second order rate expression.

### 3.3.4. Determination of pellet adsorption capacity

The experimental results are shown in Fig. 9 where the amount of metal sorbed on pellets in mg/g is plotted against the initial metal concentration in the solution in mg/L. It is clearly observed for both metals that the amount of sorbed

Table 4  
Estimated model parameters for Cu and Cd adsorption on fly ash pellets

| Cu adsorption                      |              |                       |                       |        |
|------------------------------------|--------------|-----------------------|-----------------------|--------|
| Initial metal concentration (mg/L) | $q_e$ (mg/g) | $k$ (g/mg s)          | $h$ (mg/g s)          | $R^2$  |
| 20                                 | 4.36         | $8.19 \times 10^{-6}$ | $1.55 \times 10^{-4}$ | 0.9909 |
| 40                                 | 8.90         | $3.32 \times 10^{-6}$ | $2.62 \times 10^{-4}$ | 0.9901 |
| 60                                 | 13.91        | $1.76 \times 10^{-6}$ | $3.40 \times 10^{-4}$ | 0.9928 |
| 80                                 | 17.30        | $1.68 \times 10^{-6}$ | $5.02 \times 10^{-4}$ | 0.9826 |
| Cd adsorption                      |              |                       |                       |        |
| Initial metal concentration (ppm)  | $q_e$ (mg/g) | $k$ (g/mg s)          | $h$ (mg/g s)          | $R^2$  |
| 20                                 | 4.88         | $4.12 \times 10^{-6}$ | $9.82 \times 10^{-5}$ | 0.9901 |
| 40                                 | 9.08         | $2.96 \times 10^{-6}$ | $2.44 \times 10^{-4}$ | 0.9941 |
| 60                                 | 13.40        | $1.63 \times 10^{-6}$ | $2.93 \times 10^{-4}$ | 0.9967 |
| 80                                 | 18.38        | $1.07 \times 10^{-6}$ | $3.62 \times 10^{-4}$ | 0.9934 |

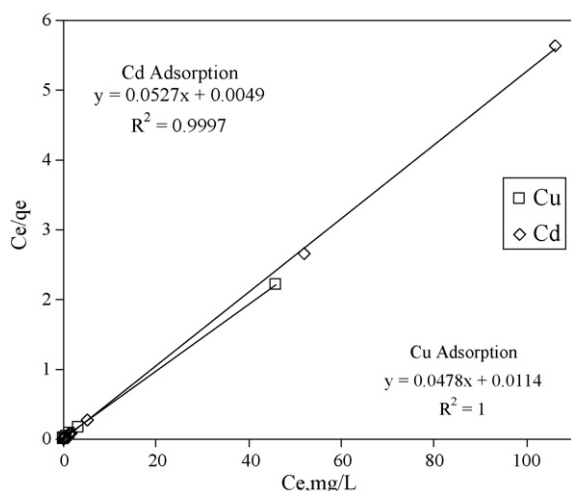


Fig. 10. Langmuirian plots of  $C_{eq}/q_{eq}$  vs.  $C_{eq}$  for copper and cadmium adsorption on fly ash pellets.

metal increased almost linearly as the initial metal concentration increased reaching a plateau which corresponded to a saturated adsorbent. The level of plateau determines the experimental estimated adsorption capacity of pellets for each metal. As it is seen in Fig. 9, the copper adsorption capacity of pellets is higher than the cadmium one.

The experimental results for both metals fit excellent to a Langmuirian type isotherm which is given with its linear form by the following equation:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_0 K_{ads}} + \frac{C_{eq}}{q_0} \quad (3)$$

where  $C_{eq}$  is the equilibrium concentration of metal (mg/L),  $q_{eq}$  the amount of metal adsorbed at equilibrium (mg/g),  $K_{ads}$  the metal adsorption reaction constant at 25 °C ( $L \text{ mg}^{-1}$ ) and  $q_0$  is the metal adsorption capacity of pellets (mg/g).

The plot of  $C_{eq}/q_{eq}$  versus  $C_{eq}$  is given in Fig. 10 where it is clearly seen that an excellent linear relationship exists for both metals indicating that the copper and cadmium adsorption on the pellets follow the Langmuir adsorption isotherm. The values of  $q_0$  and  $K_{ads}$  were calculated from the slopes and the intercepts of lines in Fig. 10 and are shown for both metals in Table 5. The calculated adsorption capacities for copper and cadmium were 20.92 and 18.98 mg/g, respectively. If they are expressed in mmol/g, the copper adsorption capacity (0.33 mmol/g) is almost twice the cadmium one (0.17 mmol/g). Taking into account that the Langmuir isotherm is derived assuming that each surface adsorption site can be occupied by only one metal species from the solution (1:1 stoichiometry), it can be concluded that the cadmium species have access to the half available surface adsorption

Table 5  
Langmuir parameters for copper and cadmium adsorption on fly ash pellets

|    | Langmuir model parameters |                  |
|----|---------------------------|------------------|
|    | $q_0$ (mg/g)              | $K_{ads}$ (L/mg) |
| Cu | 20.92                     | 4.19             |
| Cd | 18.98                     | 10.76            |

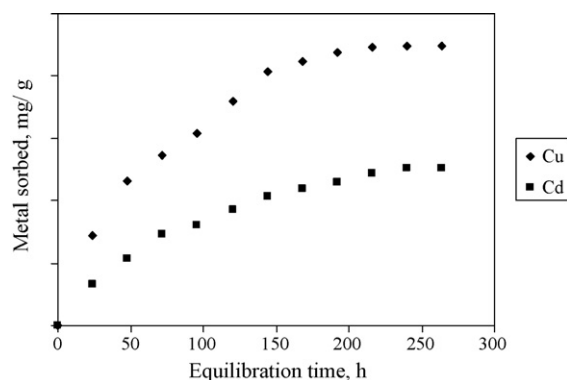


Fig. 11. Adsorption on fly ash pellets from a complex aqueous solution containing 150mg/L copper and 150 mg/L cadmium.

sites of pellets in relation to copper ones. This result cannot be attributed to the different sizes of copper and cadmium ions. Although non-hydrated cadmium ions are bigger (0.097 nm) than non-hydrated copper ones (0.072 nm), their hydrated ions have size at least 10 times smaller than the average pore diameter of pellets (8.04 nm). Taking into account that the specific surface area of pellets is attributed almost entirely to the pore surface, it can be concluded that almost the entire adsorption sites are located on the pore surface and are accessible to the hydrated copper and cadmium ions. On the other hand, the excellent fitting of experimental results for both metals to the Langmuir model points out that the pellet adsorption sites have equal activity. This observation is not consistent with the heterogeneous nature of fly ash that consists of different groups of surface adsorption sites such as  $\equiv\text{SiOH}$ ,  $\equiv\text{AlOH}$ ,  $\equiv\text{FeOH}$  and  $\equiv\text{TiOH}$ . Therefore, an explanation for the above experimental observation could be that copper and cadmium ions have preferable access to different groups of the surface adsorption sites. In order to test this assumption, an adsorption experiment was performed from a complex aqueous solution containing 150 mg/L copper and 150 mg/L cadmium ions at pH 10. The results are shown in Fig. 11. It is clearly observed that the adsorption process for both metals was decelerated substantially. The system was reaching equilibrium after almost 250 h while in the case of single metal solutions the equilibrium was achieving at 72 h. The most important observation is that copper consumed entirely its adsorption capacity on pellets while cadmium consumed only 66.5% of its adsorption capacity. This result indicates that copper and cadmium are adsorbed preferably on different groups of surface adsorption sites as it was stated also in literature [24]. As these surface adsorption sites have different surface concentrations, the metals have different adsorption capacities from single solutions. In complex solutions copper and cadmium species have a competition for the accession of the pellets pore surface which is responsible for the deceleration of the adsorption process. The more mobile copper species can access easier the pore surface and thus can reach its adsorption capacity on pellets. The cadmium adsorption in this competitive environment is inhibited and therefore cadmium cannot reach the adsorption capacity that it has in single metal solutions.



Table 6  
Properties of concrete and ashcrete blocks

| Block kind           | Replacement of cement by raw fly ash (%) | Pellets content (g) | Compressive strength (MPa) | Porosity (%) |
|----------------------|--|---------------------|----------------------------|--------------|
| Blank-concrete-I     | 0  | 0                   | 29.42–31.12                | 13.55–14.68  |
| Blank-concrete-II    | 0  | 10                  | 27.05–28.11                | 14.22–15.04  |
| Blank-ashcrete-50-I  | 50                                       | 0                   | 26.04–27.55                | 14.52–16.12  |
| Blank-ashcrete-50-II | 50                                       | 10                  | 17.08–18.04                | 16.08–20.65  |
| Blank-ashcrete-75-I  | 75                                       | 0                   | 12.01–12.30                | 15.08–16.99  |
| Blank-ashcrete-75-II | 75                                       | 10                  | 11.00–11.20                | 25.79–26.85  |
| Cu-concrete          | 0  | 10                  | 24.82–25.36                | 15.82–19.10  |
| Cu-ashcrete-50       | 50                                       | 10                  | 16.28–17.10                | 20.11–24.38  |
| Cu-ashcrete-75       | 75                                       | 10                  | 11.23–12.00                | 26.07–26.90  |
| Cd-concrete          | 0  | 10                  | 24.92–25.10                | 14.03–17.99  |
| Cd-ashcrete-50       | 50                                       | 10                  | 14.03–17.99                | 24.10–25.67  |
| Cd-ashcrete-75       | 75                                       | 10                  | 11.08–11.22                | 26.22–27.41  |

### 3.4. Desorption experiments

The experimental results showed no copper and cadmium desorption in the neutral and alkaline solutions after an equilibration time of 72 h. This was a reasonable result because under those conditions the copper and cadmium adsorption affinity on pellets is too high (Fig. 5) making the surface metal complexes extremely stable. On the contrary, high amounts of copper and cadmium were desorbed in acidic solutions as is shown in Fig. 12. The metal desorption was intensified as the extraction solution became more acidic. This was an expected result because under these conditions copper and cadmium have very small adsorption affinities as it is seen in Fig. 5 and thus the surface metal complexes can be easily decomposed.

Copper was desorbed generally to a higher extent in relation to cadmium under the same experimental conditions. This experimental result was in accordance with the higher adsorption reaction constant at 25 °C ( $K_{ads}$ ) for cadmium in relation to the copper one (Section 3.3.4) which indicates that cadmium has higher adsorption affinity on pellets than copper.

### 3.5. Stabilization of metal saturated pellets

The adsorption of copper and cadmium on pellets is a reversible process especially in the acidic area as the desorption experiments proved. This is a serious drawback because

metal loaded pellets can liberate substantial amount of copper and cadmium upon contact with acid rain causing pollution to groundwater as well as to other natural water receivers. Therefore, the stabilization of metal saturated pellets with their encapsulation in concrete structures is necessary before their disposal to industrial landfills. The experimental results are shown in Table 6. It is observed that the cement replacement with fly ash decreased the blocks' strength and increased slightly the blocks' porosity as it was expected. The addition of pellets (clean or metal saturated) in the blocks decreased their mechanical strength and increased their porosity. In any case, the measured compressive strengths were satisfactory allowing the deposition of such blocks in industrial landfills without difficulties in handling (e.g. cracking during their transportation for deposition).

The results from the desorption experiments, which evaluated the degree of Cu and Cd immobilization after the encapsulation of metal saturated pellets in the concrete and ashcrete blocks, were excellent. After 2 months in acetic acid solutions with pH values  $2.88 \pm 0.05$  and  $4.98 \pm 0.05$  as well as in pure water and a strong alkaline sodium hydroxide solution with pH 12 neither copper nor cadmium were desorbed from concrete, ashcrete-50 and ashcrete-75 blocks indicating that the risk of pollution for groundwater and other natural water receivers has been eliminated. Moreover, the blocks retained their geometrical characteristics as well as their mechanical strength indicating that their failure risk is negligible.

## 4. Conclusions

The most important conclusions from this work are summarized as follows:

- Class C fly ash like the one used in this paper is a self-cementing material that can be shaped easily in the form of pellets. The pellets after curing at ambient temperature for a period of 15 days develop satisfactory abrasion resistance as well as high relative porosity and therefore can be used as an adsorbent for wastewater treatment.
- The pellets have very good adsorption capacities for copper (20.92 mg/g) as well as cadmium (18.98 mg/g) and can be

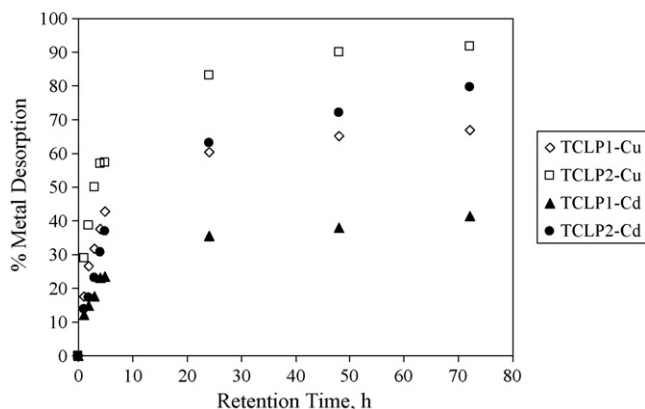


Fig. 12. Desorption of metals from saturated pellets.

used for their removal from aqueous solutions at ambient temperature. The copper and cadmium adsorption kinetics is described satisfactorily by a pseudo-second order kinetic model. The adsorption of both metals on fly ash pellets is described accurately by the Langmuir isotherm. Cadmium was proved to have higher adsorption affinity on pellets than copper.

- Copper and cadmium adsorption on fly ash pellets is a reversible process under acidic conditions and irreversible under neutral and alkaline conditions. Cadmium forms adsorbed surface complexes with higher stability than copper and for this reason is desorbed at lower extent in relation to copper.
- The metal saturated pellets can be stabilized easily in concrete blocks or in ashcrete blocks where cement was replaced to an amount of 50 to 75% by fly ash. The stabilized blocks can be disposed safely in industrial landfills having excellent mechanical behavior and negligible copper and cadmium desorption in acidic, neutral and alkaline aqueous environments.

The proposed technology can be characterized as a “green” one for the following reasons:

- (a) It exploits the hydraulic properties of an industrial solid by-product, the fly ash, which is produced in million tonnes worldwide in order to develop porous and abrasion resistant structures in the form of pellets. Moreover, it takes the advantage of the adsorption properties of fly ash in order to utilize the produced structures as adsorption means for the efficient removal of heavy metals from industrial wastewaters.
- (b) It exploits the cementitious properties of fly ash in order to encapsulate the metal saturated pellets into a concrete matrix, where a big amount of cement is replaced by fly ash. In this way excellent immobilization of pollutants is achieved and the metal loaded adsorbents can be safely disposed in industrial landfills.

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