



## ADSORPTION BEHAVIOR OF CADMIUM AND COPPER COMPOUNDS ON A MIXTURE FA:TiO<sub>2</sub>

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Fly ash (FA) with alkali modified surface, was used in wastewater treatment, for cadmium and copper immobilisation. The FA adsorption capacity can be improved, with different amounts of TiO<sub>2</sub>. The adsorption studies were carried out on single substrates (FA and TiO<sub>2</sub>) and multi proportions mixtures of FA:TiO<sub>2</sub>. The influence of the TiO<sub>2</sub> over adsorption capacity was studied by modifying the ratio FA:TiO<sub>2</sub> and by optimizing the contact time. Efficiencies over 99% were obtained after 30 minutes of adsorption. A synergism effect was obtained during the process, caused by the pH modifications towards alkaline values; the cause can be the TiO<sub>2</sub> surface activation, to negative charges by hydroxide adsorption, which favours the cation adsorption. The process was kinetically modelled (pseudo-second order kinetic and interparticle diffusion). The highest adsorption rate occurs for an optimized ratio FA:TiO<sub>2</sub> = 3:1.

### INTRODUCTION

Fly ash, one solid waste resulted in power plants is produced during burning of pulverized coal in a coal-fired boiler and is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected from electrostatic precipitators, bag houses, or mechanical collection devices such as cyclones. Worldwide, nearly 500 million tons of fly ash are annually produced, with a global recycling rate of 15%.<sup>1</sup> Only in Brasov, CHP-CET works with two boilers with 420 t/h capacity and two turbo-aggregates which generate 50 MW/each.

The common fuel contains 88% lignite and 12% methane. Thus, every year burned coal amounts 6X10<sup>5</sup> t and the fly ash resulted is about 2X10<sup>5</sup> t. An interesting possibility might be the use of FA as a low-cost adsorbent, for gas and water treatment, providing that this waste can match industrial needs. Many papers reported on the use of fly ashes for the removal of heavy metals,<sup>2</sup> dyes,<sup>3</sup> phosphate<sup>4</sup> and organic substances,<sup>5</sup> from industrial waste water. The use of different wastes

(fly ash, wood powder) with modified surface is intensively studied for heavy metal removal and literature mentions novel approaches related to cadmium, copper, lead, mercury or chromium removal.<sup>5-7</sup>

The dyes photo-degradation on n-type semiconductors as TiO<sub>2</sub> anatase is well known. Organometallic complexes are one of the most toxic dye-substances from environmental point of view and photodegradation must be combined with heavy metal removal. Adsorption of dyes on FA also started to be studied as a sustainable, low-cost solution,<sup>8</sup> while heavy metals adsorption is investigated onto TiO<sub>2</sub>,<sup>9</sup> and ternary titanium based compounds like titanates.<sup>10</sup> Therefore, a suitable solution for advanced treatment of the waters resulted in the textile industry can use a mixture of TiO<sub>2</sub> and fly ash. The paper presents the results obtained in Cd<sup>2+</sup> and Cu<sup>2+</sup> immobilization on FA-CET Brasov, chemically modified with NaOH 2N solution and added with different amounts of TiO<sub>2</sub>. Effects of the contact time and adsorbent mass on the adsorption efficiency are reported and correlated with the FA structure and

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morphology. The process kinetic is studied and it was found that a pseudo-second-order equation and inter-particles diffusion describes well all the reactions.

## MATERIALS AND METHODS

Raw Fly Ash was collected in 2008, from the electrostatic filters in the combined heat and power plant CET Brasov, Roumania. The content of the main constituents are presented in Table 1.

The total percentage of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, is 84.34% (above 70%),<sup>7</sup> thus, according the ASTM C618 classification, the fly ash –CET Brasov, is of class F.

Fly ash (4g) was washed in ultra pure water (100mL), by stirring up (100 rpm), at room temperature, for 48h, to remove the soluble compounds, until constant pH was reached, at the value of 7.8. The water resulted after washing FA had an ionic conductivity of K =2.25 mS and a TDS value of 1140 mg/L, as result of the soluble compounds dissolution. In the supernatant resulted after washing, cadmium (0.2575mg/L) and cooper (0.03974 mg/L) were found resulted from chloride (orthorhombic CdCl<sub>2</sub> (H<sub>2</sub>O)<sub>4</sub> and CdCl<sub>2</sub> H<sub>2</sub>O) and oxide (monoclinic CuO) dissolution, as the detailed XRD analysis proved, thus washing FA prior using is a necessary step.

Table 1

The composition of fly ash (FA) - CET Brasov, [%]

Compound	% in FA	Compound	% in FA	Compound	% in FA	Compound	% in FA
<b>SiO<sub>2</sub></b>	53.32	<b>Fe<sub>2</sub>O<sub>3</sub></b>	8.97	<b>MgO</b>	2.44	<b>SO<sub>3</sub></b>	1.40
<b>Al<sub>2</sub>O<sub>3</sub></b>	22.05	<b>MnO</b>	0.08	<b>K<sub>2</sub>O</b>	2.66	<b>P<sub>2</sub>O<sub>5</sub></b>	0.12
<b>Ca O</b>	5.24	<b>TiO<sub>2</sub></b>	1.07	<b>Na<sub>2</sub>O</b>	0.63	<b>LOI</b>	1.58

\*LOI: loss of ignition (corresponding to organics)

The fly ash composition and surface properties depend on many factors, including the coal source and composition, the burning process and the furnace characteristics. Therefore, a method for getting a more homogeneous surface in terms of composition, by removing the soluble compounds and surface controlled load, was proposed by long term contact of FA with alkaline solutions<sup>11</sup>. Fly ash washed was mixed, under stirring, for 48h, in NaOH 2N solution (FA/ NaOH 2N). After filtration, washing and drying at 105-120°C for 2h, the modified FA was analyzed.

The crystalline structure of the raw, water-washed and NaOH modified fly ash was evaluated by XRD (Bruker D8 Discover Diffractometer). The AFM images (Ntegra Spectra, MT-NDT model BL222RNTE) were used for surface morphology studies. The AFM was used to characterize the uniformity, grain size and pore

size distribution of the films. Image analysis was carried out by means of WSxM software, to evaluate the pore size distribution.<sup>12</sup>

The TiO<sub>2</sub> Powder (Degussa P25, Germany) was also used as substrate, mixed with modified FA. The powder is a mixture of 75% anatase and 25% rutile, and the morphology involves pores of aprox. 7 nm size and a surface area of 50% m<sup>2</sup>/g. The FA:TiO<sub>2</sub> dispersions had pH values in the range 7.8 - 6.6, decreasing with the increase of the titania content.

## ADSORPTION EXPERIMENTS

The adsorption tests were performed by batch experiments, under stirring at room temperature, at the natural pH of the dispersion, Table 2.

Table 2

The pH values of the dispersions

FA:TiO <sub>2</sub>	4:0	3:1	2.5:1.5	2:2	1.5:2.5	1:3
pH	7.8	7.4	7.1	6.5	6.6	6.6

The contact time was determined by preliminary investigations in 1g FA dispersed in 100mL cadmium (0 – 800mg/L) and respectively cooper (0 – 500mg/L) solution; the solutions were stirred up to 60 min, then the substrate was removed by vacuum filtration and the supernatant was analyzed by AAS (Analytic Jena, ZEE nit 700), at  $\lambda_{Cd} = 228.8\text{nm}$  and, respectively at  $\lambda_{Cu} = 324,75\text{ nm}$ . Similar studies were done for optimizing the ratio adsorbent mass: heavy metal solution volume; experiments covered the range 1:100 up to 7:100 g/mL.

The lowest admissible discharge concentrations are, in most national regulations set for cadmium. Therefore, the optimized adsorption conditions set for cadmium were further extended for the copper containing solutions, both for FA substrates and mixtures of FA-NaOH 2N with  $\text{TiO}_2$ .

## KINETIC STUDIES

For metal removal kinetics studies, 1 g of FA: $\text{TiO}_2$  was mixed with 100 mL of heavy metal solutions (1 mE/L) in a beaker agitated vigorously by a magnetic stirrer at constant room temperature. At appropriate time intervals (5, 10, 15, 20, 30, 45 and 60 min), stirring was briefly interrupted and the supernatant aliquots were analyzed to evaluate the residual metal compound concentration in the aqueous solution.

The metal uptake  $q$  (mg ion metal/g fly ash) was calculated using:

$$q_{\text{eq}} = (C_0 - C_t) V / m_s \quad (1)$$

where  $C_0$  and  $C_t$  are the initial and metal ion concentrations at moment  $t$  (mg/L), respectively,  $V$  is the volume of solution (mL), and  $m_s$  represents the fly ash weight (g) in dry form.

Kinetics of heavy metals adsorption was modelled using the following equations:

– pseudo first-order Lagergren equation: <sup>13</sup>

$$\log (q_{\text{eq}} - q_t) = \log (q_{\text{eq}}) - \frac{K_L}{2,303} t \quad (2)$$

where  $K_L$  is the Lagergreen constant and  $q_t$  the metal uptake at moment  $t$ .

– pseudo-second order rate equation developed by Ho and McKay. <sup>14</sup>

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where  $k_2$  the pseudo second-order rate constant of adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ) and can be evaluated from the slope of the plot. <sup>11, 15</sup> The model is mentioned in literature for  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$  adsorption on zeolites, <sup>11</sup> and of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  on humic acid. <sup>16</sup>

– the interparticle diffusion model; <sup>17</sup> describing processes on highly porous surfaces:

$$q = k_{\text{id}} t^{1/2} + C \quad (4)$$

## RESULTS AND DISCUSSION

### Fly ash characterization

The XRD spectrum, Figure1, highlights the major FA components and confirms a complex oxide structure also proving that dissolution/re-precipitation processes are occurring during substrate preparation. The results show that CaO and unburned carbon (LOI-loss of ignition) are less affected by NaOH in the reaction conditions. The reaction with NaOH leading to partial dissolution that modifies the specific surface, affects  $\text{Al}_2\text{O}_3$ , MgO and, partially,  $\text{SiO}_2$  (quartz). For the latest, the dissolution is followed by re-precipitation, solving - dissolving the tetragonal phase and forming cristobalite, an orthorhombic polymorph that can be a supplementary cause in increasing the adsorption efficiency for heavy metals due to a higher amount of edges and corners.(see also Figure 2).

These chemical and structural changes also induce surface morphology modifications, resulting in significant differences in the substrates' affinity for cadmium and copper soluble compounds, before and after treating with NaOH 2N.

The solution resulted after washing FA with water proves a significant ionic content as result of the soluble compounds dissolution. The sodium and potassium compounds (mainly oxides) are especially responsible for the slightly alkaline pH values. The morphology changes must be correlated with the surface reactions during modification and/or (re)precipitations. Washing and especially alkaline treatment is followed by a roughness decrease and large pores formation. Re-precipitation during alkaline treatment is confirmed by a shift of the pores' distribution maxima, towards lower values, Figure 2 (a) – (c).

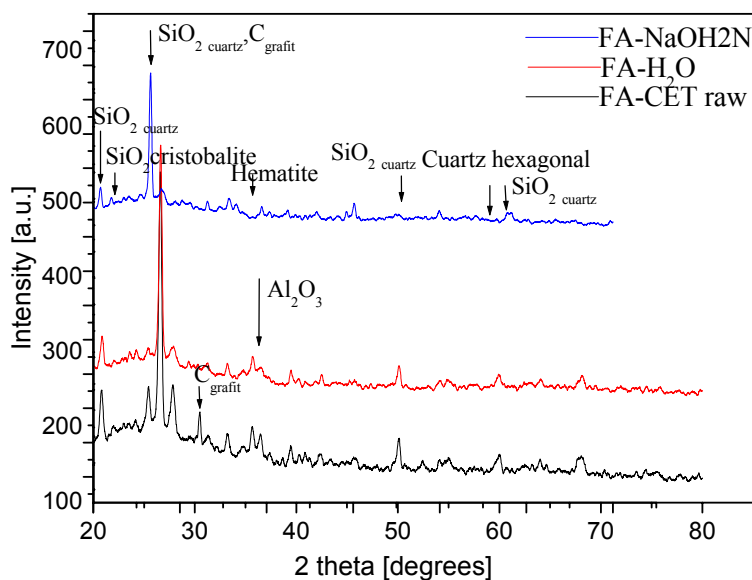


Fig. 1 – XRD patterns of FA raw, washed and treated main components.

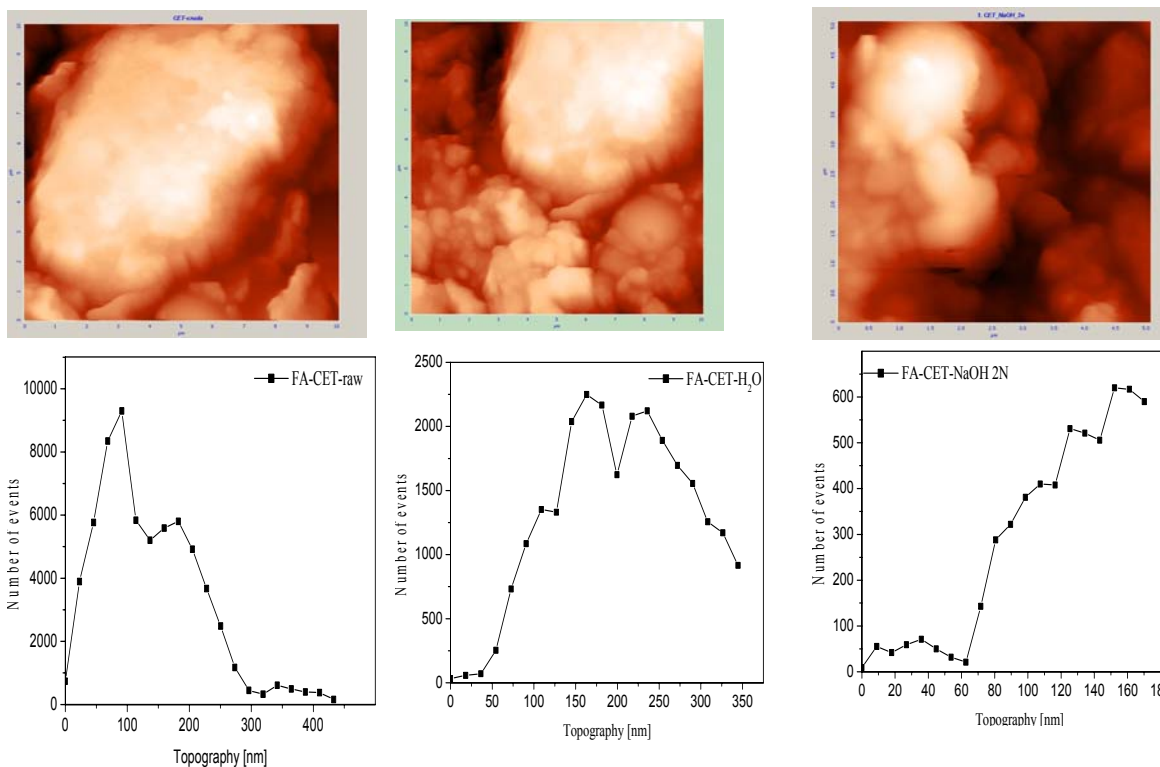


Fig. 2a – FA CET raw.  
Average roughness: 713 nm

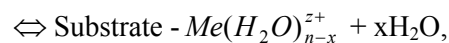
Fig. 2b – FA washed with H<sub>2</sub>O.  
Average roughness: 605 nm

Fig. 2c – FA-NaOH 2N.  
Average roughness: 393 nm

### Optimizing the adsorption on FA

The adsorption/desorption processes are complex and are strongly depending both on the substrate and on the heavy metal compound. The precipitation of Cd(OH)<sub>2</sub> starts at pH 7.8; at the working pH values (<7.8), the most likely heavy

metal compounds are the hydrated cations which can adsorb with partial or total de-hydration:



where:  $0 \leq x \leq n$ .

The adsorption efficiency,  $\eta$  and capacity,  $q_m$ , for cadmium and copper ionic compounds removal on modify FA and on mixtures of FA and  $TiO_2$  were evaluated based on the optimal time and mass balance calculation:

$$\eta = \frac{(c_{Cd}^i - c_{Cd}^e) \times 100}{c_{Cd}^i} \quad (5)$$

where  $c_{Cd}^i$  and  $c_{Cd}^e$  are the initial and equilibrium cadmium concentrations (mg/L),  $V$  the solution volume (L) and  $m$  the amount of substrate (g).

Previously reported results,<sup>18, 19</sup> showed that fly ash washed with water had poor cadmium and copper adsorption efficiency and the same is valid for the ash washed with HCl. Better results were

obtained using the fine fly ash, washed with NaOH. Efficiencies above 95% were obtained on FA modified with NaOH 4N after 5 min of contact while efficiencies of about 35% were obtained using FA modified with NaOH 2N, after 30 min., which is technologically feasible in a dynamic wastewater treatment process.<sup>20</sup> However, the use of NaOH 4N raises supplementary environmental problems and complicates the up-scalable process, therefore further studies were done for increasing the adsorption efficiency on FA modified with NaOH 2N by optimizing the ratio adsorbent mass: solution volume. The results presented in Figure. 3a and 3b, show an optimum dispersion concentration of 4:100 g/mL for cadmium and for cooper compounds.

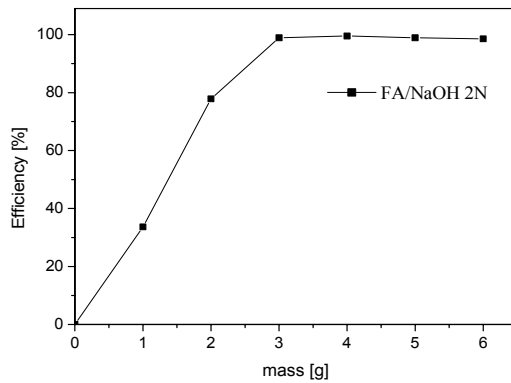


Fig. 3a – Cadmium immobilization. Efficiency vs. FA-NaOH 2N mass

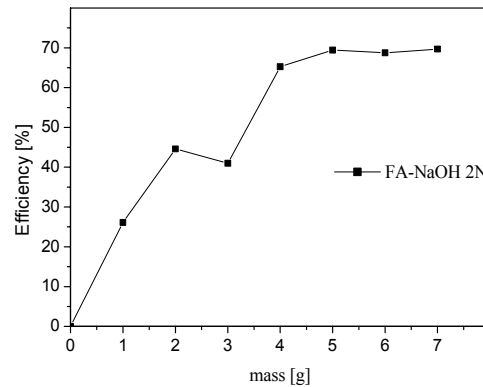


Fig. 3b – Cooper immobilization. Efficiency vs. FA –NaOH 2N mass

The adsorption studies were further carried out on multi proportion mixtures of modified FA and  $TiO_2$ . The influence of the  $TiO_2$  over the adsorption capacity was studied in 4:100 g/mL dispersions, testing substrates ratios of FA-2N:  $TiO_2$  = 3:1;

2.5:1.5; 2:2; 1.5:2.5; 1:3. The results presented in Figure 4, show that the best efficiencies for cadmium/cooper adsorption are obtained on substrates rich in modified FA (FA-2N:  $TiO_2$  = 3:1 and 2:2).

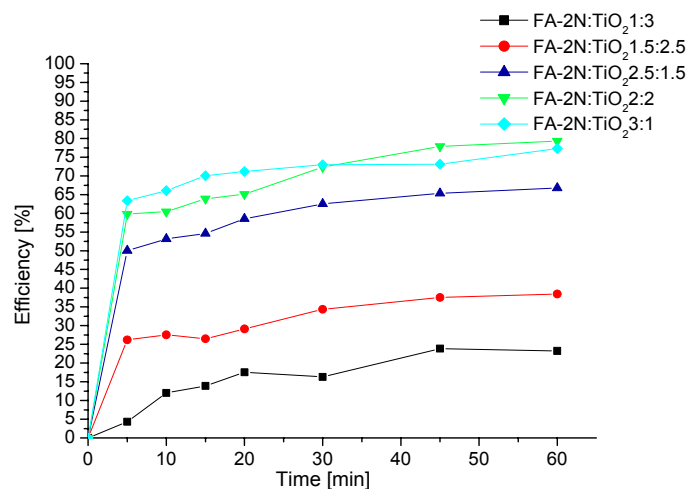


Fig. 4 – Cadmium immobilization. Efficiency vs. contact time.

Similar studies were developed for copper removal and an optimum contact time of 30 min. well suites this process, Figure 5.

Previous studies,<sup>19,21</sup> showed that the adsorption mechanism on FA can be well described by the

Freundlich isotherm and less by the Langmuir equation as result of an increased surface heterogeneity. By adding TiO<sub>2</sub> the overall heterogeneity is supplementary increased thus complex adsorption mechanisms can be expected.

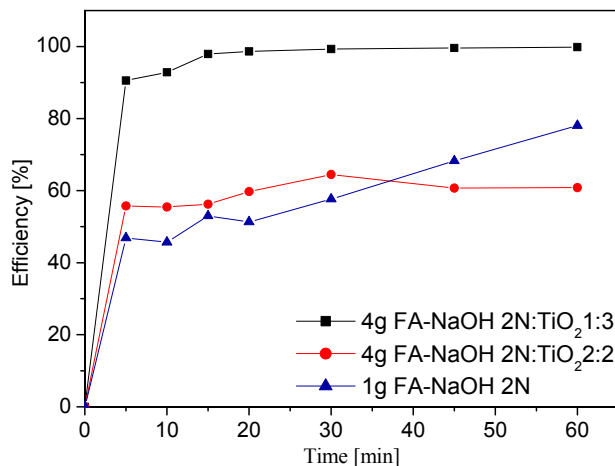


Fig. 5 – Cooper immobilization. Efficiency vs. contact time.

### Uptake kinetics of the heavy metals

Modelling studies, using eq. (2)- (4) proved that the pseudo-first order kinetic cannot describe any of the adsorption processes of cadmium and copper cationic compounds. The predominant mechanisms can be described by the pseudo-second order kinetics and interparticle diffusion, Table 3.

Considering the FA substrates, we may conclude that modifying the FA surface leads to a surface with moderate density of active sites, comparable with heavy metal compounds concentrations at the surface level. Corroborating these results with the lack of copper and cadmium affinity of the raw and water-washed FA we conclude that this behaviour is the result of the dissolution/reprecipitation processes induced during the modification(s).

Mixing TiO<sub>2</sub> with FA enhances the adsorption rate comparing with the single substrate and a synergic effect can be expected: a primary explanation can be linked with the alkaline pH, induced by the fly ash in the suspension. The TiO<sub>2</sub> zero point of charge is 6.2, thus the HO<sup>-</sup> ions (chemo)sorbs and negatively charge TiO<sub>2</sub>, resulting in an activated surface with increased affinity for cationic species. Although the pH in the batch solution allows only the cationic compounds, the pH near the substrate(s) surface can therefore be higher, favouring the cadmium precipitation as Cd(OH)<sub>2</sub> and thus increasing the substrate affinity for chemisorptions with crystallisation. These assumptions are confirmed by the adsorption rates, larger with 1-3 orders of magnitude in the mixed substrates.

Table 3

Kinetic studies of cadmium and copper removal on FA:TiO<sub>2</sub> mixed substrates

FA-2N: TiO <sub>2</sub> [g:g]	Pseudo-second order kinetics			Interparticle diffusion		
	k <sub>2</sub> [g/mg min]	q <sub>e</sub> [mg/g]	R <sup>2</sup>	K <sub>id</sub> [g/(mg min <sup>-0.5</sup> )]	C	R <sup>2</sup>
<b>Cadmium</b>						
4:0	0.0082	29.5852	0.9371	-	-	0.624
3:1	0.06976	11.5741	0.9981	0.3428	8.9438	0.9184
2.5:1.5	0.2163	10.2354	0.9967	0.4839	6.4841	0.9706
2:2	0.2213	12.2100	0.9938	0.6079	7.3416	0.962
1.5:2.5	0.6843	6.0132	0.9842	0.3877	2.8452	0.9178
1:3	3.7574	4.5208	0.9441	0.4906	0.0208	0.935

Copper						
4:0	0.008974	18.8324	0.9603	1.3925	6.9744	0.9197
3:1	25,77	13.92	1.0000	$5,8 \cdot 10^{-3}$	13.913	0.9996
2.5:1.5	34,61	24.03	1.0000	$10^{-4}$	24,027	0.9000
2:2	51,5561	7.8989	0.9983	-	-	0.7983
1.5:2.5	51,55	13.93	1.0000	-	-	0.1000
1:3	25,77	13.92	1.0000	0,024	13.91	0.9983

A parallel mechanism, with lower contribution in the overall kinetics is the interparticle diffusion that proves that the pores' dimension can easily accommodate the hydrated and rather large volume cationic species of cadmium and copper.

### CONCLUSIONS

The use of fly ash with modified surface for heavy metals removal was studied and the adsorption conditions were optimized in terms of contact time and adsorbent mass in a given volume of pollutant solution. By treating FA with alkaline solutions 2N the surface is modified by dissolution and re-precipitation reactions. By dissolution of acid oxides, the specific surface area is enhanced and activated, and the efficiency of heavy metals removal increases. The re-precipitation processes can lead to new polymorphs and provides a fractured morphology, suitable for adsorption. Adsorption of heavy metals on modified fly ash has a good efficiency and mixture of modified FA and TiO<sub>2</sub> prove to be very efficient in cadmium and copper removal, strongly depending on the titanium dioxide content.

Two parallel kinetic mechanisms could be applied for majority adsorption processes: pseudo-second order kinetics and interparticle diffusion, confirming the high heterogeneity of the substrates, even after modification with NaOH 2N.

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