

CADMIUM AND NICKEL REMOVAL FROM WASTEWATER USING MODIFIED FLY ASH: THERMODYNAMIC AND KINETIC STUDY♦

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Received: 16/01/2008

Accepted after revision: 22/02/2008

Abstract: The fly ash surface properties depend on many factors, including the coal composition, the burning process and the furnace characteristics. Developing an up-scalable process requires reproducible surface properties, less (or no) related to the above mentioned influences that can be obtained by tailoring the fly ash surface. The study presents the results obtained in Cd²⁺ and Ni²⁺ removal, using fly ash from CHP Brasov (Romania) with modified surface, prepared by long contact with alkaline solutions (NaOH 1N, 2N, 4N) and complexion agents (Complexone III, Pyrocatechol Violet). The immobilization efficiency is discussed in connection with contact time, wastewater volume: adsorbent mass ratio and ions concentration; Langmuir and Freundlich mechanisms were found to describe the adsorption processes. The process follows a pseudo-second order kinetic, for both metals, on the entire concentration range. Highly

♦ Paper presented at the fifth edition of: “Colloque Franco-Roumain de Chimie Appliquée – COFrRoCA 2008”, 25 – 29 June 2008, Bacău, Romania.

efficient adsorption, even at very low heavy metals concentrations (20 ppm), is registered for fly ash modified with NaOH.

Keywords: *wastewater treatment, fly ash, cadmium removal, adsorption.*

INTRODUCTION

Cadmium and nickel and their compounds are toxic, non biodegradable and relatively widespread in the environment and the systematic study on their removal from wastewater has considerable significance from an environmental point of view. A number of methods are available for the metal ions removal from aqueous solutions: ion exchange, solvent extraction, reverse osmosis, biological methods, chemical precipitation and adsorption on activated carbon (powder and granular), but the high costs restrict the advanced wastewater treatment in many countries [1, 2].

Recent researches were developed for the use of various industrial waste materials as low cost and efficient adsorbents for heavy metals removal.

The use of fly ash (FA), an industrial solid waste, in wastewater treatment received a lot of attention for the immobilization of heavy metal cations, mainly Cd^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} . The properties of fly ash are strongly depending on the type of coal and coal-burning process in the power plant. The differences are related to the oxide and carbon content in the fly ash and recent studies proved that the heavy metal adsorption effectiveness is enhanced by the CaO content [3, 4].

For an up-scalable wastewater treatment process, a substrate with good efficiency adsorption and with relative constant behavior is required. Modifying the fly ash surface can be a solution for reaching both goals.

The use of concentrated NaOH solutions for modifying the FA surface is reported, in processes at room temperature [5, 6], and in hydrothermal processes [7]. The chemical reactions on the FA grains surface are complex leading to composition modifications, due to dissolution and precipitation of various compounds, mainly alumina-silicates [8] and rearrangements of the oxide/carbon phases in the FA; crystalline modifications can also appear, increasing the amorphous phase; this treatment can lead (at extreme pH and temperature) to the development of ion exchanging surfaces, of zeolite type [7].

The use of highly concentrated NaOH solutions (8M [7] or pH = 13.95 [8]) can rise environmental problems and increases the complexity of the wastewater treatment technology. Therefore, alternatives must develop: either the use of less concentrated NaOH solutions for surface modification and/or the use of other surface modifiers. Heavy metals are easily reacting with chelating agents such as complexone III (the sodium salt of the ethylenediamine tetraacetic acid - EDTA), Black Eriochrome T or Pyrocatechol Violet.

The paper presents the results obtained in Cd^{2+} and Ni^{2+} immobilization on FA chemically modified with NaOH solutions of different concentration and with complexion agents.

The adsorption mechanisms are discussed by data fitting according to the Langmuir and Freundlich equations and kinetic considers the pseudo-first and -second order mechanisms and the inter-particle diffusion.

EXPERIMENTAL PART

Materials

Heavy metals stock solutions were prepared using ultra pure water (Direct - Q3, Millipore) and:

- $\text{CdCl}_2 \cdot 2.5 \text{H}_2\text{O}$ (Scharlau Chemia S.A., $M = 228.41$, <98%); $c = 20 \dots 1000$ ppm;
- $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, $M = 237.70$, 96%), $c = 10 \dots 300$ ppm;

The cations concentration was evaluated by AAS, (Perkin Elmer, Aanalyst 200) at a wave length of 228.8 nm (cadmium) and 341.5 nm (nickel).

Fly ash: Fired coal FA was collected from the Brasov CHP plant (CET), directly from the electrofilters (ELF). Raw coal fly ash consists of three types of materials: (1) chemically water stable solids (SiO_2 , FeO_x , Al_2O_3), (2) relatively water soluble solids (MeSO_4 , MeBO_3), and (3) water reactive metal-oxides (e.g., CaO , MgO , K_2O , Na_2O , etc) [9]. Ash varies from acidic to alkaline because of the chemical composition of the source coal. The composition [%] of fly ash - CET Brasov is presented in Table 1.

Table 1. The composition of fly ash - CET Brasov, [%]

Compound	Fly Ash ELF	Fly Ash and Cinder	Compound	Fly Ash ELF	Fly Ash and Cinder
SiO_2	53.32	52.84	Fe_2O_3	8.97	8.58
Al_2O_3	22.05	22.14	MnO	0.08	0.08
CaO	5.24	4.58	TiO_2	1.07	1.17
MgO	2.44	2.40	SO_3	1.40	0.88
K_2O	2.66	2.68	P_2O_5	0.12	0.13
Na_2O	0.63	0.72	LOI*	1.58	3.42

*LOI: loss of ignition (corresponding to unburned carbon and organics)

According the ASTM C618 classification, the fly ash – CET Brasov, pertains of class F because the total percentage of SiO_2 , Al_2O_3 and Fe_2O_3 , is 84.34%.

The ash was washed in ultra pure water for 48 hours, until constant pH in the washing solutions.

FA surface was modified, by batch mixing for 48 hours, of a 1/10 ratio dispersion of FA with:

- Alkaline Solutions of NaOH (Merck, 99%): $c = 1\text{N}$, 2N and 4N ;
- Complexone III solution (CIII, Rearal, 99%): $c = 10\%$;
- Pyrocatechol Violet solution (PV, Merck, 98%): $c = 0.5\%$;
- Eriocrom Blake T solution (EBT, 96%): $c = 0.5\%$.

Characterization

The FA crystalline structure was analyzed by XRD, using Bruker D8 Advance Diffractometer.

The topography of the FA surface is studied using Atomic Force Microscopy (AFM, NT-MDT model BL222RNTE). The images were taken in contact mode with Si-tips (CSG10, force constant 0.15 N/m, tip radius 10 nm).

Adsorption tests

Batch experiments were conducted, under stirring, at room temperature, to evaluate the removal efficiency of cadmium and nickel ions from the aqueous solutions. The effect of contact time, ratio FA mass/solution volume, initial metal concentration and FA surface were studied.

As reference, adsorption test, in the same experimental conditions, were done on wet activated carbon powder (Merck).

RESULTS AND DISCUSSIONS

Adsorption efficiency at various contact time, up to 60 min, are presented in Table 2, both for cadmium and nickel on raw and modified FA with NaOH 2N.

Table 2. Adsorption efficiency [%] of the heavy metal ions on FA
(1g substrate/100 mL solution; $c_{ion} = 0.01N$)

Time [min]	FA		FA modified with NaOH 2N	
	Cd ²⁺	Ni ²⁺	Cd ²⁺	Ni ²⁺
10	0.50	10.11	31.47	99.88
20	0.87	10.24	25.85	99.95
30	1.65	10.33	33.67	99.87
60	1.78	10.58	21.48	99.85

The cations adsorption efficiency strongly increases when the adsorption substrate is FA washed with NaOH 2N. Therefore, one can conclude that the predominant process on the FA surface is the heavy metal adsorption, with very good results for nickel.

Further modified FA substrates are tested, targeting the increase in the cadmium adsorption efficiency, Table 3.

Table 3. Cd adsorption efficiency [%] on modified FA and on Activated Carbon (AC)
(1g substrate/100 mL solution; $c_{ion} = 0.01N$)

Time [min]	FA / NaOH 1N	FA / NaOH 4N	FA / EBT	FA / PV	FA / CHH	AC
10	58.17	99.96	91.18	-4.74	16.51	11.62
20	76.14	99.79	93.67	-16.14	14.37	9.32
30	85.28	99.81	94.13	-0.50	14.76	7.29
60	92.99	99.86	96.38	-1.41	14.82	23.21

The results show that the complexing agents (CIII, PV) have limited efficiency in cadmium immobilization on the substrate, as result also of a weak adsorption and strong desorption.

The cadmium adsorption efficiency on FA modified with NaOH of different concentrations proves that different reactions are developed at different concentrations. The XRD analysis, Figure 1, shows crystalline modifications that can be attributed to dissolution of tetragonal (t) SiO_2 followed by re-precipitation of orthorhombic (o) SiO_2 . The XRD peaks in Figure 1 prove a complex composition, rich in various inorganic components (oxides and salts); graphite is also present in the FA, in almost constant amount in the unmodified and in the modified FA. To evaluate the contribution of the carbon content on the cadmium removal efficiency, adsorption test were done on activated carbon. The results prove that the carbon, even activated does not represent the major constituent in enhancing the efficiency.

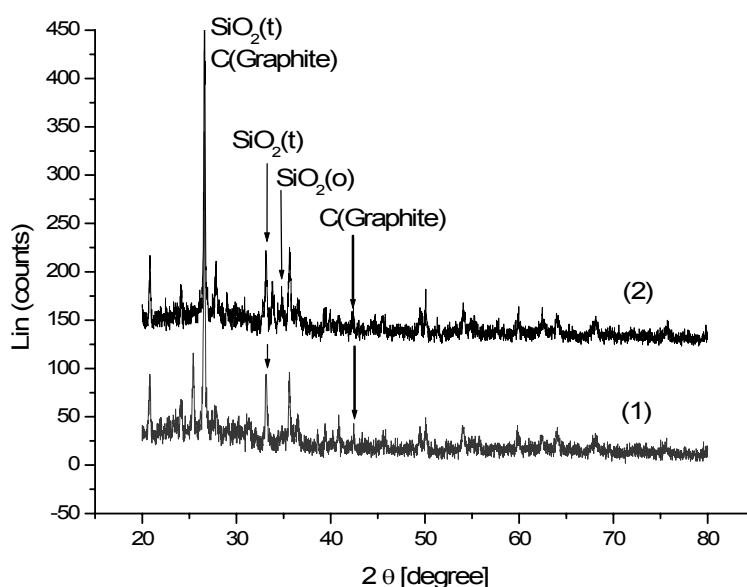
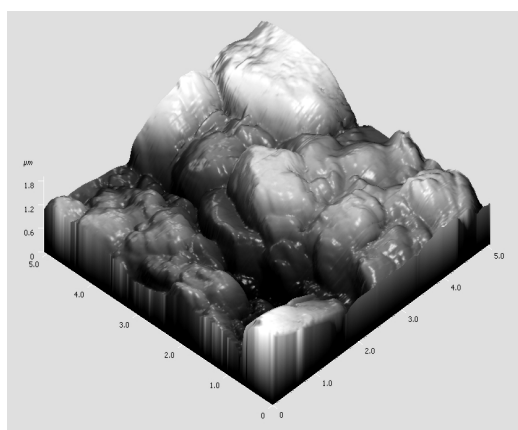


Figure 1. XRD of FA (1) and FA modified with NaOH 2N (2)

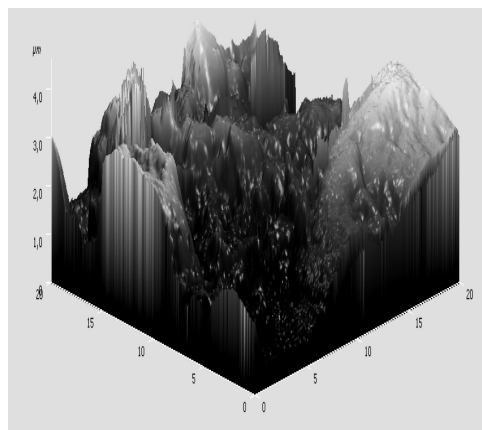
The XRD patterns indicate the dissolution of the alkali oxides and the formation of new oxides by re-precipitation (orthorhombic (o) SiO_2); these develop fractured morphologies, with more edges, consequently a surface with higher roughness, as presented in Figure 2.

The surface morphology is changed, Figure 2c, d. The raw FA consists of conglomerates of spherical particles, with diameters ranging from 1 to 30 μm . The FA modified with NaOH 2N leads to higher specific surface and increased dimension homogeneity that can explain the high efficiencies registered even at very short contact times. The morphology changes can be the result of complex dissolution – (re)precipitation processes, forming aggregated particles with diameters less than 5 μm [10].

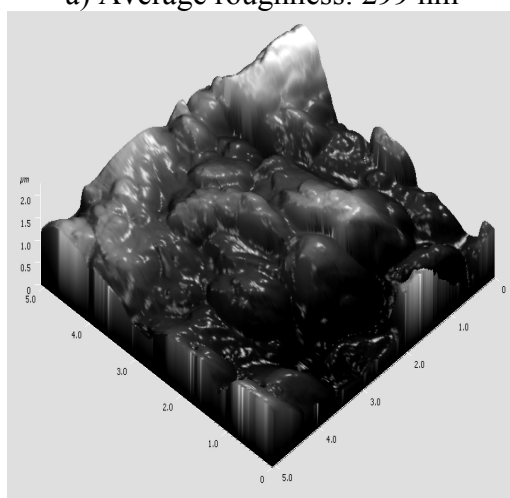
Consequently, ratios $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the FA are mainly responsible for the substrate efficiency, Table 1.



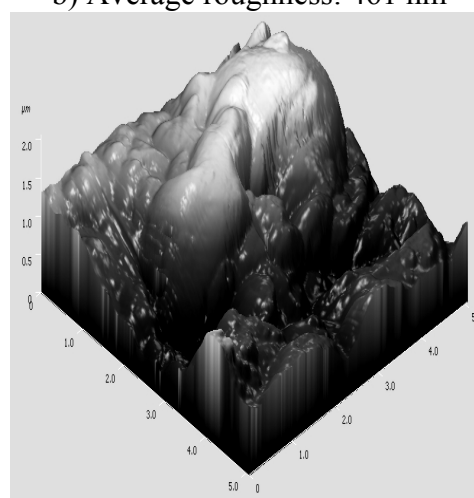
a) Average roughness: 299 nm



b) Average roughness: 461 nm



c) Average roughness: 314 nm



d) Average roughness: 393 nm

Figure 2. Surface morphology of: raw FA (a), washed FA (b), FA modified with NaOH 1N (c) and FA modified with NaOH 2N (d)

The low adsorption efficiency of FA modified with CIII and the desorption registered on FA modified with PV are the result of the development of very smooth morphologies. By using EBT the selective dissolution may be responsible for high specific surface morphologies, Figure 3. Still, the use of EBT is limited by the costs. For further optimization of the cadmium removal, experiments were done, at the optimized contact time, Table 2, by varying the FA weight mixed with 100 mL of heavy metal solution (Figure 4).

The optimized adsorption conditions are presented in Table 4.

Table 4. Optimized adsorption conditions on FA modified with NaOH

Optimized parameter	Cd^{2+}			Ni^{2+}
	FA/NaOH 1N	FA/NaOH 2N	FA/NaOH/4N	FA/NaOH 2N
Contact time [min]	60	30	10	20
Adsorbent mass [g] : 100 mL solution	2	4	1	3

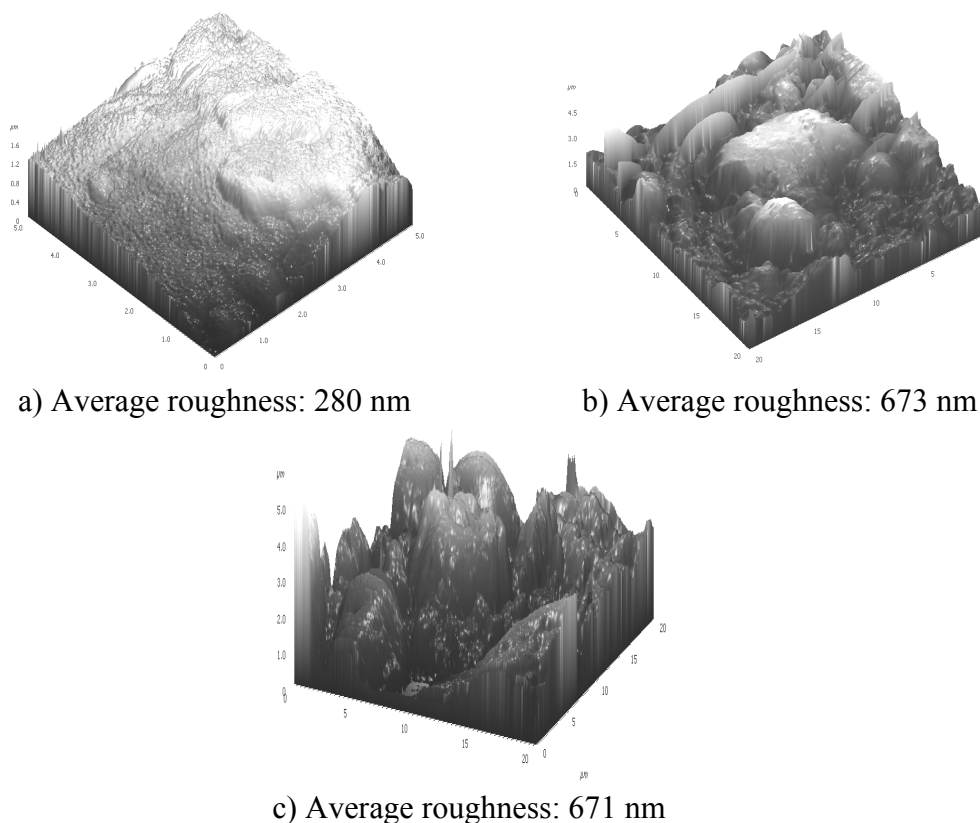


Figure 3. Surface morphology of: FA modified with CIII (a), FA modified with PV(b), FA modified with EBT(c)

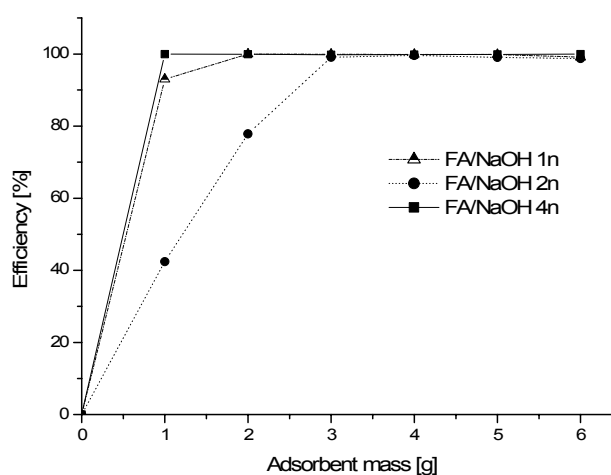


Figure 4. Cadmium immobilization efficiency vs. substrate weight

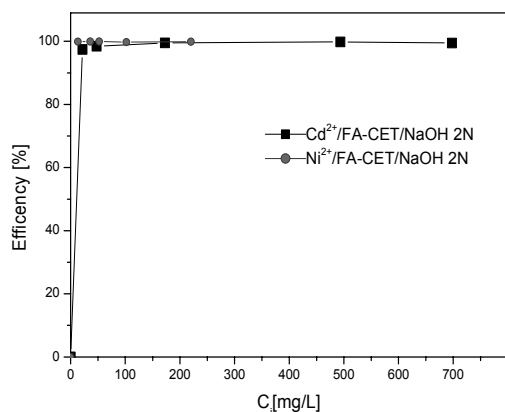
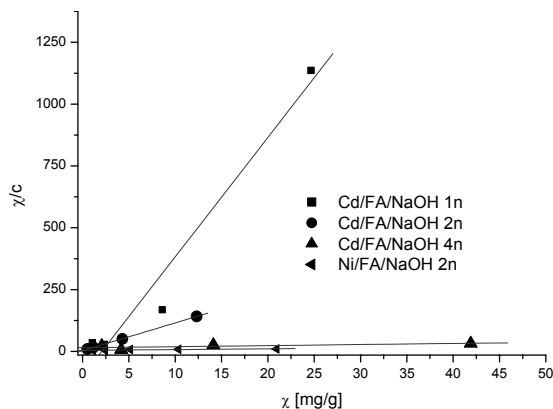
Adsorption experiments were developed for concentrations covering the extreme values that can be registered in the wastewater treatment from the electroplating industry. In the optimized conditions, the adsorption of both cadmium and nickel ions is efficient on a broad concentration range, Table 5.

Table 5. Cadmium and nickel adsorption efficiencies in the optimized conditions

C_{Cd} [ppm]	Efficiency [%]			C_{Ni} [ppm]	Efficiency [%] FA / NaOH 2N
	FA / NaOH 1N	FA/NaOH 2N	FA / NaOH 4N		
21.66	98.59	97.41	95.61	13.35	98.92
47.48	98.26	98.44	87.65	35.78	98.94
146.62	99.70	99.50	96.28	52.08	99.93
432.16	99.95	99.82	96.95	102.10	99.76
935.50	99.97	99.45	99.96	220.16	99.88

Although the most convenient adsorption conditions are registered for FA-CET/NaOH 4N, from a technological point of view, less concentrate alkaline solutions are desired. Therefore the further tests were done for the following adsorption parameters, considered as optimized and technologically feasible: 100 mL/4 g FA-CET/NaOH 2N, 30 minutes contact time. The efficiencies for cadmium removal are, in these conditions, over 97 %.

Nickel is removed from aqueous solutions (220....10 ppm solutions), using FA washed with NaOH 2N, with efficiencies above 98%. Figure 5 presents the nickel removal efficiencies from aqueous solutions.


Figure 5. Nickel removal efficiency from aqueous solutions

Figure 6. Linearization of the Langmuir isotherm

The acquired experimental data were used for identifying the adsorption mechanisms. The Langmuir model describes the absorption of both metals and the linearization (analogue of the Scatchard plot [11]), was well fitted (Figure 6); this confirms the preferential adsorption of the heavy metal cations on the oxide FA surface.

The adsorption of nickel ions on FA-CET modified with NaOH 2N solution is well modeled both by the Freundlich isotherm and Langmuir model for all the concentrations between 10 - 250 ppm.

The high value of Freundlich k parameter (10.2) shows that the nickel ions have developed strong bonds with the active adsorptions centers, most likely as chemosorption.

The Freundlich isotherm could not be fitted for cadmium on the entire concentration range.

In the optimized conditions, cadmium removal efficiencies are higher than 99%, for medium and large concentrations. For low concentration, when diffusion becomes

significant, the overall efficiencies are lower and re-circulation is needed in order to comply with the discharge regulation.

Table 6. Adsorption efficiency of cadmium and nickel cations on FA-CET/NaOH 2N

Concentration [mg/L]	Cd ²⁺	Ni ²⁺
Below 50	97.92	99.93
50...100	98.87	99.93
100...200	99.50	99.76
Over 200	99.63	99.88
Discharge concentration	0.2	0.5

The adsorption kinetics gives information on the rate of heavy metal uptake, on the adsorbent surface and supports tailoring the adsorbent surface for the target, in this case – cadmium and nickel adsorption on FA-CET/NaOH 2N (1 g/100 mL) from aqueous solutions.

Three kinetic mechanisms are usually reported for adsorption on heterogeneous substrates as is the fly ash: pseudo-first order, pseudo-second order and interparticle diffusion, expressed by equations (1) – (3) [12, 13]:

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2,303}t \quad (1)$$

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

$$q = k_{id}t^{1/2} + C \quad (3)$$

where q and q_e represent the amount of metal adsorbed at the time (t) and at equilibrium (mg/g), and k are the reaction rates.

Based on the correlation calculations, it could be proved that only the pseudo-second order kinetic can describe the process, with correlation factors, R^2 , above 0.9300, as presented in Table 7.

Table 7. The parameters of the pseudo-second order kinetic for cadmium and nickel adsorption on FA/NaOH 2N

Ion	k_2 [g/mg min]	q_e [mg/g]	R^2
Cadmium	0.00820	29.58	0.9371
Nickel	4.12232	22.03	1.0000

This mechanism confirms that the active sites *and* the metal ion concentration are of equal importance. The higher maximum adsorption capacity for nickel can be related with its ionic volume and the partial loss of hydration water, which runs differently for cadmium and nickel at the natural pH of the test solutions.

CONCLUSIONS

Fly ash surface can be modified, at room temperature, with alkaline solutions of NaOH, with different concentrations. The modification processes involves reactions of dissolution and (re)precipitation of various oxide components, leading to changes in the chemical composition, crystalline structure and surface morphology. The experiments prove that moderate NaOH concentrations (2N) are enough for developing a substrate that, in optimized conditions, insures adsorption efficiencies above 97%, for cadmium and nickel ions in a large concentration range. The oxide components are the preferential adsorption sites on the modified FA, while carbon (not affected during the modification process) contributes only in a limited amount to adsorption.

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