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Simultaneous adsorption of dyes and heavy metals from multicomponent solutions using fly ash

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ABSTRACT

In wastewaters originating from dye industry there are amounts of dyes (very common methyl orange, methylene blue—MB) and heavy metals (cadmium, copper, nickel mainly from the organo-metallic dyes). They tend to adsorb in a competitive process and modify the substrate. Advanced removal is usually proposed via adsorption and the use of modified fly ash as a substrate is sustainable solution. The main constituents of fly ash (silica, alumina, iron oxide and un-burned carbon), are the priority compounds which favour the heavy metal adsorption and are active sites in dyes' adsorption processes. The paper studies the effect of MB adsorbed on the fly ash surface on the removal efficiency of cadmium, copper and nickel ionic species from complex, multi-cationic dye solutions. The adsorption efficiency and kinetics are evaluated from the complex, multicomponent systems and possible influences are discussed. High efficiencies are obtained at low heavy metal concentrations (as it is the real case for the dyes industry) whereas at medium values, competitive processes lower the individual efficiencies of copper, nickel or cadmium from mixtures.

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1. Introduction

Dyes, pigments and heavy metals represent common and dangerous pollutants, originating in large quantities from dye manufacturing, textile as well as pulp and paper industries. They are emitted into wastewaters and produce difficult to treat water contamination, as the colour tends to persist even after the conventional removal processes. The conventional techniques used for dyes and heavy metal removal are expensive, have average efficiency and are running in sequential steps. For example, on the commercial scale the ion-exchangers and activated carbons are used, however, with certain disadvantages. The activated carbon is a great adsorbent for dyes but de-sorption and regeneration are difficult under common conditions and the overall process becomes expensive. Moreover, its efficiency in heavy metals removal is average. The modern approach towards dyes removal is connected with photo-catalysis, mainly using TiO₂-anatase.

Ion-exchange is an efficient method, with moderate selectivity since it can not only remove the heavy metal ions but exchange Ca²⁺, Mg²⁺ ions [1]. In addition, the ion-exchangers can load with dyes, thus modifying the surface and decreasing the process

reversibility. These adsorbents are efficient but not fully sustainable solution.

Recent studies [2] have shown that various fly ashes with different un-burnt carbon contents collected from the power plants can be used for sequential adsorptions of methylene blue, crystal violet, methyl orange, basic dyes and CI Reactive Red 49 from aqueous solution, because the priority compounds in fly ash favour heavy metal adsorption and develop active sites in dyes adsorption processes.

A novel technology based on a single step process is proposed, combining adsorption and photo-degradation for the simultaneous removal of both pollutants. In our studies we use a waste—"fly ash (FA)" collected from CHP Brasov (Romania), which was modified with NaOH 2N, as previously described [3]. The fly ash modification process is easy, low cost and sustainable, using alkali solutions of average concentration. By combining FA with the photo-catalysts (TiO₂) and/or adsorbents (activated carbon) a complex system, capable of simultaneous treat of dyes and heavy metals is obtained [4]. Our research followed the steps concerning heavy metals removal from single cation (Cd²⁺, Cu²⁺, Ni²⁺) solutions [4,5], simultaneous removal of cations from multication solutions using FA and FA:TiO₂ mixtures in parallel with similar studies of dyes removal via photo-degradation and adsorption. Then the mixtures of single cation solutions with dye(s) were investigated for understanding the complex influence of the components on the substrates, and the changes in mechanisms and efficiencies; a group of studies targeted the

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results obtained in Cd²⁺ and Cu²⁺ removal, using fly ash (FA) with methyl orange modified surface and its mixtures with TiO₂ and proved that the best adsorption efficiency is registered using the mixture with 25% of TiO₂ [6]. Similar studies were carried out on fly ash modified with methylene blue, MB. The efficiency was very good, both for the cations and for the dye. A new idea was born for a complex adsorption process involving cadmium, copper and nickel ionic species from multi-cationic dye solutions. This paper presents the results of the studies on the effect of MB adsorbed on the fly ash surface on the removal efficiency of cadmium, copper and nickel ionic species from complex, multi-cationic and dye solutions.

2. Experimental

2.1. The substrate

The major compounds, expressed as oxides are presented in Table 1 for the raw fly ash collected from the electro-filters of the CPH plant in Brasov (FA), Romania. The sum of the SiO₂, Al₂O₃ and Fe₂O₃ is above 70% [7], thus according to the ASTM standards, the FA is of type F.

The fly ash was washed in ultrapure water, by stirring, at room temperature, for 48 h, to remove the soluble compounds: K₂O, Na₂O, MgO and CaO. After stirring, the filtrate solution had constant pH (9.8) and conductivity (2.25 mS) with a TDS value of 1140 mg/L. Raw and washed FA shows a limited adsorption affinity for cadmium, copper and nickel as a result of high heterogeneity in the surface charge. Previous studies [8] proved that an optimum surface charge is obtained by using NaOH 2N as a modifier. The FA washed in ultrapure water was stirred for 48 h at room temperature with NaOH 2N solution (FA/NaOH 2N) followed by filtration, washing and drying, at 105–120 °C, till constant mass. This substrate was sieved and the 100 and 200 µm fractions were selected.

The FA crystalline structure was evaluated by XRD (Bruker D8 Discover Diffractometer) and AFM images (Ntegra Spectra, NT-MDT model BL222RNTE) were used for morphology studies; using the WSxM software, the pore size distribution was evaluated using the AFM data [9].

2.2. Adsorption experiments

Batch adsorption experiments were carried out under magnetic stirring, at room temperature (293 ± 1 K); considering that the solvent (water) vapour pressure at this temperature is low (0.023–0.024 bar), thermosetting was not necessary.

In all experiments, the initial MB concentration was fixed at 0.05 mmol/L, whereas the heavy metal concentration was varied up to 0.01 mol/L.

The optimal contact time was evaluated with the suspensions of 2 g FA/NaOH 2N in 100 mL of equimolar multi-cation solutions of cadmium, copper and nickel; aliquots were taken at certain moments (10, 20, 30, 45, 60, 90 and 120 min), when stirring was briefly interrupted and after decantation and filtration the volumes of supernatant were analyzed. The residual metal concentration in the aqueous solution was analyzed by AAS (Analytic Jena, ZEElit 700), at $\lambda_{Cd} = 228.8$ nm, $\lambda_{Cu} = 324.75$ nm and $\lambda_{Ni} = 232.00$ nm and

the MB concentration was evaluated by UV-vis spectrometry, on the calibration curve registered at the maximum absorption wave length ($\lambda_{MB} = 664$ nm) with PerkinElmer Lambda 25.

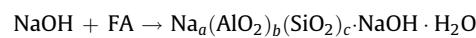
In all cases, the working pH was the natural value of the solutions, in the range of 4.8–5.3. Preliminary experiments proved that heavy metal losses due to the adsorption to the container walls and to the filter paper were negligible.

3. Results and discussions

3.1. The substrates

The XRD spectra (Fig. 1) show that the major components of fly ash are: carbon (graphite), SiO₂ in various structures (cubic and rhombohedra) combined with Al₂O₃ as rhombo H, mullite (3Al₂O₃·2SiO₂), along with γ -Al₂O₃, hematite (Fe₂O₃) and CaO. Anatas TiO₂ was also traced along with cadmium and copper compounds. Except for the alumina derivatives, the major components characterizing the raw fly ash were not removed in the modifying process. The aluminium oxide components vary from one type of substrate to another, and the alkali treatment (FA/NaOH 2N) can be responsible for partial dissolution processes.

Heavy metals and dyes removal on FA are pH dependent. The previous studies showed that the lowest Cd²⁺, Ni²⁺ and Cu²⁺ adsorption efficiency occurred when FA was treated with HCl 2N [5]; this effect is caused by a positive surface charge leading to repulsions between the surface ($\equiv SiOH_2^+$) and metal ions [10]. Moreover, silica and alumina form alumino-silicates with the pH-dependent structures. The interactions between the ash and sodium hydroxide solution are expected to be carried out according to the following reactions [11]:



when on the FA surface there can develop new active sites ($\equiv SiO^-$) and ($\equiv AlO^-$) which allow metals to form complexes at the surface (Eqs. (1) and (2)) [10]:



The MB may act as a supplementary complexion agent, which adsorbed on the FA surface can increase the affinity for heavy metals. Its almost planar structure, with three aromatic rings can act as an electron donor in the interaction with heavy metal cations.

These chemical and structural changes are mirrored in morphology modifications, resulting in large differences in the

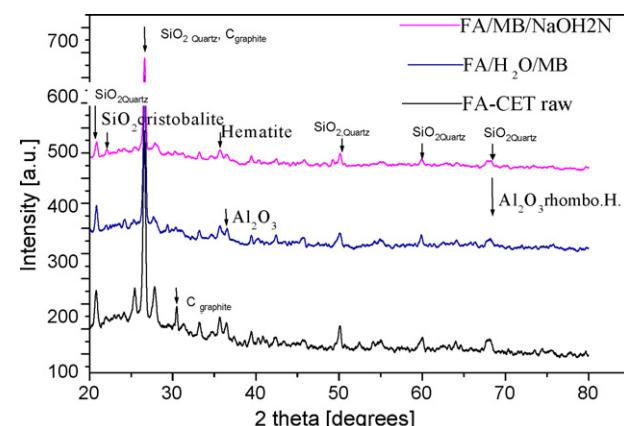


Fig. 1. XRD of raw FA, washed FA and FA modified with NaOH 2N.

Table 1
Fly ash composition.

FA composition [%]									
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	MnO	LOI ^a
53.32	22.05	8.97	5.24	2.44	2.66	0.63	1.07	0.08	1.58

^a LOI: loss of ignition.

substrates' affinity for heavy metals and dyes. Various pore size distributions and morphologies (Fig. 2) appear due to leaching of the alkaline and alumina oxides followed by the formation of new structures with an important role in heavy metals and MB adsorption.

3.2. Heavy metal adsorption

The adsorption efficiency, η , and capacity q_m were evaluated based on the optimal time and mass balance previously set:

$$\eta = \frac{(c_M^i - c_M^e) \times 100}{c_M^i} \quad (3)$$

$$q_m = \frac{(c_M^i - c_M^e) \times V}{m} \quad (4)$$

where c_M^i and c_M^e represent the initial and equilibrium heavy metal concentrations (mg/L), V the solution volume (L) and m is the amount of substrate (g).

The effect of the contact time on the efficiency of the heavy metal adsorption and MB is presented in Fig. 3a-d.

Single-component solutions, containing only one heavy metal cation can be well treated using modified FA even with a contact time of 30 min or less. This recommends the mixed (100 + 200 μm) modified FA substrate as appropriate for upscaling.

Two-component solutions of heavy metals and dye have different adsorption efficiencies as a result of two possible effects: (1) cation complexing, resulting in larger volume specie(s), thus with lower

diffusion rate towards the substrate, and/or (2) competitive adsorption between the cation species and the dye. In the first case, longer contacts would result in significant increase in the adsorption efficiency, which was not registered. The second effect is more likely and can suggest an affinity order of the species, towards the substrate: Cd > Ni > MB > Cu.

Multicomponent solutions, containing three heavy metals in the equimolar ratio and MB have a complex adsorption mechanism, with competition between the heavy metals and among these and the dye; the much lower efficiencies registered for cadmium and nickel can be the result of a competitive adsorption mainly among these two cations, having similar hydrated volume, with a small advantage for nickel. The strong increase in copper adsorption efficiency can be explained considering the largest MB affinity for the substrate; based on the results that the dye is firstly adsorbed on the substrate and then copper is adsorbed on this new layer, with good efficiency. The highest values registered in copper adsorption after 60 min (Fig. 3c) can be corroborated with the substrate saturation with MB (Fig. 3d). The larger affinity of the FA/MB substrate for copper can also be a result of smaller volume of copper, due to a lower hydration number. In aqueous media, heavy metal cations exist as hydrated complexes with a different number of water molecules. The ionic radii of the dehydrated and hydrated species are presented in Table 2, along with the hydration numbers for cadmium, copper and nickel. The hydrated structure of Cu(II) ion has been a subject of ongoing debate in the literature. Recent results [12] have shown that aqueous copper structures include not only 4–6 water molecules hydrated complexes but also clusters, containing

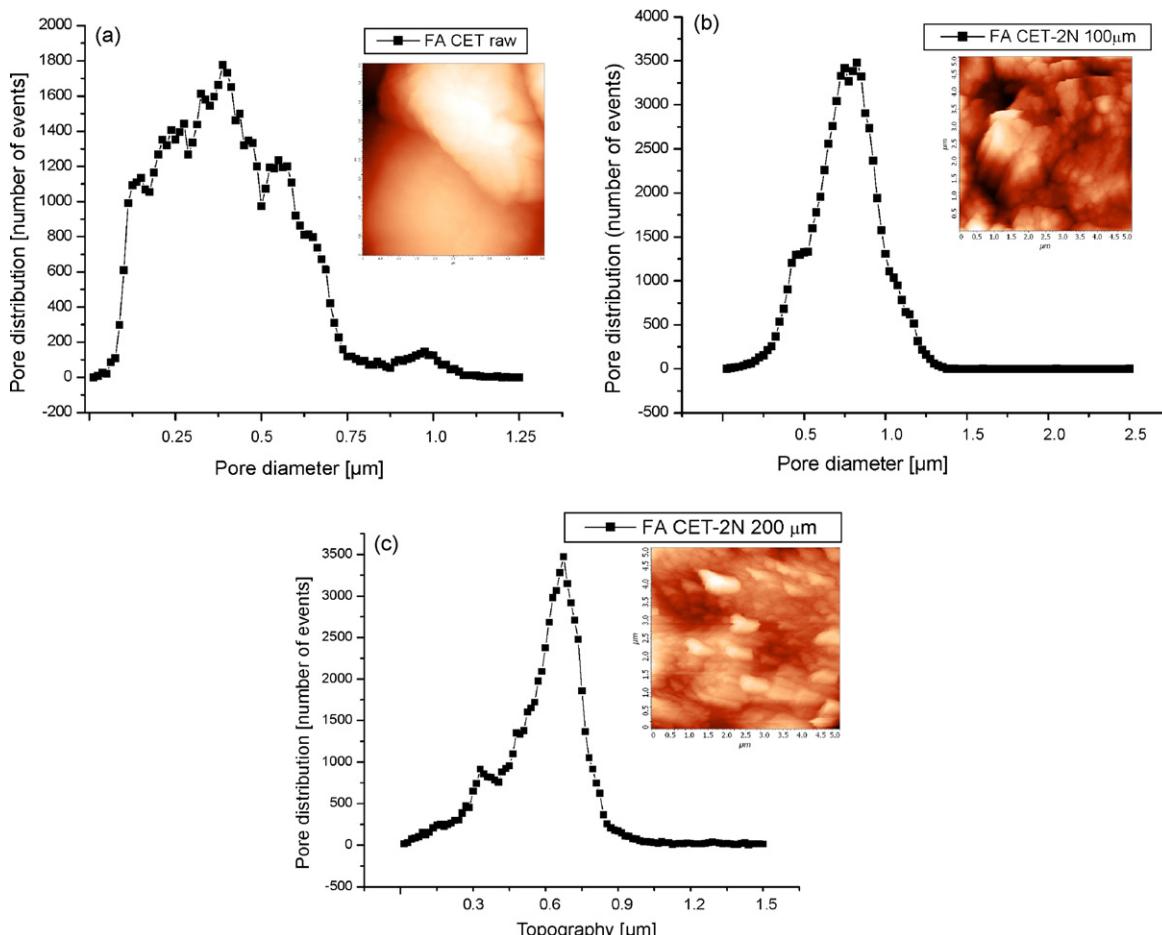


Fig. 2. The fly ash pore size distribution and morphology before and after treatment: (a) raw fly ash; (b) modified FA with NOH 2N, fraction 100–200 μm and (c) modified fly ash, fraction 0–100 μm .

Table 2

Properties of the dehydrated and hydrated heavy metal cations.

Heavy metal	Cadmium	Nickel	Copper
Dehydrated ionic radius [nm]	0.097	0.072	0.072
Hydration number	6	6	4–6
Hydrated ionic radius [nm]	0.426	0.425	0.295

up to 14 water molecules. Still, the slightly acid environment (working pH of 4.8–5.3) is responsible for low water coordination of copper, resulting in aqua-complexes with lower volume and higher mobility, compared to cadmium and nickel [13,14].

The data also show that the hydrated cadmium and nickel have a much lower affinity for the FA/MB substrate, showing for nickel actually an efficiency decrease for longer contact times, of 120 min (Fig. 3b). This can also be linked with the higher hydration number (and lower ionic degree) of these two cations. The results confirm the need for optimising the process parameters if industrial applications are targeted.

The substrate influences the adsorption process not only through its composition but also through the porosity. The 200 µm FA fraction, with narrow pore size distribution and a maximum pore diameter of 746 nm leads to better adsorption

efficiencies for both cadmium and nickel. The 100 µm fraction has smaller grains, with a broader pore distribution, centred on 842 nm, mainly as a result of the initial composition, containing predominantly soluble oxides, with lower mechanical strength. On this substrate, copper reaches adsorption efficiencies of 90% after 45 min., the values obtained on the 200 µm fraction only after 120 min of contact time. The results can lead to the conclusion that, in the defined experimental conditions, the most important factor is the substrate composition, corroborated with the heavy metal cation type and hydration.

The heavy metal adsorption could well be described by the Langmuir model [15], Eq. (5):

$$\frac{c_M^e}{q} = \frac{1}{q_m a} + \frac{c_M^e}{q_m} \quad (5)$$

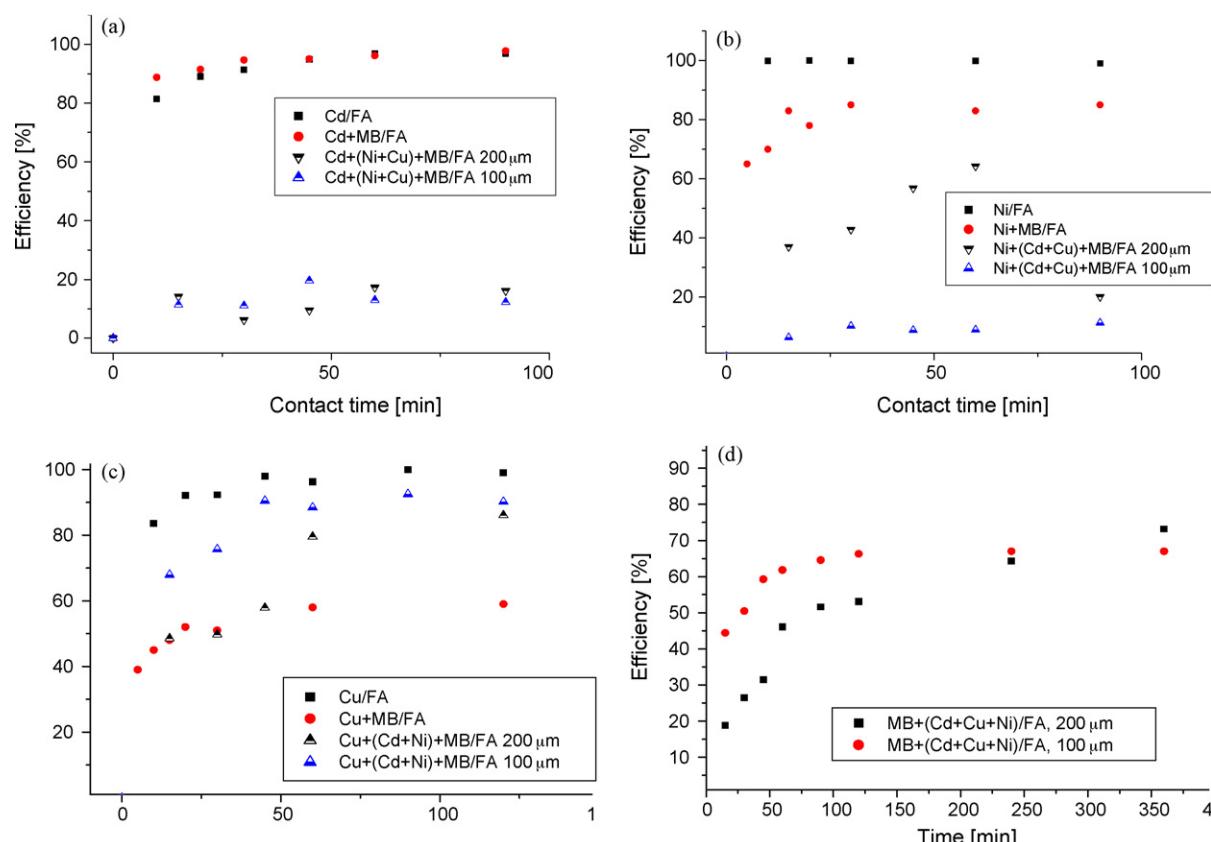
where a is the Langmuir constant related to binding energy, the affinity between the adsorbent and adsorbate, q represents the mass adsorption coefficient, whereas q_m is the maximum value of it.

The monolayer adsorption fits well with the efficiency data that show saturation after a rather limited contact time (during these experiments the contact time was set at 60 min). The Langmuir parameters are presented in Table 3.

Table 3

Langmuir parameters for the heavy metal adsorption from multicomponent systems.

	Cu/(Cd + Cu + Ni + MB)		Cd/(Cd + Cu + Ni + MB)		Ni/(Cd + Cu + Ni + MB)	
	FA-100 µm	FA-200 µm	FA-100 µm	FA-200 µm	FA-100 µm	FA-200 µm
q_m [mg/g]	12.78	10.18	6.36	3.77	1.25	1.66
a [l/mg]	0.0041	0.0123	0.0150	0.4041	0.7214	0.0936
R^2	0.9969	0.9972	0.9997	0.983	0.9983	0.9988

**Fig. 3.** Time influence on the adsorption efficiency from mixed solutions, for (a) cadmium; (b) nickel; (c) copper and (d) methylene blue.

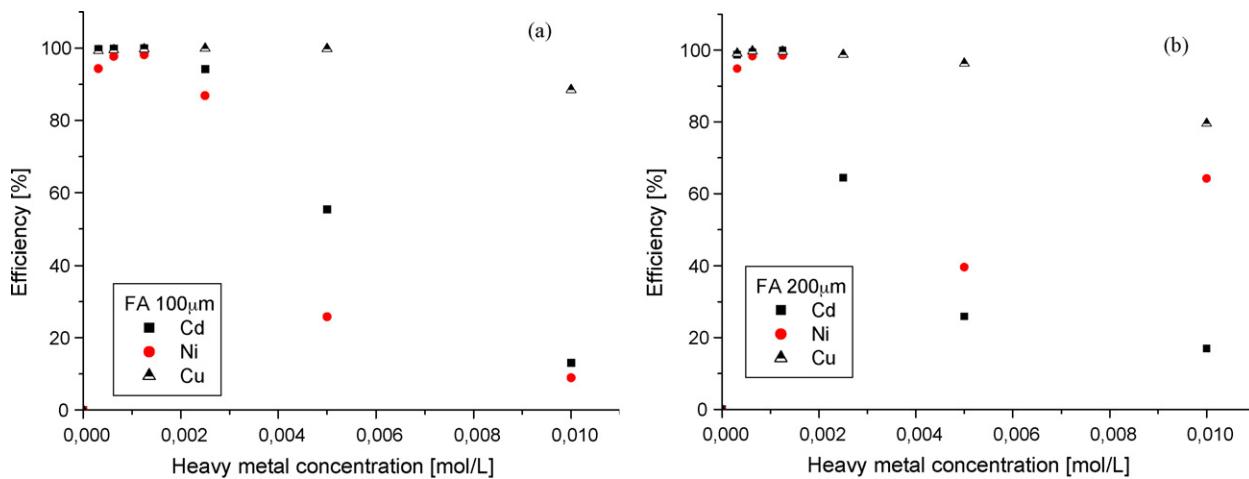


Fig. 4. Concentration influence on the adsorption efficiency on FA fractions: (a) 100 μm and (b) 200 μm .

Table 4
Kinetic parameters of the heavy metal adsorption.

Parameter	Cu/(Cd + Ni + Cu + MB)		Cd/(Cd + Ni + Cu + MB)		Ni/(Cd + Ni + Cu + MB)	
	FA-100 μm	FA-200 μm	FA-100 μm	FA-200 μm	FA-100 μm	FA-200 μm
q_e [mg/g]	13.2	11.3	3.7	3.8	1.6	2.6
k_2 [g/mg min]	0.247	1.176	0.556	5.194	4.224	0.309
R^2	0.9962	0.9946	0.8897	0.9658	0.9577	0.9568

Similar efficiency variations are obtained on both types of substrates: FA/NaOH 2N 100 and 200 μm , proving that the surface composition and charge play a key role and that morphology/porosity is of secondary importance.

High adsorption efficiencies are registered for Cd^{2+} , Cu^{2+} , Ni^{2+} and MB concentrations up to 0.001 mol/L on FA/NaOH 2N for 100 and 200 μm size as Fig. 4a and b shows.

3.3. Uptake kinetics of heavy metals

The metal uptake q_e (mg/g) was determined using the initial and momentary heavy metal concentrations:

$$q_e = \frac{(c_M^i - c_M^t) \cdot V}{m_s} \quad (6)$$

Different kinetic adsorption mechanisms were tested (pseudo-first order, interparticle diffusion) but only the pseudo-second order kinetics could well model the processes [16]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where k_2 is the pseudo-second order rate constant of adsorption ($\text{g}/(\text{mg min})$) and can be evaluated from the slope of the plot. This supports the idea of a substrate with the number of active sites in the same order of magnitude with the maximum amount of adsorbed species. Based on the linearization of the equation developed by Ho and McKay [17] the kinetic parameters were calculated and are presented in Table 4.

The maximum adsorption capacity, evaluated based on the Langmuir model and using the pseudo-second order kinetic have close values. The data show large adsorption capacity, in the experimental conditions, for the copper ion. Another important finding is that copper adsorption is rather slow compared to cadmium thus good efficiencies can be reached only at rather long contact times. The results confirm that both FA fractions have almost the same affinity, thus sieving is actually not necessary.

4. Conclusions

- Simultaneous removal of the methylene blue dye and cadmium, copper and nickel is possible on fly ash modified with NaOH 2N. A contact time of 60 min is convenient for reaching the maximum efficiencies.
- The dye adsorbs on FA and, on this new surface copper exhibits a higher affinity for the active sites compared to cadmium and nickel. The reason may be the higher mobility and ionic degree of the copper tetra-hydrated complex, compared to the hexa-complexes of Cd and Ni, at the working pH of 4.8–5.3.
- The efficiency of heavy metal adsorption does not depend on the FA fraction used. This becomes significant for the adsorption of large molecules, as it is MB.
- The pseudo-second order kinetics describes well all the processes. Large adsorption capacities are registered for copper, confirming its higher affinity for the substrate.
- High adsorption efficiencies are registered for heavy metal concentrations up to 0.01 mol/L, recommending the FA substrate for simultaneous removal of heavy metals and MB from wastewaters originating from dyes industry.
- Further combination of this substrate with a photocatalyst can lead to full removal of the dye.

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