Concurrent dyes adsorption and photo-degradation on fly ash based substrates

M. Visa · L. Andronic · D. Lucaci · A. Duta

Abstract Most of the dyes are organic compounds, with different degree of polarization and different groups with various steric effects, making their complete biodegradation slow or even impossible. Adsorption on fly ash and fly ash based substrates represents a possible alternative for simultaneous removal of dyes and heavy metals form wastewaters resulted in the textile industry. Adsorption (under visible light) and adsorption and photodegradation (under UV irradiation) studies were done on Methylene blue solutions and on their mixtures with heavy metals (copper and cadmium), in systems using fly ash as single substrate, or mixed with a wide band gap semiconductor (TiO_2). The titanium oxides and hematite content in fly ash proved to be responsible for photodegradation processes even in the absence of the TiO_2 powder, confirming that modified fly ash is a viable candidate in developing up scalable processes for advanced wastewater treatment. The kinetic and thermodynamic studies allow to calculate the parameters and to describe the complex mechanisms, involving competitive adsorption.

Keywords Fly ash · TiO_2 · Adsorption · Wastewater treatment

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1 Introduction

The textile industry is using large amounts of water in various processes (dying, rinsing, finishing) and is one of the major source of industrial wastewaters. Day to day discharge of excess wastewater with chemical complex composition (residual dyes, heavy metals, surfactants, synthetic detergents), as result of improper wastewater treatment has serious consequences over flora, fauna and human health due to the unbalance in the oxygen content. Although most of the dyes are organic compound, their complete biodegradation is slow or even impossible, since many of them have structures with aromatic rings.

Pollution by heavy metals usually comes from several industries such as the electroplating industry, rechargeable batteries, fertilizers, pesticides but also from pigments, dyes and textile operations.

To avoid the ecological flora, fauna and health problems many methods were developed for removing dyes and heavy metals: surface adsorption, chemical precipitation, coagulation and flocculation, ion-exchange, reverse osmosis, membrane nanofiltration membranes (Bowen and Welfoot 2002).

The adsorption technologies have many advantages: easy operation, inexpensive equipments, limited amounts of sludge, the adsorbents regeneration. The quality of adsorbent plays a key role and during the past years the use of substrates based on raw and modified wastes received plenty attention because it simultaneously solves two problems: the wastewater treatment and the identifying of new application as second raw materials. Suitable adsorbents for dyes and/or heavy metal removal were reported to be the red mud (Wang et al. 2005b), natural zeolite (Perić et al. 2004), peat (Ho and McKay 2004), sugar beet pulp (Mata et al. 2009), and bone char (Cheung et al. 2001). Other no conventional sorbents from agriculture have been tested for

removal colour and heavy metals from wastewater such as apple pomace and wheat straw, coir pith, corncobs or barley husks (Crini 2006).

Fly ash (FA) results in large amounts from coal burning, in the central heat and power plants (CPH). It is the fine grained fraction, collected in the electrofilters and about 60% of it is used in concrete manufacturing (Ahmaruzzaman 2010). Recent studies (Wang et al. 2005a, 2005b) show that various fly ash samples with different un-burnt carbon contents collected from CPH, can be used for sequential adsorptions of Methylene Blue, Crystal Violet, Methyl Orange, basic dyes and CI Reactive Red 49 in aqueous solution, because the priorities compounds from fly ash favors the heavy metals adsorption and act as active sites in dyes' adsorption processes.

Previous studies investigated the FA for removing heavy metals (cadmium, cooper, zinc, nickel, iron) and dyes (Methylene blue and methyl orange) from wastewaters resulted from the dye finishing industry; the results showed that raw fly ash has limited efficiency, thus fly ash surface was modified with 1N, 2N, 4N NaOH solution (Visa and Duta 2007), with NaOH and Methylene blue (Visa and Duta 2010a, 2010b) and with Methyl Orange (Visa et al. 2009).

The photocatalytic oxidation is an advanced oxidation process involving UV exposure in a system containing a wide band gap semiconductor. Optimized solutions for methylorange and Methylene blue photodegradation were previously reported using TiO_2 (Andronic and Duta 2008) and WO_3 (Visa and Duta 2010a, 2010b). The addition of oxidation agents (H_2O_2) strongly improves the process efficiency (Andronic et al. 2008) and this could be further enhanced by adding $Fe^{2+/3+}$ systems (Photo-Fenton system).

The partial or total replacement of the photo-catalyst with a compound having much lower cost, e.g. FA, while conserving the overall process efficiency represents a target that is approached in this study. For advanced removal of heavy metals and dyes we propose a novel technology based on a single step process, combining adsorption and photodegradation on FA and/or on a FA mixture with 25% TiO_2. The experiments were done on solutions containing heavy metals (cadmium and copper) and Methylene Blue (MB).

2 Experimental

2.1 The substrate

All fly ash samples are composed of glass-like porous beads, varying in chemical composition of the (a) water stable compounds (SiO_2, Fe_2O_3, Al_2O_3, TiO_2), (b) compounds with limited water solubility ($MeSO_4$, $MeBO_3$, etc.), and (c) highly soluble water compounds, mainly metal—oxides e.g. CaO, MgO, K_2O, Na_2O. Thus, the composition is mainly of

Table 1 Fly ash composition

FA Composition [%]									
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	Graphite
53.32	22.05	8.97	5.24	2.44	2.66	0.63	1.07	0.08	1.58

oxide type and the surface, although heterogeneous, has a predominant negative charge that favors heavy metals adsorption and contains active sites in the dyes' adsorption processes. The major oxides from fly ash with role in heavy metals and dyes removal are presented in Table 1. The raw fly ash was collected from the electro-filters of the CPH plant in Brasov (FA) Romania. The sum of the SiO_2, Al_2O_3 and Fe_2O_3 is above 70% (Lee and Deventer 2002), thus according to the ASTM standards, the FA is of type F and does not agglomerate in water.

The soluble compounds from raw fly ash (K_2O, Na_2O, MgO, CaO) were removed by stirring 100 g raw FA in 1000 mL ultra pure water, at room temperature, for 48 h, till the filtrate solution reached a constant pH (7.8).

Raw and washed FA show a limited adsorption affinity for heavy metals as result of a high heterogeneity in the surface charge. Previous studies (Visa and Duta 2007) proved that an optimum surface charge is obtained by using NaOH 2N as modifier. The washed FA was further stirred 48 hours at room temperature with NaOH 2N solution (FA/NaOH) followed by filtration, rinsing and drying, at 105–120 °C, till constant mass. This substrate was sieved and the 40–100 μm fraction was selected as substrate for the experiments.

A mixed substrate was prepared by adding the TiO_2 powder (Degussa P25, 80% anatase and 20% rutile) to the FA/NaOH. Previous experiments sowed that the optimized composition for heavy metals adsorption is at a FA/NaOH:TiO_2 ratio of 3:1 (Visa and Duta 2010a, 2010b).

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 (Horcas et al. 2007). Fly ash porosity and BET surface area was evaluated using a "Tri Star II 3020"—Micromeritics analyzer.

2.2 Adsorption experiments

Batch adsorption experiments were done at room temperature, under magnetic stirring, in visible light. The adsorption mechanisms and the kinetic data were evaluated on two types of suspensions:

(a) 1 g FA/NaOH in 25 mL;
(b) (0.75 g FA/NaOH + 0.25 g TiO_2) in 25 mL of complex solution of $CdCl_2$ (Cd^{2+}, 0–550 mg/L) with MB, or $CuCl_2$ (Cu^{2+}, 0–380 mg/L) with MB.

For the kinetic studies, aliquots were taken at certain moments (up to 240 min), when stirring was briefly interrupted and, after filtration on 1.5 μm filter, the supernatant was analyzed.

The residual metal concentration in the aqueous solution was analyzed by AAS (Analytic Jena, ZEEnit 700), at $\lambda_{Cd} = 228.8$ nm, $\lambda_{Cu} = 324.75$ nm.

2.3 Photocatalysis

Photodegradation studies were done on similar FA/NaOH and FA/NaOH:TiO$_2$ suspensions, under UV irradiation, using quartz glasses. The home-made reactor is equipped with three F18W/T8 blacklight tubes (Philips), emitting UVA light, typically 340–400 nm, with λ_{max} (emission) = 365 nm.

The MB solution (0–0.05 mM) was prepared dissolving the MB powder in ultra pure water. The initial and residual concentration were evaluated by UV-VIS spectrometry, on the calibration curve registered at the maximum absorption wave length ($\lambda_{MB} = 665$ nm), with a Perkin Elmer Lambda 25.

All the results obtained under visible light are denoted with (A), while the results obtained under UV irradiation have the (F) symbol.

In all experiments the natural pH was used. The pH value of the MB solutions in contact with FA/NaOH was 10.6 and in contact with the mixed system of FA/NaOH + TiO$_2$, the pH value was 10.1. Adding heavy metal salts in the MB solutions did not alter these pH values.

Preliminary experiments proved that heavy metals and MB losses due to 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 SiO$_2$ (quartz, cristobalite) combined with Al$_2$O$_3$ (as rhombo H, mullite and γ-Al$_2$O$_3$), along with bixbyite (Mn$_2$O$_3$), CaO and K$_2$O. The XRD data also show that FA contains small amounts of titanium oxide (as brookite and as non-stoichiometric Ti$_4$O$_7$) thus indicating a possible photocatalyitic activity. Supplementary, hematite (Fe$_2$O$_3$) was identified, as a possible in-situ Photo-Fenton generator. The unburned carbon graphite, as micro-sized crystallites represents a significant part of the FA and can explain the versatility of this material in various adsorption processes as also reported by Hsieh and co-workers (2000).

These components are characterizing both the raw and the modified FA. As reference, there is also presented the crystalline modifications of FA when MB is adsorbed followed by alkali treatment, FA/MB/NaOH (Visa and Duta 2009).

The alkali treatment (FA/NaOH) is responsible for the partial dissolution/ re-precipitation processes of the major components (alumina and silica) but the unburned carbon resulted as graphite, the titanium and iron oxides content does not significantly vary during the FA conditioning.

Most of the interactions between the ash and sodium hydroxide solution at room temperature (25 °C) are expected to adsorb water and alkali ions, according to the following reaction (Shawabkeh et al. 2004):
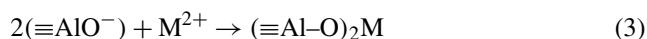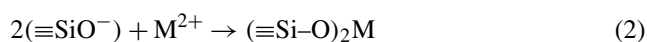
$$NaOH + FA \rightarrow Na_a(AlO_2)_b(SiO_2)_c \cdot NaOH \cdot H_2O \qquad (1)$$
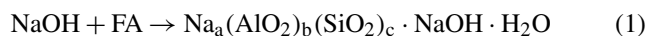
Further, on-surface reactions on FA can develop new active sites ($\equiv$SiO$^-$) and ($\equiv$AlO$^-$), allowing metals to form com-

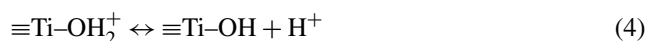**Fig. 1** XRD of raw FA and FA modified with NaOH 2N and MB
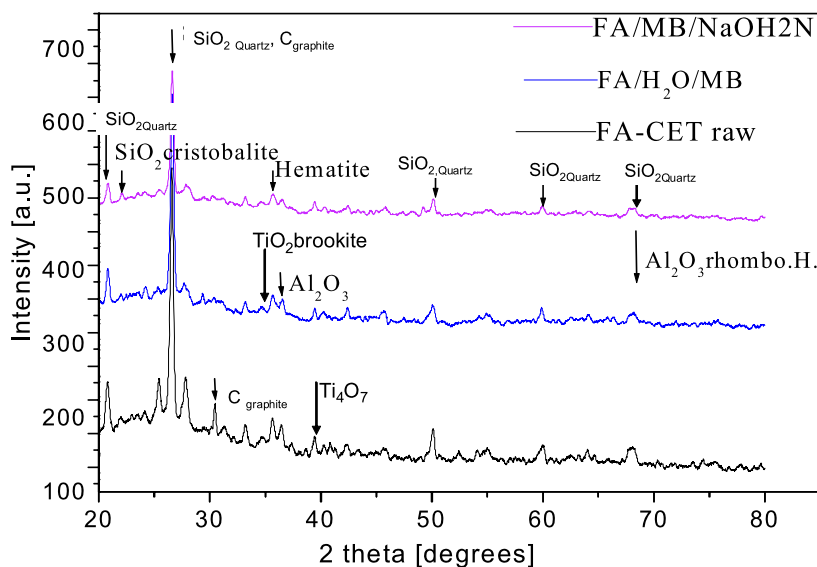
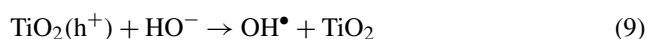plexes (2), (3), as presented by Chaizasith and co-workers, (2006):

$$2(\equiv SiO^-) + M^{2+} \rightarrow (\equiv Si-O)_2 M \qquad (2)$$

$$2(\equiv AlO^-) + M^{2+} \rightarrow (\equiv Al-O)_2 M \qquad (3)$$

According to the "site binding" theory, the surface charge on the metal oxides is created by the electrolyte ions adsorption, in protolytic equilibrium. These processes for TiO_2 can be described by the following equations (Janusz and Matysek 2006):

Adsorption:

$$\equiv Ti-OH_2^+ \leftrightarrow \equiv Ti-OH + H^+ \qquad (4)$$

$$\equiv Ti-OH \leftrightarrow \equiv Ti-O^- + H^+ \qquad (5)$$

$$\equiv Ti-OH + Ct^+ \leftrightarrow \equiv Ti-O^- Ct^+ + H^+ \qquad (6)$$

Were Ct^+ is heavy metal cation.

Photocatalysis:

$$2TiO_2 + h\nu \rightarrow TiO_2(h^+) + TiO_2(e^-) \qquad (7)$$

$$TiO_2(h^+) + H_2O \rightarrow OH^\bullet + H^+ + TiO_2 \qquad (8)$$

$$TiO_2(h^+) + HO^- \rightarrow OH^\bullet + TiO_2 \qquad (9)$$

In the FA/NaOH :TiO_2 mixture, simultaneous processes can occur:

– titanium oxide can be contaminated with alkali groups, if the zero charge point (pH_{pzc}) is higher than 6.2. Two consequences, with opposite results are thus expected: (1) the heavy metals enhances their adsorption, leading to competition with MB and (2) increase in the amount of HO radicals, the active species in MB photodegradation.
– on FA, the adsorbed MB supplementary may act as a complexion agent, increasing the affinity for heavy metals. Its almost planar structure, with three aromatic rings can act as an electron donor in the interaction with the heavy metals cations, Fig. 2.

These chemical and structural changes are mirrored in morphology modifications, resulting in large differences in the substrates' affinity for heavy metals and dyes.

The FA/NaOH specific surface is 10.95 m^2/g, and has an average pore diameter of 25 nm. The Degussa P25 TiO_2 has a high BET surface area (55 ± 15 m^2/g) and an average pore diameter of 30 nm.
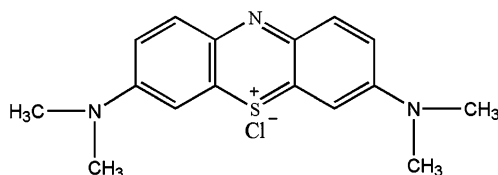
Fig. 2 Chemical structure of Methylene blue

Based on the results presented by Otero and co-workers (2008), AFM data were used to get supplementary information about the FA pore association, density and size distribution. The various roughness values, Fig. 3, appear due to
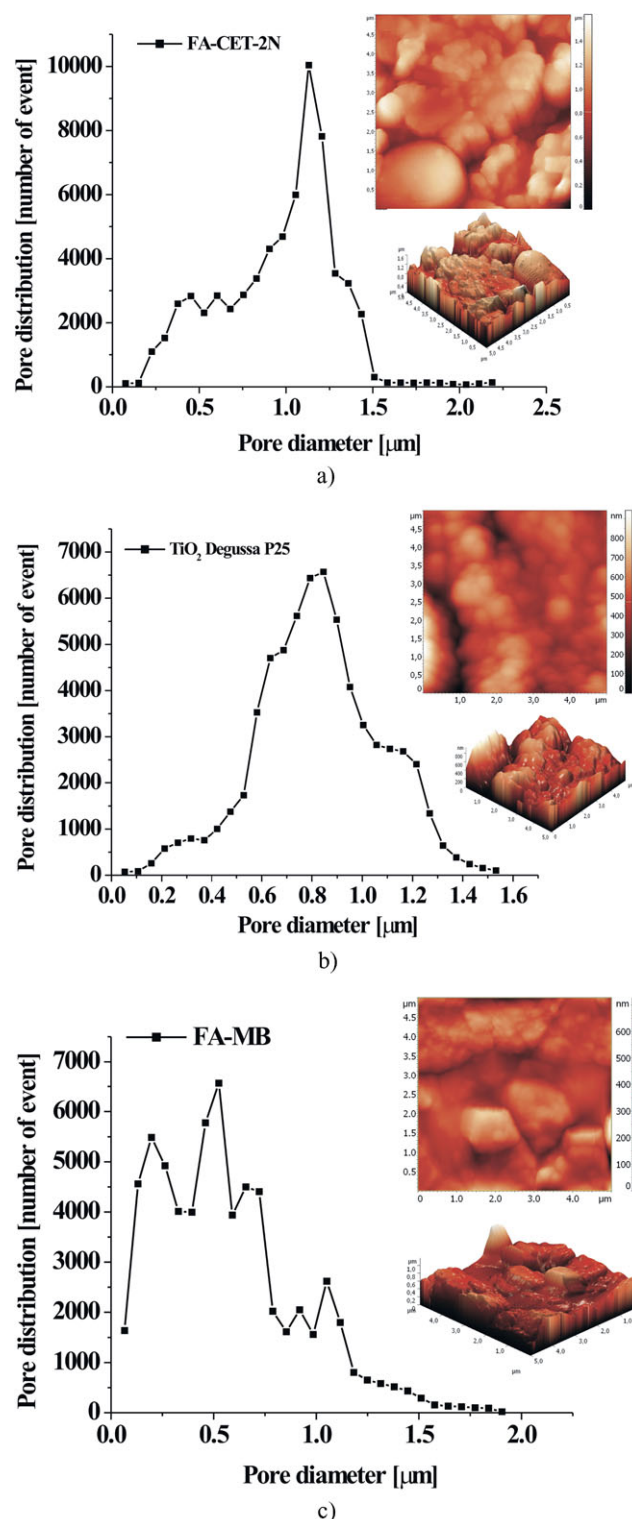
Fig. 3 The AFM topography and pore size distribution: (**a**) FA/NaOH before adsorption; (**b**) TiO_2 before adsorption; (**c**) FA/NaOH/MB
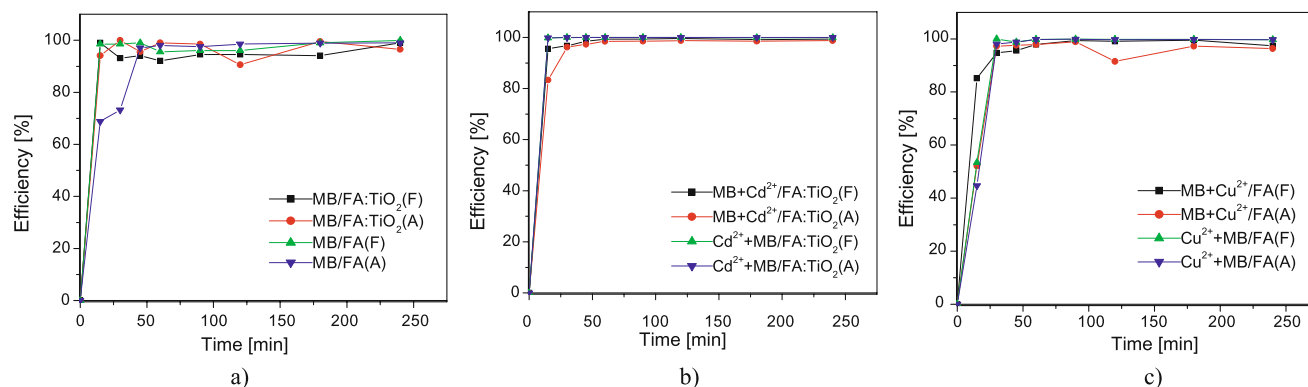
Fig. 4 Adsorption efficiency vs. time from: (**a**) MB, (**b**) Cd^{2+} (+MB) and (**c**) Cu^{2+} (+MB) solutions

leaching of the alkaline oxides and formation of new structures with important role in the heavy metals and MB adsorption.

The surface data prove that open pores associations are likely, resulting in average roughness ranging from 82 nm (TiO$_2$), up to 160 nm (FA/NaOH). Non-uniform MB adsorption is confirmed by the broad roughness distribution, Fig. 3c (corresponding to an average roughness of 106 nm).

3.2 Heavy metals and dye adsorption

The adsorption efficiency, η, was evaluated based on the concentrations of the metal (c_M) and respectively of the dye (c_{MB}) measured at the initial moment (superscript "i") and at time, (superscript "t"):

$$\eta = \frac{(c_M^i - c_M^t) \times 100}{c_M^i} \tag{10a}$$

$$\eta = \frac{(c_{MB}^i - c_{MB}^t) \times 100}{c_{MB}^i} \tag{10b}$$

The results are presented in Fig. 4(a)–(c).

Good removal efficiencies are obtained in all cases after 45 min., and further thermodynamic studies used this optimized contact time. In industrial application this optimized contact time is feasible for a dynamic flow process; supplementary, because the discharge limit for the heavy metal is very low (0.5 ppm), very high adsorption efficiencies are required, for setting up a single-step wastewater treatment processing.

The data outline that adsorption is a significant part of the MB photodegradation mechanisms as Fig. 4a shows and the increased efficiencies, obtained after 1 hour of UV irradiation support the assumption that modified FA can also act as photocatalyst and/or Photo-Fenton partner. The adsorption efficiency is little depending on the initial concentration
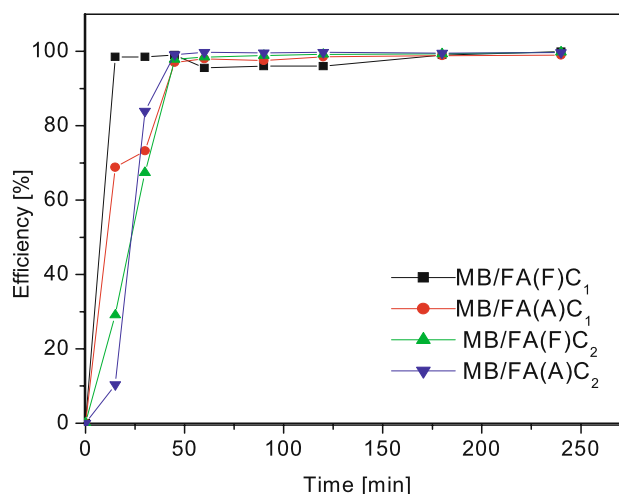

Fig. 5 Influence of the concentration of MB

($C_1 = 0.0202$ mMol/L and $C_2 = 0.0454$ mMol/L), as presented in Fig. 5.

On mixed substrates (FA/NaOH:TiO$_2$ = 3:1) the heavy metal removal efficiencies are also very good, result of the negatively charged surface of both absorbents. The copper and cadmium adsorption from single-component solutions is not affected by UV radiation (set (F), compared to tests run under visible light (set (A). Copper solutions proved to be sensitive to MB addition and the faster efficiency increase under UV irradiation can be the result of an activated FA surface due to the OH ion/radical equilibrium. The particular copper ion behavior in adsorption was previously reported and explained (comparing to cadmium and nickel) by its lower hydration radius (Visa et al. 2010). An interesting result is that MB removal is less efficient on the substrates mixture comparing to FA under UV irradiation, consequence of competitive processes.
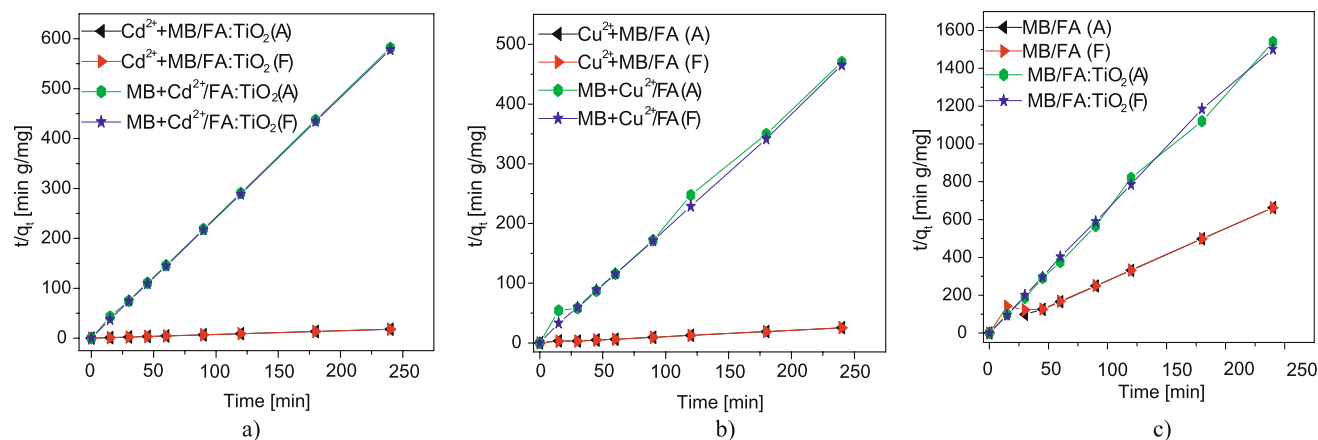
Fig. 6 The pseudo second-order kinetics of: (**a**) Cd^{2+} (+MB), (**b**) Cu^{2+} (+MB), (**c**) MB adsorption on FA/NaOH and FA/NaOH:TiO$_2$ substrates

Table 2 Kinetic parameters of the MB adsorption (A) and photodegradation + adsorption processes (F)

Parameter	MB		MB		MB/(MB + Cd)		MB/(MB + Cu)	
	(A)	(F)	(A)	(F)	(A)	(F)	(A)	(F)
Adsorbent	FA	FA	FA + TiO$_2$	FA + TiO$_2$	FA + TiO$_2$	FA + TiO$_2$	FA	FA
q_e [mg/g]	0.366	0.387	0.156	0.157	0.415	0.416	0.518	0.522
k_2 [g/mg min]	6.200	32.523	1.400	11.605	3.214	1.171	5.535	1.284
R^2	0.999	0.979	0.998	0.998	0.999	1	0.996	0.999

3.3 Uptake kinetics of the heavy metals and dye

The adsorption capacity, q_t, from a V solution volume, on an m_s amount of substrate (adsorbent), was evaluated using (11):

$$q_t = \frac{(c_{M/MB}^i - c_{M/MB}^t) \times V}{m_s} \quad (11)$$

The pseudo-second order kinetics (Ho and McKay 1999) could well model the processes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

where: k_2 is the pseudo second-order rate constant of adsorption (g mg^{-1} min^{-1}), q_e and q_t are the amount of heavy metals ions adsorbed per unit mass of the adsorbent (mg/g) at equilibrium time and time t, respectively.

The pseudo-first order kinetic, the interparticle diffusion mechanism and the Langmuir-Hinshelwood model were also tested, without positive results.

Based on (12) linearization, the kinetic curves were plotted (Fig. 6) and the kinetic parameters were calculated, as presented in Tables 2 and 3. Figure 6a shows the curve-fitting plot of the second-order adsorption process of the cadmium cation from solutions also containing MB on the mixed substrate FA/NaOH: TiO$_2$, Fig. 6b presents similar results for the copper ion, while Fig. 6c presents

Table 3 Kinetic parameters of the heavy metal removal

Parameter	Cd/(Cd + MB)		Cu/(Cu + MB)	
	(A)	(F)	(A)	(F)
Adsorbent	FA + TiO$_2$	FA + TiO$_2$	FA	FA
q_e [mg/g]	13.48	13.487	9.69	9.65
k_2 [g/mg min]	0.0007	0.0006	0.47	0.32
R^2	1	1	0.994	0.997

the kinetic data for the MB adsorption on FA/NaOH and FA/NaOH:TiO$_2$, respectively. Experiments were carried out under visible light, when only adsorption (A) can be expected and under UV illumination when also photocatalysis (F) can be employed.

The maximum uptake values for MB are much lower compared to those corresponding to copper and cadmium, but this does not lower the process viability since the usual concentration ratio between the dyes and the heavy metal concentration is 1:1000 in the wastewaters resulted in the textile industry. On the other hand, for MB the rate constants are high, especially under UV irradiation as result of adsorption followed by photodegradation. The highest value, obtained in the FA/NaOH–UV system may confirm the assumption of parallel adsorption, semiconductor photocatalysis and photo-Fenton processes, with comparable rates and with an amount of active sites comparable with the amount of species involved in the mechanisms (as the
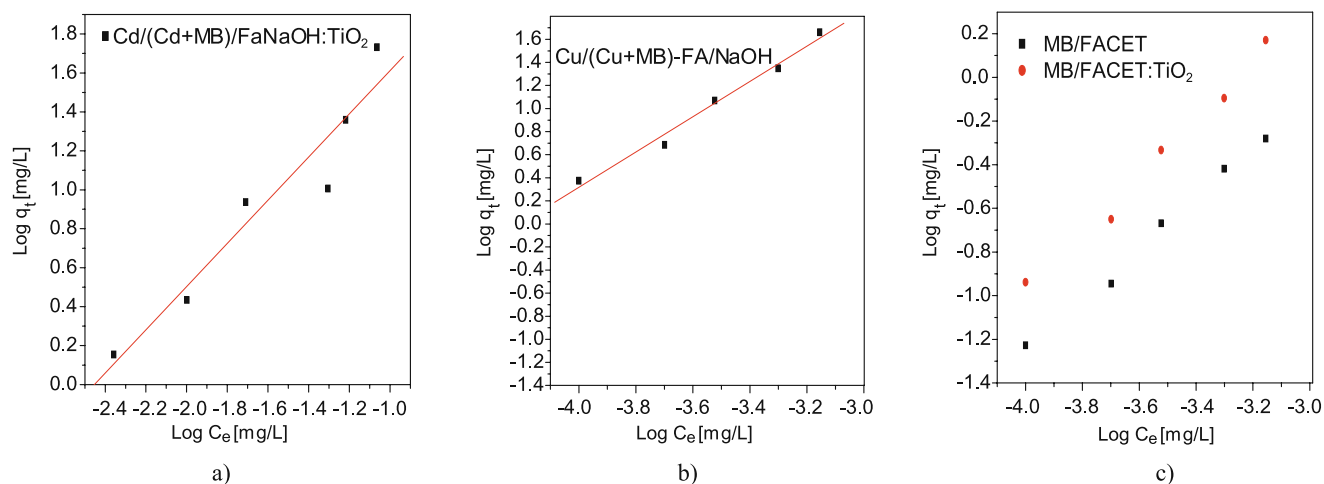
Fig. 7 The Freundlich plots for (**a**) Cd^{2+} adsorption from solutions also containing MB, (**b**) Cu^{2+} adsorption from binary solutions with MB (**c**) MB adsorption on FA/NaOH and on FA/NaOH:TiO_2 substrates

Table 4 Freundlich parameters for the heavy metals and MB adsorption from binary systems

Parameter	Cd/(Cd + MB)		Cu/(Cu + MB)		MB	MB/(MB + Cu)
Adsorbent	FA + TiO_2	FA	FA + TiO_2	FA	FA + TiO_2	FA
n	0.902	0.242	1.837	0.688	1.358	0.866
k_f	186.21	1819.70	1.20	321.07	131.13	2375.74
R^2	0.925	0.922	0.956	0.963	0.926	0.994

pseudo-second order kinetic defines). Copper may activate the adsorption system containing MB but the resulted complexes are slowly degraded under UV.

3.4 Heavy metals and dye adsorption isotherms

The heavy metals and MB adsorption data were obtained under visible light, when no photodegradation is expected. The data could not be described using the Langmuir model but could well be fitted using the Freundlich equation:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln c_e \tag{13}$$

where c_e is the equilibrium concentration, (mg/L) and q_e the amount of heavy metal ions adsorbed per unit mass of the adsorbent (mg/g) at equilibrium, k_f is Freundlich constant and is an indicator of the adsorption capacity, while the $1/n$ dimensionless parameter is a measures of the adsorption density. The Freundlich adsorption isotherms applied to the removal of Cd^{2+}, Cu^{2+} and MB from binary systems on the two types of substrates are presented in Fig. 7.

The adsorption parameters are presented in Table 4.

The substrates heterogeneity is high even when using FA and the complex adsorption mechanisms are confirmed. The Freundlich parameters indicate various adsorption affinities of the substrate(s) for the solution components with a net superiority of the modified FA.

4 Conclusions

Comparative studies developed on alkali modified FA and its mixture with TiO_2 were developed to identify the potential of these substrates for the simultaneous removal of a dye (Methylene blue) and a heavy metal (cadmium and copper, respectively).

The FA structural and morphology analysis showed that the crystalline oxides composition can be tailored by the NaOH 2N treatment, resulting in negatively charged surfaces, with open, interconnected pores, efficient in removing both the dye and the heavy metals. Under UV irradiation the dye decomposition reaches the highest efficiency, has the highest rate constant and proves a good substrate affinity supporting the assumption of FA photocatalytic activity as result of the titania and hematite content. When heavy metals are included in this system, a weak efficiency decrease is registered but the results are still very good.

The TiO_2 addition does not improve the results; therefore, we may conclude that single, modified fly ash substrates are potential low-cost, efficient substrates for the treatment of the wastewaters resulted from dyes finishing industry.

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