



Advanced treatment of wastewater with methyl orange and heavy metals on TiO₂, fly ash and their mixtures

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ARTICLE INFO

Article history:

Available online 3 March 2009

Keywords:

TiO₂
Fly ash
Methyl orange
Heavy metal

ABSTRACT

Dyes and heavy metals represent common, dangerous pollutants, resulting in large quantities in the textile finishing industry. Advanced removal of heavy metals is usually proposed via adsorption and the use of modified fly ash represents a sustainable solution. Photodegradation of dyes using anatase is largely studied and represents a process that can be up-scaled. For wastewater containing both heavy metals and dyes, an obvious treatment technology is thus the association of modified fly ash with anatase. During this process, the substrates are loaded with both pollutants and their efficiency must be quantified under these conditions. The study presents the results obtained in Cd²⁺ and Cu²⁺ removal, using fly ash (FA) with dye modified surface and its mixtures with TiO₂. The FA morphology is characterised using AFM while XRD provides the crystallinity data. The adsorption parameters (contact time, wastewater volume:adsorbent mass ratio) were optimized and the adsorption mechanisms are discussed. The experimental results indicate that adsorption of cadmium and copper ions can be significantly improved by using mixtures of FA with TiO₂. The best adsorption efficiency is registered on mixture with 25% of TiO₂.

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1. Introduction

Various methods were proposed to remove heavy metals from wastewater: biosorption using microbial cells [1], electrodialysis, electroflotation, air flotation, flocculation, chemical precipitation, ion exchange, ultrafiltration, phytoextraction, reverse osmosis and ozone oxidation, adsorption on activated carbon/natural zeolites [2], electron beam and gamma irradiation [3]. These methods are considered competitive and effective for heavy metals removal at trace quantities but the high costs restrict their applicability; thus research focuses on low cost, up-scalable solutions.

Adsorption of heavy metals and dyes on fly ash (FA) is studied as a sustainable, low-cost solution [4], while heavy metals adsorption is investigated onto TiO₂ [5], and ternary titanium based compounds like titanates [6]. Photodegradation of dyes using anatase is largely studied [7], and represents a process that can be up-scaled. For wastewater containing both heavy metals and dyes, an obvious treatment technology is the association of modified FA with titania. This makes the process more complex because heavy metals can adsorb on TiO₂ while dyes can be bonded on FA, resulting in modifications in the processes efficiencies.

The paper presents the results of heavy metals removal on FA with methyl orange modified surface and its combinations with TiO₂. The Wastewater Discharge Regulations (TM 5-814-8—developed in US and accepted, almost at the same values, in many European countries) set the following values, obtained based on the best available technology in electroplating industry: BAT_{Cd} = 0.69 mg/L; BAT_{Cu} = 3.38 mg/L. Obviously cadmium presents the highest risk and imposes the restrictions in a treatment process of wastewater also containing copper. Methyl orange photodegradation on titania and FA:TiO₂ mixtures is also investigated.

2. Experimental

2.1. The substrates

Raw FA was collected from the electro-filters of the CPH plant in Brasov, Romania. The main characteristics of FA are presented in Table 1.

The sum of the SiO₂, Al₂O₃ and Fe₂O₃ is above 70% [8], thus according to the ASTM standards, the FA is of type F.

The ash was washed in ultra pure water, by stirring, at room temperature, for 48 h, to remove the soluble compounds. After stirring, the filtrate solution had constant pH (7.8) and conductivity (2.25 mS) with a TDS value of 1140 mg/L.

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Table 1
Fly ash 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.

Because the adsorption experiments on the washed FA showed null efficiency in cadmium removal, the next step was to activate the FA surface. Previous studies [9], proved that an optimum surface charge is obtained by using NaOH 2N as modifier. The sample of washed FA were prepared as substrates for further studies, by stirring 48 h at room temperature with NaOH 2N alkaline solution (FA/NaOH 2N). Another set of samples were prepared using washed FA treated with methyl orange (MO, Merck) 0.01%, under 48 h stirring followed by filtration. Afterwards this substrate was treated with NaOH 2N under 48 h stirring (FA/MO/NaOH 2N), followed by filtration, washing with ultra pure water and drying, at 105–120 °C for 2 h.

The TiO₂ was used as powder Degussa P25 (Degussa P25, 80% anatase and 20% rutile; specific surface area 50 m² g⁻¹ and a mean particle size of 30 nm).

The crystalline structure of the substrate components was evaluated by XRD (Bruker D8 Discover Diffractometer). AFM images (Ntegra Spectra, NT-MDT model BL222RNTE) were used for morphology studies.

2.2. Adsorption experiments

Amounts of substrate (1–4 g) were added into 100 mL cadmium, respectively copper solutions (0–600 mg/L). The mixture was stirred up to 60 min. Then the substrate was removed by vacuum filtration and the supernatant was analyzed by AAS (Perkin Elmer Analyst 200), at $\lambda_{Cd} = 228.8$ nm and $\lambda_{Cu} = 324.75$ nm.

The adsorption efficiency η and capacity q_m were evaluated based on the mass balance calculation:

$$\eta = \frac{(c_{Cd}^i - c_{Cd}^e) \times 100}{c_{Cd}^i} \quad (1)$$

$$q_m = \frac{(c_{Cd}^i - c_{Cd}^e) \times V}{m} \quad (2)$$

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

For kinetics studies, mixtures of FA and TiO₂ were contacted with 100 mL of metal solutions in a beaker under magnetic stirring, at room temperature. At appropriate time intervals (5, 10, 15, 20, 30, 45 and 60 min), stirring was briefly interrupted and aliquots of the supernatant were analyzed to determine the residual metal concentration. The metal uptake q_{eq} (mg ion metal/g FA) has the same significance as q_m in Eq. (2).

2.3. Photocatalysis experiments

Methyl orange (Merck) was used for testing the photocatalytic efficiency. Photocatalysis tests were conducted in a UV reactor using 3 Phillips UV lamps for illuminating the samples. The photocatalytic experiments were done in quartz beakers using 200 mL of 0.152, respectively 0.0125 mM solution of MO. The irradiating time was 6 h. After UV illuminating, the solution of MO was analyzed using UV-vis spectrophotometer Perkin Elmer, Lambda 25, at 462 nm, based on the calibration curve. The

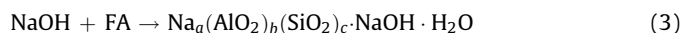
photodegradation intermediates are mostly absorbing in the IR domain, thus not overlapping their signal, at the main wavelength chosen for MO. Photocatalyst efficiency was calculated for each mixture of TiO₂ and FA by comparing the absorbance value for the solution of MO UV exposed, with the similar value of the initial MO solution. The mixture of TiO₂ and FA was 4 mg/L. The tested ratios of mixtures ranged from 100% to 0% of TiO₂.

3. Results and discussions

3.1. The substrates

The XRD spectra, Fig. 1, show that the major components of FA/NaOH are: carbon, SiO₂ in various structures (cubic, rhombohedral) and combined with Al₂O₃ as silimanite (Al₂SiO₅), mullite (3Al₂O₃·2SiO₅), along with γ -Al₂O₃, hematite (Fe₂O₃) and CaO. Anatase TiO₂ was also traced along with cadmium compounds.

Heavy metals removal onto FA is pH-dependent. The lowest Cd²⁺ and Cu²⁺ adsorption efficiency occurred when the FA was treated with HCl 2N [10]; this effect is caused by a positive surface charge leading to repulsions between the surface ($\equiv\text{SiOH}_2^+$) and metal ions [11]. Good efficiencies of heavy metals removal were obtained on FA treated with NaOH 2N solutions, at pH > 7. In this case the highest efficiency was up 99.33% after 10 min [12]. This increase in adsorption can be explained, beside the negative surface charge also by the heavy metals hydrolysis. Supplementarily, silica and alumina are forming alumino-silicates with pH-dependent structures. The reaction between the ash and sodium hydroxide solution is expected to be carried out according to the following equations [13]:



when the treated FA surface can develop new active site ($\equiv\text{SiO}^-$) and ($\equiv\text{AlO}^-$) which allows metals to be complexes at the surface (Eqs. (4) and (5)) [11].

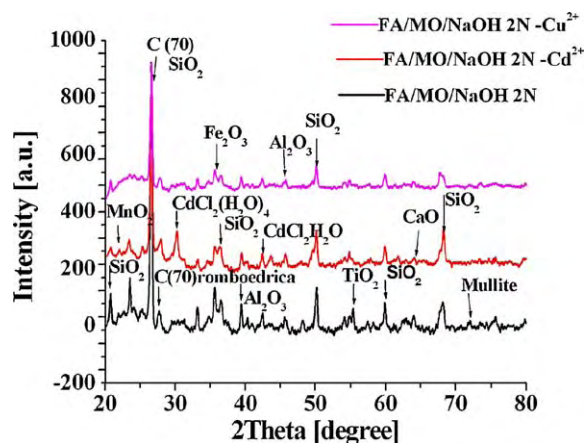


Fig. 1. XRD patterns of modified FA.

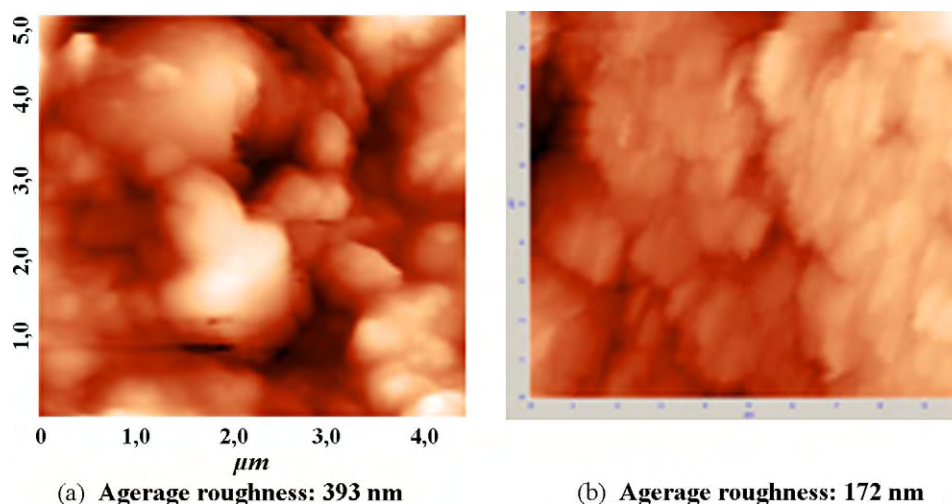


Fig. 2. FA morphology before and after treatment.

This applies to the cadmium and copper adsorption on modified FA and is proved by changes of the XRD patterns confirming that adsorption is likely to be the result of chemical modifying reactions, although without preferential dissolution of the major components. These chemical and structural changes also induce surface morphology modifications, resulting in significant differences in the substrates' affinity for Cd^{2+} and Cu^{2+} before and after treating with NaOH 2N and MO 0.01% (Fig. 2).

The average roughness varies significantly and can be explained by the dissolution/re-precipitation processes of alkaline oxides (confirmed by the high conductivity and TDS values) after treatment, leading to a surface with more uniform aspect that facilitates single mechanisms adsorptions process.

3.2. Heavy metals adsorption

Effects of the contact time and adsorbent mass on the adsorption efficiency are reported and correlated with the FA structure and morphology.

The variation in the adsorption efficiency for a 1:100 ratio FA mass:metal solution volume is presented in Fig. 3. The results allow setting the optimal contact time at 30 min, a value considered technologically feasible for both substrates and cations.

The effect of the adsorbent mass on the adsorption efficiency was previously investigated [12]. It was proved that good Cd^{2+} adsorption occurs at a dose of 4 g FA for 100 mL solution.

Therefore, the optimization tests were developed for cadmium removal, using FA with modified surface. The optimized adsorption process was then applied for solutions containing copper.

Amounts of TiO_2 catalysts added at FA can improve the cadmium and copper adsorption capacity of the substrate and solve both problems: the dyes photodegradation and the heavy metals removal.

The variation of the efficiency in cadmium and copper adsorption on various FA: TiO_2 mixtures is presented in Fig. 4.

Various amounts of TiO_2 added to FA can change the solution pH. The zero charge point for TiO_2 (powder Degussa) depends on temperature and superficial heterogeneity and is 6.17, at standard temperature [14]. Thus, at $\text{pH} > 6.17$ the surface charge is negative, favouring the cation adsorption. The data indicate a synergic effect regarding the adsorption of $\text{Cu}(\text{H}_2\text{O})_{6-x}^{2+}$ ions on the ash- TiO_2 substrates, especially at a 3:1 mass ratio of FA: TiO_2 . The same ratio proves for cadmium also high adsorption efficiencies. The partial removal of the hydration water (due to the pH decrease of the natural environment of the FA/MO/NaOH 2N by adding TiO_2)

increases the cations mobility and implicitly, the efficiency of this adsorption.

These effects are diminished when the FA content is lower and other processes became more significant, such as the $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ formation, blocking the active sites. The overall effect is in this case the decrease of the adsorption efficiency.

The highest efficiencies are obtained on two types of substrates: (1) for Cd^{2+} :FA/MO/NaOH 2N and on mixture FA/MO/NaOH

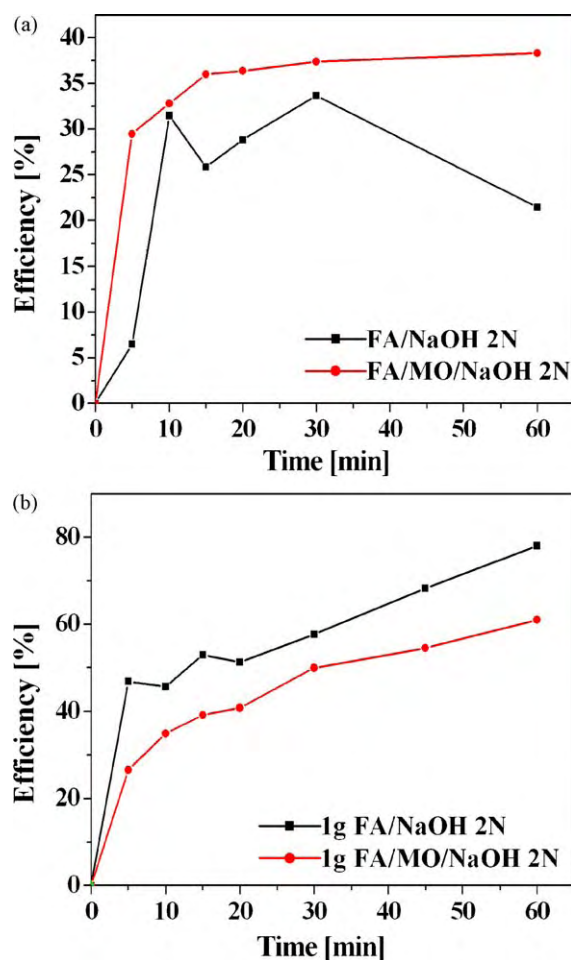


Fig. 3. Heavy metals adsorption efficiency on modified FA: (a) Cd^{2+} ; (b) Cu^{2+} .

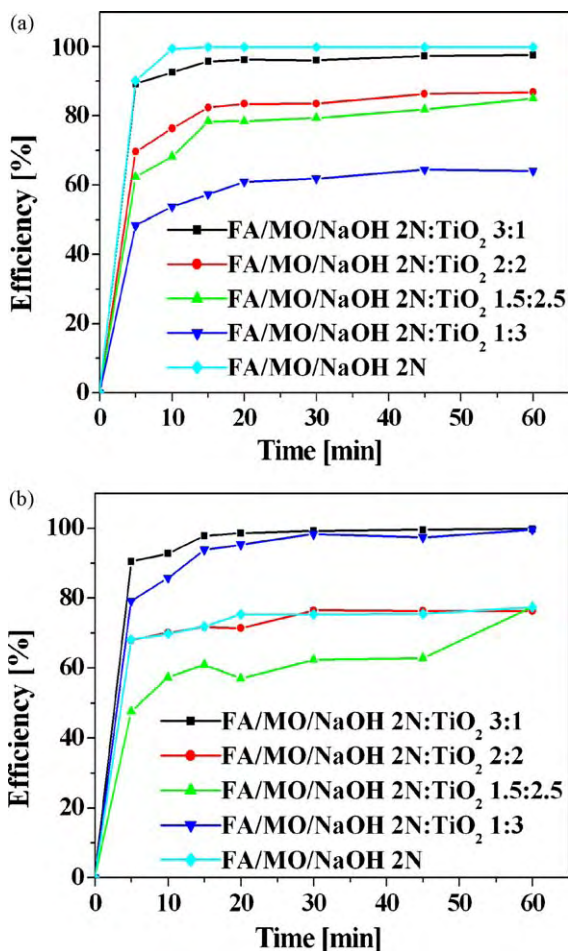


Fig. 4. Influence of amount of TiO₂ on the heavy metals removal: (a) Cd²⁺; (b) Cu²⁺.

2N:TiO₂ = 3:1 and (2) for Cu²⁺: FA/MO/NaOH 2N:TiO₂ = 3:1 and 1:3. The adsorption capacity of these substrates for Cd²⁺ were 8.3, 13.1 and for Cu²⁺ 12.6 and 5.1 mg/g.

The studies on the Cd²⁺ and Cu²⁺ removal efficiency indicated that the process was quite fast and the maximum adsorption occurred after 30 min. A contact time of 30 min is technologically feasible.

Adsorption equilibrium of heavy metals ions (Cd²⁺, Cu²⁺) can be represented by the Langmuir and Freundlich adsorption isotherm equations, respectively [15].

The Langmuir isotherm-linearisation is:

$$\frac{C_{\text{eq}}}{q_{\text{eq}}} = \frac{1}{q_{\text{max}} \cdot a} + \frac{C_{\text{eq}}}{q_{\text{max}}} \quad (6)$$

where q_{max} represents the amount of adsorbate per unit weight of adsorbent forming a complete monolayer on the adsorbent surface; a is the Langmuir constant related to binding energy, the affinity between the adsorbent and adsorbate; q_{eq} and C_{eq} shows the amount of metal adsorbed on the adsorbent and the residual metal concentration at equilibrium, respectively.

The Freundlich isotherm-linearisation is:

$$\ln q_{\text{eq}} = \ln k + \frac{1}{n} \ln C_{\text{eq}} \quad (7)$$

where k is Freundlich constant and is an indicator of the adsorption capacity and $1/n$ is a measure of the adsorption density.

Table 2

Adsorption parameters of Cd²⁺ and Cu²⁺ on TiO₂ mixtures with FA/MO/NaOH 2N.

FA:TiO ₂ (g:g)	Langmuir			Freundlich		
	a (l mg ⁻¹)	q_{max} (mg g ⁻¹)	R^2	n	k	R^2
Cadmium						
4:0	1.1791	16.6949	0.9125	0.5070	50.3732	0.9686
3:1	1.4254	13.9470	0.9924	–	–	0.3167
2:2	0.9401	9.5147	0.9996	–	–	0.4724
1.5:2.5	1.4595	11.7924	0.9955	4.6382	4.4668	0.9775
1:3	2.8127	6.8634	0.913	2.6042	4.0485	0.9407
Copper						
4:0	–	–	0.1917	–	–	0.0514
3:1	6.6269	5.1855	0.9113	0.0627	3.5727	0.9268
2:2	0.9401	9.5147	0.9996	–	–	0.4724
1.5:2.5	0.8783	9.3545	0.9994	–	–	0.4099
1:3	25.6078	7.6569	0.9992	0.4519	42.6579	0.9825

In Table 2 the results of the adsorption parameters for Cd²⁺ and Cu²⁺, on 4 g of FA/MO/NaOH 2N and/or mixtures with TiO₂ are summarized.

The results indicate that the Langmuir isotherm model can well describe the process on modified FA mixtures with TiO₂, both for cadmium and copper. These results prove that the affinity of FA and titania active sites is comparable and that chemical reactions are predominant. The substrates proved to have a larger affinity for cadmium (higher q_{max} values) as result of a higher ionic polarizability.

The kinetics of heavy metals adsorption can be modeled by various equations but the most common are:

The pseudo-first-order Lagergren equation [16],

$$\log(q_e - q_t) = \log(q_e) - \frac{K_L}{2303} t \quad (8)$$

where K_L is the Lagergren rate constant of first order (min⁻¹), q_e and q_t are the amounts of metal ion sorbed (mg g⁻¹) at equilibrium and at time t respectively.

The pseudo-second-order rate equation developed by Ho and McKay [17], with the linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where k_2 the pseudo-second-order rate constant of adsorption (g mg⁻¹ min⁻¹) and can be evaluated from the slope of the plot.

The inter-particle diffusion model can be applied in adsorption on porous materials. The amount of heavy metals ions adsorbed can be calculated with the equation [18], which has the linear form:

$$q = k_{\text{id}} t^{1/2} + C \quad (10)$$

The pseudo-first-order kinetic did not apply to any of the investigated processes. The pseudo-second-order kinetic fits very well to all the processes data while the interparticle diffusion model described almost all the experiments. These show parallel kinetics, running on small and large pores. The linear fit could not be used to match the experimental data of cadmium removal on the highly efficient substrate mixture FA:TiO₂ = 3:1, although interparticle diffusion is proved to be present in all the other experiments; this can be the result of a more complex interparticle diffusion mechanism, involving adsorption on large pores, with different rate constants, as result of different affinities. In Table 3 the kinetic constants of the adsorption mechanisms on the investigated substrates are presented.

Table 3
Kinetic parameters of the heavy metal adsorption.

FA:TiO ₂ (g:g)	Pseudo-second-order kinetics			Interparticle diffusion		
	k_2 (g/mg min)	q_e (mg/g)	R^2	K_{id} (g/(mg min ^{0.5}))	C	R^2
Cadmium						
1:0	0.0374	19.4552	0.9990	0.3883	16.208	0.993
4:0	0.5222	12.1359	0.9999	0.002	12.082	0.9768
3:1	0.1954	13.7931	0.9999	–	–	0.7387
2:2	0.0925	10.8108	0.9994	0.8014	6.8345	0.9642
1.5:2.5	0.0485	12.6742	0.9980	0.2544	10.468	0.9174
1:3	0.0699	9.6899	0.9987	0.5188	6.2898	0.9131
Copper						
1:0	0.01545	12.9366	0.9674	1.6776	1.5437	0.9552
4:0	0.0794	12.5786	0.9993	0.7631	8.3853	0.9258
3:1	0.4081	5.9988	0.9999	0.2371	4.8534	0.9366
2:2	0.1402	9.6993	0.9995	7.8009	0.316	0.9124
1.5:2.5	0.1426	9.3545	0.994	0.2467	7.6938	0.9046
1:3	0.0327	9.01713	0.9730	–	–	0.802

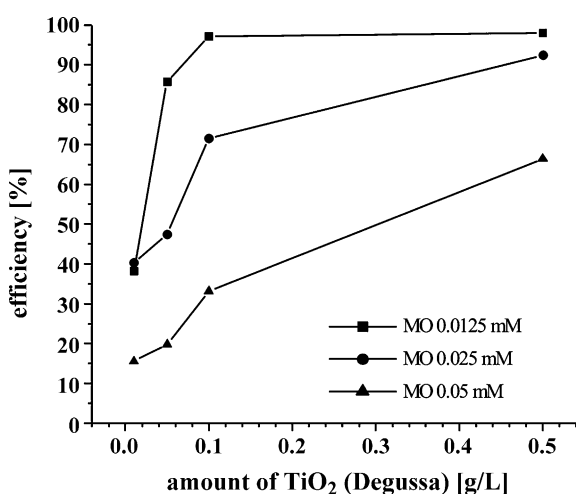


Fig. 5. Influence of the photo-catalyst amount on the MO degradation.

3.3. Methyl orange photodegradation

The next step in these studies is the dyes (MO) photodegradation on TiO₂ and mixtures of FA with Degussa powder.

Photodegradation experiments on TiO₂ proved the importance of optimizing the substrate concentration in the dispersion (Fig. 5).

The results show that 0.1 g of catalyst in 1L dispersion allows high efficiencies in average concentrated MO solutions (0.0125 mM), while by increasing the catalyst amount a slight decrease is registered in the efficiency values. Based on these

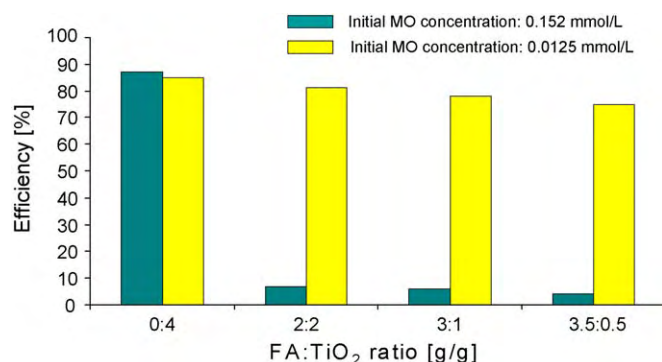


Fig. 6. Methyl orange photodegradation efficiency on FA:TiO₂ mixed substrates.

results photodegradation tests were developed on mixtures of FA and TiO₂, for two MO solutions.

The photodegradation experiments concluded that the efficiency is significantly affected by the increase in the substrate(s) concentration. This aspect is more visible for the higher MO concentrations (0.152 mM) where, for 4 g/L TiO₂, the efficiency obtained was 86.8%, lower than the value reached for the more diluted systems. Two processes can cause this behaviour: (1) the increase in the dispersion turbidity that reduces the amount of radiation effectively reaching the substrate and (2) the high MO concentration that may cause the substrate saturation, in a process where MO adsorption is a prior step to photodegradation. By increasing the FA ratio the efficiency decreases up to 4.67%. Preliminary kinetic tests developed for this system in dark (adsorption) and under irradiation (adsorption + photocatalysis) showed that the Langmuir Hinshelwood mechanism develops with comparative rate constants (in the order of magnitude of 10⁻⁴ min⁻¹) with slightly higher values for adsorption.

For lower MO concentration, of 0.0125 mM, the efficiency is less affected by the increase in the FA content: from 85.39% efficiency for the pure TiO₂ the value drops to 75.08% for the mixtures containing 0.5 g TiO₂ and 3.5 g FA, Fig. 6.

4. Conclusions

The adsorption efficiency of heavy metals on FA strongly depends on the ash surface composition and dosage, on pH, contact time, temperature, and heavy metal concentration. The experimental results indicate that adsorption of cadmium and copper ions can be significantly improved by using the FA modified with methyl orange, with negative (HO⁻) surface charge and improvement is registered when using substrate mixtures (FA/MO/NaOH 2N + TiO₂). Adsorption efficiencies over 95% were registered on 25% TiO₂ mixtures with modified FA, both for cadmium and copper adsorption.

The photodegradation experiments using methyl orange, conducted on the substrate mixtures showed that the increase of FA content does affect the process efficiency, especially at higher dye's concentration when dyes adsorption can clog the photocatalyst surface. Another reason is that FA can also block part of the UV radiation from reaching to the TiO₂ photocatalyst. For average MO concentration (0.0125 mM), close to the usual values in the primary wastewater, this effect is moderate and the lowest drop, from 85.39% to 75.08%, is registered for the mixture containing 0.5 g TiO₂ and 3.5 g FA. These results show that the dye's concentration plays a significant role in the photodegradation

mechanism and the proposed process is feasible for average concentrated pollutant solutions.

Acknowledgment

This work was supported by the Romanian National Agency for Research in the FOTO-COMPLEX 71-047/2007 grant.

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