Tungsten oxide and fly ash mixtures for single step wastewater treatment process

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In most cases, various contaminants, with different chemical composition are simultaneously released into the environment. A typical example is the dye finishing industry, where residual dyes, heavy metals, surfactants are the main pollutants in wastewaters. The use of fly ash (FA) in wastewater treatment, for heavy metals *and* dyes immobilizations, represents a good application for solving the problems of advanced treatment and the intelligent use of this waste. For advanced removal of heavy metals and dyes we propose two concurrent, simultaneous processes, of adsorption and photocatalysis based on a mixture of catalysts and fly ash. Previous results were presented when using TiO_2 as photocatalyst. This paper presents the results when using a mixture of WO_3 and FA, in a one step treatment process of wastewaters containing heavy metals and dyes. The use of this combination must consider also the effect of the heavy metals on tungsten trioxide activity, along with the parallel process involving the dyes and the fly ash. Before investigating this double process, studies on the adsorption of the individual components must be performed on substrate mixtures. We report here the cadmium and methylen blue adsorption on mixtures of WO_3 and flay ash collected from CET Brasov Romania. The process efficiency and kinetic is reported and correlated with the substrates characteristics. According to the results, WO_3 operates similarly to TiO_2, due to the similar values of the band gap energy and the band edge wavelength.

1. Introduction

The heavy metals (Cd, Cu, Cr, Ni, Zn, Hg, Pb) and the dyes are persistent bioaccumulative and toxic pollutants, resulted mainly from the metal finishing and the textile finishing industries which are considered the major contributors, due to the huge amounts of wastewaters resulted form a large number of dispersed enterprises. In this way the pollutants concentration into effluents increase up to some hundreds of mg/L and produce a variety of illnesses (respiratory problems, eczemas, cancer).

Fly ash is another pollutant, rising big environmental problems; the use of this waste as second raw material, in various applications becomes thus a sustainable solution. So far, fly ash use was reported for building materials – especially concrete. The use of fly ash as adsorbent is a novel option, intensively studied. The traditional adsorbents such as activated carbon, zeolites and oxides (TiO_2, WO_3, SnO_2) have high metal adsorption capacities, but are generally expensive. Ion-exchange is an efficient method, with moderate selectivity since it can not only remove the heavy metal ions but exchange the Ca^{2+}, Mg^{2+} ions [1]. Supplementary, in mixtures the ion exchangers can load with dyes, thus modifying the surface and decreasing the process reversibility. These adsorbents are efficiency but are not a sustainable solution.

The applications of low – cost adsorbents such as sludge ash, scrap rubber, peat, bituminous coal, activated sludge, wood, clays, and fly ash have been demonstrated

to be effective for removing heavy metals from wastewater. The use of fly ash for removal of heavy metals from industrial wastewaters was done as early as in 1975, [2].

The efficiency of fly ash as adsorbent in the wastewater treatment process is obvious and the fly ash can be obtained cheaply in large quantities, can be used both as an adsorbent and as neutralization agent [3]. 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 oxide type and the surface, although heterogeneous, has a predominant negative charge that favours heavy metals adsorption and contains active sites in the dyes' adsorption processes. Dyes advanced removal can be further improved by combining adsorption with photo-degradation on oxide photo-catalysts. The two different mechanisms can be combined in a novel technology based on a single step process, combining adsorption and photo-degradation for the simultaneous advanced removal of heavy metals and dyes. Previous studies were based on fly ash (FA) collected from CHP Brasov and (Romania), with modified surface; the optimisation studies allow to identify the conditioning process able to form relatively homogeneous surfaces by using alkaline solutions of NaOH with average concentrations (1N, 2N), in a low cost, sustainable

process, as previously reported [4,5]. Mixed substrates, combining powders of FA with photo-catalysts (TiO_2) and/or adsorbents (activated carbon) were proved to be highly efficient in dyes and heavy metals removal, [6]. These complex systems, involving different substrates and different absorbents imply, besides the main processes (adsorption and photodegradation) also secondary processes that can change the adsorbent surfaces (secondary adsorption, surface dissolution, surface precipitation).

The studies followed as first steps the heavy metals removal from single cation (Cd^{2+}, Cu^{2+}, Ni^{2+}) solutions [4,5] simultaneous removal of cations from multi cations solutions using FA, FA: TiO_2, FA : Activated Carbon or other mixtures and in parallel similar studies of dyes removal via photo-degradation and adsorption. The next level of studies involved mixtures of single cation solutions with dye(s), proving the reciprocal influence of the components on the substrates, and the changes in mechanisms and efficiencies; e.g. mixtures of FA with 25% TiO_2 were highly efficient in cadmium and copper removal from mixtures also containing methylorange or ethylene blue, [6].

Literature mentions that WO_3 is a wide band gap semiconductor with optoelectronic properties, and experimental studies proved that it can be also used as photocatalyst [7], replacing anatas TiO_2 which has a higher cost.

This study presents the results obtained in Cd^{2+} and MB removal, using fly ash (FA) with modified surface and its mixtures with WO_3.

2. Experimental

2.1. The substrates

The primary compounds of the raw FA, expressed as oxides are presented in Table 1. The 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 in the raw FA CET Brasov is higher than 70%; according to the ASTM standards [8], the FA is of type F.

Table 1. Fly ash composition.

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

*LOI: loss of ignition

The fly ash was washed in ultra pure water, by stirring, at room temperature, for 48 h, to remove the soluble compounds, up to constant pH (9.8), conductivity (2.25mS) and TDS (1140 mg/L) in the washing water. This substrate has a limited adsorption affinity for heavy metals as result of a high heterogeneity in the surface aspect and charge. Previous studies [4], proved that an optimum surface charge is obtained by using NaOH 2N solution as modifier. The FA washed in ultra pure water was further stirred 48 hours, at room temperature with NaOH 2N alkaline solution (FA/NaOH 2N) followed by filtration, washing and drying, at 105-120°C, till constant mass. The modified substrate was sieved and the 100μm fraction was further used.

The WO_3 was used as powder (99,8%) from Acros Organics.

The FA crystalline structure was evaluated by XRD (Bruker D8 Discover Diffractometer) and surface morphology was investigated by AFM (Ntegra Spectra, NT-MDT model BL222RNTE).

2.2 Adsorption experiments

The batch adsorption experiments were done on various substrates: (a) FA/NaOH 2N, (b) WO_3 , and (c) mixtures of FA and WO_3.

Amounts of substrate (1….2g) were added into 100 mL solution containing (a) Cd^{2+} (0 – 730 mg/L) and (b) Cd^{2+} and MB mixtures. Each mixture was stirred up to 90 min. and aliquots were taken at 10, 20, 30, 45, 60, 90, 120 min, when stirring was briefly interrupted. The residual Cd^{2+} concentration in aqueous solution was analyzed by AAS (Analytic Jena, ZEEnit 700), at λ_{Cd} = 228.8 nm and the MB concentration was evaluated by UV-VIS spectrometry (Perkin Elmer Lambda 25), on the calibration curve registered at the maximum absorption wave length (λ_{MB} = 664 nm).

Batch adsorption experiments were done at room temperature, under magnetic stirring. In all cases, the working pH was the natural value of the solutions. At the optimized process parameters (contact time, fly ash dosage, mixture (FA+WO_3) dosage and initial concentration of the adsorbate) kinetic studies were done and the adsorption mechanism was proposed.

Preliminary experiments proved that heavy metals 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 crystalline components in fly ash are carbon (graphite), SiO_2 (cubic, rhombohedra), Al_2O_3 (H, γ-Al_2O_3), mullite ($3Al_2O_3 \cdot 2SiO_5$), hematite (Fe_2O_3) and CaO. The crystalline structure of raw fly ash is slightly modified after washing

and alkaline treatment, confirming that dissolution affects the minority components and/or the amorphous ones.
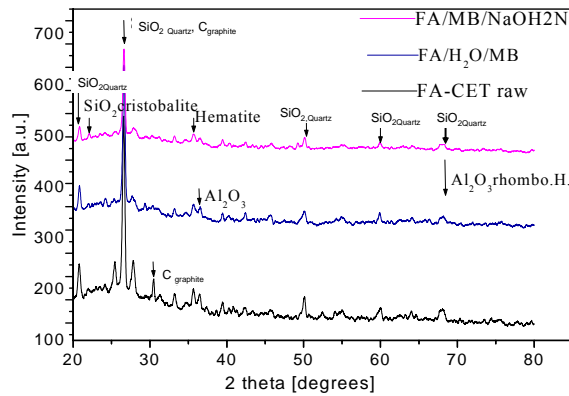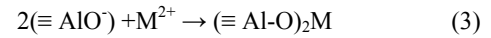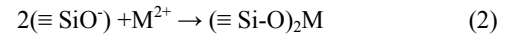

Fig. 1 XRD of raw FA and FA modified with NaOH 2N and MB

Heavy metals and dyes removal on FA are pH depended. Previous studies showed that the lowest Cd^{2+}, Ni^{2+} and Cu^{2+} adsorption efficiency occurred when the 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 [9]. Supplementary,

silica and alumina are forming alumino-silicates with pH-dependent structures. In alkali media, the interactions between the ash and sodium hydroxide solution are expected to lead to hydroxide inclusion, according to the following reaction [10]:

$$NaOH + FA \rightarrow Na_a(AlO_2)_b(SiO_2)_c \cdot NaOH \cdot H_2O \quad (1)$$
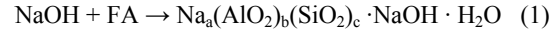
In water, the mobile Na^+ ions from the surface lattice can be solved, becoming the main component of the double layer, when on the FA surface new active site ($\equiv SiO^-$) and($\equiv AlO^-$) can develop, allowing metals to form complexes at the surface (eq. 2, 3), [9]:

$$2(\equiv SiO^-) + M^{2+} \rightarrow (\equiv Si\text{-}O)_2M \quad (2)$$

$$2(\equiv AlO^-) + M^{2+} \rightarrow (\equiv Al\text{-}O)_2M \quad (3)$$

Morphology modifications are the main results of these processes, proving large variations in the substrates' affinity for heavy metals and dyes. Various roughness values, Fig 2, appear due to leaching of the alkaline oxides and formation of new structures with important role in the heavy metals and MB adsorption.
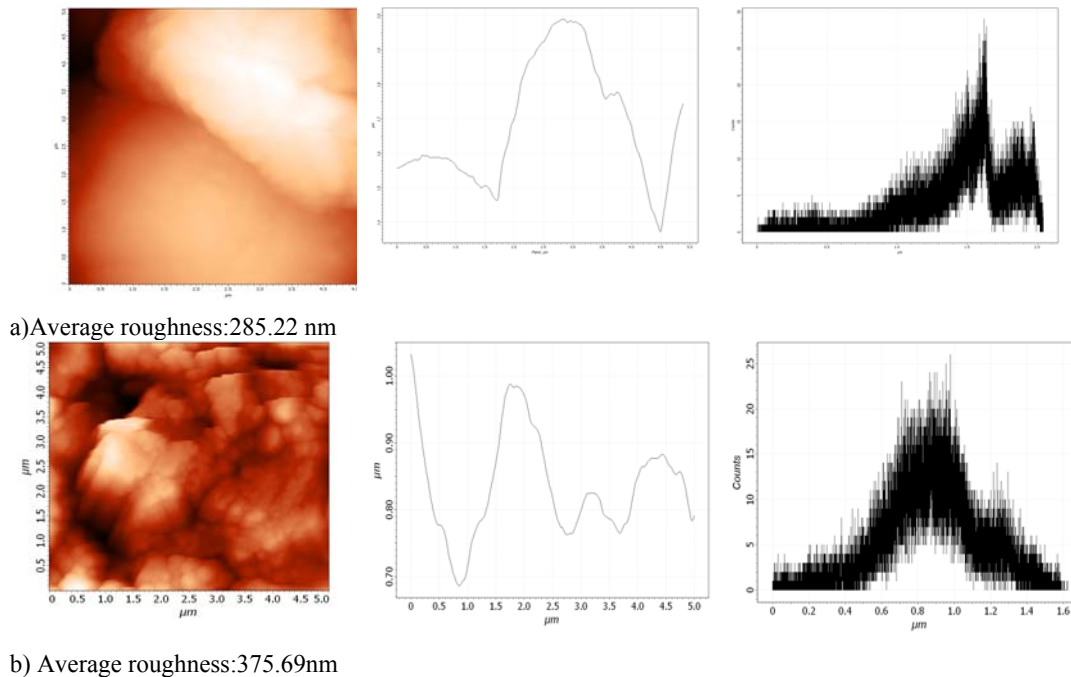

a)Average roughness:285.22 nm

b) Average roughness:375.69nm

Fig. 2. The morphology of a) raw FA b) FA/NaOH 2N

3.2 Heavy metals adsorption

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

$$\eta = \frac{(c_{Cd}^i - c_{Cd}^e) \times 100}{c_{Cd}^i} \quad (4)$$

$$q_m = \frac{(c_{Cd}^i - c_{Cd}^e) \times V}{m} \qquad (5)$$

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).

Single substrates (FA and WO_3 respectively) were used in adsorption tests as dispersions (2 and 3g) in 100 mL cadmium solutions 0.01n. High efficiencies, up 99%, are obtained when 3g FA/NaOH 2N was used for adsorption, and up 82% for the 2g FA/NaOH 2N substrate. Despite the efficiency, higher solid phase concentration has the draw back of increased turbidity that can reduce the photocatalytic efficiency, due to lowering the light amount. Therefore, further adsorption studies will be done on 2g modified fly ash.

The negative efficiency for Cd^{2+} removal on WO_3 at pH 5.8 can be explained not as desorption but as an apparent increase in the cadmium concentration due to water binding; the tungsten oxide, WO_3 can form new species of metawolframats $[H_2W_{12}O_{40}]^{6-}$,[11] or can largely host water chemisorptions forming new W=O binds, [12]. If there is a large amount of immobilized water molecules, the amount of free solvent species is strongly decreased and the cadmium equilibrium concentration is apparent higher than the initial one, in a process similar to the "salting out" effect.

On the other hand, the water absorbed is a new sources of protons $[H_3O^+]$ which disadvantageous the adsorption of heavy metals.
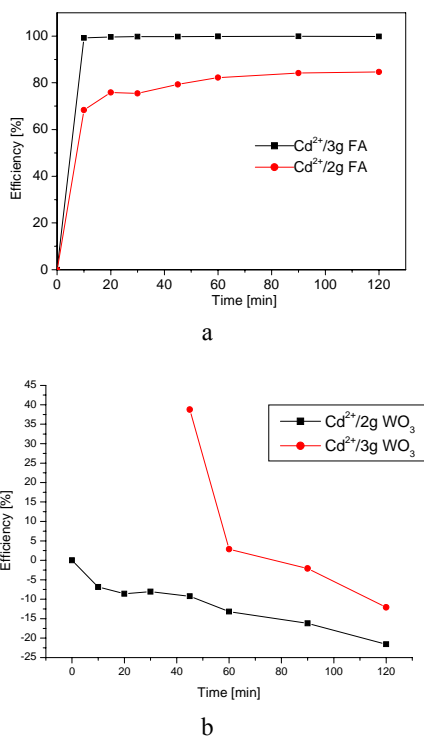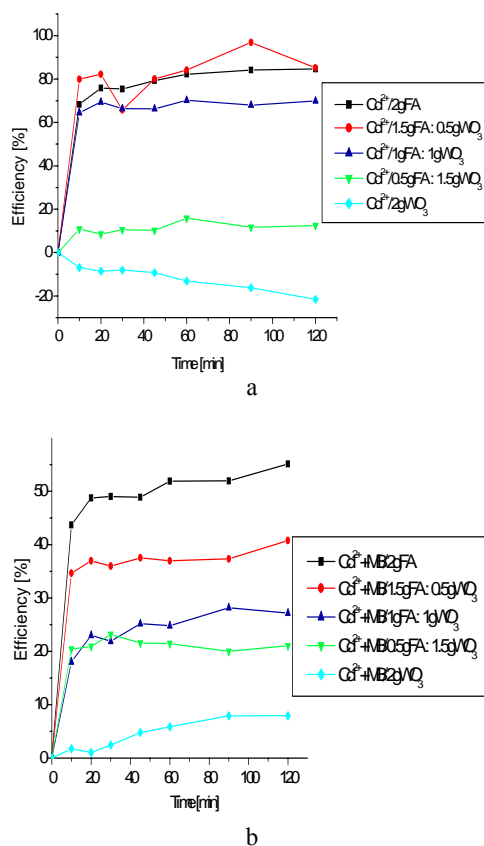

a

b

Fig. 4. Cd^{2+} immobilization efficiency vs. contact time (a) from Cd^{2+} and (b) from mixed (Cd^{2+}+MB) aqueous solutions

Amounts of WO_3 catalysts added at FA can improve the cadmium adsorption capacity of the substrate and solve both problems: the dyes photodegradation and the heavy metals removal. The results are presented in Fig 4 a) and b). The best Cd^{2+} adsorption efficiency occurs on mixtures containing 75% FA and 25% WO_3 at the pH 8.3.

The large planar structure of MB, Fig. 5, involves π electrons that can form bonds with the empty orbitals of the oxides in the FA and adsorb, modifying the substrate composition and charge when/where it adsorbs. At room temperature the adsorptions of methylene blue 0.05 mM from mixtures with cadmium has moderate efficiency, higher on substrates rich in FA, Fig. 6.
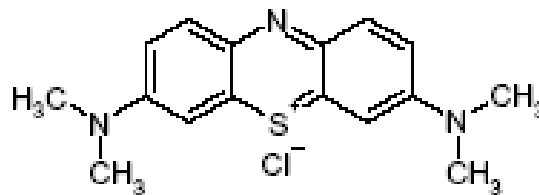

a

b

Fig.3. Cd^{2+} immobilization efficiency vs. mass of substrate: (a) FACET/NaOH 2N; b) WO_3 powder
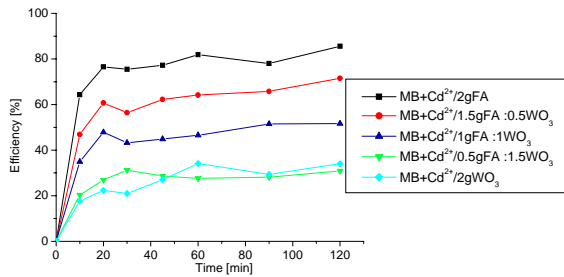

Fig.5 Methylene Blue.

Fig. 6. MB immobilization efficiency vs. contact time on varied substrates from mixture (Cd^{2+}+MB) aqueous solutions.

This adsorption conditions also influence the heavy metal adsorption. At lower Cd^{2+} concentration, the adsorption efficiency is well, Fig. 7, while at higher concentration the amount of adsorption sites becomes the limiting factor.
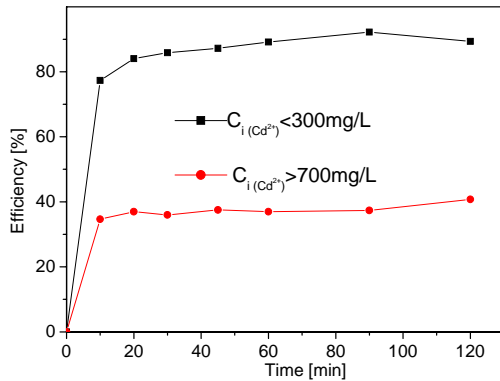

Fig. 7. Cd^{2+} immobilization efficiency vs. contact time on substrate 75% FA : 25% WO_3 from mixture (Cd^{2+}+MB) aqueous solutions.

The optimal adsorption conditions were thus defined as: contact time of 60min, 2 g of substrate (75% FA and 25% WO3) in 100mL mixed solution of cadmium and MB (0.05mM) and were further used for studies on the adsorption mechanism. The adsorption equilibrium of Cd^{2+} ions can be well represented by the Langmuir adsorption isotherm [13]. The Langmuir linearization is presented in Fig. 8:
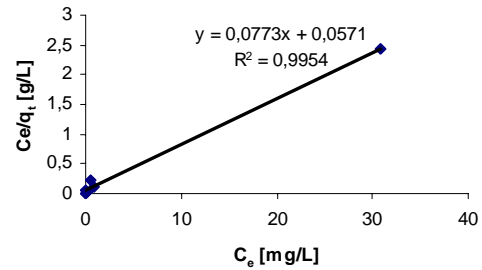

Fig. 8 Langmuir isotherm for cadmium adsorption

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

The Langmuir parameters, calculated based on the linearization in eq. (6) are q_{max} 13.021 mg/g, and a 0.0055.

3.3 Uptake kinetics of the heavy metals

The metal uptake q_e (mg/g) was evaluated based on the initial and momentary (c_{cation}^i and c_{cation}^t) heavy metal concentrations, in a given solution volume, V, on a given amount m_s of substrate:

$$q_e = (c_{cation}^i - c_{cation}^t) \cdot V / m_s \qquad (7)$$

Only the pseudo-second order kinetics, [14], could very well model the processes, on all the tested substrates:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (8)$$

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

In Fig. 9 the linearization of the equation (8), is presented on the mixed substrate that proved the highest removal efficiencies and the kinetic parameters are given in Table 2.

Table 2 Kinetic parameters of the heavy metal adsorption.

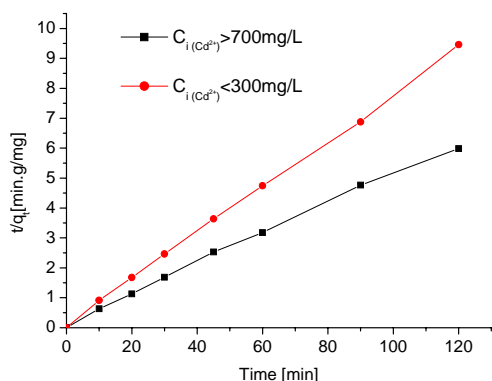| FA:WO$_3$ [g:g]	k_2 [g/mg min]	q_e [mg/g]	R^2	k_2 [g/mg min]	q_e [mg/g]	R^2
	Cadmium			**Cadmium + Methylene Blue**		
2.0:0.0	0.0424	9.7087	0.999	0.0179	19.9600	0.9973
1.5:0.5	0.0206	15.4798	0.9844	0.1565	14.5348	0.9956
1.0:1.0	0.1097	11.9617	0.9992	0.4689	10.2986	0.9939
0.5:1.5	0.1792	1.4526	0.9689	8.0650	7.8740	0.998
0.0:2.0	-	-	-	0.00257	4.9578	0.9282

Fig. 9 Kinetic curves of heavy metals adsorption on FA 75% + WO₃ 25% substrate.

These data also show that in the experimental conditions, there is a kinetic activation of the substrate by MB adsorption, resulting in increasing the maximum substrate capacity. Since there are no strong crystalline modifications, we can conclude that this is the result of an increase in the surface homogeneity due to MB adsorption. Still, the affinity is not increased and the kinetic constants are rather low.

4. Conclusions

The adsorption efficient of heavy metals on FA strongly depends on the ash surface composition and dosage, on pH, contact time, temperature, and heavy metal concentration.

Cadmium ions adsorption on alkali-modified FA has convenient efficiencies after 60 min of contact time and is strongly influenced by the MB existent in the solution, efficiency being reduced almost at half.

The FA has an open pores morphology and the adsorption efficiency of MB is good while the cadmium adsorption depends on the FA fraction used, being negative on substrates of pure WO₃, when the salting out effect can be supposed.

The pseudo-second order kinetics describes well all the processes, at average and low cadmium initial concentrations.

High adsorption efficiencies are registered for heavy metals concentrations up to 100ppm, recommending the mixture FA:WO₃ substrate for simultaneous removal of heavy metals and MB from wastewater resulted in the dyes finishing industry.

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