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Photocatalytic activity of cadmium doped TiO_2 films for photocatalytic degradation of dyes

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ABSTRACT

The TiO_2 thin films have encouraging photocatalytic activity in dyes degradation and can be used in wastewater advanced treatment. Thin films were obtained by doctor blade, for avoiding the problems raised by powder–TiO_2 leaching and separation. Hence, this technique may be viable for large volumes of low dye concentration wastewater, resulted in the textile finishing industry. Usually, these wastewaters have also a low heavy metal content (e.g. from phtalocyanine pigments) that interferes with the photodegradation. Cadmium is one often participant in the process and, in a real situation, it can adsorb on the photocatalyst surface, modifying the photocatalytic activity. The modification can be beneficial, if it results in doping. Therefore this study investigates the cadmium doping effect on TiO_2 photocatalyst. Degussa P25 TiO_2 powder and cadmium precursors were used as materials for doped TiO_2 thin films obtained using the doctor blade deposition method. Effects of TiO_2 doping with cadmium were analysed, considering the morphology, visible light response, and photocatalytic performance. The phase structure, microstructure and surface properties of the coatings were characterized by using X-ray diffraction and atomic force microscopy (AFM). The spectroscopic analysis was investigated by UV–vis techniques. The photocatalytic reactivity was evaluated by the Methyl Orange (MO) and Methylene Blue (MB) degradation on cadmium doped TiO_2. The effect of the initial dyes concentration, of the illumination time, the dopant concentration and the cadmium precursors were investigated. In this study, highest catalytic activity was found to be strongly dependent both on catalyst structure and on the dyes concentration. There is a linear correlation between the band gap energy of the cadmium doped TiO_2 films and dyes photodegradation efficiency, which allows the materials optimization for the best photocatalytic efficiencies.

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1. Introduction

Textile wastewater content varies every day due to the nature of the dyeing process and therefore it is difficult to fully characterize the ingredients. The processes, generating wastewater in a cotton textile mill are desizing, scouring, bleaching, dyeing, and printing. Azo dyes and the metal-phtalocyanides are the largest group of synthetic colorants (60–70%) and can be used to color the natural textile fibers and the resulted by-products contain both dyes and heavy metals. The conventional aerobic processes have been insufficient to degrade most azo dyes and are inefficient in heavy metals removal. Various physical–chemical techniques are available for the wastewater treatment, to eliminate dyes and heavy metals, usually in sequential steps: chemical coagulation, sedimentation and adsorption are the widely used ones, but the advanced oxidation process, e.g. photocatalysis, can also apply along with other advanced techniques are often applied [1,2].

In the past years, many catalysts like TiO_2, WO_3, ZnO and SnO_2 had been tested for the water contaminants photo-degradation [3,4]. Among these catalyst, titanium oxide is largely used in wastewater treatment but its application is still limited because the activation requires UV irradiation ($\lambda \leq 387$ nm), as a consequence of the band gap value (3.2 eV). Two factors can affect the broad use of TiO_2 as photocatalyst: (a) the solar spectrum contains only 7–10% of UV light, (b) the high recombination rate of the photoexcited electron–hole pairs in the irradiated particles limits the overall efficiency. These problems can be solved by changing the electronic structure of the photocatalyst by doping TiO_2 with transition metal ions [5,6].

In industrial wastewaters resulted in the textile industry, the heavy metals (cations or complexes), even in traces will adsorb on the photocatalyst surface. Cadmium is one of the likely heavy metals in these wastewaters. It can be adsorbed on the active sites in processes of chemisorption or it can be integrated in the TiO_2 lattice acting as a doping agent.

Some authors observed no or even negative effect of cadmium ions on the photocatalytic performance [7,8]. These effects strongly depend on the doping method and the cadmium

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concentration in the photocatalyst. Cadmium doped photocatalysts were prepared by several different techniques: impregnation method, co-precipitation, sol–gel, flame hydrolysis, plasma assisted pyrolysis, reactive magnetron sputtering, metal organic chemical vapor deposition and spray pyrolysis deposition [9,10].

The doctor blade technique can be easily employed as a fast and non-energy consuming procedure to mass production of large area titania thin films (of 5 μm in thickness) with good uniformity and reproducible properties. The doctor blade deposition is known to produce films with high adhesion and a very good photocatalytic activity due to the high surface porosity. However, a good choice of the thin film deposition parameters may yield a high quality films.

Methyl Orange (MO) and Methylene Blue (MB) are an intensely colored compounds, used in dyeing and printing textiles and are common water pollutants. This study presents the results obtained when modifying the TiO_2 surface properties by cadmium addition in small amounts and to evaluate the catalytic activity towards the degradation of MO and MB. The paper presents the parameters that influence the photoactivity, such as cadmium precursors, dopant amount, particle size, crystal phase, and band gap energy.

The results in this paper can thus give several answers to the questions of dye photodegradation form industrial wastewaters also containing small amounts of heavy metals, considering the particular situation of MO and MB in cadmium polluted water.

2. Experimental

2.1. Catalysts preparation

The materials used for catalyst preparation were: TiO_2 Degussa P25 (with BET surface area $55 \pm 15\,m^2/g$; average primary particle size around 30 nm, purity above 97% and a 80:20 anatase: rutile ratio), ethanol, acetylacetonate ($C_5H_8O_2$, 99.9%, Alfa Aesar), triton X100 (non-ionic surfactant, Sigma–Aldrich), cadmium acetate and cadmium chloride (alcoholic solution).

Thin films of cadmium doped/modified TiO_2 (Cd-TiO_2) were prepared by doctor blade; the paste was obtained by dispersing 0.5 g TiO_2 Degussa P25 powder into solutions containing ethanol, acetylacetonate, triton X100 in a volumetric ratio 10:1:1. The cadmium precursor (cadmium acetate or cadmium chloride) was added into the paste. Five different cadmium concentrations (0.1, 0.5, 1, 3, and 5% measured as atomic weight percentage) were selected. The paste was smeared on microscopy glass substrate (sample of $1.5 \times 2.5\,cm^2$) cleaned using ethanol, distilled water, acetone in successive sonication processes. After drying in air at 60 °C for about 10 min, the films were annealed in an oven at 500 °C, for 6 h. The samples were noted: Cd*x*A(*C*)-TiO_2 (where *x* represents the doping percent and *A* the cadmium acetate precursor respectively *C* the cadmium chloride precursor).

2.2. Films characterization

The structure and structural changes induced by cadmium insertions in the TiO_2 films were studied by X-ray diffraction (XRD). The XRD patterns were obtained on a Brucker D8 Discover diffractometer with CuKα radiation.

Surface morphology, roughness and microstructural properties of the thin films were evaluated by atomic force microscopy (AFM, NT–MDT model NTGRA PRIMA EC). The images were taken in semi-contact mode with "GOLDEN" silicon cantilever (NCSG10, force constant 0.15 N/m, tip radius10 nm). The AFM was used to characterize the uniformity and grain size of TiO_2 films. Image analysis was carried using a WSxM software, to evaluate the pore size distribution [11].

Absorbance measurements were recorded in the range of 200–1100 nm, using a UV–vis spectrophotometer (PerkinElmer Lambda 25 UV–vis), allowing the band gap and absorbance calculation for the catalysts.

2.3. Dyes photodegradation

The photodegradation reactor consists of a static cylindric flask, open to air. Three F18W/T8 black light tubes (Philips) (UVA light, typically 340–400 nm, with λ_{max} (emission) = 365 nm), placed annular to the photoreactor were used for photolysis.

The pollutant dyes tested in this work were Methyl Orange ($C_{14}H_{14}N_3SO_3Na$) and Methylene Blue ($C_{16}H_{18}ClN_3S$). The dyes solutions were prepared by dissolving the powder in ultra pure water (Direct-Q 3 water purification system) and were used immediately after preparation.

The photocatalytic degradation of dyes (Methyl Orange and Methylene Blue) in concentrations varied from 0.05 mM to 0.00625 mM, was employed to investigate the photodegradation effect of the Cd-TiO_2 films. Further tests were done at the natural pH values of the solutions (5.65 for MO and 6.82 for MB).

Absorbance measurements were recorded in the range of 200–800 nm, and the maximum absorption wavelength experimentally registered at $\lambda = 460$ nm for MO and $\lambda = 665$ nm for MB were used for the calibration curves and further concentration measurements.

The photodegradation efficiency was evaluated with following relation:

$$\eta = \frac{A_0 - A}{A_0} \times 100 \qquad (1)$$

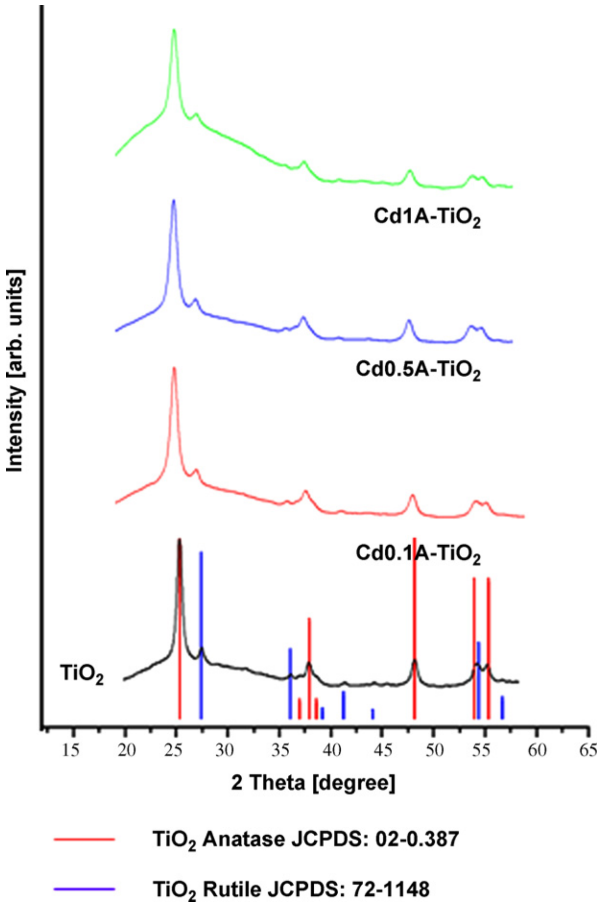

Fig. 1. The XRD patterns of the Cd*x*A-TiO_2 film.

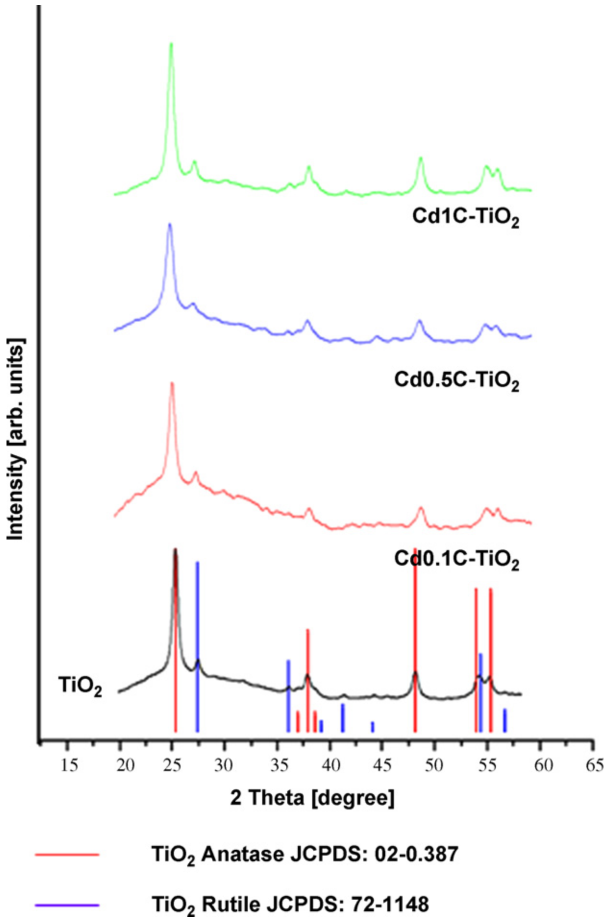

Fig. 2. The XRD patterns of the Cd*x*C-TiO_2 film.

where A_0 represents the initial absorbance of dyes solution and A represents the dyes absorbance at time t.

3. Results and discussions

The relatively low photoactivity of TiO_2 is believed to be the result of fast recombination of photogenerated electrons and holes. Structural imperfections in the TiO_2 lattice generate trap sites which may act as recombination centers, leading to a decrease in the electrons and holes concentrations. Doping semiconductors with certain transition metal ions improves the electrons trapping and inhibits electron–hole recombination. Doping must be carefully controlled because large amounts of dopant can result in stable insulators. In the case of cadmium, doping percentages higher than 3 at.% (when used cadmium acetate precursor), result in the $CdTiO_3$ formation.

3.1. *The films characterization*

The X-ray diffraction patterns of the systems, Fig. 1 respectively Fig. 2, allowed to identify the crystal phases present in the systems. Other information in the present XRD pattern concerns the influence of the cadmium dopant on the titanium oxide microstructure.

The spectra of the samples with low heavy metal percent (0.1, 0.5, 1 respectively 3.) shows the anatase (JCPDS: 02-0387) and rutile (JCPDS: 72-1148) phases, and no trace of cadmium metal, oxides or any binary compound oxides are detected. By increasing the cadmium content, a new crystalline compound ($CdTiO_3$, identified by JCPDS: 29-0277) is present in the TiO_2 lattice, observed in the XRD patterns for Cd5*A*-TiO_2, Fig. 3. Thus, doping is likely at low Cd concentrations, and chemical modification for higher Cd amounts, when also new compounds are expected. Based on these data we conclude that, for doping, the optimal percentage must be lower than 5 at.%. The photocatalytic activity of the films was tested for the sample doped in 0.1 and 0.5 respectively 1 at.%, Table 1.

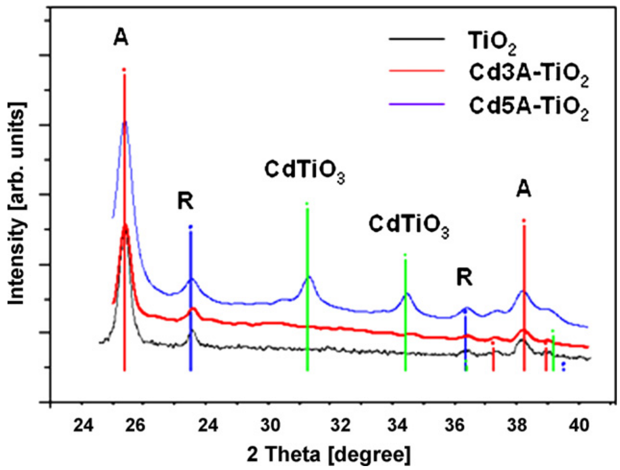

Fig. 3. The XRD pattern of the Cd3*A*-TiO_2 and Cd5*A*-TiO_2.

Table 1
The properties of cadmium modified the films.

Catalyst	UV–vis	AFM	Dye photo-degradation (%)	
	Band gap (eV)	Average roughness (nm)	MO	MB
TiO_2	3.2	133.36	12.145	31.63
Cd0.1*A*-TiO_2	3.02	128.15	32.81	40.14
Cd0.5*A*-TiO_2	3.03	131.38	28.47	39.81
Cd1*A*-TiO_2	3.10	139.17	24.13	29.03
Cd0.1*C*-TiO_2	3.08	133.5	16.13	33.42
Cd0.5*C*-TiO_2	2.95	119.02	22.05	37.62
Cd1*C*-TiO_2	2.97	150.89	17.53	30.48

Two doping mechanisms of TiO_2 with cadmium are possible: substitutional and interstitial. In the first situation some Cd^{2+} ions

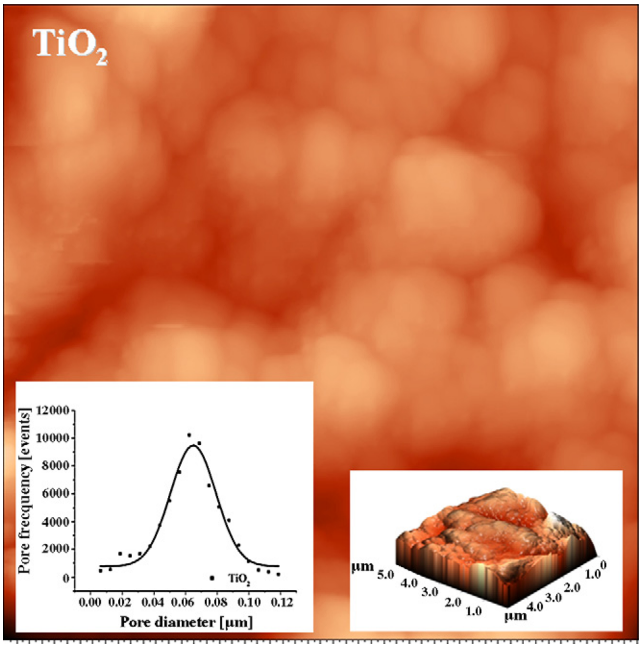

Fig. 4. The AFM image of the TiO_2 films.

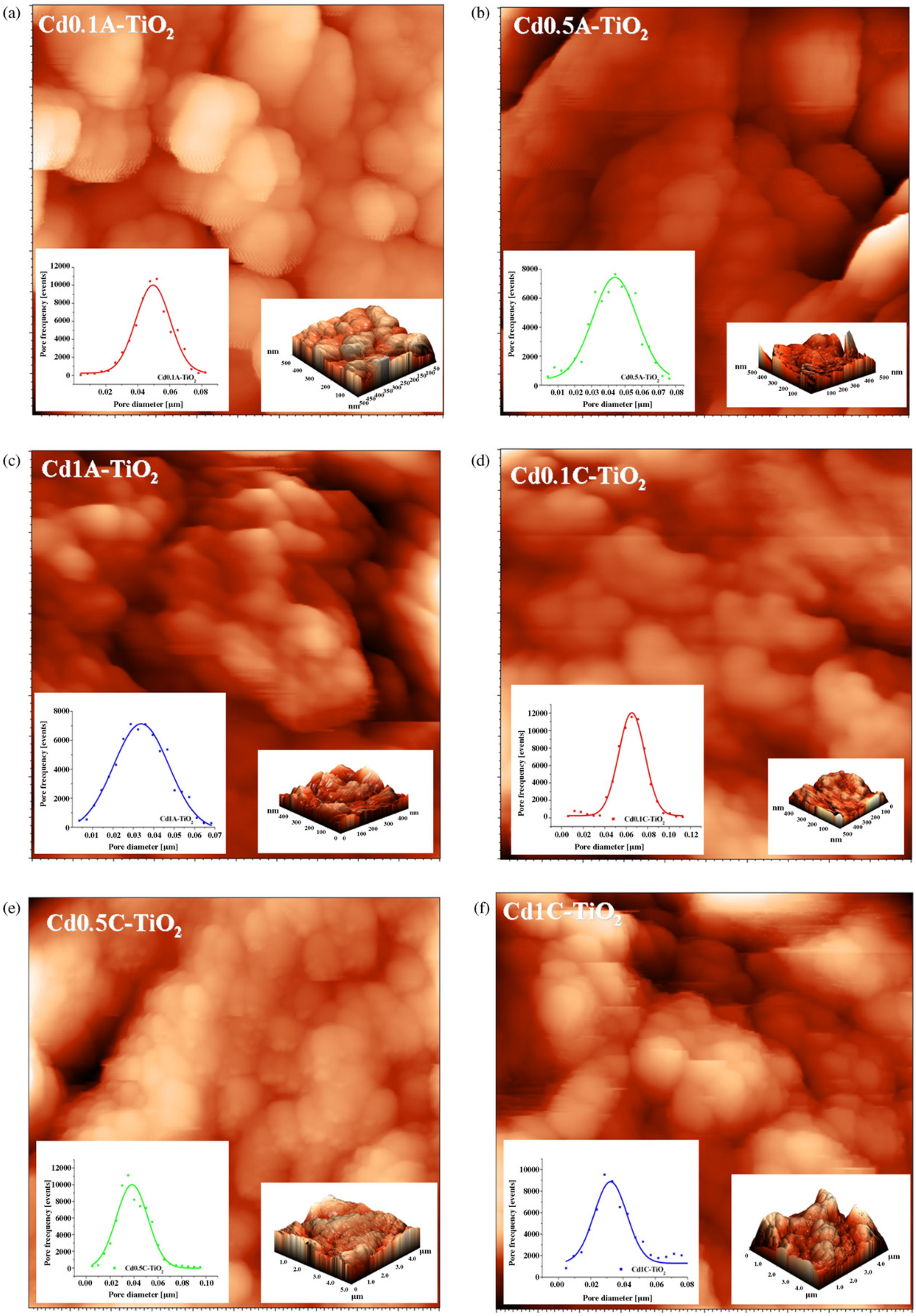

Fig. 5. The AFM images of the Cd-TiO$_2$ films.

replace Ti^{4+} (Eqs. (2) and (3)), while in the second case Cd^{2+} ions can occupy the interstitial sites of the TiO_2 lattice (Eq. (4)).

$$\mathrm{TiO_2} \xrightarrow[\mathrm{CdO}]{} \mathrm{Cd}''_{\mathrm{Ti}} + V_{\mathrm{O}}^{\bullet\bullet} + \mathrm{O}_{\mathrm{O}}^{\times} \qquad (2)$$

$$2\mathrm{TiO_2} \xrightarrow[\mathrm{CdO}]{} \mathrm{Cd}''_{\mathrm{Ti}} + V''''_{\mathrm{Ti}} + 3V_{\mathrm{O}}^{\bullet\bullet} + \mathrm{O}_{\mathrm{O}}^{\times} \qquad (3)$$

$$\mathrm{TiO_2} \xrightarrow[2\mathrm{CdO}]{} Cd''_{\mathrm{Ti}} + Cd_{\mathrm{i}}^{\bullet\bullet} + 2\mathrm{O}_{\mathrm{O}}^{\times} \qquad (4)$$

where in the Kröger–Vink notation: $\mathrm{Cd}''_{\mathrm{Ti}}$ is a cadmium ion sitting on a titanium lattice site, with two negative charge; $\mathrm{O}_0^{\times}$ is an oxygen ion sitting on an oxygen lattice site, with neutral charge; $V_0^{\bullet\bullet}$ is an oxygen ion vacancy, with double positive charge; $\mathrm{Cd_i}^{\bullet\bullet}$ is a cadmium interstitial ion, with two positive charges; V''''_{Ti} is a titanium ion vacancy, with four negative charges.

Between these two mechanisms, usually the substitutional one is the most likely to occur, considering that the Ti^{4+} radius (0.605 Å) [12] is smaller than that of Cd^{2+} (0.97 Å) [13], and allows the replacement with the formation of solid solutions. Furthermore, Eq. (4) is energetically unfavorable due to the high number of defects involved, making the cadmium ions to occupy an interstitial position in the titanium oxide lattice very difficult.

The thin films surface morphology has a pronounced effect on the photocatalytic activity. For a high photocatalytic activity, the thin film should have a porous nano-/meso-/microstructure. Porous structures can be obtained by generating loosely packed small grains; this can be controlled by adding surfactants (Triton X100). In the frame of this study, the photocatalyst morphology depends on the dopant concentration and chemical content.

Quantitative roughness measurements were obtained using AFM. Atomic force microscopy has been widely used to investigate structures of TiO_2 (Fig. 4) respectively Cd-TiO_2 on surfaces; Fig. 5 depicts 2D and 3D AFM images of Cd doped using cadmium acetate precursor (a, b and c) respectively chloride (d, e and f). The results prove that the film covers the entire area of the surface with small grains, which are uniformly distributed for the low dopant percentage (0.1 at.%), respectively randomly distributed for the other two sample types. Surface roughness increases the effective surface area of the material. This increases the active sites number and the number of defects. Relatively lower surface roughness (Table 1) presents a higher photocatalytic activity, this effect has been observed for the Cd0.1*A*-TiO_2 (Fig. 5a) sample respectively for Cd0.5*C*-TiO_2 (Fig. 5e).

The image analysis of the surface topography can provide detailed information on the surface pore structure and allows quantitative determination of the pore size distribution, Figs. 4 and 5. The pore size analysis shows that micro-, meso- and macroporosity are far from being clearly and sharply defined.

The narrow pore size distribution of films presents importance for its catalytic activity implying good homogeneity in the pore structure, mainly for Cd0.1*A*-TiO_2, respectively Cd0.5*C*-TiO_2. The pore size distribution is much broader for the other samples, indicating a more irregular and less ordered structure.

The study of the optical absorption of the investigated thin oxide films, particularly the absorption edge was used to elucidate the electronic band structure. The absorption coefficient analysis was used to obtain the optical energy gap (E_g) of the films by extrapolating the linear region of the plot $(\alpha h\nu)^2$ to zero absorption coefficient ($\alpha = 0$) [14]. The estimated band gap energy of the samples is presented in Table 1. Band gap calculations showed that implanted Cd^{2+} decreases the TiO_2 band gap. The experimental observations on the transmittance data confirm a shift of the adsorption edge with the Cd^{2+} content, Figs. 6 and 7. A blue shift is registered for the samples Cd0.5*A*-TiO_2 and Cd0.1*C*-TiO_2, while the red shift characterizes the other doped samples. These results can be correlated with the amount of defects resulted, confirming the doping process.

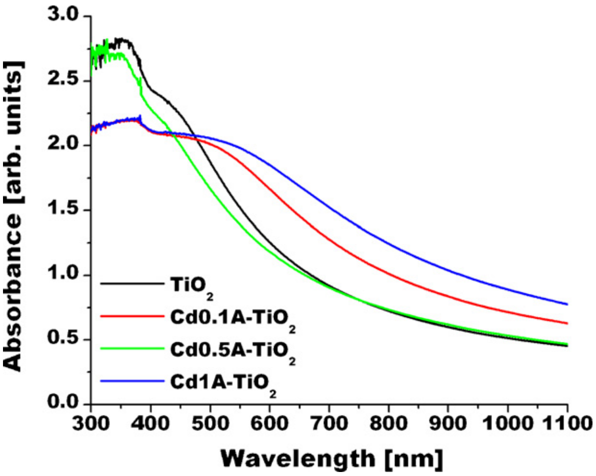

Fig. 6. Comparative absorption spectrum for TiO_2 and Cd*xA*-TiO_2 films.

3.2. *The photocatalytic activity of the films*

In water, UV-irradiated Cd-TiO_2 is able to completely destroy organic contaminants through the TiO_2 activation, according to the following reaction [15]:

$$2\mathrm{TiO_2} + h\nu \xrightarrow{k_1} \mathrm{TiO_2(e^-)} + \mathrm{TiO_2(h^+)} \qquad (5)$$

In Eq. (5), the e^- and h^+ species are the powerful reducing and, respectively oxidizing agents. During the organic compounds degradation, such as Methyl Orange and Methylene Blue, the hydroxyl radical ($OH^\bullet$), resulted in the oxidation of the adsorbed water or adsorbed OH^-, represents the primary oxidant and, in addition to oxygen, can prevent the electron-hole re-combination. The time of life of the hydroxyl radical ($OH^\bullet$) is very short, therefore, to react the dye must be near or linked to the photocatalyst substrate. Moreover, the oxidant must be convenient placed near the reactive group/groups of the dye. Therefore, the dye's structure and molecular symmetry play a key role, also the other ions solved near the substrate.

3.2.1. *The cadmium doping effect*

The cadmium modified materials present enhanced photocatalytic activity and can degrade the MO and the MB with higher efficiency than the unmodified TiO_2.

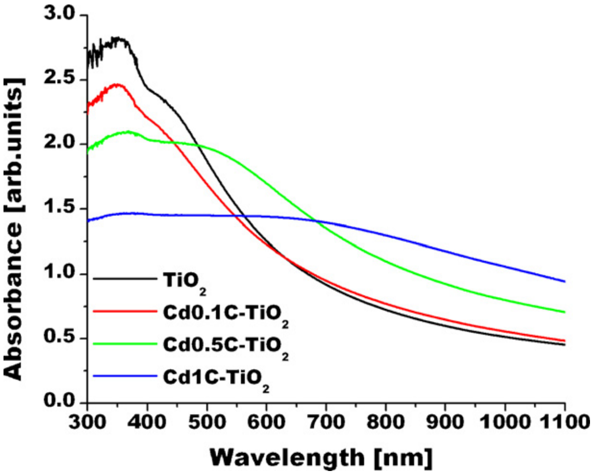

Fig. 7. Comparative absorption spectrum for TiO_2 and Cd*xA*-TiO_2 films.

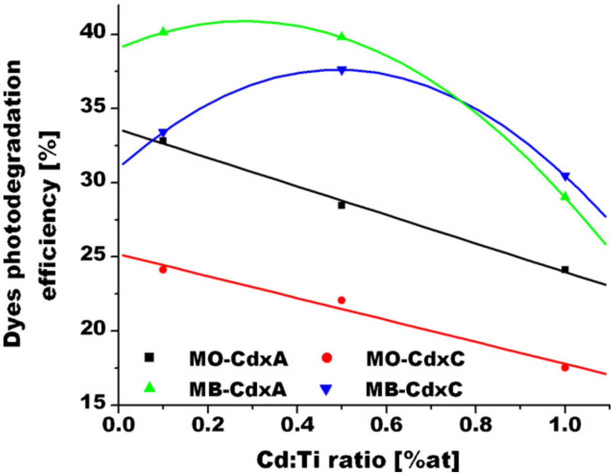

Fig. 8. Comparison between dyes photodegradation and Cd:Ti ratio.

By observing the dyes photodegradation efficiency for cadmium doped TiO$_2$ catalysts, it can be noticed that the optimum photocatalytic behavior is found to be 0.1 at.% for cadmium acetate and 0.5 at.% for cadmium chloride, Fig. 8. The lower photodegradation efficiency registered for the samples with the highest cadmium content could be also the result of a cation partial diffusion towards the surface (during annealing); cadmium rich sites are not chemically favorable for linking the dye on the surface and thus are unsuitable for photodegradation. The use of different cadmium precursors also influence the photodegradation efficiency; the highest output is registered when using cadmium acetate, and the reason can be that, during annealing in air, acetate decompose – totally or partially – forming volatile compounds and possibly traces of carbon, while chloride can be trapped in the film leading to impurification. These by-products can be responsible for the random variations in the band gap values.

The different behavior of the two dyes is also significant: while for MO the photodegradation efficiency is much higher on doped titania compared with the undoped catalyst (regardless the roughness values), for MB the increase is, at maximum, of 27% and is registered mainly on low cadmium content substrates. This supports the observation that the chemical interactions dye – active sites on the photocatalyst are important and are governed by the composition and polarity of the dye's group/groups linked to the surface.

These results are consistent with the unique structural, morphological and surface characteristics of the composite Cd-TiO$_2$ materials. The lower the average particle size and roughness of the materials, the higher the percentage of photodecomposition. The surface doping and modification effects thus appears synergetic to the charge separation process and the photocatalytic results are explained based on the mechanism that involves efficient separation of electron–hole pairs induced by the cadmium particles. This enhances the ability of the modified TiO$_2$ particles to effectively capture protons.

An experimental correlation between the band gap energy of the Cd*xA*-TiO$_2$ films and photocatalytic degradation was observed, Fig. 9. The experimental results were linear fit with a high regression coefficient (0.9970 for MO photodegradation respectively 0.9977 for MB photodegradation). The dyes photodegradation efficiency increases with the band gap decrease. By a rough extrapolation, we could thus presume that the highest dyes photodegradation efficiency could be obtain when the band gap energy is 2.6 eV for MO respectively 2.3 eV for MB degradation. These values are not completely impossible for titania; Pingxiao and colab. observed that the cadmium doped TiO$_2$, prepared by sol–gel, have a band gap energy of 2.75 eV and the photodegradation efficiency of rhodamine B (10^{-5} M) after 210 min of irradiation was 98% [9]. To be noted that these results were due to the additions of the H_2O_2 in systems that contributes to the degradation pathway by acting as an electron acceptor or as a direct source of hydroxyl radicals due to homolytic scission, fact observed by us previously [16].

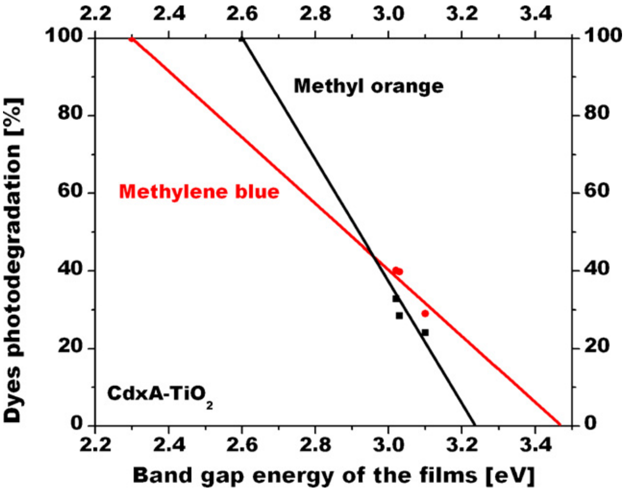

Fig. 9. Relation between band gap energy of the films and dyes photodegradation.

3.2.2. *The influence of the dyes concentration*

After optimizing the doping content of the catalyst, the photocatalytic degradation of both dyes was carried out by varying the initial concentrations of the dye from 0.00625 mM to 0.05 mM. The photodegradation activity of the Cd0.1*A*-TiO$_2$ and Cd0.5*C*-TiO$_2$ catalysts were tested and the results are presented in Figs. 10 and 11. By increasing the dye concentration, the photodegradation efficiency decreased as expected. The explanation for this behavior is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases, with direct consequence on the electron–hole formation.

3.2.3. *The influence of the photocatalyst*

By targeting up-scalable applications, a compulsory condition is to use low cost deposition techniques that can be applied for large surfaces of thin films. An alternative to the doctor blade technique,

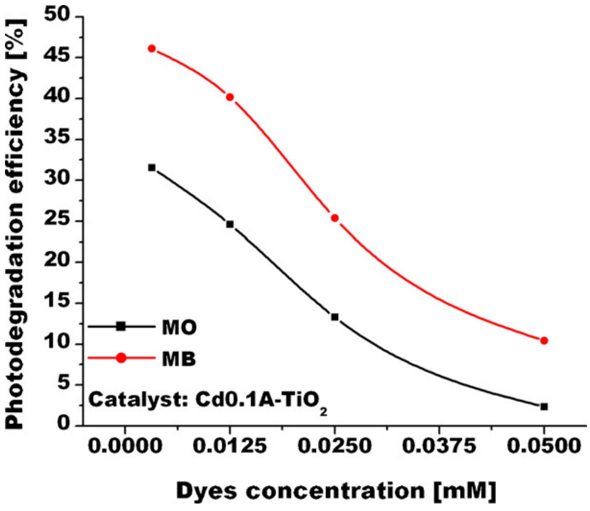

Fig. 10. The influence of the dyes concentration on the photocatalytic activity of the Cd0.1*A*-TiO$_2$ film.

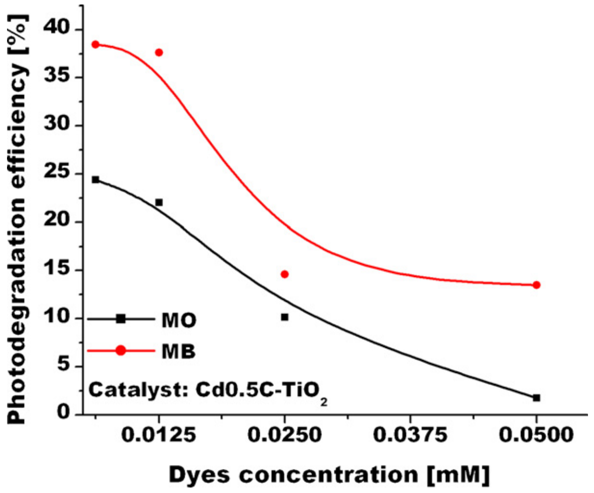

Fig. 11. The influence of the dyes concentration on the photocatalytic activity of the Cd0.5*C*-TiO_2 film.

respecting this prerequisite is the spray pyrolisys technique, SPD. The comparative photodegradation results of Methyl Orange on thin films obtained by doctor blade (Cd*xA*-TiO_2) and spray pyrolysis deposition are presented in Fig. 12. Titanium oxide was prepared by spray pyrolysis deposition (SPD) doped with cadmium using: titanium (IV) izopropoxide, cadmium acetate-alcoholic solutions, acetyl acetone, and ethanol. The deposition was done on the heated glass substrate (sample of $1.5 \times 2.5\,cm^2$), using the optimum conditions previously reported Duta et al. [17]. The films were annealed in an oven at 500 °C, for 6 h. The doping percent was 0.1 at.%, 0.5 at.% respectively 1 at.%.

The Cd-TiO_2 prepared by doctor blade presents a significantly increased degradation efficiency of the Methyl Orange (initial concentration 0.0125 mM), than the TiO_2 thin film obtains by SPD, because the doctor blade exhibit larger contact surfaces than thin dense SPD films. The higher dopant concentrations (1%) in the SPD film had as consequence the decrease in the photodegradation efficiency, confirming the assumptions made for the DB films.

Choosing one deposition technique must be subject of a benefit–cost analysis considering, beside the process efficiency, also the film thickness (much lower for the SPD films), the energy input in production, the costs of the rough materials, etc.

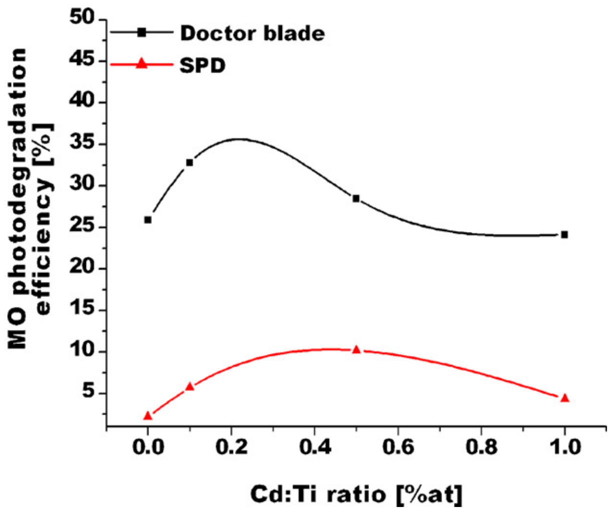

Fig. 12. The influence of the photocatalyst on the MO photodegradation.

4. Conclusions

We have prepared cadmium doped TiO_2 systems by doctor blade, using TiO_2 Degussa P25 powder and different cadmium precursors (acetate and chloride). Important differences were registered in the structural and electronic characterization of the photocatalysts, when varying the dopant (cadmium) amount and precursors type. The experiments showed that titania films prepared with cadmium acetate presents a higher photocatalytic activity than the films prepared with cadmium chloride.

In order to improve the photo-efficiency of the electronic process as well as the response into the visible part of the spectrum, TiO_2 doping with cadmium have been employed. Cadmium ions can also act as charge trapping sites and thus reduce electron–hole recombination. The effect of doping on the activity of the photocatalyst depends on many factors, e.g. the type and the concentration of dopant, the structure and the initial concentration of the dyes, the physical–chemical property of the catalyst.

There is a linear correlation between band gap energy of the cadmium doped TiO_2 films and dyes photodegradation efficiency, which conducted the experiments onto best photocatalytic efficiency of the films. The better photocatalytic activity of the Cd0.1*A*-TiO_2 films may be due to hydroxyl group on the catalyst surface and the band gap energy of the films.

The use of thin films instead of dispersed photocatalytic powders results in a decrease in dyes degradation overall efficiency; but, considering the catalyst surface available for photodegradation, corresponding to the same amount of TiO_2 powder and, respectively film, the results obtained can be considered good and can be further used in designing an up-scalable wastewater treatment processes.

Acknowledgments

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