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Cd^{2+} MODIFIED TiO_2 FOR METHYL ORANGE PHOTODEGRADATION

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Industrial wastewaters contain toxic metal ions like cadmium, that can de absorbed on the surface of the TiO_2 influencing the overall efficiency of the process. New materials with high photocatalytic process efficiency are developed. This paper presents the results of experiments done using TiO_2 thin films immersed in cadmium solutions. TiO_2 thin films were prepared by doctor blade technique and immersed in different chloride and acetate cadmium solutions. The immersion time, cadmium concentrations and post immersion thermal treatment were controlled. The influence of these parameters on the surface properties of TiO_2 thin films was studied. The thin films were characterized by atomic force microscopy (AFM) and X ray diffraction (XRD). The TiO_2 thin films were used for testing the methyl orange photodegradation efficiency after the cadmium adsorption. The thin films were exposed to UV radiation for 360 minutes, immersed in methyl orange solution of 0.0125 mM concentration.

INTRODUCTION

Large amounts of wastewaters are generated by the industry. A major part of the pollutants in these waters are represented by organic dyes that are not suitable for conventional biological treatment. As a real alternative, heterogeneous photocatalysis for dye removal presents some advantages: high photocatalytic activity, non-toxicity, high chemical stability and low cost.[1-3] The mostly used material for heterogeneous photocatalysis is TiO_2. The depurating process is based on the generation of highly active species, like •OH, that have a good oxidation potential. Titanium dioxide proved by numerous studies that can be used as an efficient photocatalyst for textile dye wastewater treatment. One possible mechanism of generating active species on the surface of TiO_2 by UV illumination is presented in the following reactions:[4]

$$TiO_2 + h\nu \rightarrow e^- + h^+, \quad (1)$$

$$h^+ + H_2O(TiO_2) \leftrightarrow \bullet OH(TiO_2) + H^+, \quad (2)$$

$$\bullet OH(TiO_2) + Dy(TiO_2) \rightarrow \text{intermediates} \rightarrow P \quad (3)$$

$$e^- + O_2 \rightarrow O_2\bullet^-, \quad (4)$$

$$O_2\bullet^- + HO_2\bullet + H^+ \leftrightarrow H_2O_2 + O_2, \quad (5)$$

$$H_2O_2 + h\nu \rightarrow 2HO\bullet \quad (6)$$

$$H_2O_2 + Dy(TiO_2) \rightarrow \text{intermediates} \rightarrow P \quad (7)$$

The mechanism suggests that first the dye molecule (organic compound and the main pollutant in the textile industry effluent) is adsorbed at the surface of the semiconductor, then under UV irradiation electrons are promoted to the conduction band from the valence band forming electron–hole pairs (1). The electrons promoted in the conduction band react with oxygen molecules and form $O_2\bullet^-$ that produce H_2O_2, and further HO• highly reactive with the dyes. Final steps (3) and (7) show the formation of intermediates followed by complete mineralization of the organic compounds. The aqueous suspension of TiO_2 presented very high efficiency, but poses one major technical disadvantage for separation of the photocatalyst at the end of the photocatalysis step. Recent studies concentrate on using TiO_2 films in order to eliminate this problem[4-5]. A simple and reproducible way to obtain TiO_2 film is doctor blade technique. It is a low cost and very easy to up-scalable technology.

Another important aspect regarding the composition of the industrial wastewaters is that it contains heavy metal ions that have a high negative environmental impact. Having these ions in the composition of the wastewaters will influence the surface of the catalyst due to adsorption. This paper explores the influence of the cadmium ions

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on TiO_2 doctor blade films in the methyl orange photodegradation. The cadmium ions could be adsorbed on the surface of the film and play a major role to stop the electron-hole pair recombination, thus the amount of active species will increase and the photodegradation process efficiency will be improved.

EXPERIMENTAL

1. Materials

The TiO_2 thin films were obtained by doctor blade technique. Precursors used were ethanol EtOH (J.T. Baker) solutions of TiO_2 Degussa P25 powder, and acetilacetonate, AcAc (2,4 pentadione 99+%, Aldrich), under previously optimized condition[6]. The substrate was microscope glass slides (Heinz Herenz). Cadmium acetate (Scharlau Chemie) and cadmium chloride (Scharlau Chemie) were used as metal ions source in the immersion step of TiO_2 thin films. Methyl orange (Merck) was used for testing the photocatalytic efficiency.

2. Preparation of surface modified TiO_2 thin films using immersion in cadmium ion solutions

The glass surface of the sample was controlled to 1.5 per 2.5 cm and was completely covered on one side by TiO_2. After annealing the thin films were immersed in aqueous solutions with different concentration of cadmium salts (0.1; 0.01; 0.001mol/L). The immersion was done in Berzelius plastic beakers using 40mL solution per one sample to avoid the metal ion adsorption on the vessel's walls. Immersion time was 6 hours and after immersion the samples were air dried followed by annealing for 6 hours at 500ºC. The samples obtained were used for photocatalytic test on methyl orange (MO).

3. Photocatalysis tests

Photocatalysis tests were conducted in a UV reactor using 3 Phillips UV lamps for illuminating the samples. The photocatalytic experiments were done in quart beakers using 25mL of 0.0125mM solution of MO. The irradiating time was 6 hours. After UV illuminating, the solution of MO was analyzed using UV-VIS spectrophotometer Perkin Elmer, Lambda 25, at 462nm. Photocatalyst efficiency was calculated for each TiO_2 thin film sample by comparing the absorbance value for the solution of MO UV exposed, with the similar value of the initial MO solution of 0.0125mM.

4. Thin films characterization

The surface modified TiO_2 thin films were characterized using XRD measurements conducted on Bruker, Advanced, D8 and atomic force microscopy (AFM) on an Ntegra Spectra, MT-NDT.

RESULTS AND DISCUSSION

1. Film characterization

The TiO_2 films obtained were analyzed using XRD and AFM techniques. In Fig. 1 the XRD spectra of doctor blade TiO_2 is presented, showing clear peaks for anatase and rutile. During the deposition step of the film the composition of the TiO_2 powder did not change, thus on the film the same product is obtained.

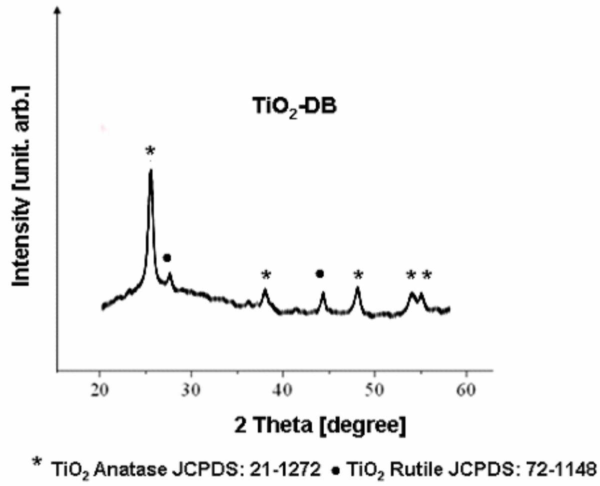


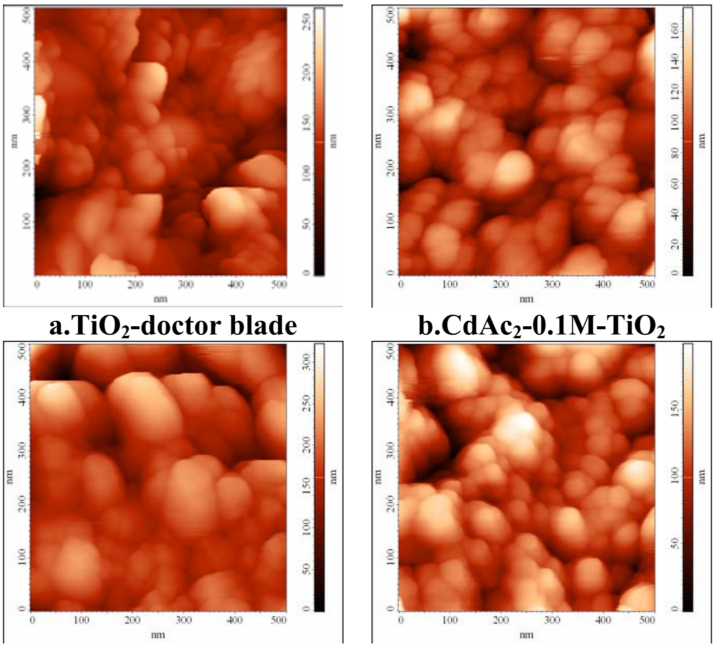
Fig. 1 – XRD spectra of doctor blade TiO_2.

Table 1

TiO_2 film properties

Catalyst	UV-VIS	XRD			AFM
	Band gap [eV]	Crystal anatase phase [%]	Crystallite (anatase) [nm]	ε [nm]	Average Roughnes s[nm]
TiO_2	3.22	74.556	137.40	0.000187	26.38
$CdAc_2$-0.1-TiO_2	3.285	73.649	143.616	0.000378	27.50
$CdAc_2$-0.1-TiO_2	3.18	76.229	144.131	0.000377	26.30
$CdAc_2$-0.1-TiO_2	3.20	78.515	151.284	0.000496	24.07

The AFM of doctor blade TiO_2 and TiO_2 immersed in cadmium acetate are presented in fig. 2. It can be seen that all samples have homogeneous, porous morphology and the roughness of the samples are almost constant and low.



a.TiO_2-doctor blade b.$CdAc_2$-0.1M-TiO_2

c.$CdAc_2$-0.01M-TiO_2 d.$CdAc_2$-0.001M-TiO_2

Fig. 2 – AFM's of TiO_2 films doctor blade and immersed in cadmium acetate.

2. Photodegradation process

The photodegradation experiments were based on using a UV reactor for exposing the films to UV radiation immersed in 40mL quart beakers. After the exposure time the films were removed and the methyl orange solution was analyzed with UV-VIS spectrophotometer to calculate the photodegradation efficiency relative to the initial methyl orange UV-VIS absorption. The efficiencies obtained for samples immersed in cadmium acetate and chloride are presented in Fig. 3. The samples immersed in cadmium acetate presented better efficiencies then the samples immersed in cadmium chloride. The best efficiency was obtained for both anions at lowest immersion concentrations.

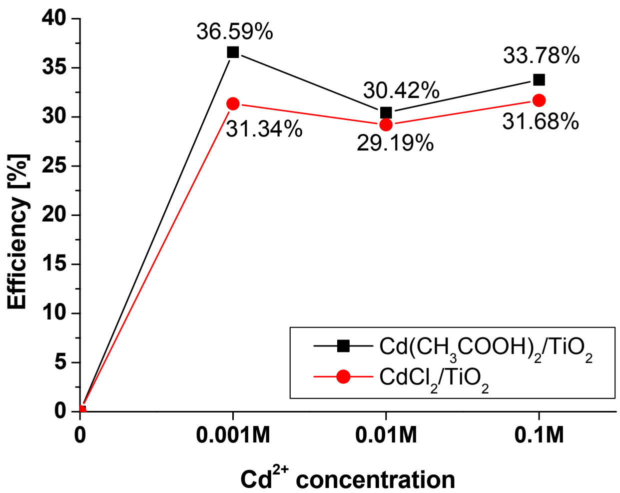


Fig. 3 – Photodegradation efficiency of TiO_2 film immersed in cadmium acetate and chloride.

On TiO_2 film unmodified with Cd^{2+} the photodegradation efficiency is 29%. Thus the cadmium adsorption improves the efficiency and doping is expected since the XRD spectra show no modifications. This effect is more significant at low cadmium concentration, again supporting the doping assumption. This effect is stronger in solutions with acetate content and the reason may be the slightly different pH values induced by the cadmium salts after hydrolysis, influencing the equilibrium in the process (2).

CONCLUSIONS

The presence of cadmium salts in industrial wastewaters can produce an increase in photodegradation efficiency by adsorption of the cadmium ions on the surface on the TiO_2 film. Special action must be taken to control the concentration of the heavy metal ions in order to obtain a higher efficiency.

Film immersed in cadmium acetate solution presented better efficiency then films immersed in cadmium chloride solution. Cadmium ions were adsorbed on the surface of the doctor blade TiO_2 films increasing the photodegradation efficiency from an average 29%, for the normal TiO_2 film to best value 36.59%, for the TiO_2 film immersed in cadmium acetate 0.001M. The best results were obtained at low concentration of cadmium salts, respectively 0.001M.

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