Reactive Black-5 Photodegradation by TiO$_2$ Thin Films Prepared by Ultrasonic Spray

N. L. Becerril-Altamirano$^1$, R. T. Hernández López$^1$, L. González Reyes$^1$, A. R. Suárez Parra$^2$, R. Ramírez López$^3$, A. Martínez Jiménez$^1$, I. Hernández-Pérez$^1$.

1División de CBI, UAM-Azcapotzalco, 02200, Cd. México, México. 2Centro de Investigación en Energía, UNAM, Temixco Morelos, 62580, México. 3Departamento de Ciencias Básicas, Escuela Superior de Ingeniería Química e Industrias Extractivas, Instituto Politécnico Nacional, UPALM, Edif. 6, 07738, Cd. México, México.

E-mail: hlrt@correo.azc.uam.mx, ihp@correo.azc.uam.mx

Abstract. Structural, optical, textural and photochemical properties of transparent TiO$_2$ thin films were investigated using XRD, AFM and DR-UV-Vis spectroscopy. TiO$_2$ films were obtained by the ultrasonic spray pyrolysis (USP) deposit technique, using corning glass as substrate and a Titanium-Acetyl-acetonate in N,N-Dimethylformamide solution as precursor. XRD patterns depicted the presence of nanostructured materials with poor crystallinity and by diffuse reflectance spectroscopy was measured the absorption profile and calculated the band gap energy of the TiO$_2$ thin films. As the layer thickness diminished, the absorption edge showed a blue shift and the band gap energy was increased. AFM studies allowed determination of irregular thin coating with different morphologies and the presence of micropores. The photocatalytic behavior was evaluated employing the Reactive Black-5 degradation as model reaction. The reaction progress was monitored following the absorbance at 315 and 597 nm of the corresponding UV-Vis absorption spectra. According with the catalytic tests, it was found that the best degradation was achieved with the film prepared at 450 C during 6 minutes.

1. Introduction

Water pollution depicts one of the most serious environmental problems since it can inhibit the photosynthetic processes by the flora in rivers, lakes and seas during the natural water cycle [1]. More than 40% of wastewater discharged belongs to the dye stuff manufacturing, printing and textile industries, moreover 70% belongs to azo dyes [2]. Therefore, textile industries have enormous demands and emissions of water to natural reservoirs. Unfortunately, during the textile and finishing process more than 20% of dyes get lost directly to discharges [1]. On the other hand, azo dyes are not biodegradables, they resist conventional treatments due to they are designed with chemical and photochemical stability [3, 4]. At the same time, this kind of dyes frequently present more than one azo group (-N=N-) joined to an aromatic ring, evidencing mutagenic and toxic effects to human and aquatic life [5, 6]. Indeed, the main physicochemical processes used to remove toxic compounds, from industrial wastewaters, are flocculation, coagulation, adsorption, and biological treatment, etc. [7]. However, the principal limitation of these processes is the partial elimination of the contaminants and the generation of another pollutants that need further treatments. Furthermore, in the last decades advanced oxidation processes (AOP) are considered to be the most viable alternative for removing
hazardous compounds since they can make strong changes on their chemical structure, reaching a deep pollutant mineralization [8-11]. Actually, heterogeneous photocatalysis, as an AOP, is considered a promising technology due to it is not specific, and therefore, it is capable to destroy a wide variety of organic and inorganic contaminants. In heterogeneous photocatalysis, the catalyst is activated by UV or Visible radiation (with the adequate frequency) to photogenerate electron-hole pairs, which participate in the redox reactions [12-15]. The conventional photocatalysis employs fine particles of semiconductor materials (TiO$_2$, Fe$_2$O$_3$, ZnO and others), but these systems presents two important drawbacks: a) slow settling velocity of the suspended powders (long retention times in the clarifiers), which limits its reuse and b) the high turbidity created by the large concentrations of powder semiconductor (in order to improve the photo conversion), with the drastically decrease in the depth of light penetration. In order to avoid these inconveniences, several techniques have been developed to immobilize the semiconductors. Among these immobilization methods, the thin film techniques appears as the most promising, such as sol-gel method and coating-drying-backing processing to obtain TiO$_2$ films of high quality and the necessary thickness [16-17]. In addition, the ultrasonic spray pyrolysis method is another of the simplest techniques for thin films preparation because it requires low equipment cost, low temperature and no vacuum requirement. Besides it also provides good thickness and uniformity over large area.

In the present study, the photodegradation of RB-5 azo-dye was carried out on a transparent TiO$_2$ thin film prepared by ultrasonic-spray pyrolysis method at different temperatures and deposition times. The photocatalytic activity of TiO$_2$ thin films was compared with the catalytic activity of TiO$_2$ nanoparticles obtained by sonochemical synthesis [18].

2. Experimental details
The experimental details were divided in sections accord to the preparation technique of TiO$_2$ and characterization.

2.1. Titanium oxide films synthesis.
The titanium oxide films were prepared by the ultrasonic spray pyrolysis technique over corning glass slides (26 x 76mm). The precursor consisted of a 0.076 M solution of Ti (IV) Acetilacetonate (Alfa-Aesar) dissolved in N,N-Dimethylformamide (Sigma-Aldrich). The aerosol was obtained by means of a conventional ultrasonic generator (0.9 Hz) and transported to the heated glass slide using a 20 mL/min of dried air flow. The film thickness was controlled varying the deposition time from 3 to 6 minutes. The temperature was controlled in the range of 400 – 450 C.

2.2. Titanium oxide nanoparticles.
All chemicals were of the highest purity available and were used as received without further purification. The titanium oxide nanoparticles were prepared by the sonochemical method, employing [(CH$_3$)$_2$CHO]$_4$Ti (TTIP, >97%) as titanium source, in a mixture of acetone-methanol 1:1. The mixture was ultrasonically treated with a Branson (model 2510) bath operating at 40 kHz during 50 minutes; the precipitate was dried under static air at 150 C, according to the methodology described previously by Gonzalez-Reyes [18].

2.3. Films Characterization.
The structural properties of the TiO2 semiconductor films were characterized by XRD in a Bruker D8 Focus diffractometer operating in the reflection mode with Cu-Ka radiation (35 kV, 25 mA) at 2º s$^{-1}$ scan rate. Atomic force microscopy in the tapping mode (AFM Digital Instruments-Nanoscope) was employed to determine the textural properties of the semiconductor films. UV-Vis absorption spectra and optical band gap energy were obtained by diffuse reflectance mode in a Dual-Beam Varian Cary I Spectrophotometer.
2.4. Photocatalytic test.
The photocatalytic assessments were carried out in a batch reactor equipped with condenser, immersion cooler and UV light lamp with a maximum emission at 365 nm. In order to evaluate the azo-dye degradation rate it was employed model solutions of RB5 dye with an initial concentration of 100 ppm, 300 µL of H$_2$O$_2$ (Mallinkrod 30% v/v) were added as oxidant agent and the pH was fitted at 2.6 pH value. The photodegradation and bleaching processes were followed by UV-Vis spectrophotometry in the range of 190 to 900 nm. The figure 1 shows the RB5 calibration curve since 0.5 to 100 ppm. The bleaching of the azo-dye solution was monitored by the absorbance maximum of the UV-Vis spectrum at $\lambda_{\text{max}} = 597$ nm and the mineralization at $\lambda_{\text{max}} = 315$ nm.

3. Results and discussion

3.1. Titanium oxide films characterization.
TiO$_2$ films in appearance look transparent and homogeneous. The optical characterization of TiO$_2$ deposited at 400°C-6 min, 450°C-3 min and 450°C-6 min are depicted in Figure 2. As can be seen in this figure, those films that were synthesized during 6 minutes show a similar spectrum, presenting two bands in the UV region, the first one at 247 nm associated with the terminal OH groups and the second one at 320 nm, which can be responsible of the O$_2p$$\rightarrow$Ti$_{3d}$ transition. On the other hand, the spectra evidence two shoulders in the visible region at 458 and 585 nm, the first one can be associated with the forbidden transitions between electrons in d orbitals and this transition allows the stabilization of the energy in all sub-levels 3d of the Ti atom. The second shoulder at 585 nm might be referred to residuals of organic ligand precursor. For the TiO$_2$ film obtained at 450°C during 3 min there is only a strong and broad absorption band located around 230-330 nm, associated to O$_2p$$\rightarrow$ Ti$_{3d}$ transition. The no well-defined absorption band at 247 nm in this film, could indicate the elimination of an important number of terminals OH groups and the formation of Ti-O-Ti compact structures. The same wide band in the visible region (around 585 nm), can be related to residual organic ligand bonds.
The optical band gap was estimated from a plot of $(\alpha hv)^n$ versus photon energy $(h\nu)$ (not showed here in) and all samples showed an indirect transition $(n = 2)$. The interception of the tangent to $[F(R)hv]^2=0$ plot gives a good band gap energy $(E_g)$ approximation and these results are summarized in Table 1. For all samples a blue shift was observed and the $E_g$ values are higher than those reported in literature $(3.2 \text{ eV})$, consequently, this effect can be associated to the quantum size effect due to small crystals of TiO$_2$. These results are in good agreement with the XRD results (see Table 1), indicating that the band gap energy is size dependent, the smaller size the higher energy.

Table 1 summarizes the principal characteristics of films deposited at 400°C during 6 min and 450°C during 3 and 6 min. The results indicate that the position of the principal reflection for all the samples was 24.815° and the FWHM show the same value for 450°C-3 and 6 min (11.6548°) versus 16.7709° for 400°C-6 min. Whereas the higher values of thickness are associated to sample obtained at 450°C by 6 min, this sample has the minor band gap energy (3.25 eV). It denotes that when the crystal size grows the band-gap decreases.

![Figure 2. Uv-Vis spectrum of 400°C-6 min, 450°C-3 min and 450°C-6 min TiO$_2$ films.](image)

| Film sample | 2 Theta (°) | FWHM (2 Theta) | Crystallite Size (θ) | $E_g$ (eV) | Thickness (μm) | Photodegradation Of RBS at 180 min (%) |
|-------------|-------------|----------------|---------------------|------------|----------------|--------------------------------------|
| 400°C/6 min | 24.815      | 16.7709        | 4.874               | 3.32       | 1.3            | 60                                   |
| 450°C/3 min | 24.815      | 11.6548        | 5.184               | 3.29       | 1.2            | 56                                   |
| 450°C/6 min | 24.815      | 11.6548        | 8.049               | 3.25       | 1.5            | 70                                   |
The diffraction plots (Figure 3) were analyzed by means of PeakFitV4 program in order to determine the position of the principal reflections and the crystallite size. It can be seen that increasing deposition temperature, amorphous phase is crystallized and oriented along [101] and [004] planes. XRD patterns were compared for both anatase, ICDD PDF 21-1272, and rutile ICDD PDF 21-1276, database cards. The results showed only the presence of the anatase phase with poor crystallinity. The Scherrer equation was used to estimate the crystallite size, as Table 1 illustrates.

The average thickness of films depends on the deposit conditions, and it was observed from atomic force microscopy, that the film obtained at the lowest temperature and deposition time is thinner. In Figures 4 to 6 are shown AFM micrographs for films obtained at, 400 °C-6 min, 450 °C-3 min and 450°C-6 min. From these analysis, it was found that the sample prepared at 400 °C by 6 minutes has a thickness around 1.3 microns. The one, which was deposited at temperature of 450 °C during 3 min have 1.2 microns of thickness and the sample synthesized at 450°C-6 min has a structure formed for nanorods with 1.5 microns (Table 2). The figure 4 shows the morphology and profilometry of the film synthesized at 400°C during 6 min. It reveals the presence of homogeneous porous material, both in shape, depth and pore diameter.

The figure 5 shows an irregular and highly rugged material of the TiO$_2$ prepared at 450 °C for three minutes. Here can be seen a surface formed by quasi-spherical particles, like valleys and mountains with heights estimated at 0.128 µm.
Figure 4. Atomic force micrograph: profilometry curve of one film region and pore structure of the TiO$_2$ thin films 3D and plane of the sample synthesized at 400 °C-6min.

Additionally, from this micrograph is evident that the surface is composed of three-dimensional aggregates, finally there is a poor porosity. In the case of figure 6, this one depicts an homogeneous morphology achieved for the sample synthesized at 450°C during 6 minutes.

Figure 5. 3D profile curve of one film region, surface structure and grain profilometry of the TiO2 thin films prepared by ultrasound spray pyrolysis at 450 °C-3min.
The surface film has a structure formed of nanorods with an average pore diameter of 36 nm and 0.5 microns in length. On the other hand, it was observed the growth of small three-dimensional aggregates.

As can be seen from Figures 4-6, the three samples are quite different, since the all samples were obtained from the same method and the same precursors, the differences in morphology, surface roughness and the porosity for each of them can be attributed mainly to the synthesis conditions, i.e. temperature and deposition time.

This result is very important in the photocatalytic behavior due to the porosity increases the surface area and improves the degradation efficiency of the catalyst.

3.2. Photocatalytic activity.
The RB5 azo-dye photodegradation was followed by the decrease of the absorption band of the solution at 597 nm wavelength. Figures 7(a) shows the photodegradation at room temperature and pH = 2.6 for all thin films and the TiO\textsubscript{2} in powder form. From this figure it was observed that all samples show two regions, initially presents a zone of low activity (around 5 to 8 min.), possibly due to the low concentration of active species on the catalyst surface. In the second zone, the reaction occurs quickly, due to the high availability of active species. The low photoactivity (60 %) of the film synthesized at 450 °C-3min can be due to the absence of the absorption band at 247 nm associated to the terminal OH groups and the absence of porosity (low specific area) depicted for this sample, while the best performance shown by the sample synthesized at 450 °C-6min can be associated to the availability of OH groups as to the high specific area generated by its structure and surface geometry (interparticle spaces). To the active region, it was found that the reaction rate can be fitted by a pseudo-first order model, as shown in Fig. 7(b), from this correlation was possible to calculate the corresponding kinetic constants of the three films: 0.005, 0.004 and 0.007 s\textsuperscript{-1} respectively.

The higher photocatalytic activity of the TiO\textsubscript{2} thin films is showed by the one prepared at 450 °C during 6 min of deposition time with a degradation of 70 mg/L of dye. This behavior can be attributed to structural and textural characteristics of the film. Finally, the photocatalytic activity of the TiO\textsubscript{2} thin films, to degrade RB5 at pH = 3, is similar to the TiO\textsubscript{2} anatase phase, 305.6 m\textsuperscript{2}/g and 4-6 nm of crystal size, prepared by sonochemical method [20].

Figure 6. AFM micrograph 3D and Profilometry curve of TiO\textsubscript{2} film region for sample obtained at 450 °C-6min.
Figure 7. Characteristic kinetic behavior of TiO2 thin films prepared by ultrasonic spray pyrolysis, (a) Photodegradation of RB5 with TiO2 NPs and TiO2 thin films prepared at 400°C-6, 450°C-3 and 450°C-6 min. (b) Kinetics of RB5 with 400°C-6, 450°C-3 and 450°C-6 min.

Conclusions
TiO2 thin films were successfully deposited on a corning glass substrate by ultrasonic spray pyrolysis technique. All thin films are partially crystallized into anatase phase and have good transparency and homogeneity. The difference in morphology, surface roughness and porosity for each of them can be attributed mainly to the synthesis conditions as temperature and deposition time. The photocatalytic behavior of TiO2 thin films can be attributed mainly to the textural characteristics. The porosity increases the surface area and improves the degradation efficiency of the catalyst. Further investigation among the different factors influencing the activity such as: crystallinity, surface area and morphology are in progress in our laboratory.

Acknowledgements
N. L. Becerril-Altamirano acknowledge to CONACYT for the and by the mobility program Santander Serfin ECOES. The authors gratefully acknowledge to Draucin Jiménez and Rogelio Elvira for the technical assistance. This work was carried out with the support of the Materials Chemistry Area from UAM-A.

References
[1] Anjaneyulu Y, Sreedhara N. C, Samuel Suman Raj D. (2005) Decolorization of industrial effluents-available methods and emerging technologies-a review. Environ Sci. Biotechnol 4:245-273
[2] Kansal S. K, Kaur N, Shing S. (2009) Photocatalytic degradation of two commercial reactive dyes in aqueous phase using nanophotocatalysts, Nanoscale Res. Let. 4,709-716
[3] Konstantinou I, Albanis T. A. (2004) TiO2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetics and mechanistic investigations. Appl. Catal. B: Environmental 49:1-14
[4] İşik M, Sponza D. T. (2004) A batch kinetic study on decolorization and inhibition of reactive black 5 and direct brown 2 in a anaerobic mixed culture. Chemosphere 55:119-128
[5] Chung K. T, Stevens S. E. J, Cerniglia C.E (1992). The reduction of azo dyes by the intestinal microflora. Crit Rev Microbiol 18:175-197
[6] Chung K. T, Stevens S. E. J. (1993) Degradation of azo dyes by environmental microorganisms and helmints. Environ ToxicolChem 54:435-441
[7] Stolz. A (2001) Basic and applied aspects in the microbial degradation of azo dyes. Appl. Microbiol Biot.56:69-80
[8] Kaneko M, Okura I. (2002) Photocatalysis: Science and Technology. Springer
[9] Ramalho R. S. (1983) Introduction to wastewater treatment processes. Academic Press Inc.
[10] Surpateanu, M, Zaharia C. (2004) Advanced oxidation processes for decolorization of aqueous solution containing Acid Red G azo dye. Central European Science Journals 2(4):573-588
[11] Scheeren C. W, Neri J. G, Paniz, and Ayrton F. Martins (2002). Comparison of advanced processes on the oxidation of acid orange 7 dye, J. Environ Sci. Health, A37(7):1253–1261
[12] Hashimoto K, Irie H, Fujishima A. (2005) TiO₂ Photocatalysis: A Historical overview and future prospects. Jap. J. Appl. Phys., 44 12 pp. 8269-8285
[13] Hoffmann M, Martin S. T, Choi W, Bahnemann D. W. (1995) Environmental applications of semiconductor photocatalysis, Chem. Rev, 95:69-96
[14] Fujishima A, Honda K. (1972) Electrochemicalphotolysis of water at a semiconductor electrode. Nature 238:37-38
[15] Bergamini R. M, Acevedo E. B, Radi de Araujo L. R., (2009) Heterogeneous photocatalytic degradation of reactive dyes in aqueous TiO₂ suspensions: Decolorization kinetics, Chem. Eng. J. 149:215-220
[16] Major S, Banerjee A, Chopra K. L (1983) Highly transparent and conducting indium-doped zinc oxide films by spray pyrolysis, Thin Solid Films 108(3):333-342
[17] Suárez-Parra R, Hernández-Pérez I, Rincón ME, López Ayala S, Roldán Ahumada M.C. (2003) Visible light-induced degradation of blue azo dye on TiO₂ / CdO-ZnO coupled nanoporous film. Solar Energy Materials and Solar Cells 76:189-199
[18] González-Reyes L, Hernández-Pérez I, Robles Hernández F., Dorantes Rosales H., Arce-Estrada E.M. (2008) Sonochemical synthesis of nanostructured anatase and study of the kinetics among phase transformation and coarsening as a function heat treatment conditions. Journal of European Ceramic Society 28:1585-1594
[19] Ge L, Xu M (2007) Fabrication and characterization of TiO2 photocatalytic thin film prepared from peroxo titanic acid sol, J. Sol-Gel Sci. and Tech. 43:1-7
[20] Kathaee A. R, Pons M, N, Zahraa O (2009) Photocatalytic degradation of three azo dyes using immobilized TiO2 nanoparticles on glass plates activated by UV light irradiation: Influence of dye molecular structure. J Hazard Mat 168:451-457