

DOI: <https://doi.org/10.18359/rfcb.5013>



How the Ti Precursor is Involved in the Effectiveness of Pt-TiO₂ Materials in Photodegrading Methyl Orange*

Julie Joseane Murcia Mesa^a ■ Mónica Sirley Hernández Laverde^b
■ Hugo Alfonso Rojas Sarmiento^c ■ Mayra Anabel Lara Angulo^d
■ José Antonio Navío^e ■ María Carmen Hidalgo López^f

Abstract: as other studies have demonstrated, improving the effectiveness of TiO₂ for environmental remediation requires that the properties of this oxide be modified using different synthesis methods. In the current study, lab-prepared TiO₂ was synthesized using the hydrothermal method and two different Ti precursors (titanium butoxide and titanium isopropoxide). After the synthesis, the obtained titania was also modified using photodeposition by platinum nanoparticles. This study aims to evaluate the effectiveness of the photocatalytic materials prepared in photodegrading methyl orange. The Ti precursors used in the TiO₂ synthesis had a slight effect on the physicochemical properties of the oxide obtained. When titanium butoxide was used as a precursor, we observed a change in the bandgap value and some material with the largest surface area. Additionally, the addition of Pt increased the absorption of TiO₂ in the visible region of the electromagnetic spectrum and slightly decreased the bandgap value of this oxide. The photocatalyst prepared using titanium isopropoxide as a precursor showed the most remarkable effectiveness in the degradation rate of methyl orange. This is the result of the lower band gap value of this material which leads to easier transport of the photogenerated charges during the photocatalytic reaction. We also observed that the addition of Pt has a detrimental effect on the effectiveness of TiO₂ in dye degradation, which may be due to possible obstruction of the dye-photocatalyst interaction on the TiO₂ surface because of the Pt nanoparticles observed by TEM. The effectiveness of commercial TiO₂ in methyl orange degradation is slightly higher than that observed in other evaluated solids.

Keywords: methyl orange; photocatalysis; titanium precursor; hydrothermal; TiO₂

Received: 15th July 2020

Accepted: 11th December 2020

Available online: 27th August 2021.

* Research article.

a PhD in Science and Technology of New Materials, Universidad de Sevilla, Spain. Member of the Catálisis group, Universidad Pedagógica y Tecnológica de Colombia (UPTC), Tunja, Boyacá, Colombia.

E-mail: julie.murcia@uptc.edu.co ORCID: <https://orcid.org/0000-0002-6237-9517>

b MS in Chemistry. BS in Food Chemistry. Member of the Catálisis group, Universidad Pedagógica y Tecnológica de Colombia (UPTC). Professor, School of Basic Sciences, Technology, and Engineering, Universidad Nacional Abierta y a Distancia, Sogamoso, Boyacá, Colombia.

E-mail: minisy71@gmail.com ORCID: <https://orcid.org/0000-0001-5353-8347>

c PhD in Chemistry Sciences, Universidad de Concepción, Chile. Member of the Catálisis group, Universidad Pedagógica y Tecnológica de Colombia (UPTC), Tunja, Boyacá, Colombia.

E-mail: hugo.rojas@uptc.edu.co ORCID: <https://orcid.org/0000-0003-3906-4522>

d PhD in Environment and Natural Resources, Universidad de Sevilla, Spain. Instituto de Ciencia de Materiales de Sevilla (ICMS), Consejo Superior de Investigaciones Científicas (CSIC), Universidad de Sevilla, Sevilla, Spain.

E-mail: anabel.larang@gmail.com ORCID: <https://orcid.org/0000-0003-1037-8448>

e PhD in Chemistry. Instituto de Ciencia de Materiales de Sevilla (ICMS), Consejo Superior de Investigaciones Científicas (CSIC), Universidad de Sevilla, Sevilla, Spain. E-mail: navio@us.es ORCID: <https://orcid.org/0000-0002-7884-1067>

f PhD in Chemistry Sciences, Universidad de Sevilla, Spain. Instituto de Ciencia de Materiales de Sevilla (ICMS), Consejo Superior de Investigaciones Científicas (CSIC), Universidad de Sevilla, Sevilla, Spain.

E-mail: carmen.hidalgo@csic.es ORCID: <https://orcid.org/0000-0001-9862-6578>

How to cite: J. J. Murcia Mesa, M. S. Hernández Laverde, H. A. Rojas Sarmiento, M. A. Lara Angulo, J. A. Navío, and M. C. Hidalgo López, «How the Ti Precursor is Involved in the Effectiveness of Pt-TiO₂ Materials in Photodegrading Methyl Orange», *Rev. Fac. Cienc. Básicas*, vol. 16, n.º 2, pp. 21-30, Aug. 2021.

Cómo el precursor de Ti está involucrado en la eficacia de los materiales Pt-TiO₂ en la fotodegradación de metil naranja

Resumen: como han demostrado otros estudios, mejorar la efectividad del TiO₂ para la descontaminación ambiental requiere que las propiedades de este óxido se modifiquen utilizando diferentes métodos de síntesis. En el estudio actual, el TiO₂ preparado en laboratorio se sintetizó utilizando el método hidrotermal y dos precursores de Ti diferentes (butóxido de titanio e isopropóxido de titanio). Tras la síntesis, el titanio obtenido también fue modificado mediante fotodeposición por nanopartículas de platino. Este estudio tiene como objetivo evaluar la efectividad de los materiales fotocatalíticos preparados en fotodegradación de metil naranja. Los precursores de Ti utilizados en la síntesis de TiO₂ tuvieron un ligero efecto sobre las propiedades fisicoquímicas del óxido obtenido. Cuando el butóxido de titanio fue utilizado como precursor, observamos un cambio en el valor de separación de banda y algún material con la mayor superficie. Además, la adición de Pt aumentó la absorción de TiO₂ en la región visible del espectro electromagnético y disminuyó ligeramente el valor de separación de banda de este óxido. El fotocatalizador preparado utilizando isopropóxido de titanio como precursor mostró la efectividad más notable en la tasa de degradación del metil naranja. Este es el resultado del menor valor de separación de banda de este material que conduce a un transporte más fácil de las cargas fotogeneradas durante la reacción fotocatalítica. También observamos que la adición de Pt tiene un efecto perjudicial sobre la eficacia de TiO₂ en la degradación del tinte, que puede ser debido a la posible obstrucción de la interacción tinte-fotocatalizador en la superficie de TiO₂ debido a las nanopartículas de Pt observadas por TEM. La efectividad del TiO₂ comercial en la degradación del metil naranja es ligeramente superior a la observada en otros sólidos evaluados.

Palabras clave: metil naranja; fotocatalisis; precursor de titanio; hidrotermal; TiO₂

Como o precursor de Ti está envolvido na eficácia dos materiais Pt-TiO₂ na fotodegradação de Metil alaranjado

Resumo: como outros estudos vêm demonstrado, melhorar a efetividade do TiO₂ para a descontaminação ambiental requer que as propriedades desse óxido sejam modificadas a partir da utilização de diferentes métodos de síntese. No estudo atual, o TiO₂ preparado em laboratório foi sintetizado utilizando o método hidrotermal e dois precursores de Ti diferentes (butóxido de titânio e isopropóxido de titânio). Após a síntese, o titânio obtido também foi modificado mediante fotodeposição por nanopartículas de platino. O objetivo deste estudo é avaliar a efetividade dos materiais fotocatalíticos preparados em fotodegradação de metil alaranjado. Os precursores de Ti utilizados na síntese de TiO₂ tiveram um leve efeito sobre as propriedades físicoquímicas do óxido obtido. Quando o butóxido de titânio foi utilizado como precursor, observamos uma mudança no valor de separação de banda e algum material com a maior superfície. Além disso, a adição de Pt aumentou a absorção de TiO₂ na região visível do espectro eletromagnético e diminuiu levemente o valor de separação de banda desse óxido. O fotocatalizador preparado a partir de isopropóxido de titânio como precursor mostrou a efetividade mais notável na taxa de degradação do metil alaranjado. Esse é o resultado do menor valor de separação de banda desse material que conduz a um transporte mais fácil das cargas fotogeradas durante a reação fotocatalítica. Também observamos que a adição de Pt tem um efeito prejudicial sobre a eficácia de TiO₂ na degradação do corante, que pode ser devido à possível obstrução da interação corante-fotocatalisador na superfície de TiO₂ em virtude das nanopartículas de Pt observadas por TEM. A efetividade do TiO₂ comercial na degradação do metil alaranjado é levemente superior à observada em outros sólidos avaliados.

Palavras-chave: metil alaranjado; fotocatalise; precursor de titânio; hidrotermal; TiO₂

Introduction

Environmental protection and the reduction of the detrimental effect of industrial activities on the environment is a priority around the world. To achieve these objectives, different alternatives have been suggested, including treating industrial wastewater containing high quantities and wide varieties of pollutants [1]. An excellent example of this problem is the wastewater from the textile industry. This industry releases large volumes of colored effluents into drains and ecosystems downriver. Azoic organic dyes present in textile wastewater are not very biodegradable under direct sunlight [2]. It has also been reported that most of these compounds do not degrade in conventional wastewater treatment plants [3]. The most commonly used methods to remove dyes from liquid effluents are biological and chemical processes such as coagulation-flocculation [4]. These treatments are not entirely effective in removing dyes [5] because of their non-destructive nature resulting from transferring pollutants from one phase to another. Therefore, it is imperative to find more efficient technologies focused on removing dyes from wastewater [3]. These dye compounds contain an azo group (N=N) usually bonded to aromatic groups (benzene and naphthalene rings) [6]–[7]. One example of an azoic dye is methyl orange (MO), which has been selected as the model molecule in the current study.

Heterogeneous photocatalysis currently represents a good choice for treating effluents containing dyes. This technology may allow for the oxidation or reduction of the azoic group in the dye molecule because of hydroxyl radicals ($\bullet\text{OH}$) or the electrons photogenerated during the photocatalytic process, respectively. The resulting breakup of the $-\text{N}=\text{N}-$ bond leads to dye discoloration [6].

During the dye photodegradation, the formation of intermediate compounds such as aromatic amines, phenolic compounds, or organic acids (acetic acid, formic acid, oxalic acid, or malonic acid) can take place. The formation of these organic acids is due to the opening of the naphthalene and aromatic rings. These acids then go through successive oxidation processes until the entire dye

molecule is mineralized with the final formation of CO_2 and water [8]. It also has been reported that the superoxide anionic radical and the dye cationic radicals are essential to the photocatalytic mineralization of the dyes [9].

The sol-gel method has been extensively used in the synthesis of TiO_2 [10]–[11]; however, other methods such as the hydrothermal procedure have been more versatile for obtaining TiO_2 modulated properties [12]. The current study evaluated different photocatalytic materials based on platinized TiO_2 on the photodegradation of MO. We also attempted to conduct an additional study of the effect of the Ti precursor selected for the hydrothermal synthesis of TiO_2 on the final physicochemical and photocatalytic properties of the obtained oxide. Pt addition was also evaluated to improve the photoefficiency in degrading MO. After considering the vast expertise of our research group in the study of these solids, we selected the photodeposition method to prepare platinized materials.

Materials and methods

Synthesis of the photocatalytic materials

We made TiO_2 powders following a previously described method [13]; first, a mix of 25/4 (v/v) of a titanium precursor and an aqueous solution of hydrofluoric acid was prepared. We used titanium tetraisopropoxide and butoxide (Aldrich 97%) as precursors, and the hydrothermal treatment was carried out over 24 hours at 200°C . The powders were then rinsed with distilled water, filtered, and dried at 100°C for 12 hours. Commercial TiO_2 from Sigma Aldrich was used without any alterations.

In order to improve the photocatalytic properties of lab-prepared TiO_2 , it was modified by platinum photodeposition [14]. We prepared a suspension of TiO_2 in a solution of H_2PtCl_6 (Aldrich 99.9%) containing 0.5wt. % of Pt. The metal photodeposition was carried out in a batch reactor using an Osram Ultra Vitalux lamp, emitting at 60 W/m^2 , as a light source. After two hours of radiation, we recovered the platinized solid by washing, filtering, and drying it at 100°C overnight. The

Table 1. Synthesized photocatalysts

Photocatalyst	Synthesis parameters
TiO ₂ (C)	Commercial material
TiO ₂ (I)	Lab-prepared material using titanium isopropoxide as a precursor
TiO ₂ (B)	Lab-prepared material using titanium butoxide as a precursor
Pt-TiO ₂ (I)	Lab-prepared material using titanium isopropoxide as a precursor and modified by a platinum addition
Pt-TiO ₂ (B)	Lab-prepared material using titanium butoxide as a precursor and modified by a platinum addition.

Source: own elaboration

samples obtained in the current study were labeled as indicated in Table 1.

Photocatalytic material characterization

The photocatalytic materials were extensively analyzed using different techniques. The experimental conditions of these analyses and the equipment used are described in detail below.

We carried out the XRD analysis using a Siemens D-501 diffractometer with a nickel filter and copper K α radiation. The measurements were performed with a scanning angle of 2θ from 10 to 80° with 0.05° passes and an elapsed time of 1 second.

The morphology and particle size of the photocatalytic materials were evaluated using Transmission Electron Microscopy (TEM) in a Philips CM 200 microscope. The samples were sonicated in an ethanol suspension for 0.17 hours before placing a drop of the sample suspension in a copper grating.

We evaluated the specific surface area (S_{BET}) by nitrogen physisorption at 77.35K in a Micromeritics ASAP 2010. For the optical properties of the materials, we used UV-Vis diffuse reflectance spectrophotometry (UV-Vis DRS) with a Varian Cary 100 spectrophotometer, an integrating sphere, and BaSO₄ as a reference. These measurements were evaluated in a wavelength range between 200 and 800 nm. The bandgap values were calculated using the Kubelka–Munk $F(R_{\infty})$ function, which is proportional to the radiation absorption. These calculations relied on the graphical function $(F(R_{\infty}) \times h\nu)^{1/2}$ Vs. $h\nu$.

The chemical composition of the synthesized materials was evaluated using X-ray fluorescence

with a Panalytical Axios spectrometer equipped with a rhodium tube as the radiation source.

Finally, we performed XPS analyses using a SPECS spectrometer with a constant energy of 40 eV and pressure of $5-6 \times 10^{-10}$ Bar and the Al K α ($h\nu$) radiation at 1486.6 eV and 250 W. The spectra obtained were analyzed using Casa-XPS software.

Photocatalytic activity evaluation

We assessed the effectiveness of the photocatalytic materials on the photodegradation of MO in the liquid phase. These reactions were carried out in a 150 mL batch reactor, equipped with a cooling jacket (Fig. 1).

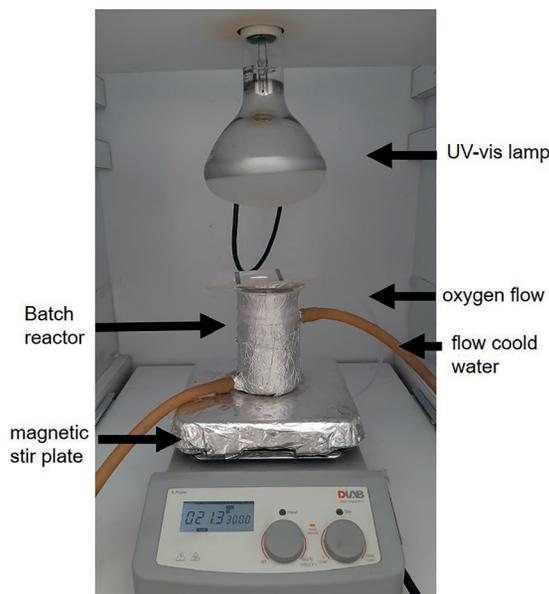


Fig. 1. Reaction system used in the photocatalytic tests.

Source: own elaboration

The experimental conditions used in the photocatalytic reactions are described as follows: 100

mL of an MO solution (25 ppm), 1 g/L of a photocatalyst, continuous oxygen flux, and 120 W/m² of light intensity. The suspension was stirred for 0.17 hours to achieve good homogenization of the photocatalyst in the reaction medium before switching on the lamp used as a light source. The total reaction time was two hours, during which we took several aliquots of the reaction solution (0, 0.25, 0.5, 1, and 2 hours). The photodegradation of the dye was evaluated by UV-Vis spectrophotometry in a Thermovision Evolution 300 spectrophotometer. We determined the dye concentration by following the behavior of the maximum absorption band of this compound located at 464 nm. The intensity of this band is directly proportional to the concentration of MO.

Results and discussion

Physicochemical properties of the synthesized photocatalysts

From the characterization performed, we could analyze the effect of using two different precursors of TiO₂ and the platinum addition on the structure, composition, and morphology of the photocatalysts synthesized. A detailed description of the results obtained by different techniques is shown below.

X-ray diffraction

The diffractograms obtained for each photocatalyst analyzed are presented in Fig. 2. Commercial titania (TiO₂(C)) presents high crystallinity with both anatase and rutile phases identified by the peaks located at the two theta positions of 25.25° and 27.44°, respectively. The lab-prepared material resulted in the detection of the anatase phase only. This result indicates that the hydrothermal method is an effective way to prevent the formation of the rutile phase during TiO₂ synthesis.

Additionally, the precursor employed in the synthesis did not have any significant influence over the crystalline phase composition or the crystallinity of the final titania obtained. These properties remained unmodified even after the platinum addition. No Pt signals were observed by XRD,

probably due to the low content of this metal and the small size of the Pt particles, as evidenced by the TEM analysis.

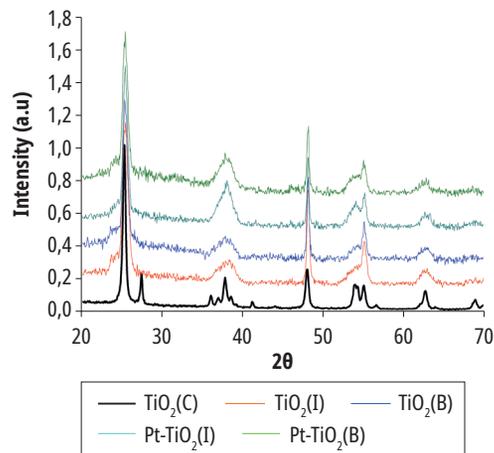


Fig. 2. X-ray diffractograms obtained for the photocatalysts analyzed.

Source: own elaboration

Transmission Electron Microscopy (TEM)

Fig. 3 shows selected images of the photocatalysts prepared. Note the dark platinum nanoparticles with a spherical shape forming agglomerates. It can also be seen that the Pt nanoparticles are heterogeneously distributed on the TiO₂ surface, with an average size of 2 to 5 nm. Any difference in the Pt particle size was observed because of the precursor employed in synthesizing these materials.

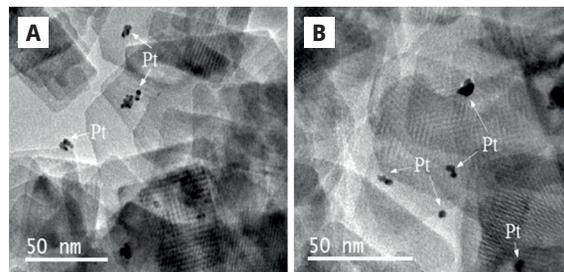


Fig. 3. TEM images for the platinumized photocatalyst analyzed. (a) Pt-TiO₂(I) and (b) Pt-TiO₂(B).

Source: own elaboration

N₂ Physisorption

A summary of the main characterization results is presented in Table 2.

Table 2. Summary of the characterization results for the photocatalysts analyzed

Photocatalyst	S_{BET} (m ² /g)	Band gap (eV)	Pt content (%)
TiO ₂ (C)	51	3.23	-
TiO ₂ (I)	91	3.10	-
TiO ₂ (B)	96	3.20	-
Pt-TiO ₂ (I)	71	3.00	0.60
Pt-TiO ₂ (B)	74	3.00	0.54

Source: own elaboration.

As shown in Table 2, lab-prepared hydrothermal materials have a larger surface area than commercial TiO₂. The TiO₂ prepared using titanium isopropoxide as a precursor (TiO₂(I)) exhibited a smaller surface area than the TiO₂ prepared using titanium butoxide as a precursor (TiO₂(B)). The addition of platinum was found to decrease the surface area of lab-prepared TiO₂, which can be due to the obstructed pores of the titania surface and the presence of Pt nanoparticles.

UV-Vis Diffuse Reflectance Spectrophotometry (UV-Vis DRS)

The characteristic absorption band of TiO₂ located between 200 and 400 nm was observed in all UV-Vis DR spectra of the photocatalysts analyzed. In this spectra analysis (Fig. 4), we could identify that the platinum addition increased the absorption of the lab-prepared TiO₂ to the visible region of the electromagnetic spectrum, which is primarily due

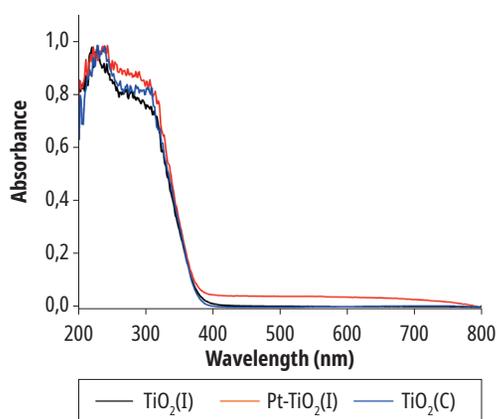


Fig. 4. UV-Vis DR spectra of the photocatalysts analyzed.

Source: own elaboration.

to the gray color of the platinized materials compared with the white starting oxide.

The bandgap values were also calculated from the UV-Vis DRS data, and the results are presented in Table 2. These values range between 3.0 and 3.23 eV after Pt addition and result in a slight decrease in the TiO₂ band gap value.

X-ray Fluorescence (XRF)

The actual amount of platinum in the samples was analyzed by XRF. The amount of platinum in the samples was slightly higher than the nominal metal loading used in the photocatalysts synthesis within the range of error of the analysis performed. We could also identify 3.6 and 5.1 % fluoride in the TiO₂ prepared using titanium isopropoxide and butoxide, respectively.

X-ray Photoelectronic Spectroscopy (XPS)

In the XPS spectra obtained in the O1s region, we observed a signal located at 529.5 ± 0.2 eV, which corresponded to surface oxygen in the crystalline net. In the Ti2p_{3/2} region, there was a signal characteristic of Ti⁴⁺ in the crystalline net, located at 458.5 ± 0.2 eV. The signals observed in the regions mentioned were unmodified neither by the titanium precursor employed in the photocatalysts synthesis nor by platinum addition.

Using XPS, the F1s region identified a signal located at 683.7 eV, which indicated fluorine on the surface. The oxidation state of Pt was determined by an XPS analysis of the Pt4f region. We noted an incomplete reduction of the metal precursor due to oxidized and reduced platinum species detected in the platinized samples. Fig. 5 shows the obtained

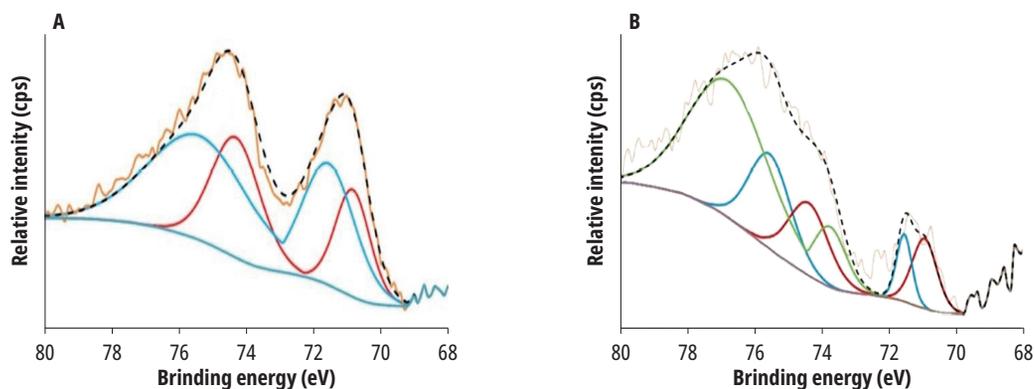


Fig. 5. xps spectra obtained in the 4f region. (a) Pt-TiO₂(I) and (b) Pt-TiO₂(B).

Source: own elaboration.

spectra and their deconvolution using the UNIFIT 2009 program.

The material prepared using titanium isopropoxide as a precursor had Pt²⁺ and Pt⁰ species (Fig. 4a). Pt⁴⁺ species were also detected in the material prepared using titanium butoxide as a precursor. From these results, we conclude that the hydrothermal synthesis directly affects the effectiveness of the platinum reduction on the TiO₂ surface.

Photocatalytic degradation of methyl orange

Fig. 6a shows the changes in coloration of the MO solution during the photocatalytic reactions using commercial TiO₂ as a photocatalyst. Fig. 6b represents the UV-Vis spectra obtained during the photocatalytic reaction using the maximum wavelength absorption of MO located at 464 nm. The photocatalytic process led to efficient dye degradation after two hours under light.

Fig. 7 shows the results obtained during the photocatalytic degradation of MO using each of the photocatalysts under study. First, a blank reaction without a photocatalyst was carried out. As commonly known and expected, this dye is sensitive to degradation under UV-Vis light [15].

When photocatalysts were used, the degradation of MO was significantly improved. The complete elimination of this dye was achieved in two hours using commercial TiO₂. When other photocatalysts were employed (*i.e.*, TiO₂ (I), Pt-TiO₂ (I), TiO₂ (B), Pt-TiO₂ (B)), we detected a remaining

concentration of MO (0.5 ppm or less). Only slight differences were observed in the effectiveness of dye degradation using the photocatalysts prepared with different titanium precursors or Pt addition. However, the TiO₂(I) photocatalyst is more effective in dye degradation than TiO₂(B).

Pt addition has a detrimental effect on the photocatalytic materials' effectiveness in degrading MO. Platinum addition also decreased the effectiveness of the lab-prepared titania using selected titanium precursors. This behavior is different from the usual behavior reported by other authors. It is often described that the addition of the metallic particles to the titania surface increases the effectiveness of this material in different photocatalytic reactions [16]-[19]. However, the overall effectiveness of photocatalysts depends on the substrate degraded, primarily due to the interaction of the pollutant molecule with this material's photocatalyst surface or surface properties. A further complete study of surface properties is still necessary to analyze this interaction in depth.

In the specific case of MO, the photodegradation is more effective with unmodified TiO₂ [20], which is primarily due to the low pH of the reaction medium. Under acidic pH, the TiO₂ surface is positively charged, which favors the interaction of the dye with the photocatalyst through a highly electronegative N=N bond from the azo group. A better dye-photocatalyst interaction leads to better adsorption of the substrate and more efficient dye degradation over bare TiO₂. Further studies

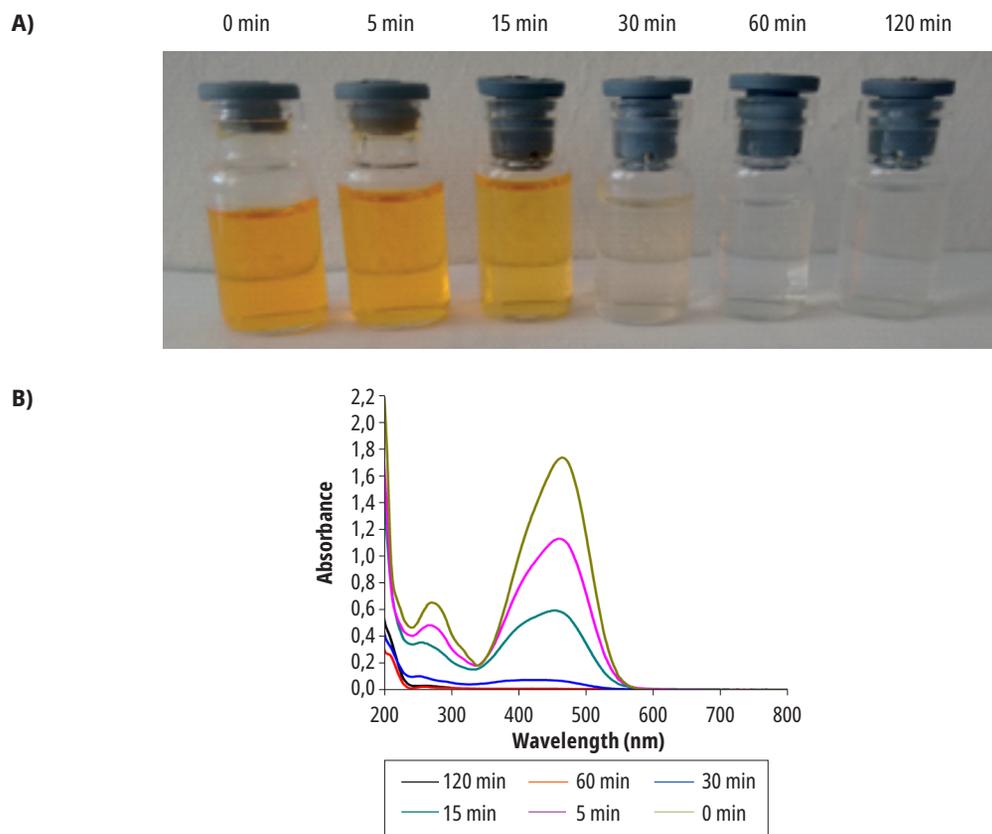


Fig. 6. Evolution in MO degradation using commercial TiO_2 as a photocatalyst. (a) Photographic record of the photocatalytic reaction and (b) uv-Vis spectra obtained during the photocatalytic reaction.

Source: own elaboration.

using FTIR could determine the active sites or dye-surface interaction of photocatalysts.

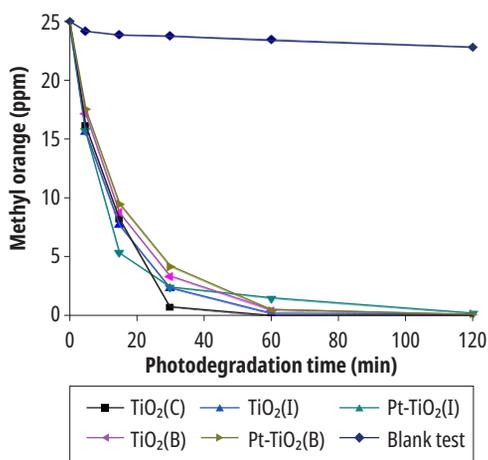


Fig. 7. Change in dye concentration as a function of the reaction time during the photocatalytic degradation of MO.

Source: own elaboration.

In the platinumized TiO_2 , the platinum nanoparticles covered the titania surface as observed by the TEM analysis. These nanoparticles can obstruct the interaction of the dye molecule with the TiO_2 surface. This hypothesis can explain the results obtained in the current study and understand why platinum addition has a detrimental effect on the degradation of MO. A further study using H_2 chemisorption can be performed to test this hypothesis.

Conclusions

We found that the precursor employed in the synthesis of titanium dioxide using the hydrothermal method has a slight effect on the physicochemical properties of the final oxide obtained. These include changes in the specific surface area, band-gap, and how the precursor employed modifies

the reduction of platinum on the TiO₂ surface. The platinum addition on TiO₂ has a significant influence over the optical and surface properties of this semiconductor. The photodeposition of platinum decreased the bandgap and increased the absorption of titania in the visible region of the electromagnetic spectrum. The parameters employed in TiO₂ can impact the effectiveness of the photocatalytic treatment in degrading MO.

Acknowledgments

The Universidad Pedagógica y Tecnológica de Colombia financed this study.

References

- [1] B. J. Cisneros, *Treatise on Water Science*. Elsevier, 2011.
- [2] M. A. Rauf, M. A. Meetani, and S. Hisaindee, "An overview on the photocatalytic degradation of azo dyes in the presence of TiO₂ doped with selective transition metals," *Desalination*, vol. 276, no. 1–3, pp. 13–27, 2011. <https://doi.org/10.1016/j.desal.2011.03.071>
- [3] I. Fechete, Y. Wang, and J. C. Védrine, "The past, present and future of heterogeneous catalysis," *Catal. Today*, vol. 189, no. 1, pp. 2–27, 2012. <https://doi.org/10.1016/j.cattod.2012.04.003>
- [4] Y. Chen, F. Chen, and J. Zhang, "Effect of surface fluorination on the photocatalytic and photo-induced hydrophilic properties of porous TiO₂ films," *Appl. Surf. Sci.*, vol. 255, no. 12, pp. 6290–6296, 2009. <https://doi.org/10.1016/j.apsusc.2009.02.004>
- [5] A. V. Vorontsov, E. N. Savinov, and J. Zhensheng, "Influence of the form of photodeposited platinum on titania upon its photocatalytic activity in CO and acetone oxidation," *J. Photochem. Photobiol. A Chem.*, vol. 125, no. 1–3, pp. 113–117, 1999. [https://doi.org/10.1016/S1010-6030\(99\)00073-8](https://doi.org/10.1016/S1010-6030(99)00073-8)
- [6] Z. Sun, Y. Chen, Q. Ke, Y. Yang, and J. Yuan. "Photocatalytic degradation of a cationic azo dye by TiO₂/bentonite nanocomposite," *J. Photochem. Photobiol. A Chem.*, vol. 149, no. 1–3, pp. 169–174, 2002. [https://doi.org/10.1016/S1010-6030\(01\)00649-9](https://doi.org/10.1016/S1010-6030(01)00649-9)
- [7] L. M. Saragiotto, H. J. Alves, O. A. Andreo dos Santos, and C. M. Macedo. "Discoloration and degradation of textile dye aqueous solutions with titanium oxide catalysts obtained by the sol-gel method," *Dyes Pigm.*, vol. 76, no. 2, pp. 525–529, 2008. <https://doi.org/10.1016/j.dyepig.2006.10.014>
- [8] Y. He, F. Grieser, and M. Ashokkumar, "The mechanism of sonophotocatalytic degradation of methyl orange and its products in aqueous solutions," *Ultrason. Sonochem.*, vol. 18, no. 5, pp. 974–980, 2011. <https://doi.org/10.1016/j.ultsonch.2011.03.017>
- [9] J. Yang, C. Chen, H. Ji, W. Ma, and J. Zhao. "Mechanism of TiO₂-Assisted Photocatalytic Degradation of Dyes under Visible Irradiation: Photoelectrocatalytic Study by TiO₂-Film Electrodes," *J. Phys. Chem. B*, vol. 109, no. 4, pp. 21900–21907, 2005. <https://doi.org/10.1021/jp0540914.s001>
- [10] S. Lee, In-Sun Cho, J. H. Lee, D. H. Kim, D. W. Kim, J. Y. Kim, H. Shin, Jung-Kun Lee, H. S. Jung, Nam-Gyu Park, K. Kim, M. J. Ko, and K. S. Hong, "Two-Step Sol-Gel Method-Based TiO₂ Nanoparticles with Uniform Morphology and Size for Efficient Photo-Energy Conversion Devices," *Chem. Mater.*, vol. 22, no 6, pp. 1958–1965, 2010. <https://doi.org/10.1021/cm902842k>
- [11] S. G. Ullattil and P. Periyat, "Sol-Gel Synthesis of Titanium Dioxide," in *Sol-Gel Materials for Energy, Environment and Electronic Applications*, S. Pillai and S. Hehir, Eds.) Springer, Cham., 2017. [Online] https://doi.org/10.1007/978-3-319-50144-4_9.
- [12] N. Jun-Nan and T. Hsisheng, "Hydrothermal Synthesis of Single-Crystalline Anatase TiO₂ Nanorods with Nanotubes as the Precursor" *J. Phys. Chem. B*, vol. 110, no. 9, pp. 4193–4198, 2006. <https://doi.org/10.1021/jp0567321>
- [13] M. A. Lara, M. J. Sayagués, J. A. Navío, and M. C. Hidalgo, "A facile shape-controlled synthesis of highly photoactive fluorine containing TiO₂ nanosheets with high {001} facet exposure," *J. Mater. Sci.*, vol. 53, no. 1, pp. 435–446, 2018. <https://doi.org/10.1007/s10853-017-1515-6>
- [14] J. J. Murcia, J. A. Navío, and M. C. Hidalgo, "Insights towards the influence of Pt features on the photocatalytic activity improvement of TiO₂ by platinisation," *Applied Catal. B, Environ.*, vol. 126, pp. 76–85, 2012. <https://doi.org/10.1016/j.apcatb.2012.07.013>
- [15] A. Peter, A. Mihaly-Cozmuta, C. Nicula, L. Mihaly-Cozmuta, A. Jastrzębska, A. Olszyna, and L. Baia. "UV Light-Assisted Degradation of Methyl Orange, Methylene Blue, Phenol, Salicylic Acid, and Rhodamine B: Photolysis Versus Photocatalysis," *Water Air Soil Pollut.*, vol. 228, no. 41, 2017. [Online] <https://doi.org/10.1007/s11270-016-3226-z>.
- [16] G. Iervolino, V. Vaiano, J. J. Murcia, L. Rizzo, G. Ventre, G. Pepe, P. Campiglia, M. C. Hidalgo, J. A. Navío, and D. Sannino, "Photocatalytic hydrogen production from degradation of glucose over fluorinated and

- platinized TiO₂ catalysts,” *J. Catal.*, vol. 339, pp. 47–56, 2016. <https://doi.org/10.1016/j.jcat.2016.03.032>
- [17] J. J. Murcia, M. C. Hidalgo, J. A. Navío, V. Vaiano, D. Sannino, and P. Ciambelli, “Cyclohexane photocatalytic oxidation on Pt/TiO₂ catalysts,” *Catal. Today*, vol. 209, pp. 164–169, 2013. <https://doi.org/10.1016/j.cattod.2012.11.018>
- [18] J. J. Murcia, M. C. Hidalgo, J. A. Navío, V. Vaiano, P. Ciambelli, and D. Sannino, “Ethanol partial photooxidation on Pt/TiO₂ catalysts as green route for acetaldehyde synthesis,” *Catal. Today*, vol. 196, no. 1, pp. 101–109, 2012. <https://doi.org/10.1016/j.cattod.2012.02.033>
- [19] N. Sakai, A. Fujishima, T. Watanabe, and K. Hashimoto, “Quantitative Evaluation of the Photoinduced Hydrophilic Conversion Properties of TiO₂ Thin Film Surfaces by the Reciprocal of Contact Angle,” *J. Phys. Chem.*, vol. 107, no. 4, pp. 1028–1035, 2003. <https://doi.org/10.1021/jp022105p>
- [20] J. J. Murcia, M. C. Hidalgo, J. A. Navío, J. Araña, and J. M. Doña-Rodríguez, “Correlation study between photodegradation and surface adsorption properties of phenol and methyl orange on TiO₂ vs. platinum-supported TiO₂,” *Appl. Catal. B Environ.*, vol. 150–151, pp. 107–115, 2014. <https://doi.org/10.1016/j.apcatb.2013.12.010>