Titanium dioxide nanoparticles for cleaning aqueous matrices

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Resumen

Este trabajo presenta el uso potencial de nanopartículas semiconductoras de dióxido de titanio (TiO2) para limpieza de matrices acuosas, contaminadas con tintes orgánicos. Fotoactivadas nanopartículas a dos concentraciones (25 ppm y 50 ppm) fueron usadas como fotocatalizadores en la degradación de azul de metileno (MB) en presencia de irradiación UV (302 nm), y agitación a 20 rpm. La degradación de azul de metileno fue monitoreada usando un espectrofotómetro UV-Vis, a 665 nm. Se observó un 97.4 % de degradación a 90 minutos cuando MB fue contactada con 25 ppm de TiO2. Resultados similares (97.8 % de degradación) fueron obtenidos después de 60 minutos de contacto con 50 ppm de TiO2.

Palabras claves: nanopartículas, dióxido de titanio, fotocatalizadores, degradación, azul de metileno.

Abstract

This work presents the potential use of semiconductors nanoparticles as titanium dioxide (TiO2) for cleaning aqueous matrices, contaminated with organic dyes. Photoactivated nanoparticles at two concentrations (25 ppm and 50 ppm) were used as photocatalysts for the degradation of methylene blue (MB) under UV irradiation (302 nm) and, agitation at 20 rpm. The degradation of MB was monitored using a UV-Vis spectrophotometer at 665 nm. About 97.4 % degradation in 90 minutes was observed when MB was contacted with 25 ppm of TiO2. Similar results (97.8 % of degradation) were achieved after 60 minutes of contact with 50 ppm of TiO2.

Keywords: nanoparticles, titanium dioxide, photocatalysts, degradation, methylene blue

Introduction

Water contamination is commonly associated to waste and organic pollutants from the city sewage and industrial activities that consumed large quantity of water to fabricate mainly textiles, papers, and plastics. Most of the colored effluents found in contaminated waters consist of organic dyes like sulfonated azo dyes and phenazine which have been reported with carcinogenic behavior. [1-4]. In this regard, the textile dyeing has generated a huge pollution problem as it is one of the most chemically intensive industries on earth, and the main polluter of clean water, after agriculture. Today, this industry is using more than 8000 chemicals in various processes of textile manufacture including dyeing and printing. Industries discharge millions of gallons of effluent containing hazardous toxic waste, full of color and organic chemicals from

dyeing and finishing salts. The colloidal matter present along with colors increases the turbidity and gives the water a bad appearance and foul smell. It prevents the penetration of sunlight necessary for the process of photosynthesis in aquatic plants. Also, the depletion of dissolved Oxygen in water is the most serious effect of textile waste as dissolved oxygen is very essential for marine life [2-5].

Conventional techniques like flocculation, coagulation, sorption, and membrane separation technologies are regularly employed in water treatments to concentrate or transfer contaminants from one phase to another without destroying the pollutants [6-7]. Therefore, photocatalysis can be considered a valuable technology to obtain a fast destruction of organic contaminants [6-7]. Some advantages of the photocatalytic approach include a quick oxidation of the pollutant molecules, lack of production of polycyclic products and final degradation of pollutants in the ppb range [8].

Exploring properties of novel materials at nanoscale; semiconductors nanoparticles have evidenced interesting optical, electronic, and catalytic properties. In this way, titanium dioxide has been widely accepted as photocatalyst due to its great quality/price ratio, chemical stability, good optical transparency, non-toxicity and, environmentally friendly nature.

Figure 1 illustrates the proposed mechanisms to degrade environmental pollutants in aqueous phase. Nanomaterials as titanium dioxide absorb photons with energy equal to or greater than the energy gap for TiO_2 bulk (3.2 eV), inject electrons from valence band (VB) to its conduction band (CB) and generate excitons or electron hole pairs (e^- / h^+). The hole (h^+) can generate hydroxyl radicals (•OH) from water and oxidize organic pollutants adsorbed onto the nanomaterials surface. The electron can react with oxygen molecules to form superoxide anions and these species react with protons (H^+) to finally generate hydroxyl radicals. Also, photoactive nanomaterials have evidenced improved performances with respect to its bulk counterpart, thanks to their high surface-to-volume ratio into a high density of catalytically active surface sites. To assure an effective degradation, photoactive nanomaterials should interact with pollutants by electrostatic interactions in aqueous matrices [9-12].

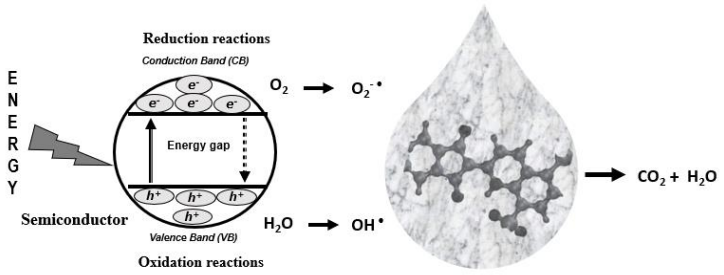

Figure 1: Proposed mechanism to degradation of organic dyes by photoactive nanomaterials.

Materials and Methods

Titanium dioxide nanoparticles

Titanium dioxide (aeroxide P25) with an average particles size of 21 nm and a surface area of 35-65 m^2g^{-1} was provided by Sigma-Aldrich.

Photocatalytic Experiments

The photocatalytic capacity of TiO_2 nanoparticles (NPs) was evaluated by using methylene blue solutions at concentrations of 15 µM. Nanoparticles were used at two concentrations, 25 ppm and 50 ppm. An 8 Watts-UV lamp (302 nm) with a power irradiation of 10mW cm^{-2} was used as the irradiation source. MB solutions in contact

with titanium dioxide nanoparticles were exposed to ultraviolet light (UV) for time intervals for a total irradiation of 120 minutes. The suspensions were gently stirred at 20 rpm at room-temperature conditions. Aliquots of the irradiated solutions were quickly withdrawn for absorbance analysis at 665 nm. A calibration curve at different concentrations of MB (1 µM, 3 µM, 5 µM, 10 µM µM, 15 µM and 20 µM) was prepared in aqueous medium, and was used to determine the concentration of dye in the experimental solutions at different time intervals. Under the same conditions, control groups in presence of light (Light control) and absence of light (Dark control) and containing 15 µM of MB were monitored at 665 nm.

Results and discussion

Transmission Electron Microscopy, Electron Diffraction (ED) and EDX analyses of titanium dioxide NPs were carried out using a JEOL-2011 hosted by the National High Magnetic Field Laboratory in Tallahassee, Florida. The results for these measurements are shown in Figures 2, 3, 4 and 5. TEM images (Figures 2, 3) of TiO_2 NPs indicate the presence of small particles with near spherical morphology as well as irregular shapes. It can be observed that particles exhibit isolated and agglomerated nanostructures with diameters less than 50 nm.

The crystallographic planes for TiO_2 are showed in Figure 4. The presence of right spots as well as ring formation suggests the presence of single and polycrystalline structures. The lattice planes that appeared were indexes to (101), (103), (200), (211) and (213) planes. These results suggest the crystalline nature of TiO_2 nanoparticles.

The EDX spectrum shows the elemental composition of TiO_2 NPs. Figure 5 evidenced predominant peaks that correspond to titanium (33.33%) and oxygen (66.67%), confirming the presence of Ti and O as main components of these nanostructures.

Semiconductors nanoparticles of TiO_2 were used to evaluate its catalytic capacity to degrade organic dyes. Standard solutions of MB (1 µM, 3 µM, 5 µM, 10 µM µM, 15 µM and 20 µM) were prepared to determine the wavelength of maximum absorbance (Figure 6). Then, these solutions were used to build a calibration curve (Figure 7) where the standards were monitored at 665 nm. The calibration curve was used to determine the concentration of MB in the experimental solutions at different time intervals. Figure 8 shows the variation of the relative dye concentration (C_f/C_i) with UV-irradiation time for MB in presence of 250 and 500 ppm of titanium dioxide NPs. The process was dependent on TiO_2 concentration and the UV-irradiation time. Control groups (Light and Dark) were slightly affected during the experiments, which indicates that the decrease in the MB concentration was mainly due to the activity of TiO_2 nanoparticles. In this way, the photodegradation of methylene blue in presence of photoactivated titanium dioxide nanostructures should occur by the production of hydroxyl radicals, a powerful oxidizing agent, which attack the MB adsorbed on the surface of TiO_2 to quickly destroy the organic compound [9-10, 13].

Figure 9 shows the degradation efficiency of TiO_2 NPs. The MB (initial concentration of 15 µM) degradation percentage was 97.4% when irradiated for 90 minutes with UV light at 302 nm, using 250 ppm of nanoparticles. An increase of concentration of TiO_2 at 50 ppm achieved the destruction of MB in 97.8%, after 60

minutes of treatment. The trends observed can be attributed to the increase of the number of active photocatalytic sites at larger quantities of nanoparticles suspended in the irradiated volume [9-10, 14].

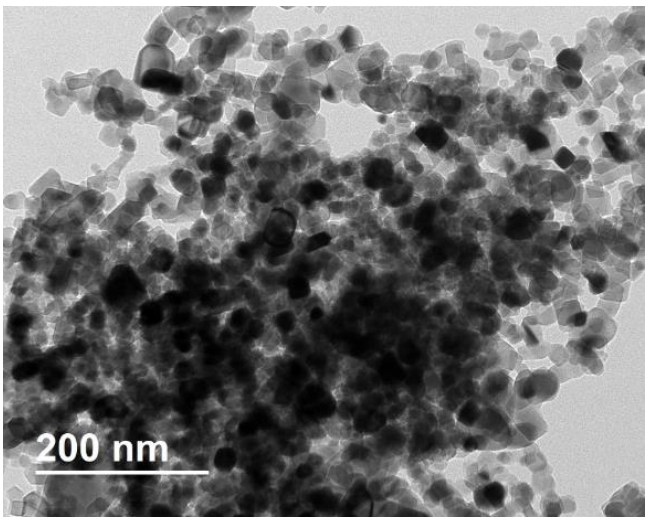

Figure 2: HRTEM images for TiO_2 NPs at 200 nm scale.

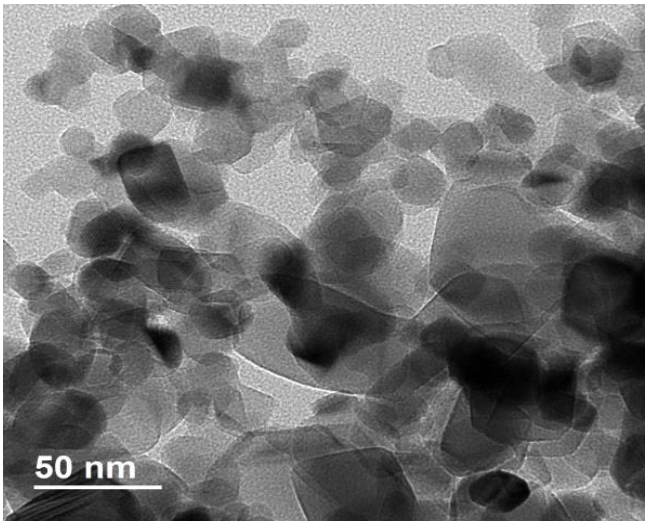

Figure 3: HRTEM images for TiO_2 NPs at 50 nm scale.

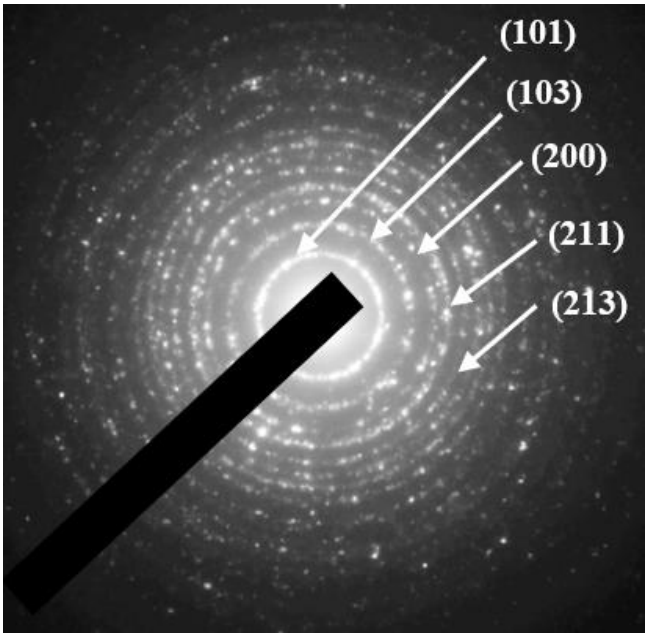

Figure 4: Energy dispersive X-ray analysis for TiO_2 NPs.

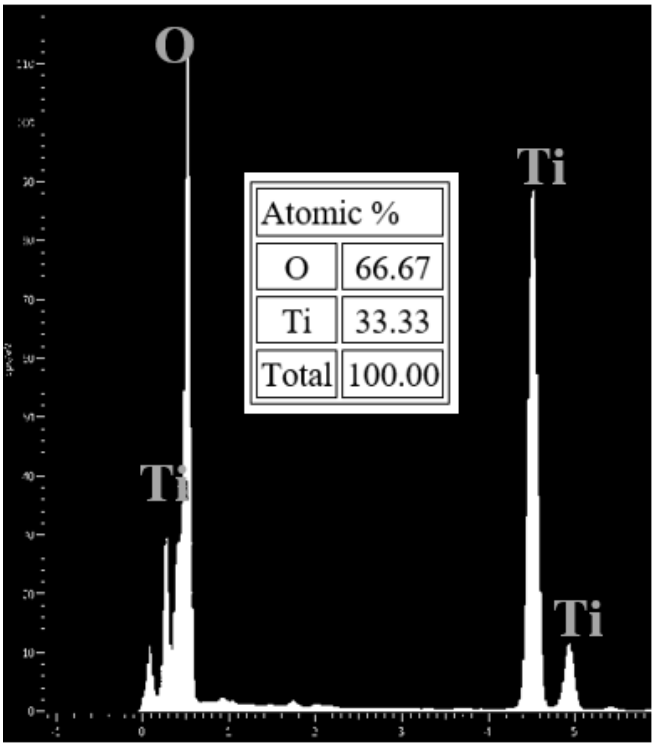

Figure 5: EDX spectrum for TiO_2 NPs.

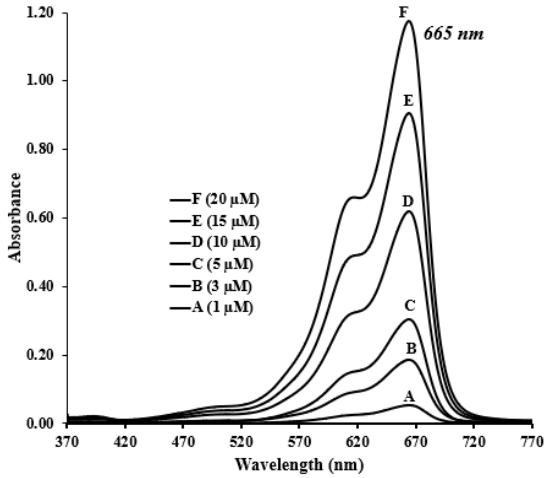

Figure 6: UV-Vis absorption spectra of MB standard solutions.

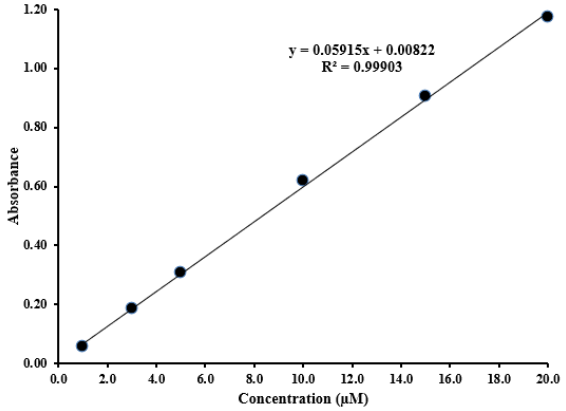

Figure 7: Calibration curve of MB at wavelength of 665 nm.

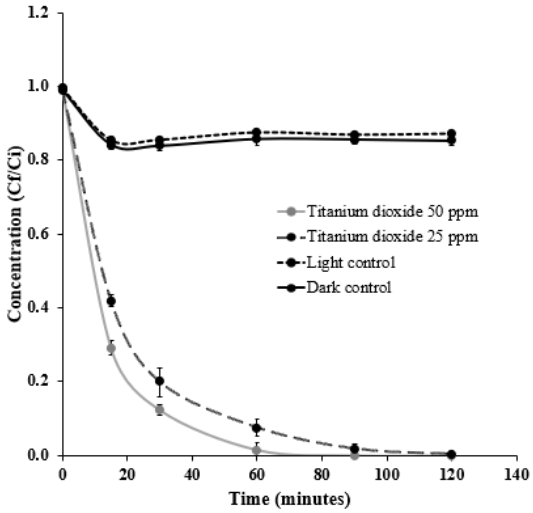

Figure 8: Effect of TiO_2 NPs concentration on Methylene Blue degradation.

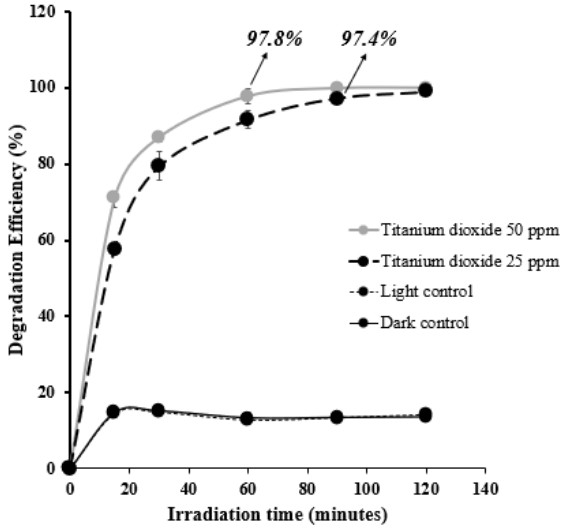

Figure 9: Degradation efficiency of TiO_2 NPs.

Conclusions

Semiconductors nanoparticles of titanium dioxide were used to degrade organic dyes as methylene blue, in aqueous phase. The photocatalytic activity was dependent of the nanoparticle's concentration, the maximum photodegradation percentage for MB was 97.8% when 50 ppm of TiO_2 was used.

References

Kant, R. (2012). Textile dyeing industry and environmental hazard. *Natural Science*, 4, 22-26.

Sohrabnezhad, S. (2011). Study of catalytic reduction and photodegradation of methylene blue by heterogeneous catalyst. *Spectrochimica Acta Part A*, 81 (1), 228-235.

Martinez, S. S., & Uribe, E. V. (2012). Enhanced sonochemical degradation of azure B dye by the electroFenton process. *Ultrasonics Sonochemistry*, 19 (1), 174-178.

Mohammadine, H., Rachid, M., Nabil, S., & Said, L. (2012). Removal of a cationic

dye-Basic Red 12-from aqueous solution by adsorption onto animal bone meal. *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 12 (1), 48-54.

Fiorentino, A., Ferro, G., Alferez, M.C., Polo-López, M.I., Fernández-Ibañez, P., & Rizzo, L. (2015). Inactivation and regrowth of multidrug resistant bacteria in urban wastewater after disinfection by solar-driven and chlorination processes. *Journal of Photochemistry and Photobiology B*, 148, 43-50.

Hamity, M., Lema, R. H., Suchetti, C. A., & Gsponer, H. E. (2008). UV-vis photodegradation of dyes in the presence of colloidal Q-CdS. *Journal of Photochemistry and Photobiology A: Chemistry*, 200 (2-3), 445-450.

El-Kemary, M., Abdel-Moneam, Y., Madkour, M., & El-Mehasseb, I. (2011). Enhanced photocatalytic degradation of safranin-O by heterogeneous nanoparticles for environmental applications. *Journal of Luminescence*, 131(4), 570-576.

Pouretedal, H. R., Nozori, A., Keshavarz, M. H., & Semnani, A. (2009). Nanoparticles of zinc sulfide doped with manganese, nickel and copper as nanophotocatalyst in the degradation of organic dyes. *Journal of Hazardous Materials*, 162(2-3), 674-681.

Alamo-Nole, L., Bailón-Ruiz, S., Luna-Pineda, T., Perales-Perez, Oscar., & Roman, F. R. (2013). Photocatalytic activity of quantum dots-magnetite nanocomposite to degrade organic dyes in the aqueous phase. *Journal of Materials Chemistry A*, 1, 5509-5516.

Alamo-Nole, L., Bailón-Ruiz, S., Cruz-Acuña, R., Perales-Pérez, O., & Roman, F.R. (2014). Quantum dots of ZnSe(S) doped with copper as nanophotocatalyst in degradation of organic dyes. *Journal of Nanoscience and Nanotechnology*, 14 (9), 7333-7339.

SamreenHeena, K., Fulekar, M.H., & Bhawana, P. (2014). Nanomaterials for Photocatalysis and their application in environmental clean-up. *International Journal of Current Research*, 7 (9), 20850-20865.

El-Kemary, M., Abdel-Moneam, Y., Madkour, M., & El-Mehasseb, I. (2011). Enhanced photocatalytic degradation of safranin-O by heterogeneous nanoparticles for environmental applications. *Journal of Luminescence*, 131(4), 570-576.

Aghareed, M., & Hussein, D. (2015). Synthesis of TiO_2 nanoparticles and their photocatalytic activity for methylene blue. *American Journal of Nanomaterials*, 3(2), 57-63.

Vallejo, W., Rueda, A., Díaz-Uribe, C., Grande, C. & Quintana, P. (2019). Photocatalytic activity of graphene oxide-TiO_2 thin films sensitized by natural dyes extracted from *Bactris guineensis*. *Royal Society Open Science*, 6, 1-17.

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