

Catalytic Photodegradation of p-aminobenzoic Acid on TiO₂ Nanowires with High Surface Area

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Abstract. Pharmaceutical personal care products (PPCP's) production and consumption have increased exponentially in recent years due to medicine and technology advances related to the development of dangerous skin diseases such as cancer. These PPCP's usually are found in wastewaters and their removal represents a very important environmental issue. With the aim of studying the possible degradation of these compounds, we have synthesized TiO₂ nanowires (rutile phase) that have been fully characterized by BET measurements, XRD and SEM and used in the photodegradation reaction of p-aminobenzoic acid (PABA). The photocatalytic degradation of PABA has been studied under different experimental conditions (i.e. catalyst loading). The photocatalytic reaction was monitored as a function of time by UV-Vis spectroscopy. The highest degradation rate occurred with 1.0 g L⁻¹ of catalyst while the reaction does not proceed without radiation or in absence of the catalyst. The present work demonstrates that p-aminobenzoic acid could be successfully degraded in a relatively short time period with high degradation percentages.

Keywords: p-aminobenzoic acid; UV-Vis spectroscopy; photocatalysis; TiO₂

Fotodegradación Catalítica de Ácido P-Aminobenzoico Mediante Nanohilos de TiO₂ de Alta Área Superficial

Resumen. La producción y consumo de productos farmacéuticos y de cuidado personal han aumentado exponencialmente en los últimos años principalmente por los avances médicos y tecnológicos relacionados con el desarrollo de enfermedades peligrosas de la piel como cáncer. Estos productos se han encontrado cada vez más frecuente en aguas residuales y su remoción representa un verdadero problema ambiental. Con la idea de estudiar la posible degradación de estos compuestos se sintetizaron nanohilos de TiO₂ en fase rutilo que fueron posteriormente caracterizados mediante medidas de área BET, DRX y SEM y usados en la reacción de fotodegradación del ácido p-aminobenzoico. La degradación fotocatalítica del ácido p-aminobenzoico se estudió bajo diferentes condiciones experimentales (por ejemplo, la concentración de catalizador). La reacción fue monitoreada mediante espectroscopía UV-Visible. La tasa de degradación más alta ocurrió con 1.0 g L⁻¹ de catalizador, mientras que la reacción no tuvo lugar en ausencia de radiación o sin el catalizador. En el presente trabajo se demuestra que ácido p-aminobenzoico puede ser degradado eficientemente en períodos relativamente cortos.

Palabras clave: ácido p-aminobenzoico; espectroscopia UV-Visible; fotocatalisis; TiO₂

Introduction

In recent years pharmaceutical personal care products (PPCP's) production have grown exponentially. PPCP's include among others, lotions, pharmaceutical drugs, veterinary products and sunscreen products (An and Zhou 2012). These PPCP's should have an active ingredient that can be organic or inorganic in nature. Because of the overconsumption PPCP's usually are found in wastewaters (Hu et al. 2011). Organic active ingredients have a chromophore responsible for the absorption of sun radiation; these include benzophenone-3, octocrylene and p-aminobenzoic acid (PABA). PABA was widely used in the 70's as a sunscreen agent but in the 80's a group of researchers found that PABA was a disruption agent against DNA cells.

With technology advances new remediation techniques have been explored and developed. Traditional remediation processes have demonstrated to be good with some organic pollutants but not enough with persistent organic pollutants such as those present in PPCP's (Lu et al. 2011). Some of the new developed technologies are the Advanced Oxidation Processes (AOP's). AOP's are carried out using a catalyst (semiconductor) with a wide band gap. •OH radicals are generated in the presence of radiation and an oxidation agent, mediated by electron-hole pairs (Vinu and Madras 2010). These hydroxyl radicals are very reactive species responsible for the degradation of organic substances. One of the AOP's widely studied is the photocatalytic degradation which has been demonstrated to be a successful technique in the degradation of phenol, organic dyes, phenanthrene and other emerging contaminants (Lin et al. 2011; Zhang et al. 2011; Rivas et al. 2012; Sharma et al. 2012).

Within photocatalytic processes there are countless alternatives to be used as semiconductor materials. Photocatalytic degradation has been studied using ZnO, ZnS, FeCu/Cu₂O and TiO₂ (Hu et al. 2011, Maji et al. 2011, An and Zhou 2012, Tang 2013). TiO₂ has been extensively used due to its appropriate band gap, cost-effectiveness, low toxicity and easy synthesizing process. Chen and Mao (2007) stated the vast uses that TiO₂ could have including photovoltaic applications, water splitting process and hydrogen storage, among others.

In this research we have synthesized and characterized TiO₂ nanowires (TiO₂ NWs) that were employed in the photocatalytic degradation of PABA. The present work demonstrates that p-aminobenzoic acid can be successfully degraded in short time periods with high degradation percentages.

Methods and Materials

Chemicals

All reagents used in the present study were of analytical grade. HCl 37% was provided by ACROS. Hydrogen Peroxide 50% was provided from Fisher Scientific. 4-aminobenzoic acid (PABA), TiCl₄, HCl 1.0 M, Acetone and Isopropyl Alcohol were provided by Sigma-Aldrich and used without further purification. Ultra pure water [(Milli-Q water, 18.2 MΩ.cm⁻¹ at 25 °C (298 K)] was used in all experiments. The substrate selected for the hydrothermal growth of TiO₂ NWs was silicon (100) wafer of p-type (boron-doped).

Experimental Procedure

In a typical synthesis of TiO₂ NWs, Si(100) substrates were rinsed with isopropyl alcohol, acetone and finally water. HCl 37% was diluted in water to 35%, then a 1:1 solution of HCl 35%:H₂O was prepared and homogenized during 10 minutes. 3.5 mL of TiCl₄ were added dropwise and kept under vigorous agitation during 15 minutes. The solution was added to a Teflon liner contained on an autoclave with the substrates placed in the bottom. The autoclave was exposed to 180 °C (453 K) during two hours. After cooling to room temperature the autoclave was open and the substrates with the TiO₂ NWs grown on the surface were rinsed several times with distilled water and dried at 60 °C (333 K) overnight. The TiO₂ NWs were characterized by Scanning Electron Microscopy (SEM), Brunauer–Emmett–Teller (BET) specific area measurements and X-Ray Diffraction (XRD).

The effect of the catalyst loading on the photodegradation reaction was studied by adding different amounts of TiO₂ NWs to a 5.0 x 10⁻⁵ M solution of PABA followed by 30 minutes of continuous stirring to allow the system to reach the adsorption-desorption equilibrium. The pH was adjusted to 3 with 0.5 M HCl. Finally H₂O₂ was added followed by bubbling air into the solution. The photocatalytic reactor consists of six light bulbs surrounding the system with continuous agitation and two mirrors to reflect the light. The photocatalytic degradation was monitored during 3 hours by taking aliquots at different reaction times that were subsequently analyzed by UV-VIS spectroscopy.

Results and Discussion

TiO₂ NWs characterization

SEM images of the synthesized TiO₂ NWs with magnifications ranging from 1,000X to 20,000X show that the synthesized catalyst is organized as single nanowires grouped in arbitrary directions (Figure 1). Each nanowire has approximately one to five microns of length and widths of ca. 300 nm. The apparent disordered growth of the nanowires leads to a material with high surface area. The Brunauer-Emmett-Teller

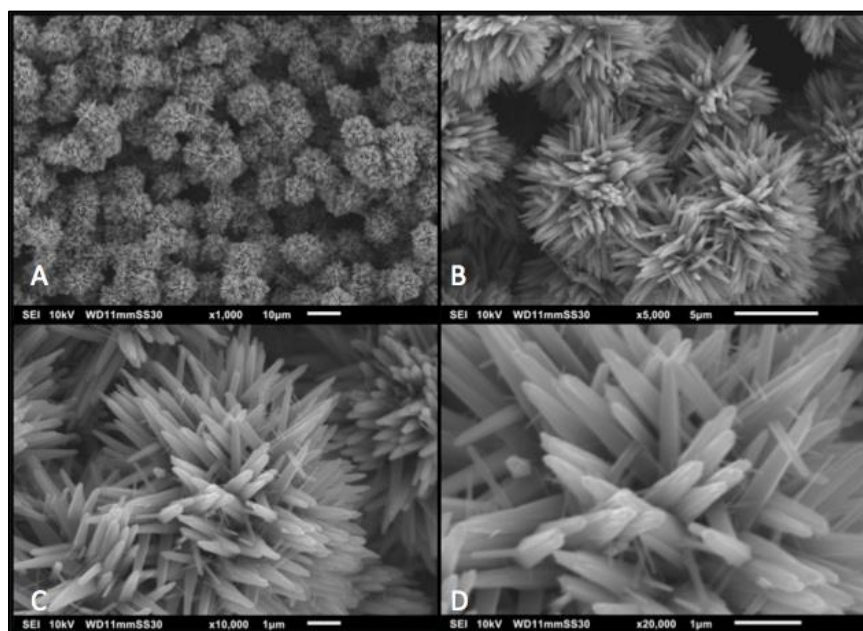


Figure 1. SEM images of the as-synthesized TiO₂ NWs obtained at different magnifications: (A) 1000X, (B) 5000X, (C) 10000X, and (D) 20000X.

(BET) surface area of the as-synthesized TiO₂ NWs was determined by N₂ adsorption-desorption isotherm measurement at 77 K. Surprisingly, the specific area of the TiO₂ NWs was found to be higher (ca. 584 m² g⁻¹) than that expected. To our best knowledge the synthesized nanowires are one of the materials based on TiO₂ with higher surface area.

The structure and crystal phase of the synthesized TiO₂ NWs have been characterized by XRD. A typical XRD pattern is shown in Figure 2. As can be seen there, the major peaks are located in the 2θ range of 20° - 70°, matching well the diffraction data of pure rutile phase since no extraneous peaks were detected.

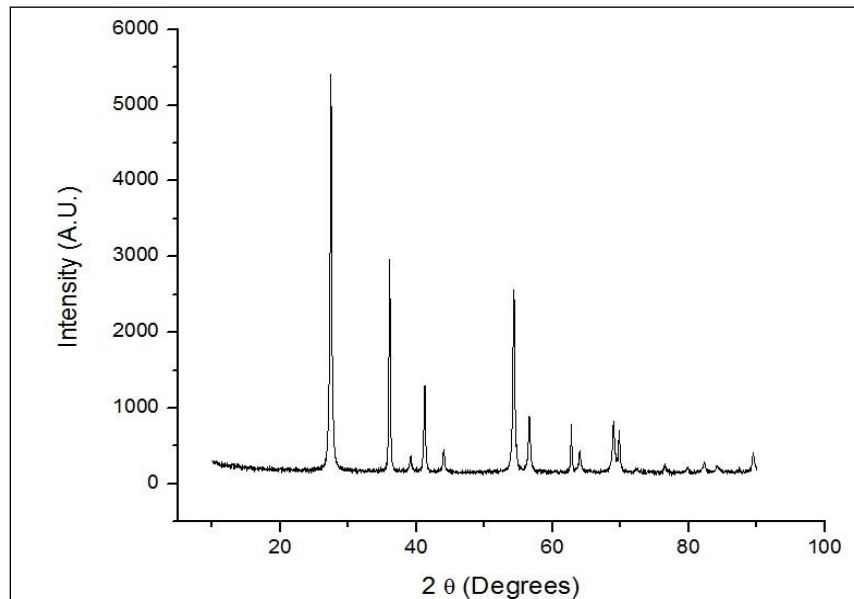


Figure 2. X-Ray diffraction pattern of the as-synthesized TiO₂NWs.

Photocatalytic Experiments

The peak at 282 nm in the UV-vis spectrum was used as the indicator of the photodegradation. The effect of catalyst loading was studied by adding different amounts of TiO₂ NWs (from 0.4 g L⁻¹ to 1.2 g L⁻¹) to the reaction mixture. The photodegradation of PABA was also tested without the presence of catalyst and without radiation source. Results obtained for the degradation of PABA under different experimental conditions (Figure 3) show that the absence of catalyst or of the irradiation source produces minimal change in the levels of PABA because the electron-hole pairs are not generated or at least not in sufficient quantity. Also in absence of the radiation source that activates the catalyst the radical species cannot be generated and the reaction does not proceed (Figure 3). Moreover, different amounts of catalyst in the reaction mixture lead, as a result, at different levels of photodegradation of PABA. The largest degradation occurs using 1.0 g L⁻¹ of catalyst (Figure 3). This result can also be seen in the final degradation percentage as a function of catalyst concentration in the reaction mixture (Figure 4).

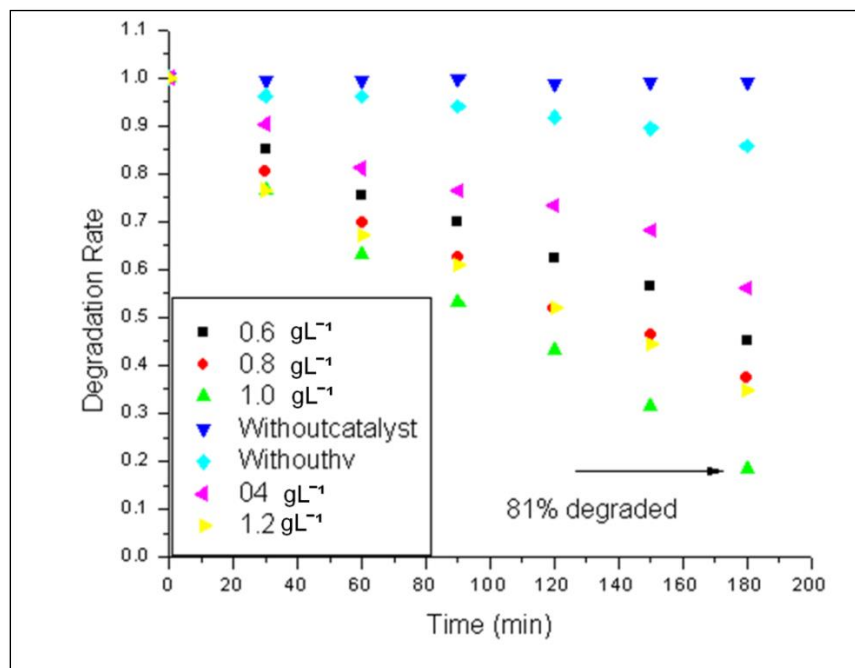


Figure 3. Study of degradation rate of PABA under different experimental conditions.

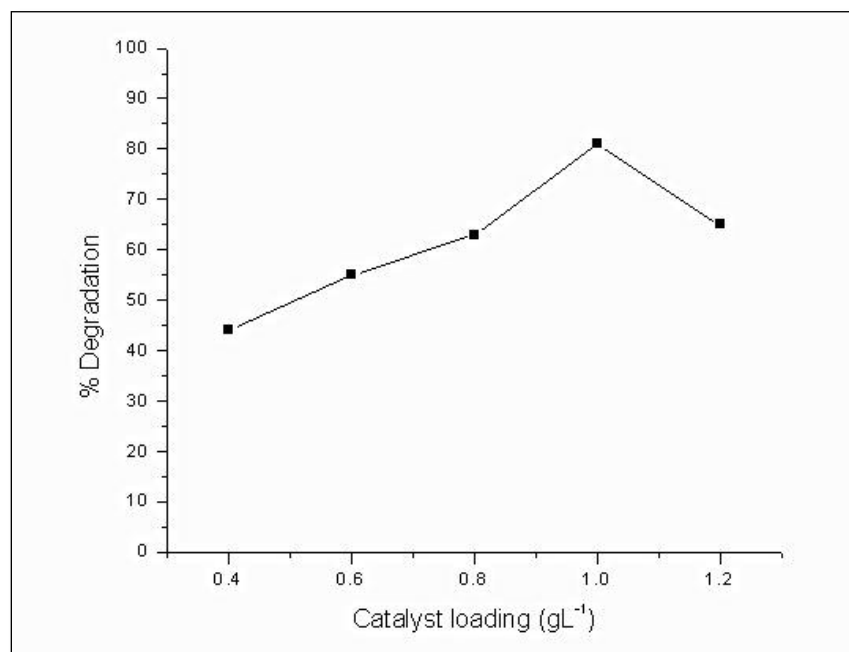


Figure 4. Degradation percentage of PABA with different catalyst loading.

Under increasing the catalyst loading the degradation rate increases until a threshold is reached (Figure 4). This occurred because the degradation rate increased with increasing catalyst loading due to more catalyst surface is available to react with the pollutant. Once the threshold is reached, the degradation rate decreased due possibly to the fact that particles of the catalyst are interacting with themselves and more molecules of PABA are still present without reacting. Also, increasing the concentration of catalyst could lead to an increment in turbidity that can produce dispersion in the incident radiation.

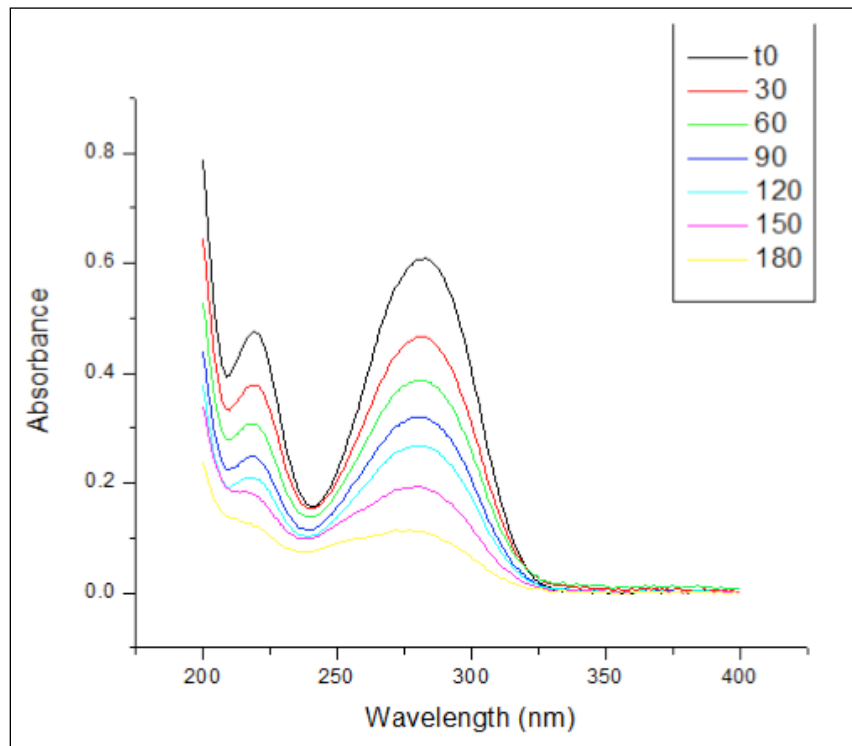


Figure 5. UV-Vis spectroscopy results corresponding to the photocatalytic degradation of PABA using 1.0 g L^{-1} of TiO_2 NWS as a function of time.

Higher catalytic activity occurred during the first 30 minutes of reaction and after that the catalysis occurred at a slower but constant pace. At 180 minutes the absorbance of PABA was much smaller which means that an effective degradation occurred in a relatively short time in comparison with other similar researches (Figure 5). It is expected that by increasing the initial pH of the reaction mixture the photocatalytic degradation increase as reported in previous researches (Mao et al. 2011, Zhou et al. 2013) since the pKa values of PABA are high.

Conclusions

TiO_2 nanowires were successfully synthesized and characterized showing high surface areas. We demonstrated that photocatalytic degradation of PABA proceed in a

relatively short period of time. However, further studies are required to better understand this catalytic process and to identify the reaction by-products.

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