Synthesis and photocatalytic activity of TiO₂ nanowires in the degradation of p-aminobenzoic acid: A comparative study with a commercial catalyst

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Abstract:

The photocatalytic degradation of p-aminobenzoic acid was studied using TiO₂ nanowires as the catalyst synthesized through a hydrothermal procedure. The as-synthesized TiO₂ nanowires were fully characterized by SEM, TEM, XRD and Raman with a very high surface area of 512 m²g⁻¹. The photocatalytic degradation of p-aminobenzoic acid was carried out under 180 minutes of constant radiation and the results were compared with P25 as commercial catalyst. Optimal experimental conditions were determined for TiO₂ nanowires with a catalyst dosage of 1.0 gL⁻¹ under acidic conditions with a 20 µM p-aminobenzoic acid solution obtaining 95 % of degradation. Under similar experimental conditions comparative studies were performed obtaining 98 % of degradation when P25 is employed. In both systems, a pseudo first order reaction was found to provide the best correlations, with constant rates of 2.0 x 10⁻² min⁻¹ and 2.4 x 10⁻² min⁻¹ for TiO₂ nanowires and P25, respectively.

Keywords: p-aminobenzoic acid, photocatalysis, TiO₂, photodegradation.

1.0 Introduction

Water pollution has emerged as a primary concern in environmental issues due to the production and consumption of pharmaceuticals and personal care products (PPCP's). The PPCP's are chemical substances resilient to traditional remediation techniques and include among others, lotions, cosmetics and sunscreen products (Zhou et al. 2013). The sunscreen products or UV-filters are frequently used because

of the concern of dangerous skin diseases caused by sun exposure like skin cancer (Ji et al. 2013a). Recent studies have identified these substances in the urine and blood from children and adults, and in indoor dust (Zhang et al. 2013, Wang et al. 2013). Also, Gago-Ferrero et al. (2013) studied the occurrence of octocrylene in marine mammals over a fifteen-years period. Their results showed this particular UV-filter was found in up to 70% of the individuals studied. Those results suggest that UV-filters residues are present in recreational waters then are absorbed through the skin and enter the bloodstream where prevail until the body secretes them.

P-aminobenzoic acid (PABA) is a UV-filter patented in 1943 but later, in the 80's, a study demonstrated that PABA caused a particular DNA damage in mammalian cells (Osgood et al. 1982). According to Wong and Orton (2011) PABA is included as one of the allergens most contained in sunscreen products. Due to the numerous recalcitrant compounds detected in recreational waters the advanced oxidation processes (AOP's) have been developed as promising decontamination methods able to generate radical species, being non-selective reactions with applications not only in liquid, but also in gaseous phase (De la Cruz et al. 2012, Ji et al. 2013a, Kontos et al. 2010). The photocatalytic process is a chemical reaction where a semiconductor acts as a catalyst when is activated with an incident radiation. This process promotes the migration of an electron from the valence band to the conduction band generating an electron-hole pair (An and Zhou, 2012). Photocatalytic reactions have demonstrated to degrade even persistent organic pollutants with high molecular weight such as dyes. Tang et al. (2013) studied the photocatalytic degradation of methyl orange using synthesized ZnO nanostructured materials, reaching 99 % of degradation modifying the catalyst shape. Other researches have employed TiO₂ to study the photocatalytic degradation of antibiotics, sunscreen products, polycyclic aromatic compounds and phenolic compounds (Zhu et al. 2013, Ji et al. 2013a, Zhang et al. 2011, Yang et al. 2010).

In this research we successfully studied the photocatalytic degradation of PABA with synthesized TiO₂ nanowires (TiO₂NWs). Additionally, and for comparative purposes, the same photodegradation study was performed with a commercial catalyst (P25) instead of TiO₂NWs.

2.0 Materials and Methods

2.1 Reagents

All reagents used in the present study were used as received. Acetone, Isopropyl alcohol 99.9%, and HCl 37% ACS Reagent were provided by Acros Chemicals. Hydrogen Peroxide 50%, TiCl_4 99.9% and NaOH $\geq 97\%$ were obtained from Fisher Scientific. 4-aminobenzoic acid $\geq 99\%$ and HCl 1.0 M standard solution were provided by Sigma-Aldrich, and P25 from Degussa (nanopowder with 21 nm particle size and $35\text{-}65\text{ m}^2\text{g}^{-1}$ surface area, $\geq 99.5\%$). All the experimental solutions were prepared using ultra pure water (Milli-Q water, $18.2\text{ M}\Omega\cdot\text{cm}^{-1}$ at $25\text{ }^\circ\text{C}$). Si(100) substrates P-type boron doped, provided by El-CAT, were used for the hydrothermal growth of TiO_2NWs . For photocatalytic experiments $0.45\text{ }\mu\text{m}$ Whatman syringe filters and quartz cells were used. Additional physical and chemical data of PABA can be found in the Supplementary Information.

2.2 TiO_2NWs synthesis

The synthesis was performed according to Cotto et al. (2013). However, modifications were performed. In a typical synthesis, Si (100) substrates were rinsed sequentially with isopropyl alcohol, water, and acetone, then dried at $60\text{ }^\circ\text{C}$. A 1:1 (v:v) solution of HCl 35 % : H_2O was prepared and magnetically stirred. After that, 3.5 mL of TiCl_4 were added dropwise and kept under vigorous stirring during 15 minutes. The solution was added to a Teflon liner contained on an autoclave with the Si substrates vertically placed in the bottom. The autoclave was exposed to $180\text{ }^\circ\text{C}$ during two hours and subsequently removed from the oven. After cooling to room temperature the autoclave was opened and the substrates with the TiO_2NWs grown on the surface were thoroughly rinsed with water, and then dried at $60\text{ }^\circ\text{C}$ overnight. Then, TiO_2NWs were removed from the Si substrates and stored on seal cups until further use.

2.3 TiO_2NWs characterization

The TiO_2NWs were fully characterized by Scanning Electron Microscopy (SEM), using a JEOL JSM6010LV operating at 20 kV. Brunauer–Emmett–Teller (BET) specific area was measured using a Micromeritics ASAP2020, according to N_2 adsorption isotherms at 77 K. The transmission electron microscopy (TEM) analyses were performed on a JEOL JEM2000FX with an accelerating voltage of 200 kV. The TiO_2NWs were ultrasound in ethanol and subsequently homogenized, and $5\text{ }\mu\text{L}$ were placed onto a copper grid coated with a lacy carbon film. Raman measurements were

acquired with a DXR Thermo Raman Microscope employing a 532 nm laser source under 5 mW power and a 25 μM pinhole aperture with a 5 cm^{-1} nominal resolution. X-ray diffraction (XRD) patterns were obtained in Theta/2Theta configuration in the range of 20-80 $^{\circ}$ at 2 $^{\circ}\text{min}^{-1}$ using a Bruker D8-Advance X-Ray Diffractometer at 40 kV and 40 mA.

2.4 Photocatalytic experiments

The reactor used for the photocatalytic experiments was a home-made type, consisting of seven spiral light bulbs and three mirrors surrounding the system. In the center of the system was placed the sample to be photodegraded (see Figure 1). The irradiation was measured about 53,000 lux.

Figure 1. Photoreactor used for the PABA degradation experiments.

The system was filled with a PABA solution to which different amounts of catalyst were added. The pH was adjusted with 0.5 M HCl or NaOH solutions, and the system was left in darkness for 30 minutes in order to reach the adsorption-desorption equilibrium (Cotto et al. 2013). Then the oxygen sources which consist of a 0.05 % solution of H_2O_2 and air bubbling were added at the time that the radiation was turned on. The photoreactor was covered with a black blanket in order to avoid any other incident radiation.

The photocatalytic reaction was maintained under constant stirring and monitored during 180 minutes by withdrawing aliquots at different time intervals.

These aliquots were filtered with 0.45 μm membrane filters and analyzed with a Shimadzu UV-2401PC spectrophotometer. As a comparative study, the same procedure was developed using P25 as commercial catalyst.

3.0 Results and Discussion

3.1 TiO_2NWs Synthesis and Characterization

TiO_2NWs were successfully synthesized, showing lengths of several microns. As shown in Figures 2a and 2b, the synthesized nanowires consisted of very branched and homogenous structures in shape and size. The highly branched structures may explain the unexpected high surface area obtained of $512\text{ m}^2\text{g}^{-1}$.

Figure 2. Characterization of TiO_2NWs . A) SEM image obtained at 10,000X magnification. B) SEM image obtained at 50,000X magnification.

At higher magnification in figure 2b is observed that each nanowire is composed of thinner nanowires of several nanometers. This is confirmed with the TEM analysis shown in figure 3 where a single nanowire exhibits a diameter of ca. 50 nm. The electron diffraction pattern (SAED) of the inset of figure 3 shows the highly crystalline nature of this material, and the absence of amorphous phase.

Figure 3. TEM image corresponding to a single TiO₂ nanowire. The inset shows the corresponding SAED pattern taken at the center of the nanowire.

The XRD of the TiO₂NWs (see Figure 4) shows a typical diffraction pattern of TiO₂ in rutile phase, showing reflections at 27.4 °, 36.0 °, 39.1 °, 41.2 °, 44.0 °, 54.2 ° and 56.3 ° that have been associated to (110), (101), (200), (111), (210), (211) and (220) planes, respectively. According to previous literature (Lin et al. 2011) anatase phase was not present.

The Raman spectrum of TiO₂NWs (see Figure 5) shows two main peaks at 444 cm⁻¹ and 608 cm⁻¹, that have been unambiguously associated to TiO₂ in rutile phase corresponding to Ti-O bond while the 236 cm⁻¹ broad band is associated to the O-O bond (Lan et al. 2012, Hardcastle 2011, Salari et al. 2011). The characteristic peaks related to anatase phase at 634 cm⁻¹, 514 cm⁻¹ and 394 cm⁻¹ were not presented confirming rutile as the unique crystal phase.

Figure 4. Typical XRD pattern obtained for TiO₂NWs, representing a pure rutile crystalline phase.

Figure 5. Raman spectrum of the as-synthesized TiO₂NWs acquired with a 532 nm laser source.

3.2 Photocatalytic experiments

3.2.1 Catalyst Loading

To determine the optimal catalyst loading, different amounts of the catalyst ranging from 0.4 gL^{-1} to 1.2 gL^{-1} were added to a PABA $50 \text{ }\mu\text{M}$ solution at pH 3. Figure 6 shows the photodegradation of PABA using P25 and synthesized TiO_2NWs at different catalyst loadings. In the case of TiO_2NWs , the degradation process increases by increasing the catalyst concentration up to 1.0 gL^{-1} reaching 77% of photodegradation. When the TiO_2NWs loading is greater than 1.0 gL^{-1} the photodegradation decreases due to system saturation, increasing the probability of interaction between catalyst particles. Also at higher catalyst loading a light screening effect may cause a dispersion of incident radiation and therefore decreasing the photocatalytic efficiency (Ji et al. 2013a, Zolfaghari et al. 2011).

Figure 6. Study of the photocatalytic degradation of PABA under different catalyst loading with synthesized and commercial TiO_2 .

When the experiments are carried out with P25 a continuous improvement in the photocatalytic degradation of PABA up to 97% is observed. However, it is noticed that the photodegradation difference obtained when the experiments are carried out with 1.0 gL^{-1} and 1.2 gL^{-1} is minimal, consistent with similar results previously reported by Mohamed et al. (2012). It is expected that if the P25 loading

increases, a lost in efficiency will occur due to the system saturation as was observed in the case of TiO₂NWs.

Under similar experimental conditions, when the as-synthesized TiO₂NWs are employed the system saturation is reached with a minor dosage suggesting that the decontaminant process can be performed with lower catalyst amount even though having acceptable results in a relatively short period of time.

3.2.2 Effect of the initial pH

The pH effect was studied by varying the initial pH from 3 to 11 and using a 50 µM PABA solution under optimal catalyst loading dosages. Table 1 shows the effects of the pH on the degradation process. As shown in Table 1, the photocatalytic process is enhanced in acidic conditions for both catalysts, achieving 97% and 77% PABA photodegradation for P25 and TiO₂NWs, respectively. The photocatalytic activity of both catalysts at acidic conditions evidenced that HCl does not have a competitive involvement in the main reaction. The poor efficiency of both catalysts at alkaline conditions could be attributed to repulsion forces between the negatively charged TiO₂ surface and PABA (Gupta et al. 2012).

Table 1. Apparent rate constants for photocatalytic degradation of PABA under different pH conditions.

Catalyst	TiO ₂ NWs	P25
pH	Rate Constant (x 10 ⁻² min ⁻¹)	Rate Constant (x 10 ⁻² min ⁻¹)
3	0.80	2.1
5	0.41	1.3
7	0.15	0.40
9	0.051	0.39
11	0.046	0.19

These results contrast with recent studies where at acidic conditions the degradation mediated by photolysis was negligible (Zhou et al. 2013). However, Ji et al. (2013b) performed comparative experiments and they established that the photodegradation enhancement under acidic conditions could be attributed to a major

contribution of $\bullet\text{OH}$ radicals in the photo-oxidation reaction. This is consistent with the fact that oxygen sources are required in order to produce radical species to enhance photodegradation. The apparent constant rates measured at acidic pH are comparable with similar researches (Ji et al. 2013b, Lin et al. 2011).

3.2.3 Influence of PABA initial concentration

The influence of the initial PABA concentration was studied in order to determine the range of optimal degradation since sunscreen products are commonly detected in water sources at low concentrations. The experiments were performed under optimum pH and catalyst loading conditions for both photocatalysts. As shown in Figure 7a, PABA can be efficiently photodegraded (ca.85%) with P25 in the range of 20 μM to 70 μM in a relatively short period of time. The photocatalytic degradation of PABA increased as the initial pollutant concentration also increases showing a maximum at 40 μM when 98% of photodegradation was achieved. Increasing the PABA concentration above 40 μM will lead to a lost in the efficiency. This happened because beyond the optimal PABA concentration the probability of PABA molecules to interact between themselves increased and less pollutant molecules are adsorbed to the catalyst surface, decreasing the photocatalytic activity.

Figure 7. Effect of the initial PABA concentration in its photocatalytic degradation. Photodegradation of PABA in the range of 20 μM to 70 μM at pH 3 under optimal catalyst loading for synthesized and commercial catalysts (A). Kinetic study of the photocatalytic degradation of PABA under optimal experimental conditions with TiO_2NWs and with P25 (B).

A 95% of photodegradation was achieved when the process was carried out in presence of TiO₂NWs. However, when PABA concentration increased the photodegradation decreased. This effect can be justified as due to the fact that the initial PABA concentration increases the generation of more organic by-products that compete for photoactive sites of the catalyst surface to be degraded (Benhebal et al. 2013). These results are in agreement with recent studies performed with a variety of photocatalysts (Mohamed et al. 2012, Roy and Mondal 2014).

Figure 7b shows that during the first 90 minutes of reaction both systems photodegraded almost at the same rate under optimal experimental conditions. However, after 90 minutes of reaction the photocatalytic activity of TiO₂NWs decreased suggesting that the system reached saturation. Both systems followed a pseudo-first order kinetic, with constant rates of $2.0 \times 10^{-2} \text{ min}^{-1}$ and $2.4 \times 10^{-2} \text{ min}^{-1}$ for TiO₂NWs and P25, respectively.

3.2.4 Control experiments

In order to determine the effect and contribution of the catalyst, radiation source and the presence of oxygen, different experimental reactions were carried out. The anoxic experiments were performed by purging the system with N₂ gas during 180 minutes (Zhu et al. 2013). The catalytic experiments were performed under darkness conditions to avoid any incident radiation while photolytic experiments were performed without the presence of a catalyst. As shown in Figures 8a and 8b, the degradation of PABA is negligible when a radiation source and oxygen sources are removed from the system, employing P25 and TiO₂NWs as catalysts. Without a radiation source the electron-hole pairs are not generated since the radiation sources are the responsible to activate the catalyst. If the photodegradation is carried out under anoxic conditions the oxygen-based radicals are not generated and therefore the photocatalysis does not proceed. If the catalysts are completely removed from the reaction mixture the photodegradation process does not proceed, as evidenced by the PABA stability along the time. This stability is also in agreement with the resilience of PABA in the environment, which is the reason why PABA is detected in surface waters.

Figure 8. Control experiments in the photocatalytic degradation of PABA using P25 (A) and TiO₂NWs (B) as catalysts.

4.0 Conclusion

During the present research PABA was photodegraded using TiO₂-based materials. The synthesized TiO₂NWs were able to photodegrade PABA up to 95%. The good catalytic activity is attributed to the high-branched levels of the material that causes an unexpected high surface area. A slight increased activity was observed when P25 was employed. This effect may be due to the fact that TiO₂NWs were synthesized as pure rutile, and P25 is produced as 70% anatase, which possesses a better catalytic activity. Also, was evidenced that a synergistic effect is responsible for the PABA degradation, since less than 10% of degradation was achieved under anoxic, catalytic or photolytic routes. The results obtained clearly show that photocatalysis could be conventionally employed in the wastewater treatment plants for the removal of recalcitrant organic compounds.

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