Photocatalytic Degradation of Sunscreen Active Ingredients Mediated by Nanostructured Materials

By

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...
Dedications

To my biological and *adoptive* family…
Acknowledgments

First of all, I will like to give thanks to my God. Thanks for giving me the strength, patience and perseverance during this entire journey. To my parents Mr Juan A Soto Morales and Mrs María M Vázquez Nistal for giving me everything what I have needed to succeed in every step of my life. Thank you for teaching me the love and passion to learn. You two are more than what I deserve. To my mentor, Dr Francisco Márquez, for being exactly what an excellent mentor is. Thank you for being so comprehensive, supportive and patient. Thank you for always believing in me even when I didn’t. To the Dean of the School of Natural Sciences and Technology, Dr Teresa Lipsett for all your support since the very first time I was in your class. Thank you for the countless conversations we have had, for listening me, and having the exact words to keep me on track.

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Abstract

LORAINÉ SOTO-VÁZQUEZ (PhD, Environmental Sciences)

Photocatalytic degradation of sunscreen active ingredients mediated by nanostructured materials (April/2016)

Abstract of a doctoral dissertation at the Universidad del Turabo.

Dissertation Supervised by Dr Francisco Márquez.

No. pages in text: 177

Water scarcity and pollution are environmental issues with terrible consequences. In recent years several pharmaceutical and personal care products, such as sunscreen active ingredients, have been detected in different water matrices. Its recalcitrant behavior in the environment has caused controversies and generated countless questions about its safety. During this research, we employed an advanced oxidation process (photocatalysis) to degrade sunscreen active ingredients. For this study, we used a 3x3 system, evaluating three photocatalysts and three different contaminants. From the three catalysts employed, two of them were synthesized. ZnO nanoparticles were obtained using zinc acetate dihydrated as the precursor, and TiO₂ nanowires were synthesized from titanium tetrachloride precursor. The third catalyst employed (namely, P25) was obtained commercially. The synthesized photocatalysts were characterized in terms of the morphology, elemental composition, crystalline structure, elemental oxidation states, vibrational modes and surface area, using SEM-EDS, XRD, XPS, Raman spectroscopy and BET measurements, respectively. The photocatalysts were employed during the study of the degradation of p-aminobenzoic acid, phenylbenzimidazole sulfonic acid, and benzophenone-4. In
all the cases, at least 50% degradation was achieved. P25 showed degradation efficiencies above 90%, and from the nine systems, 7 of them degraded at least 86%.
Resumen

LORAINÉ SOTO-VÁZQUEZ (PhD, Ciencias Ambientales)

Degradación fotocatalítica de ingredientes activos en filtros solares mediados por materiales nanoestructurados (abril 2016)

Resumen de una Disertación doctoral en la Universidad del Turabo.

Disertación Supervisada por el Dr Francisco Márquez.

No. de páginas en el texto: 177

La escasez y contaminación del agua es un problema ambiental con consecuencias terribles. En los últimos años varios productos farmacéuticos y de cuidado personal, tales como los ingredientes activos en filtros solares, se han detectado en diferentes matrices de agua. Su comportamiento recalcitrante en el medio ambiente ha provocado controversias y ha generado un sinnúmero de preguntas acerca de su seguridad. Durante esta investigación se empleó un proceso de oxidación avanzada (fotocatálisis) para degradar ingredientes activos de filtros solares. Para esto se empleó un sistema de 3x3, formado por tres fotocatalizadores y tres contaminantes. De los tres catalizadores empleados, dos de ellos fueron sintetizados. Las nanopartículas de ZnO se obtuvieron empleando acetato de zinc di-hidratado como precursor, mientras que los nanohilos de TiO₂ se sintetizaron a partir de tetrachloruro de titanio. El tercer catalizador utilizado (P25), se obtuvo de forma comercial. Los fotocatalizadores sintetizados se caracterizaron en términos de morfología, composición elemental, estructura cristalina, estados de oxidación de los elementos, modos de vibración y área superficial, usando SEM-EDS, XRD, XPS, espectroscopía Raman y medidas BET, respectivamente. Luego se emplearon estos catalizadores en el estudio de la degradación del ácido p-aminobenzoico, ácido fenilbencimidazol...
sulfónico, y benzofenona-4. En todos los casos, se consiguió al menos una degradación del 50% del contenido inicial. El catalizador P25 mostró eficiencias de degradación superiores al 90%, y de los nueve sistemas, 7 de ellos degradaron, al menos, el 86%.
Chapter One
Introduction

Clean water is a national and global priority (Cunningham and Cunningham 2009). Water is one of the most important resources for the survival of the human being. The water quality impacts the education, economy, health and population productivity (Cronk et al. 2015). Our living planet is composed nearly of 70% water, however 97% of it is seawater, which is unsuitable for drinking and for most agricultural procedures (Baird and Cann 2012). Furthermore, less than 3% of the water is freshwater, and less than 1% is available for consumption. As expected, this nearly 1% of water is not sufficient for the more than 7 billion of inhabitants of the world, since more than 90% of the freshwater is locked in glaciers and ice caps (see Table 1.1). The problem is intensified with the water demand by agriculture, which is the activity that has the highest consumption. The cumulative effects of all these factors have led to water scarcity in some regions. In consequence, this scarcity has become one of the biggest threats that our mankind has faced on its history. Furthermore, most of us are just few steps away from the access to water. However, the United Nations (UN) estimated that two-thirds of the world population will be living in water stressed countries within a decade (by 2025). A common question could be, how much water is good enough to ensure proper living and sanitation conditions for an individual? The World Health Organization (WHO) considers that 7.5 L to 20 L daily (722 L to 1930 L per year) is the minimum quantity necessary to meet the basic human needs (WHO 2016). According to WHO, in 2012 more than 600 thousand children died from diseases associated with poor water sanitation.
Table 1.1. Earth water compartments (adapted from Cunningham and Cunningham 2009).

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Water (%)</th>
<th>Average Residence Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceans</td>
<td>96.5</td>
<td>3000 to 30,000 years</td>
</tr>
<tr>
<td>Ice and snow</td>
<td>1.76</td>
<td>1 to 100,000 years</td>
</tr>
<tr>
<td>Fresh groundwater</td>
<td>0.76</td>
<td>Days to thousands of years</td>
</tr>
<tr>
<td>Fresh lakes</td>
<td>0.007</td>
<td>1 to 500 years</td>
</tr>
<tr>
<td>Other</td>
<td>0.973</td>
<td>Weeks to years</td>
</tr>
</tbody>
</table>

Also, 2.5 billion people lack access to an improved sanitation, which represents ~32% of world population. According to the WHO/UNICEF Joint Monitoring Program for Water Supply and Sanitation (JMP), an improved sanitation facility is defined as one that hygienically separates human feces from human contact. Water scarcity problem aggravates with the irresponsible use of this resource. Also, the human water use has increased about twice as fast as the population growth rate in the last 100 years (Cunningham and Cunningham 2009). Another factor to the lack of access to water is that pollution and anthropogenic activities have altered severely precipitation patterns around the world, which in consequence has caused water shortage in some areas and flood in others. Also, these anthropogenic activities have other several impacts on the use and quality of water resources, since the growth in the manufacture and use of synthetic chemicals have increased in the last decades. Many of these chemicals have contaminated the freshwater sources by direct or indirect discharge to lake and rivers, and by leakage from landfills (Manahan 2000).
According to Cunningham and Cunningham (2009) pollution can be considered as:

“... any physical, biological, or chemical change in water quality that adversely affects living organisms or makes water unsuitable for desired uses”.

Common pollutants found in water sources include, among others, heavy metals, solvents, pesticides, and organometallic compounds. Some metals are highly toxic even in diminutive concentrations. Because metals are highly resistant they can accumulate in food chains and induce a detrimental effect in the top predators. The organic pollutants include the chemicals used in the industry that usually are highly toxic. These industrial chemicals comprise pigments and common pharmaceuticals. The exposure to these organic pollutants can cause birth defects, genetic disorders, and even cancer. The real threat arises with the fact that some of these organic contaminants are very resistant to degradation (Cunningham and Cunningham 2009).

Today, the public health is under constant threat mostly by water pollution, since hundreds of different organic pollutants enter our water sources. Most of these persistent organic pollutants (POPs) are released by the industry; however, some of them also enter to the aquatic environment when people discharge them. For example, people commonly dump unwanted medicines and health supplements down the sink, or people simply consume more often these pharmaceuticals compounds at a higher rate of what the body is capable to absorb. This unabsorbed portion is discharged, or secreted, by the human body and then passed through the wastewater treatment plants (WWTPs) almost unchanged (Cunningham and Cunningham 2009). This may be the reason why several drugs, including prescription, over-the-counter,
and non-prescription drugs, have been detected in water leading from the sewage treatment plants and in surface waters (Baird and Cann 2012).

During the last years, there has been an increasing concern in the scientific community about the production, consumption and presence of the pharmaceutical and personal care products (PPCPs) in the environment. The PPCPs are chemical substances resistant to traditional remediation techniques, and include lotions, cosmetics and sunscreen products, among others (Zhou et al. 2013; Soto-Vázquez et al. 2016). The PPCPs are classified as POPs since they have been designed to be lipophilic and biologically persistent, and therefore resilient. The emission of these pollutants can present significant adverse effect to the environment and to the human health (Zhou et al. 2013). The PPCPs commonly are released through effluents from domestic sewage and hospitals (Abdelraheem et al. 2016). They are considered as emerging contaminants because of their incomplete removal in treatment plants, because of the actual status of not-regulated chemicals, and the continuous detection of these compounds in surface waters around the globe (Murgolo et al. 2015; Hu et al. 2011). The occurrence of the PPCPs may be seasonal dependent and the presence of them in the WWTPs effluents could be due to two main reasons; i) extremely high concentrations in the environment, and ii) substances highly recalcitrant to degradation (Matamoros and Salvadó 2012). These contaminants are of continuous health concerns and the situation gets worst in places where indirect potable water reuse happens. This indirect water reuse can take place through a recharge of aquifers by surface spreading, or surface water growth that serves as drinking water sources (Murgolo et al. 2015). The PPCPs have been found in several water matrices. Approximately three thousands of different substances are used as pharmaceutical ingredients (Richardson and Ternes 2014). In a recent study, De la Cruz et al. (2012)
studied the presence and removal of 32 emerging pollutants from the effluents of a treatment plant, including analgesics, antibiotics and biocides. Similarly, in a more recent study, it was evaluated the presence of several pharmaceutical drugs (Grabicova et al. 2015). The authors conclude that more than 20 drugs were present in the sites studied, and these pharmaceuticals showed a bioaccumulation potential in benthic organisms, even at low concentrations. Since these species have an important role in the food web, the uptake of PPCPs is an important exposure pathway in organisms and, of course, is not considered in determining concentrations in water-phase (Grabicova et al. 2015).

In recent years, skin health has had an increasing concern in the scientific community due to its numerous development diseases, such as cancer and allergies. Strong evidences suggest the use of sunscreens to prevent the development of melanoma (Green et al. 2011, Moyal 2012). Sunscreen products are commonly used to protect us from the incoming UV radiation from the sun and, therefore, prevent sunburn and erythema. The sunscreen products are substances that contain in their preparation an active ingredient, the UV-filter, to protect the skin from possible damage due to sun radiation. The UV-filter comes in different forms, including creams or lotions, sticks, sprays, and cosmetics. The lotions allow the greatest diversity of applications, sticks are used for lips protection and the sprays are more convenient but are less efficient (Sambandan and Ratner 2011).

The sunscreen production has surpassed this definition and currently is commonly found in other personal care products such as cosmetics, hair products, and for the protection of plastics and clothes from sunlight (Rodil et al. 2008). Some UV-filters could be in limit use or banned by government or regulatory agencies, because of their potential harmful effect to the human being (Kumar and Gupta 2013).
The sunscreen products are also classified as PPCPs and emerging contaminants, since they have been detected in raw and treated wastewaters and surface waters (Rodil et al. 2008). The environmental interest has increased in recent years due to their presence in waters and their potential harmful effect for endocrine disruption and developmental toxicity. Because of their multiple uses in a wide variety of personal care products, these compounds enter the aquatic environment either directly or indirectly from recreational activities or bathing, respectively (Richardson and Ternes 2014). Another input of the sunscreen products into surface and groundwater is from discharges of industrial and urban sources since are not degraded completely in WWTPs. Since the UV-filters have been found in several water matrices is expected that bioaccumulation and biomagnification play important roles in the fate of these organic pollutants (Jurado et al. 2014). Sunscreens agents can be classified as organic or inorganic products, according to the components present as active ingredients; however, most of them are based in organic active ingredients and, normally, contain a chromophore responsible for the absorption of UV radiation (Moyal 2012). Octyl methoxycinnamate, phenylbenzimidazole sulfonic acid (ensulizole or PBSA), benzophenone-4 (BP-4, BP4 or sulizobenzon), octocrylene, p-aminobenzoic acid (PABA) and their derivatives are some of the active organic ingredients present in sunscreens.

The continuous detection of the sunscreen active ingredients has alarmed the scientific community, as well as the regulatory agencies. Their high photostability and low biochemical degradation could lead to a dispersion of these products in the environment through several water phases and the food chain (Xue et al. 2015). As explained before, in some regions groundwater could be the main or one of the principal sources of water supplies. In a latest study, it was demonstrated that several
active ingredients, mostly benzophenone-type, are polluting the urban ground waters (Jurado et al. 2014). Also, the effect of benzophenone-3 (BP-3) in zebrafish (*Danio rerio*) was studied in a different research (Blüthgen et al. 2012). In this research was demonstrated that BP-3 could be metabolized to benzophenone-1 (BP-1), and both compounds can be accumulated in the adult fish, producing an antiandrogenic activity. Rodil et al. (2008) attributed the bioaccumulation in organisms’ tissues mainly to the lipophilic character of the active ingredients. According to Gago-Ferrero et al. (2013), several sunscreen active ingredients, such as octocrylene, can be biomagnified through the food web. The authors also conclude this active ingredient accumulates in the liver of Franciscana dolphins (*Pontoporia blainvillei*) at high concentration levels, and a pollutant transference can occur through the placenta, according to the results obtained in the study performed in Brazil.

The aquatic environment is not the only matrix in which the sunscreen components are detected. Benzophenone-type active ingredients have been also detected in dust samples around the globe, specifically in South Korea, China, Japan and USA (Wang et al. 2013). Furthermore, and unexpectedly, according to the authors, the estimated daily intake of benzophenone compounds through indoor dust ingestion was higher for USA inhabitants than for the Asian counterparts, and was attributed to the continuous use of PPCPs in the US population. In contrast, Zhang et al. (2013) reported that lower concentrations of benzophenone-type sunscreen active ingredients were detected in urine samples from US population samples, in comparison with the Chinese ones. In the numerous analyses performed by the authors, they concluded that notably higher concentrations of BP-3 were found in frequent PPCPs users. The real struggle of these benzophenone-type organic pollutants is that they can be transferred from the mother to the fetus, since these
substances were detected in twenty pairs of samples of maternal and fetal cord blood (Zhang et al. 2013). According to Kumar and Gupta (2013), BP-3 can be absorbable through the skin and cause endocrine disruption. In a similar way, Kunisue et al. (2012) studied the association between the occurrence of endometriosis and the exposure to UV-filters. They conclude that elevated exposures to some benzophenone-type sunscreens may be associated with increased chances of a positive endometriosis diagnosis. Furthermore, the authors investigated the presence of different benzophenone metabolites in over 600 urine samples, and they concluded that some of them were present in over 80% of the samples.

As stated before, there are several organic active ingredients in the sunscreen products. One of them is PABA, which was patented in 1943 as an effective UVB filter, and rapidly became very popular as one of the first active ingredients to be widely used in commercial sunscreens. The first authors to publish the antagonistic effect of PABA were Osgood et al. (1982), when they presented a study on DNA damage of certain mammalian cells, caused by the active ingredient. After several researches PABA uses has declined because of photosensitivity and its high rate of contact allergies limits its use (Chrétien et al. 2010; Sambandan and Ratner 2011, Kumar and Gupta 2013). According to Wong and Orton (2011), PABA is included as one of the allergens most contained in sunscreen products. Today, according to the 21 CFR Part 352, PABA is approved by the US Federal Drug Administration (FDA) as a sunscreen agent, in a limited use of 15% in USA (Sambandan and Ratner 2011). Because PABA is still FDA approved, several sunscreen products or PABA derivatives can be found and detected in surface waters (Xue et al. 2015). PABA or its derivatives, such as octyl-dimethyl-p-aminobenzoic acid, are known carcinogenic, and can trigger photoallergic processes (Kumar and Gupta 2013; Gilbert et al. 2013).
Also, PABA derivatives have showed several inconveniences, such as the ability to release free radicals and, in turn, cause DNA damage (Kumar and Gupta 2013).

As expected, PABA is very stable, and is this stability under solar irradiation can explain the difficult to degrade or remove it using traditional treatment methods (Xue et al. 2015). The PABA derivative most commonly used is octyl-dimethyl-p-aminobenzoic acid and, as occurs with PABA, has showed several inconveniences, including the high reaction rate with chlorine at neutral pH, forming chlorine-by-products which, in turns, cause mutagenic effects (Richardson and Ternes 2014). Moreover, according to Gilbert et al. (2013), the fact that PABA produces reactive oxygen species (ROS) in the presence of phosphate-buffered saline solution (PBS) should be of worrying, since PBS mimics the human extracellular fluid, which means that PABA has a potential to exhibit cytotoxic activity in the extracellular fluid.

Similarly to PABA, PBSA has been associated with the production of ROS and thymine dimer formation, and is considered also as an emerging contaminant (Hanson et al. 2006). However, the maximum concentration approved for PBSA is 4%, less than what is reported to PABA (Kumar and Gupta 2013). Meanwhile, European Commission established a maximum concentration for PBSA of 8% (EC 2008). PBSA is a water soluble UV-filter, with a strong absorption in the UV-B spectral region (290-320 nm) (Abdelraheem et al. 2015). Due to the continuous input into the environment through PPCPs discharge and incomplete elimination during waste water treatments, PBSA has been detected in concentrations up to ~2.7 μg L$^{-1}$ (Rodil et al. 2008, Ji et al. 2013a). One of the most serious concerns about this compound is the ability to photogenerate reactive oxygen species, such as $^{1}\text{O}_2$ and $\text{O}_2^{-}$ and, therefore, producing DNA damage (Ji et al. 2013a; Ji et al. 2013b). In fact, the generation of these oxygen radicals was proposed by Zhang et al. (2010), using a
theoretical approach based on the density-functional theory (DFT). Also, Bastien et al. (2010) concluded that PBSA offers a good photoprotection, but it is also capable of generating photosensitization, causing oxidation of guanine bases by UV-A and UV-B radiation. Grabicova et al. (2013) determined the concentration of PBSA relatively high in swimming pools and rivers, with concentrations up to 13 μg L$^{-1}$ and 500 ng L$^{-1}$, respectively.

As exposed previously, the aquatic fauna may be bioaccumulating these contaminants, and transferring them to the next generation or to predators (Abdelraheem et al. 2015). The accumulation of this UV-filter was confirmed in a recent research when the authors determined, after conducting a chronic toxicity test, that PBSA concentrations in fish plasma, liver and kidneys were elevated after 21 and 42 days of exposure. Also, exposure to PBSA changed various biochemical parameters and enzyme activities in the fish plasma (Grabicova et al. 2013). PBSA also is very resistant to traditional remediation techniques, since was detected in the WWTP in raw and treated samples, with significant increase during July month, which could be attributed to an increase in recreational activities that require sunscreen products for the individual photoprotection (Rodil et al. 2008). Also, when the analyses were performed in water matrices of sea and river, this UV-filter was also detected during July, which agrees with what exposed previously, confirming the recalcitrant performance of PBSA. Furthermore, in a recent research performed in Spain, the presence of several PPCPs in raw wastewaters was determined. According to the authors, eleven contaminants were not efficiently removed in the WWTPs tested, and their median concentrations in effluents still surpassed the 0.1 μg L$^{-1}$, including the UV-filters PBSA and BP-4 (Rodil et al 2012). From the total of 53 compounds determined, BP-4 was one of the most concentrated.
BP-4 belongs to the group of benzophenones, which are one of the most common UV-filters found in sunscreen products. Most of these compounds are water insoluble; however BP-4 is an exception. BP-4 is a FDA approved in concentrations up to 10% (Kumar and Gupta 2013). However, at much lower concentration (i.e. 5%), several irritant reactions have occurred (Wong and Orton 2011). Similar to PABA and PBSA, BP-4 has demonstrated to be very resistant, since in a recent research was detected in relative high concentrations in river, sea and wastewaters (raw and treated effluents), with an apparent increase during July, which is a high season month (Rodil et al. 2008). Furthermore, from the nine UV-filters tested, BP-4 was the only one detected in seawater during March, which is catalogued as a low season month. Among all the benzophenone-type UV-filters, benzophenone-3 is the most common. However, BP-4 is becoming increasingly incorporated into PPCPs formulations, and now is one of the most common sunscreen allergens identified (Wong and Orton 2011; Stiefel and Schwack 2014). Furthermore, BP-4 has been detected in swimming pools, rivers and recreational ponds, in concentrations up to 390 ng L\(^{-1}\) (Grabicova et al. 2013). The authors also established that BP-4 is one of the UV-filters more commonly detected in German surface waters. These results are in agreement with Jurado et al. (2014), since they determined BP-4 as one of the UV-filters in major concentration, polluting urban ground waters.

Few studies are available regarding the effect of BP-4 in organisms. However, it is well known that BP-4 led to the alteration of gene expression of adult males of zebra fish, including the genes involved in steroidogenesis (Zucchi et al. 2011). Also, the authors demonstrated BP-4 interferes with the sex hormone system. Nevertheless, the authors employed concentrations of BP-4 much higher than those normally found in the environment. However, due to the prevalence in the aquatic
environment, the pollutant may have an additive effect and may pose a serious public health hazard, due to its potential endocrine disrupting effect (Zucchi et al. 2011, Liu et al. 2016). This prevalence may also be the reason why BP-4 was detected in all the samples tested in raw and treated wastewaters in median concentrations of ~2.1 and 1.2 μg L$^{-1}$, respectively, and in 75% of the surface waters (Rodil et al. 2012). Other researchers have detected BP-4 in concentrations as high as 5.1 μg L$^{-1}$ (Wick et al. 2010), which again could lead to serious health hazards.

Typically, the water resistance of sunscreens is very low, retaining from 10 to 30% of the product on the skin after one immersion in water, which means that about 70% of the product will remain in the water (Esbenshade et al. 2010). The presence of these POPs in treated effluents from WWTPs indicates that existing techniques are not effective at removing UV filters (MacManus-Spencer et al. 2011; Gago-Ferrero et al. 2012; Jurado et al. 2014). For example, the mean removal of PBSA from WWTPs is about 21%, and cannot be removed from water by any biological treatment system (Grabicova et al. 2013). These substances are usually retained in the sewage sludge, and after might be used as fertilizer (Gago-Ferrero et al. 2013). With concentrations of UV filters accumulating in water sources and swimming pool waters, an efficient method for the degradation of sunscreen compounds in water would be a desirable application (Esbenshade et al. 2010).

Several remediation techniques exist up to date, however, most of them are not capable to remove the POPs. Nowadays, there are some in situ remediation techniques where, basically, the containment method restrains the dirty liquid/water wastes, with an impermeable layer to divert clean water from the wastes. When the pollutants are too deep then the pollutants can be precipitated or solidified (Cunningham and Cunningham 2009). The WWTPs work somehow different from
the *in situ* methods. In the WWTPs, the first step consists of a primary treatment, producing the physical separation of solids from the waste stream. The effluent from the primary treatment flows into an aeration tank and it is mixed with a bacteria-rich slurry. In this stage, the treatment consists of a biological degradation of dissolved organic compounds (Cunningham and Cunningham 2009). Few municipalities employed the advance, or third treatment. In this, specific substances are removed from the partially cleaned water before the final disinfection (Baird and Cann 2012).

Water can be purified from small particles by microfiltration and ultrafiltration, where a membrane of small pores, mainly from 0.002 to 10 μm diameter, is employed (Baird and Cann 2012). In terms of drugs or PPCPs, one of the most effective degrading methods is the chlorination (Baird and Cann 2012). However, chlorination is not suggested because chlorine can react with both, the parent compound and their by-products, leading to higher toxicity in water due to chlorinated-by-products (Abdelraheem et al. 2015).

Beside chlorination, other traditional remediation techniques include bioremediation, pump-and-treat and adsorption methods, among others. The bioremediation consists in the use of biochemical agents, mainly microorganisms, to degrade the organic pollutants. The pump-and-treat consists in pumping out the contaminated groundwater, treat the pollutants, and return the cleaned water to the system. The adsorption methods consist in the use of activated carbon to adsorb the pollutants; however, this method does not allow the destruction of the contaminant. Some of the main disadvantages of these traditional methods are that the toxicity of the compounds is not reduced, and the difficult to dispose the sludge produced in the process (Cotto-Maldonado et al. 2013). As expected, these conventional methods often are not capable to deal with POPs (Baird and Cann 2012). For example, Beel et
al. (2013) studied the biotransformation of BP-4, and even, after five days of treatment, BP-4 was still present in more than 90% of the initial content.

Because of this, sophisticated techniques such as Advanced Oxidation Processes (AOPs) have been widely studied in recent years, due to its capability to oxidize a wide range of substances and to meet the current needs of effective water treatment methods (Teh and Mohamed 2011; Krishnakumar and Swaminathan 2011). AOPs represent a group of methods classified by their ability to generate •OH radicals, which are strong oxidizing agents. Some of the advantages of these techniques involve the complete mineralization of the pollutant into CO₂ and water, no waste disposal problem, works perfectly at mild temperatures, and being non-selective reaction with applications not only in liquid, but also in gaseous phase and soil remediation (Baird and Cann 2012; Rajamanickam and Shanti 2012; Khataee and Kasiri 2010, Soto-Vázquez et al. 2016; Murgolo et al. 2015). Furthermore, the AOPs can be employed as pre-treatment, in combination with other methods, or as a post-treatment for the degradation of POPs (De la Cruz et al. 2012). In recent years, the AOPs have experienced a tremendous interest due to the fact that they are considered a real alternative to traditional remediation techniques. The AOPs include ozonation, sonolysis, Fenton processes, and heterogeneous photocatalysis, among others (De la Cruz et al. 2012).

The ozonation is considered as a promising technology for the effective removal of a variety of PPCPs (Liu et al. 2016). Ozonation is an oxidation process in which the oxidizing agent used is ozone. The main advantage of this AOP is the high oxidation potential of ozone in the decomposition of organic compounds. However, the excessive cost, high-energy usage, and low solubility in water (and ozone decomposition in water) makes the treatment a non-cost-effective and non-suitable for
water treatment (de Souza et al. 2010; Sumegová et al. 2015; Woan et al. 2009; Manahan 2000).

The sonolysis is another alternative method for remediation of aqueous environments. The sonochemical degradation of organic pollutants generally involves the chemical effect of ultrasound that arises when a sound wave passed through an aqueous media. As an AOP, highly reactive species of •OH are formed due to a transient collapse of the cavitation bubbles generated by the ultrasound wave, and then, react in a non-selective reaction (Madhavan et al. 2010; Merouani et al. 2010). However, according to Ma (2012), one of the major disadvantages of this method consists in an insufficient generation of •OH radicals. Due to this, and because this method tends to fail in the mineralization of the organic compounds, is necessary to couple with other methods, for example with Fenton processes (sono-Fenton). The Fenton processes use the Fenton’s reagent (H$_2$O$_2$ + Fe$^{2+}$) to oxidize the organic pollutants (Vinu and Madras 2010). The Fenton process works by producing •OH radicals through the H$_2$O$_2$ splitting by Fe salts. In the case of sono-Fenton reaction, the addition of H$_2$O$_2$ is not necessary, since the water splitting is assisted by ultrasound and, in consequence, H$_2$O$_2$ is produced (Madhavan et al. 2010). Fenton reaction seems to be a viable option, however, most of the photo-Fenton studies deal with the process carried out under very acidic conditions (pH <3.4) in order to maintain the iron salts soluble in water (De la Cruz et al. 2012). In order to achieve these conditions, the polluted water should be pre-treated since, under normal conditions, the wastewater is not at this acid pH and, additionally, a post-neutralization step is required. These pre- and post-treatments increase the remediation costs and, therefore, make these procedures less attractive.
The heterogeneous photocatalysis is a varied research field that includes organic synthesis, water splitting, and environmental remediation (Gaya and Abdullah 2008). The remediation of organic pollutants has experienced a tremendous interest in recent years. Vinu and Madras (2010) reported an exponential growth in the publications regarding photocatalysis from 1990, with less than one-hundred publications, to 2010 with more than three thousand publications. Furthermore, they defined photocatalysis as:

“...the acceleration of the rate of chemical reactions (oxidation/reduction) brought about by the activation of a catalyst, usually a semiconductor oxide, by ultraviolet (UV) or visible radiation”.

The photocatalytic mechanism involves the generation of valence band holes (h+) and conduction band electrons (e-) after an irradiation source (hv) impinges over a semiconductor surface and produces its activation. This activation is accomplished if the incoming photons have energy equal or greater than the semiconductor band gap energy. The generated e- and h+ pairs now are responsible for the reduction-oxidation (redox) reactions in the media (Vinu and Madras 2010). Generally, the media contain oxygen which can be reduced after reacting with the e- in the conduction band, forming the superoxide radical, while the oxidation takes place in the valence band, when the h+ are responsible to degrade (oxidize) the organic compounds (i.e. pollutants) (see Figure 1.1). Also, it should be noticed that if H2O2 is present in the medium it could react in presence of the hv and produce •OH.
The photocatalysis, as an alternative remediation method, provides major advantages, such as offering a good-substitute for the energy-intensive conventional methods; capability to degrade the pollutants, even the POPs, in contrast with conventional methods that only transfer from one medium to other; and application in aqueous, gaseous and solid matrices (Kabra et al. 2004). As mentioned before, the photocatalysis has experienced an exponential growth and interest in the last decade. For example, it has been proved to be very effective in the photocatalytic degradation of solvents, antibiotics, azo dyes, phenolic compounds and drugs of abuse in aqueous media (Zolfaghar et al. 2011; Elmolla and Chaudhuri 2010; Sobana et al. 2013, Yang et al. 2010; Kuo et al. 2015). As it was showed in these researches, the efficiency in the photocatalytic degradation will depend from system to system, according to the interactions between the photocatalyst and the organic pollutant. For example, in the photocatalytic degradation of the solvent N-methyl-2-pyrrolidone, the optimum degradation was achieved at conditions of neutral to acidic pH, while in the photocatalytic degradation of several antibiotics the optimum experimental pH was 11.
(Zolfaghari et al. 2011; Elmolla and Chaudhuri 2010). However, photocatalysis as a remediation technique, can also be applied to degrade volatile organic compounds in the gaseous phase and polycyclic aromatic compounds in soil surfaces (Kontos et al. 2010; Gu et al. 2012).

Unfortunately, very little is known about photocatalytic degradation of sunscreen products as pollutants. Esbenshade et al. (2010) studied an alternative method to remove sunscreen compounds, including PABA, from swimming pools. They used TiO$_2$ nanotubular array electrodes exposed to UV radiation. Some experimental conditions during the catalytic reaction, including pH and the potential applied to the electrode, were evaluated. In this study, 88.4% reduction of PABA, and 98.7% reduction of 4-methylbenzylidene, were achieved, according to the total organic carbon (TOC) results. Recently, the transformation of PABA, through reactions that are mediated by simulated solar radiation, has been studied (Mao et al. 2011). Here, the effect of some ions and natural organic matter, such as nitrate and bicarbonate, were studied. Their results suggest that the photodegradation of PABA in the water environment will be affected, due to the presence (or absence) of organic matter and ions in the medium. This was confirmed by Xue et al. (2015), since they reported that natural ions showed an impedance effect in the degradation of PABA. However, in the latter research, a different and more complex method, composed of a radiation source with iron ions and persulfate, was employed, achieving 99%+ degradation.

In a similar manner, the photochemical degradation of PBSA was investigated under different initial pH conditions. The authors concluded that the photochemical transformation of PBSA, mediated by direct photolysis, might be the important pathway in the photodegradation of this UV-filter (Ji et al. 2013b). The same authors,
but in a different research, investigated the photocatalytic degradation of PBSA with P25 suspensions (Ji et al. 2013a). They determined that approximately 80% of the TOC was removed, suggesting that photodegradation proceeds in a very quick path, but the mineralization took longer period of time. Finally, Abdelraheem et al. (2015), reported acceptable degradation results regarding PBSA when a UV-254 nm/H₂O₂ system was employed. The degradation of PBSA, by a photochemical procedure, may produce up to fourteen by-products, mainly by a hydroxylation or desulfonation step in the degradation (Abdelraheem et al. 2016).

The researches on the photocatalytic degradation of BP-4 are less common, however, the biotransformations of BP-4 have been studied (Beel et al. 2013). In this study the authors investigated the aerobic biodegradation of BP-4, however, the pollutant remains almost constant during the first five days of treatment. These results can be improved, since by a photocatalytic approach, BP-4 could be degraded in few hours. BP-4 is structurally very similar to BP-3. Gago-Ferrero et al. (2013) studied the ozonation and peroxone oxidation of BP-3 in water, and they reported that pH might be a major parameter in the reaction.

Little information about sunscreens as pollutants, their environmental fate, and relevant information about how it can be degraded are available. Because of this, studies are necessary to understand the chemistry, the reaction kinetics, and how the parameters involved in the process affect the photocatalysis.

In recent years the photocatalytic degradation of pollutants has been studied from a chemical and environmental point of view. A variety of catalysts have been proposed and studied, such as ZnS, Fe₃O₄, TiO₂ and ZnO. Zinc sulfide, or ZnS, has been employed in the photodegradation of organic dyes, whereas Fe₃O₄ was used in the arsenic removal of drinking water (Maji et al. 2011; Yavuz et al. 2010). Similarly,
TiO$_2$ has been widely used due to the fact that is a low cost catalyst, chemically inert and stable, with a high photoefficiency (Teh and Mohamed 2011; Umar and Aziz 2013). According to Kumar et al. (2010), the specific morphology of TiO$_2$ could be controlled varying the synthesis conditions, such as the nature of the substrate, the surface roughness, the nature of the precursor and concentration, and reaction temperature. TiO$_2$ can be found in nature as rutile, which is the most common form, however, special attention is also given to the anatase phase. With band gap energies of 3.0 and 3.2 eV, for rutile and anatase phases, respectively, TiO$_2$ has been employed in numerous photocatalytic processes, which include degradation of phenantrene, toxic compounds, chloroaromatic compounds, and antibiotics (Teh and Mohamed 2011; Zhang et al. 2011; Yang et al. 2010; Lu et al. 2011; Zhu et al. 2013). As explained above, TiO$_2$ can be obtained by countless methods; however, several commercial forms are also available. One of these commercial forms is P25, which is a combination of anatase: rutile (70:30).

Similar to TiO$_2$, another well-proved photocatalyst is ZnO. With a band gap of 3.2 eV, this compound has been described as a highly efficient and non-toxic catalyst, with environmental applications due to the low cost and thermal stability (Ong et al. 2013). As in the case of TiO$_2$, the photocatalytic degradation of p-nitrophenol, using ZnO as catalyst, has been recently studied (Rajamanickam and Shanthi 2012). The syntheses of ZnO nanoparticles have been conducted by several methods. Banerjee et al. (2012) used zinc acetate in alcohol solutions in an ultrasound bath for two hours at 65 °C. They observed that the morphology, as well as the particle size, varied, depending on the alcohol used during the synthesis reaction. Also, the nanoparticles obtained were employed in the photoremediation of Cr$^{6+}$. Furthermore, ZnO nanoparticles have been synthesized from a reaction of zinc metal.
with methanol and ethanol solutions at low and high temperatures, respectively (Shah 2008, Shah and Al-Shahry 2009). Additional synthesis routes that have been explored include the sonochemical methods, to obtain specific morphologies such as nanorods, nanoflowers and nanospheres, with zinc nitrate hexahydrated as precursor. The desirable structures were obtained by controlling some experimental parameters, including the ultrasound time and precursor concentrations (Jung et al. 2008). Due to the wide band gap of ZnO, this compound has been used as catalyst in the photodegradation of organic pollutants, even with those having heavy molar masses (Tang 2013).

The goal of this research was to study, in a bench-model, the potential use of environmentally friendly catalysts for the remediation of surface waters, polluted by sunscreen active ingredients, employing a home-made photoreactor. The first stage of the research aims to synthesize ZnO nanoparticles and TiO$_2$ nanowires. In both cases, the presence of nanostructured materials with high surface area to maximize the adsorption of the sunscreen active ingredient over the catalysts surfaces was required. In the photocatalytic experiments (stage II), the goal was to study the degradation reaction of three sunscreen active ingredients, by using UV-vis and fluorescence spectroscopies, in order to determine the properties and efficiency of the catalysts previously synthesized. For these purposes, PABA, PBSA and BP-4 were chosen as target organic pollutants. Several factors were considered in order to determine the major variables responsible for the photodegradation process. In the third, and final stage, comparative experiments using a commercial catalyst (P-25, Degussa) were performed (see Figure 1.2). The research mentioned above in the three stages described a 3x3 system (3 catalysts x 3 organic pollutants).
Figure 1.2. Stages description of the 3x3 system, used in the present research.
Chapter Two

Methods and Scientific Instrumentation

This chapter is focused on the scientific techniques employed during this study. The techniques discussed here include spectroscopy, microscopy and surface area measurements. Spectroscopy techniques comprise UV-vis, fluorescence, X-ray photoelectron spectroscopy (XPS), energy dispersive spectrometry (EDS), Raman spectroscopy; microscopy technique refers to scanning electron microscopy (SEM). Some of these instrumentations are available at Universidad del Turabo in Gurabo, Puerto Rico. However, few analyses were performed at Universidad Autónoma de Madrid and the Universidad de Puerto Rico, Río Piedras Campus.

2.1 UV-vis Spectroscopy

Ultraviolet-visible (UV-vis) spectroscopy has been employed in research and industrial laboratories over the past decades due to cost-effectiveness, ease of analysis and rapidness. The molecules exhibit electronic energy levels that are broadly separated and only if the molecule absorbs a photon of higher energy, meaning a shorter wavelength, can excite or promote the molecule from a ground level ($E_0$) to a higher level of energy ($E_1$, $E_2$, …) (see Figure 2.1.1). The incident radiation provides the necessary energy to promote the excitation of the molecule electrons. The absorption of UV-radiation results from the excitation of bonding and non-bonding electrons. Every organic molecule has, at least, one single bond. The single bonds are commonly known as sigma bonds and these are very stable. Sigma bonds usually are not affected by UV-radiation. Double bonds need four electrons, two are part of a sigma bond and the other two correspond to a pi bond ($\pi$ bond).
Electrons in pi bonds are more easily to excite to higher energy levels, consequently, organic compounds with a longer conjugated system tend to absorb at higher wavelengths (Wade 2005).

![Energy Levels Diagram](image)

Figure 2.1.1. Excitation process of a molecule from $E_0$ (ground energy level) to $E_1$ or $E_2$ (excited states).

(Adapted from Skoog et al. 2006).

The bonding types of a known analyte can be associated with the absorption spectra. Maximum absorption of a molecule occurs at a specific wavelength that depends on the chemical structure of the molecule according to Woodward-Fieser rule (Wade 2005). For example, aromatic systems absorb very intensely in the UV region due to the presence of $\pi$ electrons in its structure. When aromatic structures are bonded to strong chromophores such as carbonyl or nitro groups, the resultant is a characteristic UV spectrum. A chromophore is a molecule that absorbs UV-radiation because of the presence of an unsaturated functional group capable to exhibit an $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition. However, for a specific structure determination, UV-vis spectroscopy must be supplemented with other scientific techniques such as mass spectrometry or nuclear magnetic resonance.
UV-vis spectroscopy is based on the measurement of the absorbance of an analyte of interest. Basically, absorbance is defined as the logarithm of the quotient obtained from the incident radiation and transmitted radiation (see equation 2.1.1). The transmitted radiation is inversely proportional to the concentration of the substance of interest (Skoog et al. 2006).

\[ A = \log \left( \frac{P_0}{P} \right) \]  

Equation 2.1.1,

where \( A \) is the absorbance, \( P_0 \) is the intensity of the incident radiation, \( P \) is the intensity of the transmitted radiation by the sample and the ratio \( P_0/P \) is defined as transmittance (see Figure 2.1.2).

Absorption of radiation is linear under the same parameters of analysis, according to Beer-Lambert law (see equation 2.1.2). Maintaining the same path length, the absorbance is linear with the concentration since the molar absorptivity is a constant for given conditions.

\[ A = \varepsilon b C \]  

Equation 2.1.2,

where \( \varepsilon \) is the molar absorptivity in \( \text{L mol}^{-1} \text{cm}^{-1} \), \( b \) is the path length in cm and \( C \) is the concentration of analyte given in \( \text{mol L}^{-1} \). Since all the parameters remain constant, UV spectroscopy represents a valuable technique for quantitative analysis. However, Beer-Lambert law has several limitations such as the fact that it is applicable only when the analyte is at relative low concentrations (less than 0.01 M).
UV-vis spectroscopy is of great importance in organic and inorganic systems with good sensibility at low concentrations ($10^{-5}$ M). Due to this fact, the UV-vis spectroscopy is a fundamental scientific technique in rate experiments where a change in concentration of a substance is measured as a function of time at a fixed wavelength (Skoog et al. 2006).

The components of the UV-vis spectrophotometers depend on the applications of the instrument and vary from instrument to instrument. In a wide description a spectrophotometer consists of a radiation source that passes through a monochromator and then splits into two identical rays that each one hit the reference and sample cells individually. The transmitted radiation from the sample cell is compared to that in the reference cell. The signal output passes to a photomultiplier (PM) and then is transduced to a resultant UV-spectrum (Skoog et al. 2006) (see Figure 2.1.3).
Figure 2.1.3. Diagram of a common UV-vis spectrophotometer (Adapted from Skoog et al. 2006).

The UV-vis spectroscopy in this research was used as a primary analytical technique to determine the photodegradation of organic compounds in presence of catalysts. The UV-vis spectrophotometer used during this research was a Shimadzu UV-2401PC spectrophotometer (see Figure 2.1.4). The instrument is located at the Universidad del Turabo, and was used with two quartz cuvettes with a path length of 1 cm in the UV range, mainly at 200-400 nm, at room temperature.

Figure 2.1.4. UV-vis spectrophotometer used in this research. Model Shimadzu UV-2401PC spectrophotometer.
2.2 Fluorescence Spectroscopy

The fluorescence is a spectroscopy technique often used as a complement of UV-vis spectroscopy. It is frequently used to determine the compounds concentration, to study the progress of reactions, and to quantify inorganic and organic species in trace amounts since fluorescence shows sensitivity with detection limits up to three orders of magnitude in comparison with absorption spectroscopy (Skoog et al. 2006). In general, when the matter absorbs radiation it can emit light as part of the process of relaxation from an excited state to a ground state, this process is called luminescence.

A molecular electronic state in which all the electron spins are paired (antiparallel) is said to be a singlet state \( S_n \), where \( n \) denotes the energy level. When a pair of electrons absorbs energy they reach an excited state. If the electrons preserve the spins they are promoted to a singlet-excited state (denoted as \( S_n^+ \)). However, if one of the electrons change the spin by an intersystem crossing, a triplet state is formed (denoted as \( T_n^* \)) since the Pauli Exclusion Principle states that no pair of electrons in an atom can have the same set of four quantum numbers (Skoog et al. 2006). The radiation can only be absorbed in very small units named quanta, so the efficiency of the process is guided by the quantum efficiency, \( \Phi_E \) (Equation 2.2.1).

\[
\Phi_E = \frac{\text{number of quanta emitted}}{\text{number of quanta absorbed}} \quad \text{Equation 2.2.1},
\]

Therefore, the total number of quanta deactivated by radiative and non-radiative processes should equal the number of quanta absorbed.

Atkins and De Paula (2010) defined a sequence of short reactions that shows the absorption of radiation and deactivation processes (See Equation 2.2.2 to 2.2.4).
Absorption: $S_0 + h\nu_i \rightarrow S_n^*$  
Equation 2.2.2,
Internal conversion: $S_{\nu n}^* \rightarrow S_{\nu 0}^*$  
Equation 2.2.3,
Fluorescence: $S_n^* \rightarrow S_0 + h\nu_f$  
Equation 2.2.4,

Once a molecule absorbs energy and gets into the excited electronic state different processes can happen. The first step occurs when a molecule in ground state ($S_0$) absorbs an incident radiation ($h\nu_i$) and reaches a $S_n^*$. If the molecule has acquired too much energy, then it needs to lose the excess of energy by collisions (internal conversion). In this moment the molecule is passing from a higher vibrational level in the excited state ($S_{\nu n}^*$) to a ground vibrational level of the excited state ($S_{\nu 0}^*$). After that, the molecule in the $S_n^*$ returns to the $S_0$ by fluorescence, releasing photons of energy $h\nu_f$. The result is that fluorescence always occurs as transitions from the lowest vibrational energy level of an excited singlet state to different vibrational energy levels of the ground state (Kasha’s rule) (Sauer et al. 2011). A molecule can return to the ground state by a combination of several steps and the preferred route will be the one that permits the less lifetime of the molecule in the excited state (Skoog et al. 2006).

All the electronic transitions that involve the fluorescence process occur in the singlet states. Transitions involving a change of spin, and consequently the appearing of triplet states ($T_n$), are associated with phosphorescence, another form of luminescence (see Figure 2.2.1). In this research we are focused only in luminescence by fluorescence which is guided by the molecular structure of the target compounds and the chemical environment impact over that substance. These factors affect the intensity of emission when fluorescence occurs. Furthermore the compounds that exhibit the most intense fluorescence contains aromatic functional
groups with $\pi \rightarrow \pi^*$ transitions. The temperature of the sample also interferes with the quantum efficiency, since high temperatures increase the frequency of collisions, and hence improves the probability for deactivation by external conversion and not by fluorescence.

![Jablonski Diagram regarding luminescence phenomena](image)

Figure 2.2.1. Jablonski Diagram regarding luminescence phenomena (Adapted from Skoog et al. 2006).

Also the fluorescence of aromatic compounds with acidic or basic substituents are highly influenced by the pH conditions because the protonated or deprotonated forms of the compound can exhibit different emission intensities. The presence of dissolved oxygen has an important effect on the fluorescence. This is because oxygen is responsible for fluorescence quenching, due to oxidation capability of the fluorescing species (Skoog et al. 2006). From a practical point of view, the first step to generate fluorescence is the absorption of radiation to create the different excited states. In fact, because of this, the excitation spectrum of a target compound is essentially very similar to an absorption spectrum obtained with similar experimental
conditions. In this research the fluorescence spectroscopy was used as a complement to UV-vis spectroscopy to study the photocatalytic process.

The fluorometer used in this research was a Varian Cary Eclipse fluorescence spectrophotometer (see Figure 2.2.2). This instrument is located in the Puerto Rico Energy Center (PREC) at the Universidad del Turabo, and was used with a quartz cuvette of 1 cm path length at room temperature.

![Fluorometer used in this research. Model Varian Cary Eclipse fluorescence spectrophotometer.](image)

**Figure 2.2.2.** Fluorometer used in this research. Model Varian Cary Eclipse fluorescence spectrophotometer.

### 2.3 Raman Spectroscopy

Raman spectroscopy, usually called Raman, is a useful technique for the characterization of semiconductor materials. As in Infrared (IR) spectroscopy, two essential vibrational bonds are found in Raman, stretching and bending (see Figure 2.3.1). Stretching vibrational modes require more energy so occurs at higher frequencies, commonly above 1500 cm\(^{-1}\), and bending vibrational modes occur mostly at fingerprint region, below 1500 cm\(^{-1}\) since require less energy. During a Raman analysis the samples are excited to a virtual excited state with a laser radiation source. This arises from the fact that the molecules in the ground vibrational level can absorb a photon of energy and re-emit or scatter a photon (Skoog et al. 2006).
Most of this scattered radiation will have the same frequency as the incident radiation. However, a small portion will be scattered at a different energy and is said to be at a shifted frequency from the incident radiation. If the scattered radiation is of lower or higher frequency than the excitation radiation it is called Stokes Scattering or Anti-Stokes Scattering, respectively. Furthermore, the photon scattered can be of an exact frequency as the radiation source and is named Rayleigh scattering. Because Anti-Stokes lines are much less intense than its counterpart Stokes scattering, the second ones are commonly used in the Raman spectra.

Figure 2.3.1. Common vibration modes found on IR and Raman spectroscopies. A) Stretching mode, B) Bending mode (Adapted from Smith and Dent 2005).

Raman and IR spectroscopies are quite similar and complementary however they differ in the chemical-physical phenomena necessary to analyze a sample. IR absorption requires a change in the dipole moment and a radiation of the exact frequency can interact with the molecule and promotes it to an excited vibrational state. On the contrary, a material to be Raman active must show a change in the polarizability of the molecule during the vibration. Polarizability is the capability of
the electron cloud surrounding the molecule to change its shape during the application of an external source such as an incident radiation (see Figure 2.3.2). This is the fundamental difference between Raman and IR spectroscopies.

![Figure 2.3.2. Polarizability effect of the electron cloud. A) Change in the electron cloud, Raman Active, B) No change in the electron cloud, not active in Raman.](Adapted from Smith and Dent 2005).

In overall, for centrosymmetric molecules no strong IR active transitions are in common with active transitions in Raman and vice versa; this is known as the mutual exclusive principle. This means that an active transition on Raman spectroscopy cannot be active in the absorption of IR. For non-centrosymmetric molecules some vibrational modes may be, both, Raman and IR actives (Huheey et al. 1997). This explains the fact that symmetric and homo-atomic bonds are generally well characterized by Raman spectroscopy.

Raman spectroscopy is a powerful research technique that has been applied for qualitative and quantitative analyses of both, organic and inorganic materials. Raman spectroscopy has the advantage over IR spectroscopy of displaying strong signals on metal-oxygen bonds, and is superior in the analysis and characterization of inorganic...
systems. Also aqueous matrices can be analyzed by Raman spectroscopy because water is not Raman active but a powerful IR absorber (Skoog et al. 2006).

In a Raman instrument, the radiation sources commonly used are lasers because the high intensity is necessary to produce significant scattering with a reasonable signal-to-noise (S/N) ratio. Sources with shorter wavelengths have the advantage to produce more intense scattering, however the fluorescence interference can obstruct some regions of interest in the Raman spectrum. The near IR lasers are commonly used to diminish this interference since they can be operated at higher power without the fluorescence effect (Skoog et al. 2006).

The Raman spectrometer used in this research was a Thermo DXR Raman Microscope, equipped with a 532 nm laser (see Figure 2.3.3). The instrument is located in the Molecular Science Research Center at the University of Puerto Rico.

![Figure 2.3.3. Raman spectrometer used in this research. Model Thermo DXR Raman Microscope.](image)

2.4 Scanning Electron Microscopy

For surface characterization the techniques with sources based on ions, molecules or electrons are most powerful than photons because this assures that the
measurement is restricted only to the materials surface and not to the bulk. This is guaranteed because a photon will penetrate much more a sample in comparison with an electron of the same energy (Skoog et al. 2006). One of the most useful instruments for morphological and topographical characterization of micro and nanostructured materials is the scanning electron microscope (SEM).

In order to ensure the mean free path and the directionality of the electrons produced by the electron gun, the instrument must work under constant vacuum, usually $10^{-6}$ torr. During the process of obtaining an SEM image an electron beam is focused onto a solid surface sample and rastered in the $X$ and $Y$ direction from above ($Z$ axis), and then the information recovered is translated into an image of gray tones (Skoog et al. 2006). While this occurs, several types of signals are generated when a beam of electron strikes on the sample surface, for example the emission of backscattered electrons (BE) and secondary electrons (SE) that are useful during the image construction process (see Figure 2.4.1).

![Figure 2.4.1. Generation of BE, SE and X-ray signals when an electron beam impinges over a sample surface during SEM analysis (Adapted from Skoog et al. 2006).](image-url)
This detail makes the SEM a versatile instrument since several analyses can be performed to construct an image of the surface based on the emission of the BE and SE. When an electron beam strikes the sample surface some of them remain in the solid, however a certain number of electrons eventually leave the surface as BE. Another group of electrons, the SE, can also leave the sample but these represent the 20-50% of the total of the BE generated (Skoog et al. 2006). In Figure 2.4.1 also is shown the X-ray signal produced from the sample when the primary electron beam strikes the sample. However, these will be discussed in the EDS section.

The SE are typically of low energy, up to 50 eV, and only can escape from a region within few nanometers from the surface. SE are commonly used for topographic contrast, texture, smooth analyses, etc (Zhou et al. 2007). Moreover, the image obtained depends largely from the accelerating voltage, sample matrix, spot size and aberration corrections that can distort the image. Some lens aberration includes astigmatism and chromatic correction. The chromatic aberration occurs when electrons of different energies focus on different focal points. The astigmatism correction is an amendment in the strength of the lens when they are asymmetrical and the spot size influences in the depth of field; smaller spot size produces a higher depth of field.

A second equally valuable way to produce an image in SEM is by detecting the BE. The BE have the advantage over SE that provide information about morphological and chemical composition of the material surface. These electrons are more energetic since they leave the surface with energies greater than 50 eV. Elements with higher atomic numbers have more positive charges on the nucleus and this causes that more electrons are backscattered causing a more intense signal (Zhou et al. 2007). In consequence, elements with higher atomic numbers will be
backscattered with higher yield than the lighter ones resulting in brighter zones. When the sample morphology is considerably smaller the field emission SEM (FE-SEM) is the best choice for getting a high resolution. FE-SEM can provide topographical information up to 1,000,000X and a resolution of few nanometers. In FE-SEM, the electron beam is produced by a field emission source that is about 1000 times smaller than in a standard SEM. As a result, the image quality is markedly better, providing high or ultra-high resolution.

The analysis of a material surface with electron microscopy is easy to do with conducting samples because their capability to flow electrons greatly reduces charging artifacts. If this occurs, the sample could be coated with a metallic thin film of approximately 10 nm-thick by sputtering. For this study, a SEM and FE-SEM were used to examine the morphology of the as-synthesized materials as well as to determine their structural dimensions. For this research a JEOL JSM-6010LA and a Philips FED XL-30S systems were used (see Figures 2.4.2a and 2.4.2b). The first is located in the PREC at the Universidad del Turabo, and the second at the Universidad Autónoma de Madrid.

Figure 2.4.2. Scanning electron microscopes used in this research: a) SEM Model JEOL JSM-6010LA and b) FE-SEM Model Philips FED XL-30S.
2.5 Energy Dispersive Spectrometry

The elemental composition is as much as important as the morphology and structure determination. One of the most widely used techniques for this purpose is the Energy Dispersive Spectrometry (EDS or EDX). This technique provides qualitative chemical information regarding the chemical composition on the surface layer of the sample. It is quite difficult to predict how deep the electrons will penetrate into the sample since it is governed by the accelerating voltage and the sample matrix. However, this can be studied individually for each matrix by a Monte Carlo simulation (Gauvin 2006). The EDS technique detects the X-rays emitted from the sample when an electron beam strikes the sample (MEE 2001). These emitted electrons are characteristic for each element and its shell. The EDS technique usually is coupled with the SEM. When the electron beam collides with the sample, electrons from the sample surface are ejected. This process generates vacancies that are filled by electrons from outer shells. After that, X-rays are emitted to balance the energy differences between the two shells, and these emitted X-rays are finally detected by the EDS system (see Figure 2.5.1).

Most of the surface spectroscopy techniques require a vacuum system to assure a long free path of the electrons to strike the sample, as previously stated in the section 2.4. Also, the vacuum environment keeps the surface free from adsorbed contamination and gases such as CO₂ and O₂ (Skoog et al. 2006). Even at vacuum environment this process can occur but at a lower rate.

According to Rutherford-Böhr atom model, the electrons orbit is around a positive nucleus. The electron shell nearest to the nucleus is known as K shell and the second shell is the L shell (see Figure 2.5.1). The electron occupying outer orbitals, such as M, are less directly involved in the production of X-ray spectra since these
result from electron transitions between inner orbits. The EDS nomenclature usually identifies the X-ray lines indicating the shell containing the inner vacancy and a Greek letter that states the level of importance (α, β, etc). For example, the Zinc primary X-ray line for the K shell is identified as Kα.

Figure 2.5.1. Process of generating a useful X-ray signal during an EDS analysis (Adapted from Hafner 2013).

Most of the times EDS is used as a qualitative technique in order to find what elements are present in the sample. This is a fast technique since a complete spectrum can be obtained in seconds. Frequently are found spectral interferences during the sample analysis, specifically at the low energy region. The presence of spectrum artifacts such as sum peaks and escapes peaks make hard the ability to differentiate unequivocally between two or more spectral lines (CFAMM 2015). In order to determine unambiguously a spectral line, a complete analysis should be done, assigning, if possible, more than one energy line to the elements of interest (Kα, Kβ, L family, etc.). Also the accelerating voltage used during the analysis influences on the detected elements. An optimum accelerating voltage (in kV) is determined by the
expected elements present in the sample, since it must be at least twice the excitation energy of the elements.

An alternative application of EDS is the elemental mapping. During the EDS analysis the electron beam raster a very small point (or pixels) of the sample area. The pixels and area analyzed depend on the resolution selected, frames and magnification. The resulting data obtained are converted into an image analog to the SEM images but *painted* in different colors. Each color is assigned to each one of the detected elements. This analysis is very useful to determine the degree of homogeneity in the sample.

In this research the EDS was used to determine the elemental composition of the synthesized catalysts. The EDS used for this research was an EDAX Genesis 2000, located in the Molecular Science Research Center, at the Materials Characterization Center, Inc. facilities.

### 2.6 X-ray Photoelectron Spectroscopy

Similar to EDS, the X-ray photoelectron spectroscopy (XPS), also known as ESCA, is used to determine the elemental composition of samples. The XPS technique has the particularity to give information from only the first 1 to 10 nm of the top layer of the sample. Since this experimental technique analyzes the material surface, the vacuum conditions are stricter than EDS because oxidation of the material can occur due to the presence of water and oxygen in normal ambient conditions.

The XPS signal is produced when an electron gun is directed to a target, mostly magnesium or aluminum, producing the X-rays. These X-rays are then monochromatized and well-focused on the sample of interest. During the XPS analysis this incident beam of a monochromatic X-ray source impinges over the sample surface and ejects electrons from their orbits. In a similar manner as occurs in
EDS, in XPS an electron from an outer shell fills the vacancy. After that, an Auger or XPS electron is emitted in accordance with the principle of conservation of energy (see Figure 2.6.1). Finally, the kinetic energy (KE) of the ejected electron is measured and the binding energy, which is characteristic from the atom and orbital that emits the electron, can be determined according to the following formula:

\[
\text{Binding Energy} = h\nu - KE - w \quad \text{Equation 2.6.1},
\]

where KE is the kinetic energy, \( h\nu \) is the energy of the incident X-rays and \( w \) is the work function of the spectrometer.

![Figure 2.6.1. Process of generating a photoelectron during the XPS analysis (Adapted from Moulder et al. 1995).](image)

During the study of XPS, the analyzer is operated as an energy window commonly known as pass-energy (PE) accepting only electrons within this range (Moulder et al. 1995). In general, the binding energy is more likely to be higher for
electrons from the K shell of atoms of higher atomic numbers because of the increased positive charge of the nucleus (Skoog et al. 2006).

The XPS analysis consists of a low-resolution plot over a wide energy range commonly known as survey. A narrower energy range, with higher resolution, can be obtained with multiplex analyses. The peak position and shape also gives information about the chemical environment and state of the element. The area under each XPS peak or line is proportional to the relative amount of that element in the sample. Furthermore, the peak shape indicates the chemical state or states for that element in the sample, since the variations in the elemental binding energies are a result from differences in the polarizability of the compound and can be used to identify the different chemical states of the material surface (Moulder et al. 1995). Also the peak shape is often used as an indicator of the chemical states present in the sample, since a broad peak implies a change in the number of chemical bonds in the sample.

The XPS spectrum can be complex due to the presence of XPS lines, and also Auger lines. During the Auger process an electron vacancy is generated. Then another electron from an outer shell fills the vacancy and simultaneously another electron from the same outer shell is ejected (see Figure 2.6). The XPS spectra also can present other additional signals such as X-ray satellites, ghost lines and shake-up lines. These are less probable phenomena to occur but possible. Satellites peaks occur only when a non-monochromatic source is employed. When analyzing XPS data all these artifacts should be carefully studied and also taking into account the possibility that the sample can get charged. For this purpose, an analysis should always be done considering that the C1s transition (present in all samples) must be at 284.5 eV (Briggs and Seah, 1990). A different value is an indication that the sample was charged during the XPS acquisition and corrections should be done.
In this research the XPS was used as a complement to EDS spectroscopy to determine the elemental composition of the catalysts and the chemical environment. In this investigation a PHI Quantum 2000 XPS system was used using a PE of 117.40 eV (for survey analysis), and 58.70 eV (for multiplex analysis). The instrument is located in the Molecular Science Research Center at the Universidad de Puerto Rico (see Figure 2.6.3).
Figure 2.6.3. X-ray photoelectron spectrophotometer used in this investigation. Model PHI Quantum 2000 XPS.

2.7 X-ray Diffraction

The X-rays are a type of electromagnetic radiation of high energy produced by several ways. Commonly in an X-ray tube, electrons produced by the cathode are accelerated toward an anode, usually made of Cu or Mo. When the electrons collide with the target, part of the energy is converted to X-rays. This process is highly ineffective since only 1% of the energy is used to produce X-rays and the remainder is lost as heat (Suryanarayana and Grant Norton, 1998). When the X-rays interact with the sample matter a scattering is produced. Due to the highly ordered nature of crystalline structures, constructive and destructive interferences result, and a diffraction pattern is produced (Skoog et al. 2006).

When an X-ray hits a crystal matter at an angle θ, part of the beam is scattered by the atoms of the surface. Another portion pass through the sample onto a second layer and again part of the radiation is scattered. When the sample possesses a highly ordered crystal structure with an interplanar distance, d, a cumulative effect occurs and the incident beam can be diffracted (see Figure 2.7.1). A crystal can show
constructive interferences if, when the X-ray strikes it, the Bragg’s equation is satisfied. The Bragg’s equation (See Equation 2.7.1) states that when two beams of exact wavelengths hit two different atoms they will be scattered and one of the beams will travel until a lower layer equal to a distance of $2dsin\theta$. A constructive interference will occur, and therefore diffraction, if the distance $2dsin\theta$ equals to an integer multiple of the wavelength (see Figure 2.7.1) (Skoog et al. 2006)

$$n\lambda = 2dsin\theta$$  

Equation 2.7.1,

where $n$ is a positive integer, $\lambda$ is the wavelength of the incident wave, and $d$ is the interplanar distance.

![Diagram](image)

Figure 2.7.1. Diffraction of a signal during the XRD analysis (Adapted from Skoog et al. 2006).

Not all solids exhibit highly ordered structures, when this occurs the solid is said to be amorphous. Since amorphous structures do not exhibit ordered crystal structure, a destructive interference occurs resulting in diffractograms with no
noticeable signal. A highly ordered crystal has different planes according to the position of the atoms in the unit cell. Planes of three integers known as indices h, k and l define the crystal structures. A given set of indices cut the a-axis, b-axis and c-axis in h, k and l segments, respectively (see Figure 2.7.2). A zero means that the planes are parallel to the respective index. This information is enclosed and well defined by a special nomenclature in crystallography known as the Miller Indices.

\begin{align*}
D &= \frac{K\lambda}{\beta \cos(\theta)} \quad \text{Equation 2.7.2,}
\end{align*}

Figure 2.7.2. Axes of the unit cell (Adapted from Huheey et al. 1997).

The analysis of X-ray diffraction (XRD) provides powerful information about the crystal structure of the sample, lattice parameters, and crystal size. The qualitative information provided is based on the diffraction pattern and the line positions for every XRD signal obtained. Since every crystal structure has an unique diffraction pattern, an exact match with a reference compound means identical crystal structure (Skoog et al. 2006).

The XRD analysis is also useful to estimate accurately the crystal size of the material using the Scherrer Equation (See Equation 2.7.2).
where $D$ is the crystallite size in nm, $K$ is a constant relevant to shape normally taken as 0.9, $\lambda$ is the X-ray wavelength which usually is employed (0.154 nm), $\beta$ is the full width height maximum (FWHM) in degrees, and $\theta$ is the Bragg angle of the peak used for the crystallite size determination. According to Monshi et al. (2012), particle size is not synonym for crystal size, and using the Scherrer Equation it is possible to calculate only the crystallite size since XRD is sensitive to the crystal inside the particles.

In this research the XRD was used to determine the crystal structure of the catalysts employed. For these purposes, a XRD Bruker D8 Advance was used in the 20 range of 20-80 ° at a scan speed of 2.0 ° min$^{-1}$, with a scan step of 0.02 °. The incident radiation employed was 1.54 Å (Cu Kα). The instrument is located in the PREC at the Universidad del Turabo (see Figure 2.7.3).

![Figure 2.7.3. X-ray diffractometer used in this research. Model Bruker D8 Advance.](image)
2.8 Brunauer-Emmett-Teller (BET) Measurements

The surface area measurement is an important property of every material in chemistry since it can affect the performance of the material. In catalysis is desired a material with high surface area to promote a better performance during the reaction process. Highly branched structures and nanoparticles are common examples of materials with high BET area, denoting the space available for the reaction to occur.

There are few methods to determine the surface area of a solid material. Commonly is measured by passing an inert gas, such as nitrogen, over the sample, which is adsorbed on the material surface by weak Van der Waals interactions (see Figure 2.8.1). The specific surface area is then estimated from the amount of nitrogen adsorbed in relation to the pressure.

![Figure 2.8.1. Adsorption process for the BET analysis.](image)

The physical adsorption of the adsorbate (the gas molecules) onto a solid material surface (the adsorbent) is the basic principle of the BET measurements to determine the specific surface area of the material under study. The BET measurements are employed as an extension of the Langmuir equation, since it is applied to the adsorption of a molecular monolayer to determine the surface area. In order to employ this approach, several assumptions should be considered; the gas
molecules can be adsorbed on a solid in layers infinitely, and there is no interaction between each adsorption layer.

In this research a Micromeritics ASAP 2020 was employed and the materials synthesized were analyzed by the BET isotherm at 77 K using nitrogen as the adsorbate gas (see Figure 2.8.2). The instrument is located at the Universidad Autónoma de Madrid, Spain.

Figure 2.8.2. Surface area and porosimetry analyzer used in this research. Model Micromeritics ASAP 2020.
Chapter Three

Synthesis and characterization of nanostructured materials

This chapter is focused on the preparation, synthesis and characterization of the TiO$_2$NWs and ZnONPs catalysts. The chapter includes the materials and reagents employed, and the specific conditions for the characterization of each material and every technique used. All reagents used in this study were used as received without further purification. All the experimental solutions were prepared using ultra pure water (Milli-Q water, 18.2 MΩ cm$^{-1}$ at 25 °C).

3.1 Synthesis of TiO$_2$ nanowires (TiO$_2$NWs)

The reagents used for the synthesis of TiO$_2$NWs were acetone, isopropyl alcohol 99.9 %, TiCl$_4$ 99.9 % and HCl 37 % were provided by Acros Chemicals. Si(100), 300 µm thickness, p-type, single-side polished, provided by EL-CAT Inc. USA, were used as substrates for the material growth.

TiO$_2$NWs were synthesized by a facile hydrothermal route, using TiCl$_4$ as the Ti precursor, according to the method described by Cotto-Maldonado et al. (2013), with slight modifications. In a typical synthesis Si(100) substrates were rinsed with isopropyl alcohol, water and acetone, and dried at 60 °C. A 1:1 (v/v) solution of HCl 35% and water was prepared and magnetically stirred for 15 minutes. Then, 3.5 mL of TiCl$_4$ were added dropwise, and the reaction was kept under stirring for additional 15 minutes. The solution was then transferred to a Teflon liner and placed into stainless steel autoclaves. The Si(100) substrates were placed vertically inside the Teflon liner and the autoclaves were closed tightly (see Figure 3.1.1). The autoclaves were placed in the oven for 2 hours at 180 °C, and then were removed.
After cooling to room temperature the autoclaves were opened, and the Si(100) substrates with the TiO$_2$NWs grown on the surface were rinsed with water, at least three times, and left to dry at 60 °C. The TiO$_2$NWs were then stored in sealed cups until further use.

Figure 3.1.1. Synthesis procedure of TiO$_2$NWs: a) Autoclave used for the synthesis; b) Si(100) substrates employed for the TiO$_2$NWs growth; c) Si(100) are placed vertically inside the Teflon liner; d) Si(100) with the TiO$_2$NWs grown on the surface, after synthesis reaction; e) as-synthesized TiO$_2$NWs (optical image at a magnification of 100 X).
3.1.1. TiO\textsubscript{2}NWs characterization

The synthetic procedure described above provided nanowires of very homogenous size and shape. According to the SEM images, recorded at 10 kV and 20 kV, highly branched wires were obtained (Figure 3.1.2). In Figures 3.1.2a and 3.1.2b is observed the homogeneous growth of the TiO\textsubscript{2}NWs across the Si(100) substrate. At higher magnifications (see Figure 3.1.2c) is observed the branching level of the TiO\textsubscript{2}NWs, which can explain the unexpectedly high surface area obtained of 457 m\textsuperscript{2} g\textsuperscript{-1} (up to 512 m\textsuperscript{2} g\textsuperscript{-1}). Also is noticed that each nanowire is composed of narrower wires, according to Figure 3.1.2d.

![Figure 3.1.2. SEM images of the synthesized TiO\textsubscript{2}NWs: a) TiO\textsubscript{2}NWs grown on the surface of a Si(100) substrate, at 100 X; b) detail of the homogeneous growth of TiO\textsubscript{2}NWs, at 1000 X; c) as-synthesized TiO\textsubscript{2}NWs are highly branched, at 10 000 X; and d) each nanowire is composed of narrower wires, as shown at 50 000 X.](image-url)
These nanowires begin to growth from the first 30 minutes of reaction as single wires, and then connect among each other (see Figure 3.1.3a). After 45 minutes of reaction, the branched structure begins its organization (see Figure 3.1.3b).

Figure 3.1.3. Study of the growth process of TiO$_2$NWs: a) single wires started to connect among themselves from 30 minutes of reaction; and b) after 45 minutes of reaction, the single nanowire begins its organization.

The elemental composition was obtained with an accelerating voltage of 20 kV and it showed the presence mainly of Ti-K, Ti-L and O-K transitions, corresponding to the TiO$_2$ (see Figure 3.1.4). Also, it was noticed a minimal contribution of Cl-K, attributed to the presence of chlorine during the synthesis reaction (from hydrochloric acid and titanium tetrachloride). In the EDS analyses no foreign elemental signal was detected, suggesting the elemental purity of the synthesized TiO$_2$NWs.
Figure 3.1.4. EDS results for the as-synthesized TiO$_2$NWs.

The elemental mapping results are shown in Figure 3.1.5. The SEM image of the analyzed area is shown in Figure 3.1.5a, where the darker area (upper left) corresponds to the carbon tape where the sample was placed. This agrees with the major carbon concentration detected on the sample, illustrated with red color (see Figure 3.1.5b). Moreover, the Ti and O distribution through the sample is very homogeneous and is intensified on the nanowires surface, as presented in yellow and green colors, respectively (see Figures 3.1.5c and 3.1.5d). The Cl content is also distributed homogeneously on the TiO$_2$NWs surface, although less intense, as displayed in blue color (see Figure 3.1.5e). When an overlay image is obtained, it is noticed that the nanowires are composed mainly of Ti and O, with a very homogeneous distribution. The presence of C in this overlay is due mainly to the carbon tape and possible carbon surface contamination, and it is presented for color contrast purposes (see Figure 3.1.5f).
Figure 3.1.5. EDS mapping images for TiO$_2$NWs: a) SEM image of the as-synthesized TiO$_2$NWs; b) carbon contribution, shown in red color; c) titanium contribution, shown in yellow color; d) oxygen contribution, shown in green color; e) chlorine contribution, shown in blue color; and f) elemental overlay image.

Similar results were obtained by XPS analysis. In Figure 3.1.6 is shown the survey result with noticeable photoelectron energies for Ti and O, and weak signals for C and Cl, below 600 eV. The weak carbon signal labeled as C1s was corrected at 284.5 eV. Furthermore, Auger peaks were recorded for O (O KLL) and Ti (Ti LMM), above 900 eV.
The photoelectron peaks of Ti 2p, with binding energies at 458.5 and 464.3 eV, have been identified previously as Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively for Ti(IV) species, characteristic of TiO$_2$ (Noh et al. 2012). The symmetric shape of 2p photoelectron energies suggests that only one chemical state of Ti is present (see Figure 3.1.7a).

The O1s photoelectron transition is characterized by having an asymmetric shape, with a main line at ca. 529.8 eV, characteristic for metal oxides, that is in agreement with the presence of TiO$_2$ (Moulder et al. 1995). A weak shoulder at ca. 531.2 eV can be attributed to organic contamination, or to the presence of a hydroxide component adsorbed on the material surface (Regonini et al. 2010) (see Figure 3.1.7b).
Figure 3.1.7. XPS multiplex results for the as-synthesized TiO$_2$NWs: a) Ti2p; and b) O1s.

The diffraction pattern was obtained in the 2-theta range of 20° to 80°, at a scan velocity of 2° min$^{-1}$ and a step size of 0.02°. The XRD analysis demonstrated the crystallinity and purity of the TiO$_2$NWs. The XRD of the TiO$_2$NWs (see Figure 3.1.8) shows a typical diffraction pattern of TiO$_2$ in rutile phase, showing reflections at 27.4°, 36.0°, 39.1°, 41.2°, 44.0°, 54.2° and 56.3° that have been unambiguously associated to (110), (101), (200), (111), (210), (211) and (220) planes, respectively, according to the International Centre for Diffraction Data in the reference card JCPDS No. 21-1276 (Soto-Vázquez et al. 2016). As stated by previous literature (Lin et al. 2011), anatase phase was not present since, according to the reference card JCPDS No.21-1272, the main characteristic peak of this crystalline structure (at ca. 25.3°, corresponding to (101) plane), was absent.
Figure 3.1.8. XRD pattern corresponding to the as-synthesized TiO$_2$NWs.

This crystalline structure is confirmed by Raman spectroscopy (see Figure 3.1.9). The Raman spectrum was recorded with a 532 nm laser source operating at 5 mW power focused with a 50X objective. Two main peaks were observed at ca. 444 and 608 cm$^{-1}$, associated to TiO$_2$ in rutile phase, were observed corresponding to Ti-O vibrations. Additionally, a broad band at ca. 236 cm$^{-1}$, associated to the O-O vibration, has been observed (Lan et al. 2012, Hardcastle 2011, Salari et al. 2011). The characteristic peaks of the anatase phase at 634 cm$^{-1}$, 514 cm$^{-1}$ and 394 cm$^{-1}$, were not present, confirming rutile as the unique crystal phase existing in the as-synthesized TiO$_2$NWs.
Based on the SEM-EDS, XPS, BET measurements, XRD and Raman results, it is concluding that branched wires were obtained with a pure rutile crystalline structure and high surface area.

3.2 Synthesis of ZnO nanoparticles (ZnONPs)

For the synthesis of ZnONPs the reagents used were NaOH 98.9%, zinc acetate dihydrate, and ethanol 95%, provided by Fisher Scientific. The ZnONPs were synthesized using an eco-friendly method, via precipitation. A precursor solution was prepared diluting 4 g of zinc acetate dihydrate in 150 mL of water. In a separate Erlenmeyer flask, 1.17 g of NaOH were diluted in an aqueous solution of 12.5% ethanol (v/v). The two solutions were magnetically stirred for 30 minutes, and then the NaOH solution was added slowly into the precursor solution. The reaction was kept under vigorous stirring for two hours at room temperature. After that, a white solution was formed and then it was centrifuged several times at 7,000 rpm for 10 minutes, and dried at 60 °C overnight. Next, the synthesized material was calcined at 300 °C for 15 minutes, and stored in sealed cups until use.
3.2.1. ZnONPs characterization

The as-synthesized ZnONPs were characterized to determine among others the morphology, elemental composition and crystal structure. As shown in the FE-SEM image of Figure 3.2.1a, the calcined ZnONPs exhibit particle aggregates of less than 1 µm. However, at higher magnifications was observed that individual particles could be classified as particles of sphere-shape morphology of ca. 50 nm (see Figure 3.2.1b). The very small size of the ZnONPs provided a material with a surface area of 406 m² g⁻¹ (up to 413 m² g⁻¹).

Figure 3.2.1. FE-SEM images obtained for calcined ZnONPs: a) aggregates of particles are shown at 75 000X; b) at higher magnification (200 000X) is observed that aggregates are composed of sphere-like particles of ca. 50 nm.

The elemental composition was measured at 20 kV; the nanoparticles showed the presence mainly of Zn-K, Zn-L and O-K transitions, expected for ZnO (Ong et al. 2013) (see Figures 3.2.2a and 3.2.2b). Furthermore, the presence of carbon, attributed to the interference of the carbon tape where the sample was placed and possibly to contamination on the sample surface, was also detected. After calcination of the ZnONPs, the carbon content drastically decreased, implying the removal of the zinc salt and other impurities after the calcination step (see Figure 3.2.3). Neither sodium
(from NaOH), nor another element was detected, indicating that the nanoparticles are exclusively composed by zinc and oxygen.

Figure 3.2.2. EDS results for ZnONPs: a) ZnONPs after drying at 60 °C; and b) ZnONPs after calcination at 300 °C for 15 minutes.

Figure 3.2.3. EDS comparison of the carbon contribution of ZnONPs, after drying and calcination.

A mapping analysis was performed to the ZnONPs calcined. The darker area of the SEM image corresponds to the carbon tape, as confirmed in Figures 3.2.4a and 3.2.4b, where the greater density of carbon, shown in green color, matches with the carbon tape. The particles aggregates, and therefore the ZnONPs, are composed of O
and Zn in a homogeneous distribution, with O in magenta color and Zn in yellow color (see Figures 3.2.4c and 3.2.4d). Finally, the overlay image shows that ZnONPs are composed of Zn and O with homogeneous distribution; carbon content is shown for contrast purposes (see Figure 3.2.4e).

Figure 3.2.4. EDS mapping images for calcined ZnONPs: a) SEM image of the ZnONPs; b) carbon contribution; c) oxygen contribution; d) zinc contribution; and e) elemental overlay image.

Similarly, by Raman spectroscopy (see Figure 3.2.5) was confirmed that the calcined nanoparticles are made mainly of ZnO. As can be seen there, it is shown a sharp peak at ca. 436 cm\(^{-1}\), and two weak bands at ca. 382 and 331 cm\(^{-1}\) that have
been assigned to the characteristic hexagonal wurtzite structure of ZnO (Rai et al. 2012, Lu et al. 2012).

The wurtzite crystalline structure and the removal of zinc salt were confirmed by XRD analyses of the ZnONPs (dried and calcined). The diffraction pattern was obtained in the 2-theta range of 20 ° to 80 °, at a scan velocity of 2 ° min⁻¹ and a step size of 0.02 °. The purity of the ZnONPs increases if the samples are calcined, since additional diffraction signals detected were attributed to the zinc precursor (Saravana et al. 2013). However, these diffraction signals are no longer detectable after the calcination step (see Figure 3.2.6).

The diffraction pattern of the calcined ZnONPs in Figure 3.2.6b showed signals at 31.8 °, 34.4 °, 36.2 °, 47.5 °, 56.6 °, 62.9 °, 66.4 °, 67.9 °, 69.1 °, 72.6 ° and 77.0 °, that were assigned to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) reflections, respectively. According to literature, all these diffraction signals have been indexed to wurtzite crystalline structure (Kumar et al. 2013, Tang 2013, Ong et al. 2013, Gomez-Solís et al. 2015).
Figure 3.2.6. XRD patterns corresponding to ZnONPs: a) ZnONPs, dried at 60 °C; and b) ZnONPs, calcined at 300 °C.

The survey analyses performed by XPS are shown in Figures 3.2.7a and 3.2.7b for ZnONPs dried and calcined, respectively. Similar results were obtained in both samples, showing strong signal of Zn and O. Furthermore, Auger lines were detected for Zn and O, and identified as Zn LMM and O KLL, respectively. A weak carbon signal, labeled as C1s, was corrected at 284.5 eV.

Figure 3.2.7. XPS survey results corresponding to ZnONPs: a) ZnONPs dried; b) ZnONPs calcined.

The multiplex analyses for Zn showed intense peaks around ca. 1020.8 and 1020.9 eV, corresponding to the ZnONPs after drying and calcination, respectively (see Figures 3.2.8a and 3.2.8b). This transition was ascribed to Zn 2p$_{3/2}$, characteristic of Zn (II), and consistent with the presence of ZnO, as reported by
previous studies (Lu et al. 2012, Xu et al. 2002, Li and Wang 2010). The Zn 2p\textsubscript{3/2} in the calcined ZnONPs, is characterized by having a sharp and symmetric shape, indicating that Zn (II) bound to oxygen is the only chemical state present in the sample. In contrast, this same peak in the dried ZnONPs exhibited an additional signal at 1024.9 eV, revealing that at least a second chemical state for Zn is present in the sample. This may be attributed to the presence of residual starting material, or to the formation of intermediate Zn products during the synthesis reaction. In Figure 3.2.8b also is shown a second peak at ca. 1044.0 eV, due to the spin-orbit coupling effect, that has been ascribed to the Zn 2p\textsubscript{1/2} transition, confirming that the Zn (II) species is the only present in the sample (Lu et al. 2012, Jamali-Sheini 2012).

![Figure 3.2.8. XPS multiplex results corresponding to Zn 2p: a) ZnONPs, after drying; b) ZnONPs, after calcination.](image)

The multiplex analysis for O1s is shown in Figures 3.2.9a and 3.2.9b (ZnONPs dried and calcined, respectively). Both samples showed asymmetric peaks with maxima at ca. 529.5 eV, corresponding to oxygen bound to Zn (II) (Moulder et al. 1995, Xu et al. 2002). The asymmetric shape indicates that at least two oxygen species are present in both samples. The O1s peak, corresponding to ZnONPs, shows
a shoulder at 531.0 eV that can be attributed to organic contamination on the sample surface, or to the presence of –OH substances adsorbed to the surface.

Figure 3.2.9. XPS multiplex results corresponding to O1s: a) ZnONPs, after drying; b) ZnONPs, after calcination.

In contrast, a second intense peak was identified at 531.3 eV in the dried ZnONPs, that was attributed to the presence of residual starting material, due to the well-fitting with O1s signal observed in the zinc acetate precursor (see Figure 3.2.10).

Figure 3.2.10. XPS multiplex results obtained for O1s, when the dried ZnONPs sample is compared with the starting material.
Based on the FE-SEM, EDS, BET measurements, XRD, Raman and XPS results, it was concluded that ZnO particles, with less than 100 nm and crystalline structure, were obtained after a calcination step, and therefore are appropriate to be used in the photocatalytic experiments.
Chapter Four

Photocatalytic experiments: Results & Discussion

This chapter is focused on the photocatalytic activity of the synthesized catalysts, described in the previous chapter. Also P25, a commercial catalyst, is introduced for comparison purposes. A description of the photoreactor employed, experimental parameters, and physical-chemical characteristics of the organic pollutants and the catalysts can be found as well. All reagents used in this study were used as received, without further purification. All the experimental solutions were prepared using ultra pure water (Milli-Q water, 18.2 MΩ cm$^{-1}$ at 25 °C).

4.1 Photocatalysis procedure

The photocatalytic activity of the ZnONPs, TiO$_2$NWs and the commercial P25 was evaluated by performing several experiments for the degradation of PABA, PBSA and BP-4. In a typical experiment, a determined catalyst amount is added to a pollutant solution. The concentration ranges to be studied was determined according to the calibration curves prepared for PABA, PBSA and BP-4 (see Figures 4.1.1 to 4.1.3). For all the calibration curves $R^2$ values were 0.999 or higher. The $R^2$ is a statistical measure that indicates how the obtained data fits in the proposed equation or regression line. The $R^2$ values generally ranged from -1 to +1. Negative values indicate that the data (y values), or the response obtained is inversely proportional to the treatment (x values). Positive values in the $R^2$ indicates the response and treatment and directly proportional one to another. As much as the $R^2$ is close to +/- 1 the better the data fits to the regression line proposed. Since all of the values are 0.999 or higher the response (absorbance in UV-Vis spectroscopy) is directly proportional to the treatment (concentration of the organic pollutants).
Figure 4.1.1. PABA calibration curve

Figure 4.1.2. PBSA calibration curve

Figure 4.1.3. BP-4 calibration curve
In all the experiments, the initial concentration ranged from 10 to 80 µM. The pH was adjusted with 0.5 M NaOH or HCl, and then, the solution was kept in darkness inside the photoreactor during 30 minutes, in order to reach the adsorption-desorption equilibrium. After that, the oxygen sources which consist of air bubbling and a dilute solution of 0.05% H₂O₂ were added. The air bubbling was kept constant during all the experiment. Once the oxygen sources were added, the radiation was turned on and the photoreactor was covered with a blank blanket to avoid any other radiation interference. The photocatalysis progress was followed during three hours by taking aliquots every 30 minutes, starting at minute 0. The aliquots were filtered with 0.45 µm membrane filters in order to remove completely the solids in solution that arose from the catalysts. The aliquots were analyzed by UV-vis spectroscopy. Furthermore, PABA and PBSA aliquots were stored in amber vials in order to confirm the results by fluorescence spectroscopy. All the experiments were performed in triplicate and the degradation % was calculated according to the following formula:

\[
\text{Degradation \%} = \left( \frac{A_0 - A_{180}}{A_0} \right) \times 100 \quad \text{Equation 4.1,}
\]

where \( A_0 \) and \( A_{180} \) are the absorbances at \( \lambda_{\text{max}} \) for the compound of interest at time 0, and after 180 minutes of reaction, respectively. The \( \lambda_{\text{max}} \), as well as other physical and chemical characteristics, and the absorption and fluorescence spectra, can be found in Table 4.1 and Figures 4.1.4 to 4.1.6. Also in Table 4.2, basic characteristics of the photocatalysts employed can be found.
Table 4.1. Physical and chemical properties of the organic pollutants studied in this research.

<table>
<thead>
<tr>
<th>Physical/Chemical Characteristics (Merck Index 2006)</th>
<th>PABA</th>
<th>PBSA</th>
<th>BP-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₇H₇NO₂</td>
<td>C₁₃H₁₀N₂O₃S</td>
<td>C₁₄H₁₂O₆S</td>
</tr>
<tr>
<td>Molecular weight (g mol⁻¹)</td>
<td>137.14</td>
<td>274.30</td>
<td>308.31</td>
</tr>
<tr>
<td>λ_max (nm) (observed)</td>
<td>283</td>
<td>302</td>
<td>286</td>
</tr>
<tr>
<td>Solubility in water at 25 °C</td>
<td>1 g 170 mL⁻¹</td>
<td>260 mg L⁻¹</td>
<td>1 g 4 mL⁻¹</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>187.0-187.5</td>
<td>410</td>
<td>145</td>
</tr>
</tbody>
</table>

Figure 4.1.4. Structure and spectroscopy results for PABA: a) Chemical structure; b) UV-vis spectrum; c) Fluorescence excitation spectrum; and d) Fluorescence emission spectrum.
Table 4.2. Basic properties of the photocatalysts used in this research.

<table>
<thead>
<tr>
<th>Physical/Chemical Characteristics</th>
<th>TiO$_2$NWs</th>
<th>P25</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline structure</td>
<td>Rutile</td>
<td>70:30</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>(experimental)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Band gap energy (ev)</td>
<td>Anatase:Rutile</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>(Vinu and Madras 2010)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(experimental)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface area (m$^2$ g$^{-1}$)</td>
<td>406</td>
<td>50</td>
<td>457</td>
</tr>
<tr>
<td>(experimental)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Zhu et al. 2013) (experimental)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.1.5. Structure and spectroscopy results for PBSA:
a) Chemical structure; b) UV-vis spectrum; c) Fluorescence excitation spectrum; and d) Fluorescence emission spectrum.
Figure 4.1.6. Structure and spectroscopy results for BP-4: a) Chemical structure; and b) UV-Vis spectrum.

4.2 Photoreactor description

The reactor used for the photocatalytic experiments was a home-made type, consisting of seven spiral light bulbs (SATCO, 55 W, natural light, 5000 K). The system is surrounded by three mirrors to concentrate the radiation output of the light bulbs, which was measured to be about 53,000 lux. In the center of the system was placed a stirring machine and the sample solution to be photodegraded (see Figure 4.2.1).

Figure 4.2.1. Photoreactor used during the degradation experiments (Adapted from Soto-Vázquez et al. 2016).
4.2.1 Experimental parameters

The photocatalytic degradation of the organic pollutants chosen was studied by varying several experimental parameters. For this, the effect of the catalyst loading was considered. The optimal catalyst loading determined was then used as a standard loading in further experiments. After, the initial pH was varied with NaOH and HCl. Finally, the photocatalytic degradation reaction was studied at different initial concentration of the pollutants, in the µM range. Once defining the optimal experimental parameters, it was evaluated the contribution of other possible reaction routes such as catalysis and photolysis. Furthermore, the reaction was evaluated in anoxic conditions to determine the relevance of the oxygen sources in the reaction system. The differences in the obtained experimental data were evaluated according to ANOVA-1 way, with α=0.05, and Minitab 17 software.

4.3. Results and discussion

4.3.1 p-aminobenzoic acid

4.3.1.1 Effect of catalyst loading

In this research the first sunscreen active ingredient studied was PABA. The catalyst loading effect was investigated by adding different amounts of the catalyst to a 50 µM at a pH of 3 for TiO₂ (NWs and P25), and at a pH of 7 for the ZnONPs. As shown in Figure 4.3.1a, the photocatalytic degradation of PABA with TiO₂NWs increased as the catalyst loading also increased, reaching up to ca. 77 % of photodegradation. The optimal catalyst loading of TiO₂NWs was determined to be 1.0 g L⁻¹; above this catalyst loading a decrease in the photodegradation was observed due to system saturation, which increases the probability of interaction between catalyst solid particles. Furthermore, above the optimal catalyst loading a dispersion
of the incident radiation may occur and, therefore, less favorable is the process to occur (Ji et al. 2013a, Zolfaghari et al. 2011). A continuous decrease in the PABA absorbance, and therefore the concentration, was observed through the time. This implies that the process employed produces a constant degradation (see Figure 4.3.1b). For further photocatalytic experiments of PABA, and TiO$_2$NWs as the catalyst, a standard amount of 1.0 g L$^{-1}$ was used.

Figure 4.3.1. Photocatalytic degradation of PABA with as synthesized TiO$_2$NWs and commercial P25 at different catalyst loadings: a) effect of TiO$_2$NWs loading; b) photocatalytic degradation through the time at different TiO$_2$NWs loadings; c) effect of P25 loading; d) photocatalytic degradation through the time at different P25 loadings.

When the experiments were carried out with P25, an apparent saturation point was not observed, and the photocatalytic degradation achieved 97% (see Figure 4.3.1c). However, it is expected that if the P25 loading increases above 1.2 g L$^{-1}$, a
lost in efficiency will occur because it was noticed that the photodegradation difference obtained when the experiments are carried out with 1.0 g L\(^{-1}\) and 1.2 g L\(^{-1}\) is minimal, consistent with similar results previously reported by Mohamed et al. (2012). As occurs with the TiO\(_2\)NWs, a continuous decrement through the time is observed. Furthermore, similar degradation patterns were obtained at 1.0 g L\(^{-1}\) and 1.2 g L\(^{-1}\), confirming minimal differences between the two loading conditions (see Figure 4.3.1d). For further photocatalytic experiments of PABA, and P25 as the catalyst, a standard amount of 1.2 g L\(^{-1}\) was used.

When the ZnONPs was employed, a similar degradation pattern, but less effective, was observed in comparison with P25. The photocatalytic degradation results of PABA with ZnONPs were very similar at different catalyst loadings (see Figure 4.3.2a). A maximum PABA removal was obtained at 1.2 g L\(^{-1}\) where ca. 40\% was degraded. Furthermore, all the experimental results obtained when the ZnONPs loading was varied, ranged from 33 to 40 \%. As shown in Figure 4.3.2b the reaction progress through the time is similar at different catalyst loadings. The low photocatalytic degradation obtained for PABA, when ZnONPs was used as the catalyst, may be justified as possibly due to the fact that the reaction proceed below the optimal load for this specific pollutant. In previous results was demonstrated that the optimal catalyst loading for the ZnONPs was 5 g L\(^{-1}\) when degrading an azo dye (Sobana et al. 2013). Nevertheless, in that research was demonstrated that at 1.0 g L\(^{-1}\) the degradation obtained was ca. 50\%, with a slight increase in comparison to our results. For the upcoming experiments regarding the ZnONPs-PABA system the standard catalyst loading chosen was 1.2 g L\(^{-1}\) since it demonstrated the highest photocatalytic performance.
Figure 4.3.2. Photocatalytic degradation of PABA with ZnONPs at different catalyst loadings: a) effect of catalyst loading; and b) photocatalytic degradation through the time at different catalyst loadings.

### 4.3.1.2 Effect of initial pH

After determining the influence of the catalyst loading, the optimal dose was used, for each catalyst, to investigate the pH effect in the solution. For this study, a 50 µM PABA solution was prepared, and the pH was adjusted ranging from 3 to 11, with 0.5 M HCl or NaOH. As shown in Figure 4.3.3a, the photocatalytic activity is greatly enhanced at highly acidic environments when the TiO$_2$NWs is employed. In alkaline conditions, degradation experienced a significant decrease (from 77 % at pH 3 to less than 10 % at pH 11). Also it is observed that at pH 9 and 11 almost the same photodegradation pattern was obtained, with minimal removals, in contrast to pH 3 and 5, in which a continuous degradation was observed (see Figure 4.3.3b).
Figure 4.3.3. Photocatalytic degradation of PABA with as-synthesized TiO$_2$NWs and P25 at initial pH: a) effect of pH with TiO$_2$NWs; b) photocatalytic degradation through the time at different initial pH with TiO$_2$NWs; c) effect of initial pH with P25; and d) photocatalytic degradation through the time at different initial pH with P25.

The poor efficiency of the TiO$_2$NWs at alkaline conditions may be due to the presence of repulsive forces between a negatively charged TiO$_2$ surface and PABA, since the pKa of the pollutant is ~4.7 at neutral to alkaline conditions, and forms its anionic species (Gupta et al. 2012, Mao et al. 2011, Mirzaei et al. 2012) (see Figure 4.3.4). As occurs with TiO$_2$NWs, the photocatalytic degradation of PABA in presence of P25 significantly experiences a decrease to ca. 50% at neutral to alkaline conditions. The zero point charge (zpc) of P25 is reported to be 6.25 (Ji et al. 2013a). This means that at pH < pH$_{zpc}$, the surface of P25 is positively charged, and at pH > pH$_{zpc}$ the surface will be charged negatively, according to the following reactions (Zhu et al. 2013, Umar and Aziz 2013):
At neutral and alkaline environments both species (P25 and PABA) are negatively charged and, therefore, their interaction is not allowed due to the presence of repulsive forces, producing a decrease of the degradation rate. 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 \( \cdot \text{OH} \) 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. According to Rajamanickam and Shanthi (2012) the \( \cdot \text{OH} \) radicals in acidic environments can be formed by the following reaction:

\[
\text{H}_2\text{O} + h^+ \rightarrow \cdot \text{OH} + H^+ \quad \text{Reaction 4.3}
\]

The photocatalytic degradation of PABA with P25 through the time showed a similar pattern, however, in this case, the degradation of PABA at pH 7 and 9 was very similar and then decreased at pH 11 (see Figure 4.3.3d). The effect of pH was
shown to have a relevant influence on the photodegradation process. Moreover, this can be confirmed by the ANOVA-1 way analyses where, in both cases, p value< α (0.000 and 0.007 for TiO$_2$NWs and P25, respectively).

Different results were obtained when the ZnONPs were employed as the catalyst, varying the initial pH of the solution. As shown in Figure 4.3.5a, the photocatalytic process is not favorable at highly acidic conditions, with degradation rates of ca. 20% at pH 3. This result agrees with Roy and Mondal (2014) and Sobana et al. (2013), where the maximum degradation was obtained at neutral to alkaline pH. This may be caused by two reasons: (1) at acidic environments ZnO may undergo dissolution, which decreases its photocatalytic activity (Nilamadanthai et al. 2013); and (2) under acidic conditions, ZnO can undergo a photo-corrosion process, decreasing its reactivity (Devipriya and Yesodharan 2010).

Figure 4.3.5. Photocatalytic degradation of PABA with ZnONPs at different initial pH conditions: a) effect of initial pH after 180 minutes of irradiation; and b) photocatalytic degradation through the time at different initial pH.

Rajamanickam and Shanthi (2012) reported similar results; however their process was enhanced at high alkaline environments (i.e. pH 11). They attributed the
improved photocatalytic activity to the formation of •OH radicals according to the following reaction:

$$\text{OH}^- + \text{h}^+ \rightarrow \text{•OH}$$  \hspace{2cm} \text{Reaction 4.4}

Under harsh pH conditions (pH 3 and 11), the photocatalytic process was not favorable since both species in the reaction are positively or negatively charged, respectively. As shown in Figure 4.3.5b during the first 90 minutes of reaction, the process is almost the same at pH 5, 7 and 11. However the degradation rate at pH 11 became slower after this time. This may be due to repulsive forces between the negatively charged surface of the ZnONPs and, possibly, the generated PABA by-products, which also can be negatively charged.

4.3.1.3 Effect of initial PABA concentration

After determining the catalyst loading and pH influence on the photocatalytic reaction, the optimal dose and pH were used for each catalyst. Our third experimental parameter investigated was the effect of the initial PABA concentration. For this study, different PABA solutions, at concentrations from 20 to 70 µM, were prepared, and the pH was adjusted to 3 for the TiO$_2$NWs and P25, and to 7 for the ZnONPs.

The initial concentration of PABA remarkably influences on the photodegradation process. In presence of TiO$_2$NWs, the photocatalytic degradation was very efficient, with ca. 95% of PABA removal. It is worth noting that when PABA concentration increased the photodegradation rate experienced a relevant decrease to ca. 50%. This occurs because of the fact that the initial PABA concentration increases the generation of more organic by-products that compete with the photoactive sites of the catalyst surface to be degraded (Soto-Vázquez et al. 2016,
As can be seen in Figure 4.3.6a, the photodegradation efficiency exceeds 85% below an initial PABA concentration of 40 µM. However, at even lower concentrations (below 20 µM), 90% degradation was achieved. The result obtained is similar to previous results reported when TiO$_2$ is employed as the catalyst by degrading amaranth and p-chlorophenol (Gupta et al. 2012, Nguyen and Juang 2015). When the initial PABA concentration is 20 µM a 50% degradation was achieved during the first 30 minutes of reaction, and 90% at approximately 90 minutes of reaction (see Figure 4.3.6b). During the second half of the experiment (from 90 to 180 minutes of reaction time), when only ~10% of initial PABA concentration is still present, was observed that the reaction rate decreased considerably. This can be attributed to the competition for active sites of the TiO$_2$NWs from the remaining PABA molecules and by-products. Because of this same reason is observed that the degradation rate at 70 µM is relatively slower in comparison with lower concentrations. The reaction progress through the time is very similar when the reaction is carried out from 30 to 50 µM. In all cases the degradation obtained with TiO$_2$NWs was above 50%.

The reaction progress can also be observed in the UV-vis, emission and excitation spectra through the time (for a single experiment under optimum experimental conditions) as shown in Figures 4.3.6c, 4.3.6d and 4.3.6e. In these Figures is confirmed the fact that the degradation process is faster during the first half of reaction. Also, after 90 minutes of reaction time, the individual spectra become indistinguishable one from another.
Figure 4.3.6. Photocatalytic degradation of PABA with TiO$_2$NWs at different initial pollutant concentrations: a) effect of initial PABA concentration; b) photocatalytic degradation through the time; c) UV-vis spectra under optimal experimental conditions; d) fluorescence emission spectra under optimal experimental conditions; e) fluorescence excitation spectra; and f) determination of pseudo-first order kinetic reaction.

A similar study was performed to evaluate the photocatalytic degradation of PABA with P25 at different pollutant concentrations. Under optimum initial PABA concentration, the photodegradation achieved was ca. 98%. Similar results were reported previously when ZnS was used as the catalyst to degrade Rose Bengal,
achieving 99% degradation (Maji et al. 2011). Furthermore, under all the initial concentrations tested the minimum photodegradation obtained was 85% (see Figure 4.3.7a). In contrast as observed with TiO$_2$NWs, it was noticed that the photodegradation increased as the initial PABA concentration also increased. However, after reaching a maximum degradation at 40 µM it is observed that the degradation decreased from ~98% to ~86%. This may be caused due to the fact that the interaction between the P25 particles and PABA molecules can be enhanced at 40 µM. Below this concentration, the interaction between P25 particles was improved, while above this concentration the PABA molecules saturate the P25 surface. Moreover, it is demonstrated that when the photocatalysis was carried out at 40 µM, or less, a degradation of 50 to 70% was reached during the first 30 minutes of reaction time (see Figure 4.3.7b). Nevertheless, at 20 µM, the PABA concentration remains almost constant since ca. 15% was degraded during the following 150 minutes of reaction. Under optimum conditions, after 120 minutes of reaction the photodegradation obtained was almost negligible, since no noticeable change was observed in the PABA absorbance. This is confirmed with the UV-vis, emission and excitation spectra, shown in Figures 4.3.7c, 4.3.7d and 4.3.7e.

The photocatalytic degradation of PABA with P25 followed a kinetic of pseudo-first order, with almost a perfect fit ($R^2=0.99$), similar to the results obtained with TiO$_2$NWs. The apparent rate constant was estimated to be $2.4 \times 10^{-2}$ min$^{-1}$ (see Figure 4.3.7f). Also, the half time was calculated according to equation 4.2,

$$t_{1/2} = \frac{0.693}{k}$$

where $k$ is the apparent rate constant in min$^{-1}$. 

Equation 4.2,
Figure 4.3.7. Photocatalytic degradation of PABA with P25 at different initial pollutant concentrations: a) effect of initial PABA concentration; b) photocatalytic degradation through the time; c) UV-vis spectra under optimal experimental conditions; d) fluorescence emission spectra under optimal experimental conditions; e) fluorescence excitation spectra; and f) determination of the pseudo-first order kinetic reaction.

The half time obtained for the PABA during its photocatalytic degradation with P25 was approximately 29 minutes, which agrees with the result shown in Figure 4.3.7b for the individual progress plot for 40 µM. This result contrast with that reported by Gu et al. (2012), when the half times for the photocatalytic degradation of
phenanthrene with TiO$_2$ ranged from 38 to 53 hours. Furthermore, our result showed an apparent slower half time life when is compared with the results reported for the photolysis of PABA (Mao et al. 2011). As in the case with P25, a similar pattern was obtained when the photocatalytic process was carried out with ZnONPs, since a slight increase was observed from 20 to 30 µM. The photocatalytic degradation of PABA increased from ca. 35% to 70%, under optimum experimental conditions, with ZnONPs. Moreover, the photodegradation was enhanced from 20 to 40 µM when, at least, 65% photodegradation was obtained (see Figure 4.3.8a). These results are slightly lower in comparison with other photocatalytic researches that obtained up to 97% of degradation of organic dyes with ZnO (Saravanan et al. 2013). The photocatalytic process took the same degradation pattern through the time, at different initial PABA concentrations, as shown in Figure 4.3.8b. Also, when the initial concentration of PABA ranged from 20 to 40 µM the degradation proceed at almost the same rate, since the three individual experiments results were very similar to each other. The photocatalytic activity of the ZnONPs seems to occur at a slower rate in comparison with TiO$_2$, however, the process showed a constant degradation through the 180 minutes of reaction time. This is also established according to Figures 4.3.8c, 4.3.8d and 4.3.8e, where is observed that the decrease in PABA concentration (according to the absorbance and fluorescence intensity) occurs at a slower pace, in comparison with TiO$_2$. However, the ZnONPs surface was not saturated during the process since the degradation observed through the different reaction times remains constant. From Figure 4.3.8c is observed a minor shift from 283 to 266 nm in the $\lambda_{\text{max}}$ of PABA, in comparison with Figures 4.3.6c and 4.3.7c. This shift occurred due to the different optimum pH conditions, determined for each catalyst.
Figure 4.3.8. Photocatalytic degradation of PABA with ZnONPs at different initial pollutant concentrations: a) effect of initial PABA concentration; b) photocatalytic degradation through the time; c) UV-vis spectra under optimal experimental conditions; d) fluorescence emission spectra under optimal experimental conditions; e) fluorescence excitation spectra; and f) determination of the pseudo-first order kinetic reaction.

At neutral to alkaline conditions, the PABA anionic species should be dominant, as demonstrated earlier in Figure 4.3.4. This dominant anionic species may generate a change in the $\lambda_{\text{max}}$ observed during the UV-vis analyses. The dominant
anionic form of PABA, at neutral to alkaline conditions, was reported in a previous research (Zhou et al. 2013).

In the fluorescence spectra (Figures 4.3.8d and 4.3.8e) was not observed the formation of a second signal through the time. This suggests that the photoproducts formed were also rapidly degraded during the process, or that PABA was mineralized. The photocatalytic degradation of PABA reached a maximum of 70% degradation with ZnONPs and showed a kinetic of pseudo-first order, with an apparent constant of $4.7 \times 10^{-3}$ min$^{-1}$, and $R^2=0.96$.

In latest studies a photolytic procedure in presence of organic matter was employed to degrade PABA (Zhou et al. 2013, Mao et al. 2011). The authors conclude that one possible pathway for the PABA degradation is the polymerization of an intermediate product and the hydroxylation of PABA. Also, in both researches, three to four photoproducts were detected after long periods of reaction times (ca. 36 hours). The non-selective attack of the hydroxyl radicals may promote the hydroxylation of PABA and produce a main by-product identified as a PABA hydroxylated compound (PABA with an additional hydroxyl group). PABA TOC reduction also was achieved in a third research, when a complex environment composed of persulfate, Fe$^{2+}$ and a UV-system was employed (Xue et al. 2015). According to the authors, PABA can be completely degraded into CO$_2$, water and nitrate. Once again, is established that the degradation of PABA undergoes a sequential hydroxylation pathway.

The photocatalytic results shown above demonstrated that PABA can be efficiently degraded in at least 70% during 180 minutes (see Figure 4.3.9a). Moreover, under the conditions studied, TiO$_2$ (NWs and P25) was able to degrade PABA with similar results (p value=0.95) and comparable rates as shown in Figure
4.3.9b. As shown, after 90 minutes of reaction time, the degradation obtained is negligible when TiO₂NWs and P25 were employed, since the greatest degradation was obtained during the first 30 minutes of reaction time. As discussed early, a slower but constant pace was observed when the photocatalytic degradation was carried out with ZnONPs. Under optimum experimental conditions for each catalyst, the results obtained with TiO₂NWs, P25 and ZnONPs seems to be similar with a few differences among them. However, these differences cannot be attributed to randomness or to statistical differences, since the p value obtained was 0.05, and therefore a trustable conclusion about the differences observed cannot be made.

![Figure 4.3.9](image.jpg)

**Figure 4.3.9.** Study of the photocatalytic degradation of PABA with different catalysts: a) comparison of the degradation percent after 180 minutes of irradiation with different photocatalysts; and b) comparative photocatalytic degradation process through the time for the three photocatalysts studied.

**4.3.1.4 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. 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 any catalyst (Soto-Vázquez et al. 2016). It was demonstrated that the degradation of PABA undergoes mainly a photocatalytic process, since the degradation by photolysis and catalysis was negligible when the TiO$_2$NWs, P25 and ZnONPs were employed, as shown in Figures 4.3.10, 4.3.11 and 4.3.12, respectively. Under anoxic conditions the reactions did not proceed due to absence of oxygen in the reaction mixture. The lack of oxygen under these conditions prevents the formation of oxygen-based radicals and therefore the degradation is not produced. The persistence of PABA in the environment is demonstrated since without the presence of the catalyst the concentration remains almost constant along the 180 minutes of reaction time.

Figure 4.3.10. Comparison of the degradation results of PABA under optimal experimental conditions, and control experiments with TiO$_2$NWs.
Figure 4.3.11. Comparison of the degradation results of PABA under optimal experimental conditions, and control experiments with P25.

Figure 4.3.12. Comparison of the degradation results of PABA under optimal experimental conditions, and control experiments with ZnONPs.
4.3.2 Phenylbenzimidazole sulfonic acid

4.3.2.1 Effect of catalyst loading

The second organic pollutant studied in this research was PBSA. As with PABA, the catalyst loading effect was investigated by adding different amounts of the three catalysts used to a 50 µM solution, adjusted to pH 5 for TiO\textsubscript{2} (NWs and P25) and pH 9 for the ZnONPs. When TiO\textsubscript{2}NWs was employed in the photocatalytic degradation of PBSA, the results obtained were similar in comparison with PABA. In this case, the degradation reached an optimal catalyst loading at 1.0 g L\textsuperscript{-1}, as shown in Figure 4.3.13a. However, it must be noticed that the degradation results obtained in comparison with PABA were much lower since less than 30 % of degradation was obtained in all the conditions. This optimum catalyst loading was determined according to the graphical representation of degradation vs. catalyst loading. However, it should be observed that all the degradation results obtained were very close to each other, since these results ranged 22 and 29 %. The remarkable differences in the photodegradation results may be due to the fact that PBSA is a much larger molecule in comparison with PABA. Due to the larger size of PBSA molecules, the amount of these molecules adsorbed by surface area of the catalyst (TiO\textsubscript{2}NWs) is clearly lower (Guillard et al. 2003). Furthermore, PABA and PBSA are structurally different; PABA has a strong electron donor functional group (-NH\textsubscript{2}). The presence of the –NH\textsubscript{2} group in the molecule can intensify its resonance and therefore the degradation efficiency. In contrast, PBSA has a strong electron-withdrawing group (–SO\textsubscript{3}H), which has demonstrated to retard the degradation efficiency (Fathinia et al. 2010). As can be seen in Figure 4.3.13a, the degradation rate increased with increasing the catalyst loading up to 1.0 g L\textsuperscript{-1}; at higher catalyst
loadings the degradation rate experienced a significant decrease. This behavior can be explained due to the fact that the addition of surplus catalyst material also results in the deactivation of activated molecules by collision with ground state molecules (Benhebal et al. 2013).

Although the final degradation of PABA and PBSA were different, the catalytic processes through the time are similar, since a continuous removal of the pollutants was observed (see Figure 4.3.13b). At catalyst loading of 1.0 g L$^{-1}$ it was observed that the degradation from 30 to 90 minutes was slightly less efficient. This may be caused because the photoproducts during the first minutes of reaction may be competing for the TiO$_2$NWs photoactive sites. Since the maximum degradation was achieved with 1.0 g L$^{-1}$ this amount was used as the standard dose for the upcoming photocatalytic experiments of PBSA with TiO$_2$NWs.

In the case of P25 a similar degradation pattern was obtained, in comparison with the TiO$_2$NWs, and the optimal catalyst loading was determined to be 1.0 g L$^{-1}$, similarly to the reaction conducted with TiO$_2$NWs (see 4.3.13c). When the catalyst dose increased to 1.2 g L$^{-1}$ a slight decrease in the degradation rate was observed, suggesting that the system reached a saturation point. This result can be explained by the light screening effect, that is caused when the excess of solid particles from the photocatalyst scatter or reflects the incoming photons from the radiation, necessary to activate the catalyst. The P25 solid particles have a mean particle size of 25 nm and usually this small size tends to form aggregates, decreasing the contact surface area between the pollutant molecules and the photocatalyst and, in this way, reducing the photodegradation (Ji et al. 2013a). In comparison with PABA, was obtained a lower optimal catalyst loading. However, as stated before, a minimum of 95% degradation of PABA was obtained when the catalyst loadings ranged from 1.0 to 1.2 g L$^{-1}$. In
contrast, a minor degradation, up to 90%, was obtained in the case of PBSA under the same catalyst loading conditions. This result agrees with the fact that PBSA molecules are larger and can saturate the catalyst surface and, consequently, cause a decrease of the photocatalytic efficiency.

Figure 4.3.13. Photocatalytic degradation of PBSA with as synthesized TiO$_2$NWs and commercial P25 at different catalyst loadings: a) effect of catalyst loading with TiO$_2$NWs; b) photocatalytic degradation through the time at different catalyst loadings of TiO$_2$NWs; c) effect of catalyst loading with P25; and d) photocatalytic degradation through the time at different P25 loadings.

The optimal catalyst loading reported by Ji et al. (2013a), with an optimal dose of 2.0 g L$^{-1}$ for the system P25 – PBSA, was very different to the reported in this research. The photocatalytic processes through the time, under all catalyst loading conditions, showed a similar pattern, as occurs with the degradation of PABA with
P25. The commercial P25 catalyst was able to degrade PBSA in a continuous manner (see Figure 4.3.13d). As can be seen there, when the degradation is carried out with catalyst loadings of 1.0 and 1.2 g L$^{-1}$, the obtained results are quite similar. However, with 1.0 g L$^{-1}$ is observed a greatest degradation during the first 30 minutes of reaction (A/A$_0$ decreased from 1.0 to ~0.6). The standard amount of catalyst for the following experiments was chosen to be 1.0 g L$^{-1}$, since a maximum degradation was observed with very similar results in comparison with 1.2 g L$^{-1}$, and hence less photocatalyst should be used.

The ZnONPs activity towards the photodegradation of PBSA showed an intermediate efficiency, in comparison with the commercial and as-synthesized TiO$_2$. Differently to TiO$_2$, the ZnONPs did not reach an apparent saturation point. As shown in Figures 4.3.14a and 4.3.14b, the photocatalytic degradation was constant and was not observed a decrease in the photocatalytic rate through the time. This result suggests that the system under study could be able to sustain a higher catalyst loading. Sobana et al. (2013) reported the almost complete degradation of an azo dye in 120 minutes. However, their experimental setup conditions for these results include a much higher catalyst loading of 5 g L$^{-1}$ which turns their system in a non-cost effective procedure to transfer in a real environment. The enhancement rate in our results may be due to the increase of catalyst particles in the illumination area, which promotes the catalyst photoactivation (Krishnakumar and Swaminathan 2011). Similar to our results, Nilamadanthai et al. (2013) demonstrated that the photocatalytic activity of ZnO increased as the catalyst weight % was also increased. However, the authors decide to use a catalyst loading of mid-concentration to avoid the light screening effect and possible agglomeration of the nanoparticles. In our case, we decided do not increase the amount of catalyst added (above 1.2 g L$^{-1}$), even
when the system seems capable to tolerate higher doses, in order to keep similar 
photocatalytic conditions for the three photocatalysts used. Furthermore, if the 
catalyst loading is increased, the study could be not cost-effective to perform, since 
the expenses will increase because of the requirement of more reactants to produce 
even more catalyst materials. Because of this, the maximum catalyst loading was 
used as the standard amount of ZnONPs to photodegrade PBSA.

**Figure 4.3.14. Photocatalytic degradation of PBSA with ZnONPs at different 
catalyst loadings: a) effect of catalyst loading after 180 minutes or irradiation; 
and b) photocatalytic degradation through the time at different catalyst loadings.**

**4.3.2.2 Effect of initial pH**

In order to evaluate the influence of the pH in the photocatalytic degradation 
of PBSA, different experiments were performed with the optimal dose. A 50 µM 
PBSA solution was prepared, and the pH was adjusted from 3 to 11 with 0.5 M HCl 
or NaOH. The photocatalytic degradation of PBSA was very similar when P25 and 
TiO$_2$NWs are employed at different pH, since the optimal pH was determined to be 5 
for both catalysts (see Figures 4.3.15a and 4.3.15b). The sunscreen PBSA exhibits a 
pKa close to 4.0 and, when the pH is increased above 4.0, the sulfonic group is 
deprotonated and the anionic PBSA specie, PBSA-H, is formed (Ji et al. 2013b) (see
Figure 4.3.16. PBSA showed a different optimal pH, in comparison with PABA. At highly acidic environment, pH 3, both species are positively charged, and the lack of electrostatic attraction between TiOH$_2^+$ and PBSA leads to a less efficient reaction (Ji et al. 2013a). In both systems was observed that, when the pH is increased to 5, the photodegradation increased substantially. This occurs because, at this pH (and above), the PBSA-H species is formed, and then a negatively charged species is present in the system. These opposites charges of PBSA-H and TiO$_2$ improve the interaction between themselves, which facilitates the adsorption of PBSA molecules on the TiO$_2$ surface, and consequently the increase of the degradation process. When the pH is at neutral or alkaline conditions, both substances predominate in its anionic form and, once again, the repulsion forces prevail and the photodegradation experiences a decrease. This result contrast with previous researches, where was reported that optimum pH was 8.5. However, according to the authors, this result was unexpected since repulsion forces were anticipated to diminish the photodegradation, as occurs with our results (Ji et al. 2013a). In a different research Ji et al. (2013b) supported the conclusion that the PBSA degradation by a photolytic route was enhanced at pH 12.5. This result contrasts with the obtained in the present research, since no catalyst was employed and therefore the repulsion forces between substances in the system are reduced. Furthermore, in our system, the extreme alkaline conditions make the electrostatic repulsions much stronger, which masked or out- competed with the •OH radicals formed and, therefore, decrease the degradation.

It should be noticed that, although degradation pattern through the different pH is similar between the as-synthesized and commercial TiO$_2$, the experimental results were very dissimilar. Under optimum catalyst loading and pH conditions, P25 and TiO$_2$NWs were able to degrade ca. 90% and 30%, respectively. The higher
catalytic activity shown by P25 could be attributed to the fact that TiO$_2$NWs were identified as a pure rutile crystalline structure, and P25 is a commercial catalyst with a content of 70:30 anatase:rutile ratio. Anatase exhibits a larger band gap than rutile (~3.2 eV for anatase and 3.0 eV for rutile) and this may cause an improvement in the oxidation capability of the catalyst and, consequently, a greater photodegradation result (Murgolo et al. 2015, Luttrell et al. 2014). In general, anatase shows a stronger photocatalytic activity than rutile, however, the reasons are still debated. For the upcoming photodegradation experiments, an optimum pH of 5 was chosen when TiO$_2$ (NWs and P25) are employed as the catalyst.

The photocatalytic activity of the ZnONPs in the degradation of PBSA was also tested at different pH environments. As expected, and similar as with PABA; the degradation is reduced at pH 3 (see Figure 4.3.15c). As commented before, the pH of solution plays an important role in the process, since at acidic pH the photocatalysis is greatly reduced, and enhanced at neutral or alkaline conditions, reaching a maximum at pH 9. A similar trend was observed by Krishnakumar and Swaminathan (2011), when ZnO was employed for the degradation of dyes. Furthermore, was observed that at pH 7, 9 and 11, similar results were obtained with degradation rates above 50%. This may be due to the presence of large quantities of OH$^-$ ions on the ZnONPs surface, favoring the formation of •OH radicals. This occurs because, once the ZnONPs are activated, the band holes can react with either water or the hydroxyl ions adsorbed on the surface of the catalyst to generate the •OH radicals, which are strong oxidants (Elmolla and Chaudhuri 2010). Then, these radicals promote the degradation of PBSA according to the following reaction (Chu et al. 2012):

\[
\text{•OH} + \text{PBSA} \rightarrow \text{PBSA photoproducts}
\]

Reaction 4.5
Figure 4.3.15. Photocatalytic degradation of PBSA with different photocatalysts: a) TiO$_2$NWs; b) P25; c) ZnONPs and; d) photocatalytic degradation through the time at different initial pH using ZnONPs.

Figure 4.3.16. Equilibria of PBSA at different pH conditions (Adapted from Ji et al. 2013a, Ji et al. 2013b).

In the study of the photocatalytic degradation of PBSA through the time is observed that, at neutral pH, the degradation of PBSA occurs rapidly during the first 30 minutes of reaction, where almost 35% was degraded (see Figure 4.3.15d). After this time, the photodegradation rate was reduced greatly. This result may suggest that the PBSA photoproducts (as shown in reaction 5) are mainly organic compounds that
are competing for ZnONPs active sites. In contrast, at pH 9, the degradation occurs at a slow but constant rate through the time, reaching the maximum degradation observed (ca. 54%). Several saturation points were observed during the degradation process at different stages of the reaction. For example, at pH 3 is observed a saturation point after 150 minutes, where the degradation, in comparison with 180 minutes, is almost the same; this similar trend was observed with PABA. Comparably, at pH 5 is observed a saturation point from 120 to 150 minutes. The results showed in this Figure confirmed what was observed in Figure 4.3.15c, where is shown the degradation efficiency of the system at different pH environments after 180 minutes of treatment. In general, the lowest degradation was observed at pH 3, then an increase was observed when the pH increased up to 9, and finally the photodegradation decreased at pH 11. For the upcoming experiments the optimal pH chosen was 9.

**4.3.2.3 Effect of initial PBSA concentration**

The photocatalytic degradation of PBSA was studied in the range of 10 to 50 µM, employing the optimal catalyst dose and initial pH for each catalyst. The photocatalytic degradation of PBSA showed a relatively low efficiency when the TiO$_2$NWs were employed, and was enhanced only when the initial PBSA concentration was 40 µM where ca. 86% of degradation was achieved. This result was unexpected, since under other initial PBSA concentrations, the degradation results were less than 40%. As shown in Figure 4.3.17 the photocatalytic process is greatly improved when the initial concentration is 40 µM. This result contrasts with the study performed with PABA, since the TiO$_2$NWs was able to degrade more than 50% at all the concentrations studied. In a similar research is reported that the higher degradability of some dyes could be due to the presence of carboxylic groups that can
react via a photo-Kolbe reaction (Khataee and Kasiri 2010). Also, it could be possible that the chemical structure of PBSA cannot be adsorbed properly onto the nanowires, diminishing the photodegradation rate. The kinetic information obtained from the plots in Figure 4.3.17 is shown in Table 4.3. The higher kinetic constant obtained concurs with the fact that the photodegradation was highly enhanced when the initial PBSA concentration is 40 µM.

![Figure 4.3.17. Evaluation of the photocatalytic activity of the TiO$_2$NWs at different initial PBSA concentrations.](image)

**Table 4.3. Kinetic results for the photocatalytic degradation of PBSA with TiO$_2$NWs, according to a kinetic of pseudo-first order.**

<table>
<thead>
<tr>
<th>Initial PBSA concentration (µM)</th>
<th>Kinetic constant (x 10$^{-3}$ min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.8</td>
<td>0.63</td>
</tr>
<tr>
<td>20</td>
<td>2.9</td>
<td>0.68</td>
</tr>
<tr>
<td>30</td>
<td>2.5</td>
<td>0.98</td>
</tr>
<tr>
<td>40</td>
<td>11.3</td>
<td>0.94</td>
</tr>
<tr>
<td>50</td>
<td>1.8</td>
<td>0.94</td>
</tr>
</tbody>
</table>
When the reaction was carried out with P25, the photodegradation rate ranged from 89% to 99.5%. Furthermore, the photocatalytic degradation results of PBSA were higher than 97% in the range of 10 to 40 µM, with a maximum of 99.5% at 20 µM (see Figure 4.3.18a). When the initial concentration is 50 µM, a decrease of the photodegradation was observed, since a higher yield of intermediates can be expected, which are capable of react with the P25 active sites, and compete as well for the incident photons (Ji et al. 2013a). A slight increase was observed when the initial PBSA concentration increased from 10 to 20 µM. This result suggests that the interaction of PBSA molecules with P25 solid particles are enhanced at 20 µM, and maybe at 10 µM the interaction of P25 particles among themselves caused a slight decrease in the degradation process.

The enhancement of the degradation activity at 20 µM is shown in Figure 4.3.18b, when it is observed that 90% of the initial PBSA content was degraded during the first 30 minutes of treatment. Obviously, after the first 30 minutes, the reaction rate decreased since only ~10% of the initial content was still present. This pattern was observed in all the reactions when the highest degradation was observed during the first 30 minutes of reaction time. The decrement of the degradation rate was also observed starting at 90 minutes, 120 minutes, and 60 minutes, when the initial concentrations were 10, 30 and 40 µM, respectively. These times also coincide when the degradation was close to 90% in all cases. The degradation of PBSA at 50 µM occurs at a constant rate through the time, in contrast with the other conditions. This occurs because the initial PBSA concentration was so high that the system was not able to degrade 90% in less time, as occurs when the initial concentration is 20 µM. UV-vis and fluorescence spectroscopy (see Figures 4.3.18c and 4.3.18d) confirmed that the highest degradation of PBSA was measured during the first half
hour of reaction. A minimum progress in the photodegradation rate was observed in the next samples. Moreover, after 120 minutes, the individual spectra become indistinguishable one from another. Our results are similar to those described by Ji et al. (2013a), using P25 for the photocatalytic degradation of PBSA. However, our results showed an increased degradation rate, since they reported ca. 80% degradation after 60 minutes of reaction time.

Figure 4.3.18. Evaluation of the photocatalytic activity of P25 at different initial PBSA concentrations: a) effect of the initial PBSA concentration after 180 minutes of irradiation; b) study of the photocatalytic degradation through the time; c) UV-spectra under optimal experimental conditions; and d) fluorescence emission spectra under optimal experimental conditions.

ZnONPs also showed excellent photocatalytic results, obtaining +90% when the initial PBSA concentration was 20 µM or below (see Figure 4.3.19a). Moreover, under all the initial concentrations tested, the photocatalytic degradation was above
50%. In the case of ZnONPs is observed that the photocatalytic degradation decreases by increasing the initial PBSA concentration. As mentioned before, it is probable that at higher concentration a greater yield of photoproducts is formed, that can be adsorbed on the ZnONPs surface. These photoproducts, and the remaining un-photodegraded PBSA molecules, then compete for the a) incident photons, and b) photoactive sites. Moreover, if these photoproducts interact among themselves, or with PBSA molecules, the degradation also can decrease since the photodegradation is related to the probability of •OH radical reacting with the pollutant molecules.

Since the catalyst amount, radiation source, and power are constants for all the initial PBSA concentration experiments, the generation of hydroxyl radicals can be assumed to be constant and, consequently, can be presumed that the probability of PBSA molecules to interact with these radicals decreases at higher concentrations (Krishnakumar and Swaminathan 2011). Additionally, progressive photodegradation rates, with similar trends, were observed when the initial PBSA concentration is 10 and 20 µM (see Figure 4.3.19b). Furthermore, ~30% was able to be photodegraded in the first 30 minutes, when the initial concentration is below 40 µM. An atypical increase was observed from 60 to 90 minutes, when the initial concentration was 40 µM. This can be attributed to the formation of photoproducts that absorb in the UV region, near PBSA, with a higher molar absorptivity coefficient according to the Beer-Lambert law, which will cause a higher absorbance even when a photoreaction is occurring. The progressive degradation through the time is observed in Figures 4.3.19c and 4.3.19d. A similar trend in the UV-spectrum was observed in a previous research where ZnO was used for the photocatalytic degradation of methylene blue (Chu et al. 2012). However, in that research, ZnO was able to photodegrade the dye in four hours, reaching less than 90% degradation. As shown in the UV-vis and
excitation spectra, the intensity of the individual plot at 180 minutes is near to 0, which implies that almost all the initial PBSA has been degraded. At the best of our knowledge, this is the first research on the photocatalytic degradation of PBSA employing ZnO as catalyst.

Figure 4.3.19. Evaluation of the photocatalytic activity of ZnONPs at different initial PBSA concentration: a) effect of the initial PBSA concentration after 180 minutes of irradiation; b) study of the photocatalytic degradation through the time; c) UV-spectra under optimal experimental conditions; and d) fluorescence excitation spectra under optimal experimental conditions.

The studies regarding photodegradation of sunscreen active ingredients are scarce. However, few authors have reported that progressive attacks of PBSA by hydroxyl radicals can result in cleavage or ring opening by-products. The AOPs often yield numerous degradation intermediates and photoproducts due to the non-selective reaction of the radicals with the organic pollutant (Ji et al. 2013a). Depending on the
nature of the photoproducts, their formation and degradation varies from one to another (Abdelraheem et al. 2016). Also the AOPs can be able to mineralize the parent compound because of the successive and non-selective attacks.

In the case of PBSA it can be mineralized into water and CO₂. Moreover, the sulfonic group can be released as SO₄²⁻, and the nitrogen atoms of the imidazole structure into NH₄⁺, and NO₃⁻; however, this may occur at a much lower rate than the degradation of the parent compound (Ji et al. 2013a). According to a recent study, the formation of NH₄⁺, and NO₃⁻ species depends on the pollutant chemical structure and the presence of catalysts, since typically the nitrogen atoms are converted into inorganic N, in the form of NH₄⁺, and due to a consecutive photo-oxidation, the NO₃⁻ is generated (Abdelraheem et al. 2016). Ji et al. (2013a) reported that only 17% of the total organic carbon (TOC) was removed, even when most of the parent compound was degraded. Furthermore, in recent studies is reported that only ~30% of the total sulfate was mineralized when ~90% of PBSA was degraded (Abdelraheem et al. 2016). These results suggest that the photoproducts obtained can be even more photoresistant, and probably requires longer period of treatment. According to Ji et al. (2013a) the photocatalytic degradation of PBSA with TiO₂ leads to few intermediates, including the imidazole ring cleavage and carboxylic acids. Moreover, they reported the elimination of the intermediates, suggesting that, after a longer period of irradiation time, it is a promising technique for the PBSA removal. Similar results were reported by Abdelraheem et al. (2016), where they concluded that, generally, the PBSA degradation includes the pollutant hydroxylation, sulfonate elimination and ring opening.

Our photocatalytic degradation results demonstrated that PBSA could be efficiently degraded in at least 86% (see Figure 4.3.20a). The statistical analysis
showed that the differences observed after 180 minutes of treatment with the different photocatalysts can be attributed to randomness, since p value > 0.05 (p value=0.189). However, in the study of the photocatalytic degradation of PBSA, under optimum experimental conditions, is observed that at 30 minutes of treatment the pollutant removal is ~30% with the as-synthesized catalysts, and ~90% with P25.

![Figure 4.3.20: Study of the photocatalytic degradation of PBSA with different catalysts: a) Comparison of the degradation rate after 180 minutes of irradiation with different photocatalysts; and b) comparative photocatalytic degradation process through the time for the photocatalysts studied.](image)

**4.3.2.4 Control experiments**

As explained with PABA, to determine the effect and contribution of the catalyst, radiation source and the presence of oxygen, different experimental reactions were performed. The control experiments with TiO$_2$NWs and P25 were carried out at pH 5, with a catalyst loading of 1.0 g L$^{-1}$. For the TiO$_2$NWs, P25 and ZnONPs, the initial PBSA concentration was 40, 20 and 10 μM, respectively. The control experiments with the ZnONPs were carried out with a catalyst loading of 1.2 g L$^{-1}$ at pH 9. The experimental results showed that the degradation of PBSA undergo mainly
by a synergistic effect of the radiation, catalyst and oxygen sources for TiO$_2$NWs, P25 and ZnONPs, as shown in Figures 4.3.21, 4.3.22, and 4.3.23, respectively.

Figure 4.3.21. Comparison of the degradation results of PBSA under optimal experimental conditions, and control experiments with TiO$_2$NWs.

Figure 4.3.22. Comparison of the degradation results of PBSA under optimal experimental conditions, and control experiments with P25.
Figure 4.3.23. Comparison of the degradation results of PBSA under optimal experimental conditions, and control experiments with ZnONPs.

Under anoxic conditions the reaction does not proceed in any system, as expected, since without the presence of oxygen the radicals cannot be formed. Also, the photolytic route is almost negligible, as PBSA concentration remains constant throughout the degradation process, confirming the stability of this pollutant against the photolysis treatment (Abdelraheem et al. 2016). This result is consistent with the fact that PBSA is a very resistant organic compound, and under environmental relevant conditions is stable. These results agree with previous findings when it was shown that a photolytic route was not efficient under the pH conditions used in this research (Ji et al. 2013b). The different catalysts studied show to degrade less than 20% in 180 minutes, without the presence of a radiation source. The results obtained with the as-synthesized and commercial catalysts coincide with Ji et al. (2013a), where also it was demonstrated that the degradation proceeds through a photocatalytic route.
4.3.3 Benzophenone-4

4.3.3.1 Effect of catalyst loading

The last organic pollutant studied in this research was BP-4. The photocatalytic degradation of this persistent organic pollutant was studied by adding different amounts of the catalyst to a 60 µM solution, at pH 5, in presence of TiO$_2$NWs and P25, and pH 7, using ZnONPs as catalyst. The photocatalytic degradation of BP-4 with TiO$_2$NWs showed a higher optimal catalyst loading in comparison with PABA and PBSA under similar conditions. The degradation of BP-4 showed higher efficiency as the catalyst loading increased (see Figure 4.3.24a). At the lowest catalyst loading condition, the system was inefficient, degrading less than 15% of the initial BP-4 content. Furthermore, as the catalyst loading increased, higher degradation was obtained, reaching ca. 60% when 1.2 g L$^{-1}$ was used. Studies regarding the photocatalytic degradation of BP-4 are scarce, however, several researches are being reported on the study of the degradation of benzophenone-type organic pollutants. For example, recently, it was reported that up to 99% of benzophenone could be degraded using from 3 to 4 g L$^{-1}$ (Escobar et al. 2010). This seems to be a more efficient system; however, these higher catalyst concentrations may not be a practical condition to transfer into a real environment because of the excessive solid particles in the medium, inducing an increase in the treatment costs.

The trend observed in Figure 4.3.24a may suggest that the interaction between BP-4 molecules and TiO$_2$NWs is enhanced when the catalyst loading increased. No apparent saturation is expected to be occurring in the catalyst surface, since the trend is increasing continuously and no decrement was observed. As stated before, when the catalyst loading is 0.4 g L$^{-1}$ the degradation rate showed a minimum. This also can be confirmed since the degradation obtained during the first 30 minutes is
negligible, and ca. 5% degradation was obtained during the first 60 minutes of reaction (see Figure 4.3.24b). Moreover, when the catalyst loading is 0.8 to 1.0 g L\(^{-1}\) the degradation percent and trend observed are very similar. During the first 60 minutes of reaction time, the degradation progress observed was very similar for catalyst loading ranging from 0.6 to 1.2 g L\(^{-1}\). However, after 60 minutes of treatment, the degradation rate from 0.6 to 1.0 g L\(^{-1}\) showed a decrement, contrary to the trend observed at 1.2 g L\(^{-1}\). This may suggest that the highest catalyst loading of 1.2 g L\(^{-1}\) is necessary to provide additional active sites to the photoproducts obtained that compete in the degradation. This competition, and the lack of active sites at catalyst loadings from 0.6 to 1.0 g L\(^{-1}\), may explain the decrement in the degradation progress through the time. Because of this, for further experiments regarding BP-4 and TiO\(_2\)NWs, the standard catalyst concentration to be used will be 1.2 g L\(^{-1}\). As mentioned before, excessive catalyst loading may not be necessary to degrade BP-4.

When P25 was employed, the photocatalytic degradation reached ca. 90% in all cases. Furthermore, at 0.6, 0.8, 1.0 and 1.2 g L\(^{-1}\), degradation results of 97, 99, 99.3 and 99.5% were obtained, respectively (see Figure 4.3.24c). The almost constant trend observed from 0.6 to 1.2 g L\(^{-1}\) may suggest that P25 reached a saturation point. However, this trend may not be associated with a saturation point since a decrease in degradation was not observed. Instead may be associated to the system efficiency, since almost 100% degradation was obtained in the four cases. It is expected that at higher catalyst loading (2 or 3 g L\(^{-1}\)) a decrement in degradation could be observed, due to the light screening effect caused by the solid particles suspended in the media. Furthermore, when the catalyst amount added ranged from 0.6 to 1.2 g L\(^{-1}\), a degradation rate of BP-4 of ca. 50% was obtained during the first 60 minutes of reaction time (see Figure 4.3.24d). It is observed that very similar trends were
observed when the reactions were carried out with 1.0 or 1.2 g L$^{-1}$, specifically during the first 30 minutes of reaction time, and from 120 to 180 minutes. However, in the range of 0.6 to 1.2 g L$^{-1}$, the degradation efficiency after 180 minutes of treatment was very similar, agreeing with the result reported in Figure 4.3.24c. At all catalyst loading conditions, a continuous degradation was observed, suggesting that saturation conditions were not reached. However, the greatest degradation step was observed during the first 30 minutes of reaction (from 20 to 50% degradation). After this, the degradation is continuous but less dramatic, which suggests the production of organic by-products in the reaction that may compete for active sites of the catalyst.

According to the analyses performed with ANOVA-1 way, statistical differences are obtained when employing different catalyst loadings from 0.4 to 1.2 g L$^{-1}$, since the p value obtained was 0.013. However, when the same statistical analysis is performed with the photocatalytic degradation results ranging from 0.6 to 1.2 g L$^{-1}$, it can be concluded that the differences observed can be attributed to randomness (p value > 0.05, 0.522). Because of this result, for the upcoming experiment a standard catalyst loading of 0.6 g L$^{-1}$ was used because similar results can be obtained with less catalyst material, making the treatment cost-effective.

The photocatalytic degradation of BP-4 with ZnONPs showed different results. As shown in Figure 4.3.25 similar results were obtained with all the catalyst loading conditions with a maximum at 1.0 g L$^{-1}$. However, it should be noticed that less than 20% of degradation was obtained at all conditions after 180 minutes of treatment. This may be caused because a) poor interaction between the ZnONPs and BP-4, and b) excessive concentration of BP-4, specifically for this catalyst. Several authors have modified the chemical-physical properties of various semiconductors by doping the materials.
Figure 4.3.24. Photocatalytic degradation of BP-4 with as synthesized TiO$_2$NWs and commercial P25 at different catalyst loadings: a) effect of catalyst loading with TiO$_2$NWs; b) photocatalytic degradation through the time at different catalyst loadings of TiO$_2$NWs; c) effect of catalyst loading with P25; and d) photocatalytic degradation through the time at different P25 loadings.

In previous studies Georgekutty et al. (2008) synthesized ZnO and Ag-doped ZnO. They reported an increase in the photocatalytic degradation of an organic dye if the ZnO was doped. Since every system (catalyst-pollutant) behaves different under a set of parameters, it could be possible to increase the photocatalytic degradation rate of BP-4 using doped-ZnONPs as catalyst. However, this doping process increases the research costs because most of the doping materials are based on Au, Ag and Pt. Since the maximum degradation was obtained with 1.0 g L$^{-1}$, the experiments with ZnONPs were performed adding this amount of catalyst to the system.
4.3.3.2 Effect of initial pH

The effect of pH was studied for BP-4 photocatalytic degradation. Using a catalyst dose of 1.2 g L⁻¹, and 0.6 g L⁻¹ for TiO₂NWs and P25, respectively, the initial pH was varied from 3 to 11 (i.e. 3, 5, 7, 9 and 11). The photocatalytic degradation of BP-4 with TiO₂ (NWs and P25) showed similar trends, as discussed previously with PBSA. The reaction process is greatly enhanced at acidic environments (i.e. pH 5) (see Figures 4.3.26a and 4.3.26c). Under optimal catalyst loading and pH conditions, BP-4 can be successfully degraded up to 60% with TiO₂NWs and ca. 100% with P25. Under neutral to alkaline conditions, the photocatalytic degradation rate with TiO₂NWs experienced a marked decrease, below 10%. Under these neutral-alkaline conditions, the degradation results obtained were very similar, almost constant. The greatest decrement observed occurs when the pH increases from 5 to 7, reducing the degradation rate from 60% to ~10%. These results contrast with a recent research based on the removal of BP-4 by ozonation (Liu et al. 2016). In this study, the BP-4 removal was enhanced by increasing the pH. In the case of photocatalysis, the optimal pH will differ according to the specific interactions between the organic pollutant and...
the catalyst. As reported in the literature, BP-4 has two pKa’s; pKa$_1$ (corresponding to the sulfonic group) has been reported below 1. Since we did not work at pH conditions below 1 the pKa$_1$ is not expected to cause any interference. The second pKa was determined experimentally by De Laurentiis et al. 2013, and reported to be 7.3.

Considering our experimental conditions, even under acidic harsh conditions, BP-4 was studied as its anionic, or double anionic form (see Figures 4.3.27). The enhancement of the photocatalytic degradation of BP-4 with TiO$_2$ at acidic conditions could be explained because of the fact that, below neutral pH, TiO$_2$ was positively charged on its surface because its zpc=6.25. At pH$>|$zpc the TiO$_2$ surface is negatively charged, as well as BP-4, according to Figure 4.3.27. Because of this, the interaction catalyst-pollutant will be avoided due to repulsion forces. Also, the degradation process at pH 3 and pH 5 showed similar trends, with increased degradation at pH 5 (see Figures 4.3.26b and 4.3.26d). Moreover, very similar trends were observed during the reaction progress at pH 7, 9 and 11 for TiO$_2$NWs, and at pH 7 and 9 for P25. As can be seen in Figures 4.3.26b and 4.3.26d, slight variations in the slopes, during the reaction progress at different pH conditions, can be observed for both catalysts. These variations could be attributed to several reasons: a) pH variations during the reaction process and, b) formation and competition of organic photoproducts.
Figure 4.3.26. Photocatalytic degradation of BP-4 with TiO$_2$NWs and commercial P25 at different initial pH conditions: a) effect of initial pH with TiO$_2$NWs; b) photocatalytic degradation through the time at different initial pH with TiO$_2$NWs; c) effect of initial pH with P25; and d) photocatalytic degradation through the time with P25, by varying the initial pH.

As expected, different results were obtained when the ZnONPs were employed in the photocatalytic degradation of BP-4. As shown in Table 4.4, the photocatalytic degradation of BP-4 with ZnONPs at different initial pH conditions reached the maximum degradation rate at neutral pH. The optimal pH conditions
determined for each catalyst were expected to be different, since ZnO and TiO\textsubscript{2} showed different catalytic activity, as shown with the previous organic pollutants studied. These results suggest that interaction between ZnONPs and BP-4 molecules is enhanced, experiencing the maximum increase at pH 7.

Table 4.4. Kinetic results for the photocatalytic degradation of BP-4 with ZnONPs, according to a kinetic of pseudo-first order.

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Kinetic constant (x 10^{-3} min^{-1})</th>
<th>R\textsuperscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.2</td>
<td>0.97</td>
</tr>
<tr>
<td>5</td>
<td>2.3</td>
<td>0.94</td>
</tr>
<tr>
<td>7</td>
<td>4.1</td>
<td>0.99</td>
</tr>
<tr>
<td>9</td>
<td>1.4</td>
<td>0.92</td>
</tr>
<tr>
<td>11</td>
<td>1.2</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Surprisingly, the photodegradation obtained at pH 5 seems to be higher in comparison with the photodegradation at pH 9. This could be explained because at pH 9 ZnO may be negatively charged and BP-4 is present in its double anionic form. In contrast, in the range of pH 3 to 7 ZnO, possibly it is positively charged, and the interaction is enhanced due to the fact that BP-4 is present in its mono-anionic or double anionic form. For the following experiments, the degradation of BP-4 with ZnONPs was carried out at pH 7.

4.3.3.3 Effect of initial BP-4 concentration

The effect of the initial BP-4 concentration on the photocatalytic degradation was studied in the range of 10 to 80 μM. The BP-4 was degraded in ca. 90% when the initial concentration was below 20 μM, employing TiO\textsubscript{2}NWs (see Figure 4.2.38a). A similar trend was observed in the photocatalytic degradation of PABA with
TiO$_2$NWs. The photocatalytic activity was enhanced at lower initial concentrations, suggesting that the interaction between TiO$_2$NWs and BP-4 increased under these conditions. The decrease observed in the photocatalytic degradation rate may be associated to the photoproducts formed in the process. Also, at higher concentrations, the TiO$_2$NWs surface may be saturated with BP-4 molecules. In consequence, some BP-4 molecules cannot interact with the catalyst surface, producing a decrease of the photodegradation rate. This result is in agreement with the results reported by Mohamed et al. (2012), since they reported an increase in the photocatalytic degradation of methylene blue at lower concentrations of the pollutant. Since the catalyst dose, irradiation time and intensity remains constant, the concentrations of the photogenerated radicals should remain practically constant. This fact means that a constant radical’s concentration is available to react with higher amounts of the organic pollutants and therefore the photocatalytic degradation efficiency decrease (Nguyen and Juang 2015). The TiO$_2$NWs was able to degrade BP-4 with a degradation rate of ca. 50% when the initial concentration of this organic pollutant is up to 60 µM.

The photodegradation process of BP-4, using an initial concentration of 20 µM, reached degradation levels in the range of 30 to 40%, approximately, during the first 30 minutes of reaction (see Figure 4.3.28b). Furthermore, at these initial concentrations the trends observed through the time were very similar. At very higher concentrations (i.e. 80 µM), the highest photocatalytic degradation occurs during the first half hour of reaction. After that, the photodegradation experienced a decrease, possibly due to the interaction of BP-4 molecules and its photoproducts. However, a very constant degradation was observed when the initial concentration was 60 µM, which confirms the ability of the catalyst to degrade the by-products and the parent
compound at this concentration. These results confirm that the photocatalytic degradation is a promising technique at lower concentrations (Nguyen and Juang 2015). Under optimum experimental conditions (20 µM, pH 5, and a catalyst loading of 1.2 g L^{-1}) an apparent kinetic constant of 1.29 x 10^{-2} min^{-1} was determined, according to a pseudo-first order reaction, with an R^2 > 0.99 (see Figure 4.3.28c). This apparent constant seems to be higher in comparison with previous results published on the degradation of p-chlorophenol, methyl orange, and phenanthrene in soils (Nguyen and Juang 2015, Wilson et al. 2012, Gu et al. 2012).

The photocatalytic degradation of BP-4, at different initial concentrations employing P25, showed even higher photodegradation results. As shown in Figure 4.3.28d, under all initial BP-4 concentrations, at least 80% degradation was measured. Furthermore, the photocatalytic degradation achieved was +95%, when the initial concentration was at 60 µM or below, and ca. 100% at 20 µM. The trend observed in the photocatalytic degradation of BP-4 is very similar in comparison with TiO_2 NWs. The methods employed lead to the photocatalytic degradation in 180 minutes. These results suggest that the degradation occurs in a slower rate in comparison with the ozonation process that degrades BP-4 in less than 10 minutes (Liu et al. 2016). However, ozonation procedure may not be a plausible remediation solution since it requires an ozone generator equipment and, therefore, higher operational costs (de Souza et al. 2010, Sumegová et al. 2015). In a different research, the biotransformation of BP-4 was studied (Beel et al. 2013). The authors reported that BP-4 was biotransformed within 14-21 days after spiking the samples with ca. 65 µM of the organic pollutant. This agrees with the fact that traditional remediation techniques, such as biodegradation, are not capable to remove the persistent organic pollutants in an efficient manner.
Figure 4.3.28. Evaluation of the photocatalytic degradation of BP-4 at different initial pollutant concentration with the TiO$_2$NWs and P25: a) photocatalytic degradation with TiO$_2$NWs; b) study of the photocatalytic degradation through the time with TiO$_2$NWs; c) determination of the pseudo-first order kinetic reaction under optimal experimental conditions; d) photocatalytic degradation with P25; e) study of the photocatalytic degradation through the time with P25; and f) determination of the pseudo-first order kinetic reaction under optimal experimental conditions.
In contrast, the advanced oxidation techniques are very proficient since we demonstrated that BP-4 can be degraded in 3 hours vs 14-21 days in comparison to biodegradation. Moreover, similarly to PABA results discussed previously, ~90% degradation was obtained in 90 minutes, when the initial concentration was 10 µM, and ca. 50% degradation during the first 30 minutes of reaction (see Figure 4.3.28e). As can be seen there, the degradation rates at 20 to 40 µM were very similar, with 90% degradation at 120 minutes. The degradation process through the time becomes undistinguishable one from another after 120 minutes, when the initial concentrations ranged from 10 to 40 µM. The photocatalytic degradation of BP-4 with P25 showed constant degradation rates through the time, with minor saturation interferences through the time. Since P25 was able to degrade BP-4 in at least ~82% under all the initial concentrations, 10 µM was chosen as the optimal initial concentration. Under optimal experimental conditions (0.6 g L⁻¹, 10 µM and pH 5) was obtained an apparent constant rate of $3.21 \times 10^{-2}$ min⁻¹ (see Figure 4.3.28f).

Following equation 4.2, $t_{1/2}$ of BP-4 under optimal experimental conditions using P25 as the catalyst, was measured to be ~21.6 minutes, which is in agreement with the results shown in Figure 4.3.28e. This result represents a much lower half time of BP-4, in comparison with the days and weeks that it may stay in sunlit, shallow freshwaters during summer time conditions (De Laurentiis et al. 2013). Figure 4.3.29 shows the photodegradation of BP-4 when TiO₂NWs and P25 are employed. As can be seen there, TiO₂NWs was able to degrade BP-4 at a very constant rate through the time. When P25 is employed, the absorbance of BP-4 at $\lambda_{max}$ is close to 0, and the individual plots become undistinguishable, which means that most of the initial BP-4 content has been degraded.
Figure 4.3.29. Photocatalytic degradation results obtained by UV-vis spectroscopy, under optimal experimental conditions: a) TiO$_2$ NWs; and b) P25.

The photocatalytic degradation of BP-4 with ZnONPs showed a similar trend in comparison with the TiO$_2$ catalysts studied and discussed above, however, lower degradation rates were observed (see Figure 4.3.30a). Under lower initial BP-4 concentrations, the photocatalytic degradation was enhanced, reaching the ca. 53%. By increasing the concentration above 20 µM, the efficiency experiences a marked decrease (see Figure 4.3.30b). As explained previously, this can be caused because of the organic photoproducts formed and a possible saturation at the catalyst surface. At lower initial concentration, the photodegradation occurs at a constant rate, with a similar pattern, as shown in Figure 4.3.30b. Furthermore, at 40 µM the trend observed could be described as atypical, since the relative absorbance of BP-4 remains almost constant from 30 to 90 minutes and then degrades. Also, at higher concentrations was observed that the degradation process stopped at 60 minutes, which can be attributed to the deactivation of active sites of the photocatalyst caused by the slow diffusion of the generated intermediates (Fathinia et al. 2010). Also, high concentration of pollutants reduces the photonic efficiency, and consequently the degradation is also reduced because the photocatalytic oxidation depends on it (Umar and Aziz 2013, Gaya and Abdullah 2008). As occurred with the previous
photocatalysis studies, the degradation of BP-4 with ZnONPs follows a pseudo-first order kinetic, with an apparent constant rate of $4.1 \times 10^{-3} \text{ min}^{-1}$, which looks slower than the reported for TiO$_2$ (see Figure 4.3.30c). This result is confirmed by the photodegradation process through the time shown in Figure 4.3.30d, where is observed a constant degradation occurring at a slower rate pace.

![Figure 4.3.30](image)

Figure 4.3.30. Evaluation of the photocatalytic degradation of BP-4 at different initial pollutant concentration with ZnONPs: a) photocatalytic degradation at different initial BP-4 concentrations; b) photocatalytic degradation through the time; c) determination of the pseudo-first order kinetic reaction under optimal experimental conditions; and d) UV-vis spectra obtained under optimal experimental conditions.

Based on our experimental results, the photodegradation of BP-4 reached (at least) the 50% in three hours, and ca. 90% when a TiO$_2$ catalyst was employed (see Figure 4.3.31a). The ZnONPs seems to be less effective in the degradation. This effect may be attributed to the chemical-physical interactions and properties of the
catalyst and the organic pollutant, since every system (photocatalyst-substrate) behaves different. The statistical analyses showed that the photodegradation processes are statistically different (p value<0.05, 0.032), confirming that the efficiency of the system depends on the nature of the catalyst and its interaction with the organic pollutant to be degraded. The photocatalysis of BP-4 with TiO$_2$NWs and P25 showed similar results after 180 minutes of reaction time; however, in a comparison of the efficiency through the time, was observed that P25 seemed to show a faster rate (see Figure 4.3.31b). As can be seen there, the photocatalysis of BP-4 with ZnONPs occurs at a constant but slower rate.

Figure 4.3.31. Photocatalytic degradation of BP-4 with different photocatalysts: a) after 180 minutes of irradiation with different photocatalysts; and b) study of the photodegradation using different catalysts.

At the best of our knowledge, this research represents the first study involving the degradation of BP-4 by a photocatalytic approach. Therefore, it is not possible to establish a reaction mechanism or possible by-products based on literature review. Nevertheless, Liu et al. (2016) proposed a mechanism based on the degradation of BP-4 through an ozonation process. In this study, the first step of the degradation mechanism occurs by a hydroxylation step guided by an attack of a hydroxyl radical.
in the \textit{para} position with respect to the sulfonic group (or \textit{meta} position with respect to the methoxy group). Then, further hydroxylation steps can generate additional by-products. Other mechanism steps suggested by the authors include the desulfonation, demethylation and oxidation reaction, which transform the \textit{-OH} groups into carbonyl groups.

\textbf{4.3.3.4 Control experiments}

In order to evaluate alternative routes for the degradation of BP-4, such as photolysis and catalysis, control experiments were performed under optimal experimental conditions. These experiments were performed at pH 5 for TiO$_2$ photocatalysts; with an initial BP-4 concentration of 10 and 20 \(\mu\text{M}\) for the P25 and as-synthesized nanowires, respectively. The concentrations used were 1.2 g L$^{-1}$ (for TiO$_2$NWs), and 0.6 g L$^{-1}$ (for P25). The degradation of BP-4 with TiO$_2$NWs occurs mainly by a photocatalytic route, since the contribution of the photolysis and catalysis was practically negligible (see Figure 4.3.32a). The role of a catalyst in any reaction is to accelerate the reaction rate without being consumed in it (Kabra et al. 2004). As shown, when the reaction is carried out by photolysis a negligible effect is produced, since the efficiency is very low in comparison when a catalyst is present. Also, in absence of oxygen \(~20\%\) was degraded, suggesting that photogenerated oxygen radicals are the most important species in the reaction pathway. Similar results were obtained when P25, with alternative degradation routes producing low yields (~10\% degradation) (see Figure 4.3.32b). These results demonstrate the stability of BP-4 under normal conditions, and can be used to explain the high levels of BP-4 in urban wastewaters (Jurado et al. 2014).
Figure 4.3.32. Comparison of the degradation results of BP-4 under optimal experimental conditions, and control experiments: a) with TiO$_2$NWs; and b) with P25.

Similar results were obtained when the ZnONPs was employed. In this case, and similarly to P25, less than 10% of degradation was obtained by an alternative route (see Figure 4.3.33).

Figure 4.3.33. Comparison of the degradation results of BP-4 under optimal experimental conditions, and control experiments with ZnONPs.

As shown in this Figure, an apparent increase in the relative absorbance was observed during the catalytic reaction. This effect can be attributed to a minimal
degradation of BP-4, producing photoproducts that absorbs in similar UV-regions with higher molar extinction coefficients, increasing the absorbance even when the degradation is occurring. Also Cotto-Maldonado et al. (2013) attributed an apparent decrease in degradation to a desorption process of the organic pollutant from the catalyst surface.

4.4 Summary of results

The persistent organic pollutants are emerging contaminants with highly variable entries in the environment. More important, the traditional remediation techniques are not capable to degrade them because of the chemical stability of these compounds (Teh and Mohamed 2011). The problem aggravates with the fact that less than 1% of water is available for consumption (Cotto-Maldonado et al. 2013). During the photocatalytic experiments of the organic compounds studied is expected that several reactions occur as a cascade. First, when the radiation source (see Figure 4.1.1.1) impinges over the catalyst, an electron is photoexcited, and the electron-hole pair (e⁻ + h⁺) is generated. After that, the oxygen present undergoes a reduction reaction and forms a superoxide species (•O₂⁻). However, this super reactive species also can be protonated to form a hydroperoxyl radical (HOO•) (Gaya and Abdullah 2008). It should be noticed that in our system we also have H₂O₂, which reacts in the presence of a radiation, hν, and forms two •OH by a homolytic cleavage. This chain of reactions occurs as follows:

\[
\text{Photoexcitation: Catalyst } \rightarrow e^- + h^+ \quad \text{Reaction 4.6}
\]
\[
\text{Oxygen reduction: } O_2 + e^- \rightarrow •O_2^- \quad \text{Reaction 4.7}
\]
\[
\text{Superoxide protonation: } O_2•^- + H^+ \rightarrow \text{HOO•} \quad \text{Reaction 4.8}
\]
\[
\text{H}_2\text{O} + h^+ \rightarrow •\text{OH} + H^+ \quad \text{Reaction 4.9}
\]
\[
\text{Homolytic cleavage: } \text{H}_2\text{O}_2 \xrightarrow{h\nu} 2 •\text{OH} \quad \text{Reaction 4.10}
\]
Also, depending on the pH conditions, additional •OH can be formed according to reactions 4.3 and 4.4 described earlier. The oxidation reaction for our organic contaminants, OCs, (PABA, PBSA and BP-4), occurs as follows:

\[
\text{OC} \xrightarrow{\text{i) catalyst}} \text{Intermediates} \xrightarrow{\text{ii) } h\nu \geq E_{bg}} \text{Subsequent oxidation} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \ldots \quad \text{Reaction 4.11}
\]

The successive reactions showed above demonstrated that our OCs studied in this research experience a degradation process, stimulated by the presence of the catalyst (TiO$_2$ or ZnO), the radiation source on the photoreactor and the presence of oxygen source(s). The cumulative effect of the seven light bulbs used brings photons of energy higher to the band gap energy ($h\nu \geq E_{bg}$), which produces the photoexcitation reaction (Vinu and Madras 2010). This process degrades the parent compound and, by subsequent oxidation processes carried out by enormous quantities of radicals formed the intermediates, these compounds are also degraded until the mineralization process occurs, producing water, CO$_2$, and inorganic compounds with N or S as products, depending of the OC studied. This is possible since, by definition, the photocatalytic process is a non-specific reaction, so in the presence of intermediates and parent compound, both organic species could be successfully degraded.

The photocatalytic systems employed during this research were able to degrade all the organic contaminants in more than 50%. Furthermore, PABA was degraded in at least 70%, PBSA in 86% and BP-4 in 52%, as shown in Table 4.5 and Figure 4.4.1. Also, in the nine systems employed, 7 of them achieved +86% degradation.
Figure 4.4.1. Comparison of the photocatalytic degradation results of the three different contaminants with three photocatalysts (3x3 system).

The commercial P25 achieved +90% degradation for the three contaminants, the as-synthesized TiO$_2$NWs degrades the three contaminants in at least 86%, and ZnO degrades 2 of 3 contaminants in +70%. The apparent higher efficiency of TiO$_2$ versus ZnO could be because the latter is less photostable than TiO$_2$ (Cotto-Maladonado et al. 2013). According to Vinu and Madras (2010), ZnO can undergo a decomposition process caused by the valence band holes, according to reaction 4.12.

\[
\text{ZnO} + 2h^+ \rightarrow \text{Zn}^{2+} + \frac{1}{2} \text{O}_2 \quad \text{Reaction 4.12}
\]
Table 4.5. Summary of the photocatalytic degradation and kinetic results.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Optimal experimental conditions</th>
<th>Degradation (%)</th>
<th>$K$ ($10^{-2}$ min$^{-1}$)</th>
<th>$R^2$</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-aminobenzoic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$NWs</td>
<td>1.0 g L$^{-1}$, pH 3, 20 μM</td>
<td>95.1</td>
<td>2.00</td>
<td>0.909</td>
<td>35</td>
</tr>
<tr>
<td>P25</td>
<td>1.2 g L$^{-1}$, pH 3, 40 μM</td>
<td>98.4</td>
<td>2.40</td>
<td>0.996</td>
<td>29</td>
</tr>
<tr>
<td>ZnONPs</td>
<td>1.2 g L$^{-1}$, pH 7, 30 μM</td>
<td>70.0</td>
<td>0.47</td>
<td>0.960</td>
<td>147</td>
</tr>
<tr>
<td>Phenylbenzimidazole sulfonic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$NWs</td>
<td>1.0 g L$^{-1}$, pH 5, 40 μM</td>
<td>86.4</td>
<td>1.13</td>
<td>0.945</td>
<td>61</td>
</tr>
<tr>
<td>P25</td>
<td>1.0 g L$^{-1}$, pH 5, 20 μM</td>
<td>99.5</td>
<td>3.13</td>
<td>0.803</td>
<td>22</td>
</tr>
<tr>
<td>ZnONPs</td>
<td>1.2 g L$^{-1}$, pH 9, 10 μM</td>
<td>93.8</td>
<td>2.07</td>
<td>0.868</td>
<td>33</td>
</tr>
<tr>
<td>Benzophenone-4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$NWs</td>
<td>1.2 g L$^{-1}$, pH 5, 20 μM</td>
<td>89.5</td>
<td>1.29</td>
<td>0.999</td>
<td>54</td>
</tr>
<tr>
<td>P25</td>
<td>0.6 g L$^{-1}$, pH 5, 10 μM</td>
<td>97.5</td>
<td>3.21</td>
<td>0.989</td>
<td>22</td>
</tr>
<tr>
<td>ZnONPs</td>
<td>1.0 g L$^{-1}$, pH 7, 10 μM</td>
<td>52.1</td>
<td>0.41</td>
<td>0.994</td>
<td>169</td>
</tr>
</tbody>
</table>

When P25 is employed all the contaminants reached a half-life time of less than half an hour, which concurs with the fact that the top-3 reaction rates constant corresponds to the systems that are employing P25. Also, all the optimal catalyst loadings ranged from 1.0 to 1.2 g L$^{-1}$, except for the P25-BP4 system. The TiO$_2$ photocatalysts play a better role in the reaction at acidic pH, while ZnO acts better at neutral to alkaline conditions since at low pH can undergo a photocorrosion of the material. Our photocatalytic degradation results of PBSA were similar in comparison to recent researches, where a photocatalytic route and UV-254nm/H$_2$O$_2$ were employed (Ji et al. 2013a, Abdelraheem et al. 2016). In the case of PABA, apparent
slower degradation rates were observed in comparison with a Fenton system and similar kinetic constants were obtained by Xue et al. (2015).
Chapter Five

Conclusions

The UV-filters, or the active ingredients of the sunscreen products, are commonly found in almost every product that we consume, from pharmaceuticals personal care products to clothes. UV-filters are often added to these products to protect them from sun radiation and to avoid the photodegradation of the material. The overproduction, and the frequent consumption of sunscreen products, has led to its detection in several media, such as urban groundwater, sewage sludge, organisms’ tissues and human blood. Nowadays, sunscreen products are an effective tool to protect us against skin cancer and other dangerous skin diseases caused by sun radiation. However, its highly recalcitrant behavior in the environment has caused countless controversies and generated a multitude of questions about its safety. These, and other, organic compounds have been detected in the water effluents of the wastewater treatment plants, which indicates that traditional techniques are not capable to remove them.

In this research we provided an alternative method to remove these organic pollutants in an aqueous media. The photocatalysis, as an advanced oxidation process, was successfully employed in the degradation of three active ingredients used in UV-filters; these were p-aminobenzoic acid, phenylbenzimidazole sulfonic acid, and benzophenone-4. The photocatalytic degradation was studied employing three different catalysts: TiO$_2$ nanowires, ZnO nanoparticles and P25 (a commercial TiO$_2$ catalyst). The first two catalysts were synthesized, and characterized prior the photocatalytic tests which comprises the first stage of this research. In this stage we aimed, and achieved, to synthesize ZnO nanoparticles and TiO$_2$ nanowires.
The TiO$_2$ nanowires were obtained after following a hydrothermal procedure, employing TiCl$_4$ as the precursor. The synthesis was performed in an autoclave during two hours at 180 °C in an acidic environment. It was demonstrated these wires began to growth at 30 minutes of the reaction as individual wires and then continue to organize as a branched structure. The individual wires were observed as elongated structures with a crystalline phase of pure rutile, according to the XRD and Raman results. Furthermore, the nanowires were composed of Ti and O according to the EDS and XPS analyses. As stated in the objectives, a high surface area was accomplished for the TiO$_2$NWs with an average surface area of 457 m$^2$ g$^{-1}$.

In the case of ZnO nanoparticles, very homogeneous sphere-like particles were observed, with sizes of ca. 50 nm. The small size of these particles may be influenced in the high surface area obtained of 406 m$^2$ g$^{-1}$. A calcination step was followed in order to remove all the reactant materials from the final product. This was confirmed with XPS and XRD analyses where was demonstrated the presence of the precursor, zinc acetate dehydrated was shown, when the synthesis was carried out without the calcination step. Furthermore, the presence of NaOH in the ZnONPs was not detected which suggests the well removal with and without the calcination step. The final product obtained after the calcination step was identified as ZnO, with a wurtzite crystalline structure according to the Raman and XRD results. As explained above, in both cases, the presence of nanostructured materials with high surface area was achieved. This high surface area was necessary to maximize the adsorption of the sunscreen active ingredients over the catalysts surfaces and therefore enhancing the photocatalytic procedure.

After this, during the second and third stage of the research performed, the as-synthesized materials, and the commercial photocatalyst, were employed for the
photocatalytic degradation of PABA, PBSA and BP-4. The goals of these stages were
accomplished after considering several factors that affect the photocatalytic process.
It was demonstrated that the catalyst identity and loading, initial pH and initial pollutant concentration will influence the degradation results since the degradation results ranged from 52 to 99.5%. Specifically, the initial pH demonstrated to be a significant parameter since the degradation is highly influenced due to the repulsive forces that can be formed if the substrate and the catalyst are equally charged. For example, it was demonstrated that the TiO$_2$NWs degraded PABA 77% under optimum catalyst loading at pH 3, but less than 10% of degradation was achieved at pH 11 because at highly alkaline environments both substances are negatively charged. The objectives of the second and third stages were achieved in the 3x3 system (3 photocatalysts x 3 organic pollutants). All the systems employed were capable to degrade at least the 50% of the organic pollutant. Moreover, PABA and PBSA was degraded in at least 70%. From the three catalysts employed, P25 seems to show a higher efficiency in comparison with the nanowires and nanoparticles, having photocatalytic degradation yields above 90% in all the organic pollutants.

The organic contaminants removal by this technique showed to be a promising decontamination method, since in 78% of the systems employed (7 out of 9) 86% photocatalytic degradation (or higher) was achieved. This degradation results occurred mainly because of a synergistic effect caused by the presence of oxygen sources, the catalyst and radiation. Furthermore, it is established that the contribution of other degradation routes, such as catalysis and photolysis, were negligible. This may be the reason why the POPs are very resistant to degradation since all these conditions do not occurs naturally, and the photolytic route showed to be inefficient in all cases degrading less than 20% in 180 minutes.
Overall, all the objectives and goals of the research were met since environmentally friendly catalysts were synthesized and characterized. The morphology, elemental composition, diffraction pattern, and surface area were determined for both photocatalysts synthesized. These synthesized photocatalysts, and the commercial catalysts were proved to be efficient in the photocatalytic performance. All the $t_{1/2}$ were determined to be less than 180 minutes which is much less in comparison to traditional remediation techniques. Furthermore, in seven cases the $t_{1/2}$ were close to one hour or less.

In order to implement this technique in a real environment, several precautions have to be taken into account, such as the initial pH in the system, since as mentioned above, this parameter is one of the major factors affecting the reaction efficiency. Furthermore, for future researches based on these methods, the photoproducts of these organic pollutants should be identified in order to establish a clear toxicity reduction, in comparison with the parent compounds. There is no established mechanism that will occur during all the degradation procedures. For instance, every reaction may take a different pathway every time. However, predominant pathways and photoproducts can be identified for every organic pollutant. In the case of PABA, the non-selective attack of the hydroxyl radicals may promote its degradation and the formation of a photo-product identified as the hydroxylation form of itself. Similar results are expected for PBSA since the hydroxylation of this organic compound could be one of the major paths in the degradation process. PBSA has a more complex chemical structure in comparison with PABA and therefore the photoproducts formed may be more varied including a ring opening step, and a desulfonation step. Similar to PBSA, BP-4 has a $-\text{SO}_3\text{H}$ which is expected to be released as part of the degradation process. Unfortunately, the experiments regarding
the photocatalytic degradation of BP-4 are scarce, in consequence little information about the possible degradation route is available.

Also, in order to make this cleaning step more cost-effective, a pilot study considering the recyclability of the photocatalysts could be performed to establish the cycle’s number that the same catalyst could be employed without losing efficiency in the system implementation. As a final recommendation, total organic carbon analysis also can be implemented in order to evaluate the mineralization progress along the reaction pathway. If necessary, the irradiation time or treatment can be increased in order to maximize the mineralization: degradation ratio. In summary, we can conclude that all the objectives of this research were achieved, since the photocatalytic activity of the three different catalysts were proved in the degradation of the sunscreen products active ingredients in an aqueous media.

As demonstrated during this research, the photocatalysis technique showed an extraordinary efficiency in the degradation and removal of organic pollutants including sunscreens active ingredients. The continuous detection of PPCPs in WWTPs effluents and surface waters demonstrated the need for advanced methods for removing emerging contaminants since the traditional techniques are not capable of. Traditional techniques such as bioremediation, pump-and-treat, and adsorption methods are not able to reduce the toxicity of these compounds since the organic compound is only transferred from a physical state to other (i.e. liquid to solid). In contrast the AOPs, including the photocatalysis, deals with the chemical transformation of the structure and therefore the toxicity can be reduced in short period of times (i.e. hours, t_{1/2} of minutes). Moreover, the photocatalytic procedure is able to mineralize the organic compounds into CO_{2}, water, and inorganic N and S. Finally, the photocatalytic degradation of organic pollutants is efficient in mild
conditions without the need of high temperatures or pressure systems and works perfectly at mid-low concentrations as demonstrated in this research degrading 50% or more in all the cases, 70% or more in 8 of 9 cases, and 89.5% or more in 6 of 9 cases.
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