UNIVERSITAT DE BARCELONA

HETEROGENEOUS PHOTOCATALYTIC DEGRADATION OVER TITANIUM DIOXIDE OF TOLUENE IN GAS PHASE AND DIPHENHYDRAMINE IN LIQUID PHASE

MASTER FINAL PROJECT

MASTER OF ENVIRONMENTAL ENGINEERING

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Abstract

Scientific studies on photocatalysis started about two and a half decades ago. Titanium dioxide (TiO_2), which is one of the most basic materials in our daily life, has emerged as an excellent photocatalyst material for environmental purification. In this study, current progress in the area of TiO_2 photocatalysis, mainly photocatalytic air and water purification are discussed together with some fundamental aspects.

In the air purification line it was set-up an installation for descontamination of toluene in gas phase. It was explained the experimental method to carry out different experiments and the experiments performed. Moreover, it was created a new chromatographic method to analyze toluene in GC-2010. Best results showed 97% of recovery with 0.5 L/min of toluene during 10 minutes and it desorbed with Vortex during 10 minutes without photocatalytic reaction. But after some deficiencies were found in the installation and in this work it were proposed some enhancement options to study different variables involved in photocatalytic process in gas phase (photolysis, adsorption, total flow rate, radiation and concentration of pollutant).

In the water purification line the degradation of diphenhydramine hydrochloride (DPH) by TiO_2 photocatalysis was studied under different radiation sources: UVC (λ=254 nm), black blue lamps (BLB, λ=365 nm), simulated solar radiation (SB, Solarbox) and CPCs, at pilot plant scale with sunlight. Photolysis shows an important role in the DPH abatement under UVC radiation (31.5% of DPH conversion) but mineralization was not observed. Different TiO_2 concentrations (0.05, 0.1 and 0.4 g/L) were used in SB device and the best results were obtained for 0.4 g/L: 35.7% of DPH conversion and 9.8% of TOC removal, after 60 min of irradiation. The UV-Vis/H_2O_2/TiO_2 process represents an improvement with respect to the photocatalytic process (without H_2O_2). Thus, at 60 min with 150 mg/L of H_2O_2, 62.6% of DPH conversion (kinetic constant $15.05 \cdot 10^{-3}$ h^{-1}) in SB was achieved instead of 35.7% obtained without H_2O_2. Concerning the energy consumption in the useful wavelength range, SB and BLB reactors displayed the best ratios (mg DPH removed/kJ): 0.10 and 0.12, respectively, with 0.4 g/L of TiO_2. Finally, reaction intermediates were identified and DPH photo-degradation pathway was proposed.

Keywords: air purification, water purification, toluene, diphenhydramine hydrochloride, titanium dioxide, UVC, BLB, SB, CPC.

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Notation

AOPs	Advanced Oxidation Processes
BLB	Black Blue Lamp
BOD	Biological Oxygen Demand)
BTX	Benzene-Toluene-Xilene
CB	Conduction Band
COD	Chemical Oxygen Demand
CPC	Collector Cilindric Parabolic
CS_2	Carbon disulfide
DPH	Diphenhydramine hydrochloride
ECs	Emerging contaminants
EEA	European Environment Agency
ELV-DE	Environmental Limit Value of daily exposure
ELV-SD	Environmental Limit Value of short duration
$HO^{\cdot}$	Hydroxyl radical
H_2O_2	Hydrogen peroxide
HPLC	High-performance liquid chromatography
INSHT	Instituto Nacional de Seguridad e Higene en el Trabajo
PPCPs	Personal Care Products
SB	Solarbox
TiO_2	Titanium dioxide
TOC	Total Organic Carbon
UVA	Ultraviolet radiation longwave
UVB	Ultraviolet radiation halfwave
UVC	Ultraviolet radiation shortwave
VB	Valence Band
VOCs	Volatile Organic Compounds

1. INTRODUCTION

1.1.Atmospheric pollution

Since years 60’s, atmospheric pollution started to become in a mainly social concern. “The air is considered polluted when the presence in it of a foreign substance or a significant change in the proportion of its compounds are so severe, that can cause effects or discomfort known as harmful in the light or current knowledge scientists” (European Council, 1967).

The emission of contaminant substances into the atmosphere, from natural and anthropogenic sources, can affect the health of the people, material degradation and ecosystems. The atmospheric pollution is a both local and international problem. Air pollution poses the single largest environmental health risk in Europe today. Air pollutants can affect the area where they are formed but may be transported over long distances, and they may affect large areas. Some pollutants persist in the environment for long times and they may accumulate in the environment and in the food chain, influencing humans and animals not only via air intake, but also via water and food intake. This means that it is a complex problem that poses a multiple challenges in terms of management and mitigation (EEA, 2015).

1.1.1. BTX compounds

VOCs (volatile organic compounds) are one of the indoor and outdoor air pollution sources. These compounds, after the suspended particles, have the most frequency and variety of emissions (Rostami & Jonidi Jafari, 2014). Some VOCs are used as solvents in industrial operations and processes (Mathur *et al.*, 2007). BTX (Benzene, Toluene and Xylenes) are VOCs considered as predominant pollutants and have adverse effects on the health and environment (Franco *et al.*, 2012). These substances affect the environment and directly on human health. BTX may cause effects on the central nervous system, respiratory, genome and excretory system (Mathur *et al.*, 2007).

1.2.Water pollution

Water is fundamental to survival on earth. About 75% of the earth’s surface is covered by water, but only a small fraction is really available for human consumption. Increasing water demand from the world population has become a major global concern (De Luca *et al.*, 2013). In recent decades, the scarcity of water resources has become more and more evident and led to reclaimed water use in a variety of applications (Laws *et al*, 2011).

Effluent of municipal wastewater treatment plants is considered a good source of water for potential reuse. However, quality requirements for reusable water (Díaz-Cruz & Barceló, 2008) include an absence of toxic compounds that generally escape conventional wastewater treatment (Teske & Arnold, 2008). In order to promote reusability, the water should be free of emerging contaminants (ECs) (De Luca *et al*., 2013).

1.2.1. Emerging contaminants

Emerging contaminants (ECs) is used to define different types of compounds, including newly developed substances, compounds that have been newly discovered in the environment, often due to analytical developments and compounds that have only recently been categorized as contaminants (Lindsey *et al*., 2001; Petrovic *et al*., 2006; Richardson, 2007).

According to Mirada (Miranda *et al., 2014)* the topics of great concern related to such substances are their bioaccumulation and persistence.

They are also resistant to conventional wastewater treatment, and are found in effluents at concentrations generally ranging from 0.1–20.0 $\mu g \cdot L^{-1}$ (Gómez *et al*., 2007; Martínez-Bueno *et al*., 2007). Due to the low concentration in which they are found in nature, they are also called micropollutants.

ECs include a wide array of compounds such as pharmaceuticals, household chemicals, personal care products (PPCPs), disinfection byproducts, insecticides, and pesticides, some of which are suspected endocrine disruptors. Pesticides have a wide spectrum of applications. Due to their physicochemical properties, they are found in all compartments of the environment (De Luca *et al*., 2013).

1.3.Legal framework

In Spain, improving air quality is considered a fundamental line in environmental policy of Departamento de Agricultura, Alimentación y Medio Ambiente. Due to the effects of air and water pollution may produce on human health and ecosystems. During the last years, efforts have been made for reducing emissions of pollutants in atmosphere and water. However, certain problems persist related to air and water quality. Within the legal framework regulating the atmospheric and water pollution, the main laws are shown below.

1.3.1. Legal framework of air

The current legislation on air is scattered in a wide variety of legislative tools that have different levels of competition.

European Regulations

- Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe.
- Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air.

National Regulations

- Ley 34/2007, de 15 de noviembre, de calidad del aire y protección de la atmósfera.
- Real Decreto 678/2014, de 1 de agosto, por el que se modifica el Real Decreto 102/2011, de 28 de enero, relativo a la mejora de la calidad del aire.

For toluene there is not rule regulating the emission and immission levels. The only recommendation that may serve as reference is the value used in the context of risk prevention, showed in Table 1.I (INSHT, 2007).

Table 1.I. Environmental limits of toluene. [Source: INSHT]

Toluene	
ELV-DE	50 ppm (192 mg/m^3)
ELV-SD	100 ppm (384 mg/m^3)

1.3.2. Legal framework of water

In many developed countries there are laws designed to ensure sustainable use of water. On this basis, Directive 2000/60 / EC is one of the most important tools on the conservation of water quality in Europe.

The current legislation on water is scattered in a wide variety of legislative tools that have different levels of competition.

European Regulations

- Directive 2000/60/EC of 23 of October of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy.
- Directive 2009/90/EC, of 31 of July 2009, laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status.

National Regulations

- Real Decreto-ley 11/1995, de 28 de diciembre, por el que se establecen las normas aplicables al tratamiento de las aguas residuales urbanas.
- Real Decreto 1620/2007, de 7 de diciembre, por el que se establece el régimen jurídico de la reutilización de las aguas depuradas.

In other regulations are defined the emissions levels and disposal of different pollutants. However, regulations on emission levels of emerging contaminants in water have not been completed yet and are being updated and improved.

1.4.Advanced Oxidation Processes (AOPs)

AOPs rely the high reactivity of hydroxyl radical ($HO^{\cdot}$) to drive oxidation processes and to achieve complete degradation and full mineralization of several organic pollutants (Legrini *et al.*, 1993). Hydroxyl radical is among all oxidant species the second most reactive after fluoride (E^{o}= 2.80 V) and being non-selective it can attack almost any organic compound including those that make up living cells (Forero *et al.*, 2005).

AOPs can be divided in **photochemical processes** if radiation has a participation in the process or **non-photochemical processes** if no radiation is required as detailed in Table 1.II

Table 1.II. Typical AOPs system [Source: Adapted from (Litter & Quici, 2010)]

Photochemical	Non-photochemical
O_3/UV	Ozonation at alkaline pH (>8.5)
H_2O_2/UV	Ozone + catalyst
O_3/H_2O_2/UV	Fenton
Photo-Fenton	Non-thermal plasma
TiO_2/UV	Ultrasonic cavitation
Photolysis	
TiO_2/H_2O_2/UV	

Finally, the main advantages of these techniques are shown:

-It is produced a chemical change of the pollutant. And it is degraded.

-It can be achieved a total mineralization of the pollutant (the pollutant is destroyed).

-These may be used to treat contaminants at very low concentration.

1.5.Heterogeneous photocatalysis

The heterogeneous photocatalysis is an oxidative process with a growing interest in environmental applications for removal of organic contaminants.

However, to understand that means the term of photocatalysis, it is necessary to point out some concepts. Firstly, it is called catalysis to chemical phenomena that generate a permanent change in the molecules. In this order of ideas, a catalyst is a substance that affects the rate of reaction of a decisive process, which has a high selectivity on the molecules on which it operates (Cámara, 2012).

Then, it can say that the photocataysis is a process that aims to absorbing radiant energy to a solid which is generally a semiconductor broadband (*Bandgap* E_G high) that not go through any chemical change and which generates a series of chemical reactions involving the degradation of the pollutant. (Nan *et al.*, 2010). TiO_2 is a semiconductor with a *Bandgap* of about 3.0eV, UV light (with wavelengths shorter than ∼400nm) can create pairs of electrons and holes.

When a semiconductor-based photocatalyst (TiO_2) is irradiated by light photons that have energy equal to or higher than the photocatalyst band gap energy, there is an absorption of these photons and an electron (e^-) is transferred from the valence band to the conduction band, leaving a hole (h^+) in the valence band. The valence band hole can react directly with the pollutant molecule or can produce hydroxyl radicals, while the electron in the conduction band will react mainly (O_2) present in the fluids phases (Méndez-Arraiga, 2009).

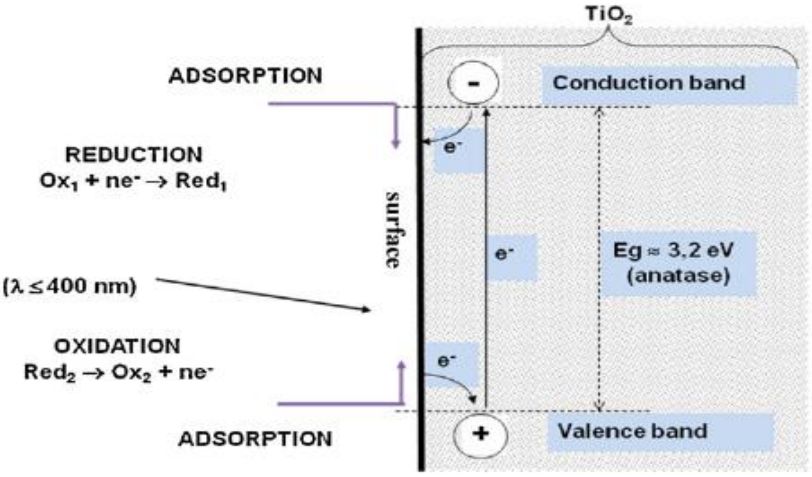


Figure 1. 1. Steps of a photocatalytic reaction in a solid semiconductor particle: (1) light photons of energy h***υ*** matching or exceeding the semiconductor band-gap; (2) excited electron, e^-, migrates from valence band (VB) to conduction band (CB) leaving a hole, h^+, in the valence band; (3) h^+ migrates to surface and initiate oxidation reactions; (4) e^- migrates to surface and initiates reduction reactions; (5) charge carrier recombination liberating heat. [Source: Cámara,2012].

1.5.1. Reaction kinetics

Chemical kinetics is an area of physical chemistry that takes over the study of speed reactions. That is to say to know how to change the speed of the reactions under variable conditions and what molecular events are made through the general reaction.

This speed is not constant and depends on several factors such as the concentration of the reactants, the presence of a catalyst, the reaction temperature and the physical state of the reactants (Atkins & Paula, 2006).

One of the most important factors is the concentration of the reactants. If there are more particles in a same volume, there will be more collisions between particles per unit time and therefore the reaction rate is faster.

If the absorption of contaminant on the surface of the photocatalyst is very low, the process can be described by first-order kinetics (Romero *et al.*, 2015):

$$-\ln\left(\frac{c}{c_o}\right) = k_{ap} * t \qquad \text{(Eq.1)}$$

Where c_o is the initial concentration at time=0, c is the final concentration and k_{ap} is apparent first order kinetic constant (Eq.1).

2. JUSTIFICATION

The great industrial and demographic development of recent decades has led to an unsustainable increase of energy and raw materials consumption that negatively affects the environment due to the large amount of waste and pollutants generated.

The technologies currently used for degradation of these compounds present some inconveniences due to the generation of toxic intermediates creating the problem of effluent disposal beyond the high cost. Moreover, many technologies do not destroy the contaminants. Solely the pollutants are separated from the fluid phase. Thus, once separated these pollutants, they have to be treated.

Among the advanced oxidation processes, photocatalysis is an attractive and innovative technique with growing interest in its application for the removal of many organic and inorganic compounds (Crap, Huisman *et al*., 2004). In addition, as it allows the use of sunlight as a source of UV radiation there is a significant reduction of energy costs and operation. The most employed photocatayst is titanium dioxide (TiO_2) due to its cost effectiveness, inert nature and photostability.

In the one hand, in water line AOPs can remove many types of micropollutants and can be used to attain the levels of reuse parameters required by legislation. In this context, the treatment of secondary effluents could minimize the discharge of micropollutants into the receiving waters and thus improve the overall secondary effluent quality for possible reuse (De Luca *et al*., 2013). In this study, diphenhydramine (DPH) was chosen as a model compound to represent micropollutant in synthetic water.

In the other hand, every time the levels of many atmospheric pollutants are higher and they have to be eliminated in the most sustainable way. In this context, heterogeneous photocatalysis has been recognized over the recent decades as one of the most promising technologies for air treatment. In this project it has been analyzed one of the compounds that form the BTX fraction (toluene), due to the specific characteristics of these compounds and their affection both the environment and public health.

3. OBJECTIVES

In the previous sections of this work it has highlighted the problems resulting from the presence of contaminants in the environment and the need to develop oxidation technologies capable to reduce the concentration of these pollutants.

3.1.General objective

The main objective objective of this project is to evaluate the degradation of DPH in liquid phase and toluene in gas phase by means of heterogeneous photocatalytic process.

3.2.Specific goals in gas phase

Specific objectives in gas phase are based on:

- To start up of the installation.
- Definition and development of required analytical techniques.

3.3.Specific goals in liquid phase

Specific objectives in liquid phase are based on photocatalytic degradation of DPH:

- To use different radiations (solar with Collector Cilindric Parabolic (CPC), simulated solar with Solarbox (SB), ultraviolet radiation shortwave (UVC) and ultraviolet radiation halfwave or Black Blue Lamp (UVB or BLB).
- To use different concentrations of TiO_2.
- To add different concentrations of peroxide (H_2O_2).

4. GAS PHASE

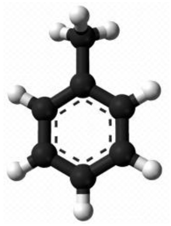
4.1.MATERIALS, EXPERIMENTAL AND ANALYTICAL METHODS AND PROCEDURES

4.1.1. Chemicals and reagents

Toluene

On the one hand, toluene in liquid phase was purcheased from Sigma-Aldrich (Spain). On the other hand, toluene in gas phase was purcheased from Abelló Linde, S.A. (Spain). CAS No.: 108-88-3. The main features of toluene bottle are presented in Table 4.III.

Table 4.III. Chemical properties of toluene.

Toluene	
Molecular weight	92.1381 (g/mol)
Formula	C_7H_8
Molecular structure	
Boiling point	383.8 K 111 (^{o}C)
Concentration of toluene diluited in dry air	1,117 (mg/m^3)
Type of bottle	Linde 40 liters
Filling pressure	35.271 (bar)
Stability	24 months

<u>Other chemicals and reagents</u>

Table 4.IV. Chemical properties of all other reactives used in this work.

Name	CAS No.	Formula	Supplied by	Purity (%)	Used in/for
Carbon disulfide	75-15-0	CS_2	Sigma-Aldrich	99	Desorption of toluene
Titanium dioxide P-25	13463-67-7	TiO_2	Sigma-Aldrich	>85	To impregate the mortars

Following ths study by Shen (Shen *et al.*, 2012) ultra-fine (nano-scale) titanium dioxide PC105 (Anatase) was used in this study for surface treatment. The used catalyst is titanium dioxide (TiO_2), because it appeared in the literature as the best for this type of experiments (Angelo *et al*. 2013).

4.1.2. Experimental and analytical methods

4.1.2.1. Preparation of mortars

Previously carrying out experiments is necessary to make the test pieces of concrete on which the catalyst (TiO_2) is supported. For this work, which is in the initation phase, was chosen a impregnation method very easy following the study by Shen (Shen *et al., 2012).* The concrete chosen is Portland (Beissier, S.A.) with a water-cemet ratio of 0.29, to a target porosity of 25%. The water-cement ratio was chosen based on the recommendation from study of Shen. The dimensions of mortars are 8.8 cm x 12.5 cm x 0.7 cm, as it can be noted in Figure 4.2. After 36 hours, when the cement is dry, it applied on it the catalyst. Test performed in this study consisted on water and 5% concentration of TiO_2. According to Shen work concrete with this concentration of TiO_2 it can produce between 94% and 98% compound reduction. Moreover, also in this study it is noted that 4 g of TiO_2 per 465 cm^2 - surface area (86.1 g/m^2) - worked effectively at removing pollutants.

Figure 4.2. Mortar of cement with 5% concentration of TiO_2.

However, the durability of the Shen's method is low. For this reason, as reference, a list of photocatalytic film preparation methods has been assembled in Table 4.V.

Table 4.V. Preparation of TiO_2 active surface layers.

Method	Author
Sol-gel	Negishi *et al*., 1995 Tada *et al*., 1997
Spray-pyrolysis	Ohko *et al*., 2001
Electrophoretic deposition	Yanagida *et al*., 2005
Chemical bath deposition	More *et al*., 2008
Electron-beam evaporation	Yang *et al*., 2004

Method	Author
Plasma spray	Toma *et al*., 2008
Anodic oxidation	Chen & Zhao, 2009
Inorganic- organic graded film	Takami *et al*., 2002

4.1.2.2. Toluene extraction

The adsorption of toluene is done by activated carbón contained in a tube. The tubes recommended for this type of adsorption are Anasorb CSC. They have high surface area and they are suitable for sampling a wide range of compound nonpolar (INSHT, 2007). The main features are presented below:

- Activated carbon 100 mg (section A) /50 mg (section B).
- External diameter: 6 mm.
- Internal diameter: 4 mm.
- Length: 7 cm.
- Separators: foam/foam/fiberglass

Activated carbon tubes are made of glass. Both ends are closed to the flame. These tubes contain two sections of activated carbon which are separated by a portion of polyurethane foam of 2 mm (section A) and 3 mm (section B).

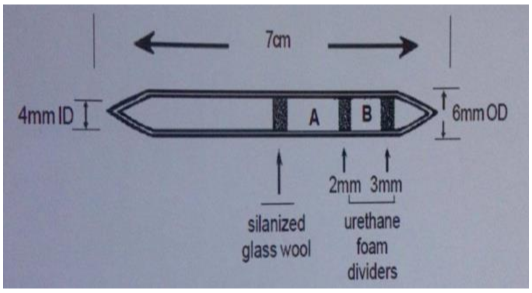


Figure 4.3. Scheme of activated carbon tube

The extraction procedure is as follows:

1. Breaking the tube ends
2. To connect the pump to one tube ends (where there is fiberglass).
3. To start up the pump. This has to regulate to 200 mL/min.
4. To disconnect the pump and to remove the activated carbon tube.

4.1.2.3. Toluene desorption

Chemical desorption is carried out with carbon disulfide. Thus, the tolune adsorbed on activated carbon can be extracted. The general procedure is the next:

1. To add 1 ml of desorbent dissolution in a threaded tube and to close it immediately.

2. To break the activated carbon tube at one end. The glass wool is romoved and this is discarded.

3. Finally, to add two sections of activated carbon and two polyurethane foams in the threaded tube. Again, to close the tube immediately.

Once this is done, different techniques to improve desorption were tried.

A) It was used a Vortex (VWR-VV3) during 10 minutes.

B) It was used a ultrasound tip (BANDELIN SONOPLUS UW 2070) during 5, 10 and 20 minutes.

C) It was used a centrifuge (Centrifuge 5804) during 10 and 30 minutes.

D) Shaking with hands the threaded tube during 30 minutes.

Finally, a dilution 1:10 was made in order to obtained the toluene concentration is in the range of detection cromatograph.

4.1.2.4. Gas chromatography analysis

The model of gas chromatograph is SHIMADZU GC-2010 PLUS. It was created a method for analyzing toluene in gas chromatograph. The method was created according to "*Guía de selección de columnas Agilent J&W para GC"* and Ramirez work (Ramirez, *et al*., 2010). In addition, CSIC and UB technical services staff were contacted to check both of the operation of the chromatograph and toluene method. Finally, different ramps of temperature were tried. The main characteristics of toluene method are shown below.

- **Column:** TRB-624
- **Dimensions:** 30m x 0.32m x 1.8µm
- **Maximum column temperature:** 260 ^{o}C
- **Injection mode:** split
- **Injection volume:** 1 µL (10.00 µL syringe)
- **Injection temperature:** 250 ^{o}C
- **Purge flow:** 3 mL/min
- **Split ratio:** 5

- **Column oven temperature program:**

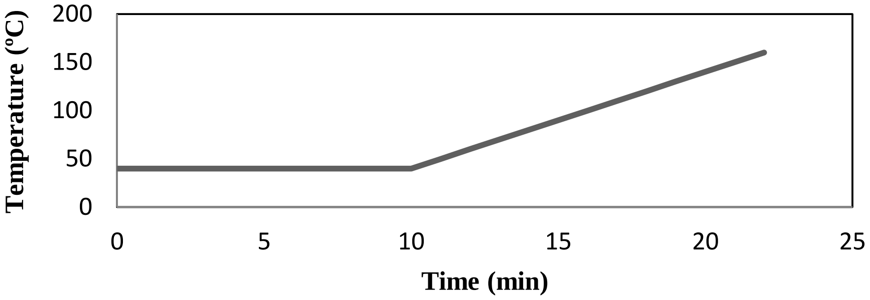


Figure 4.4. Column oven temperature program of toluene method

- **Makeup gas:** He
- **Makeup flow:** 30 mL/min
- **H_2 flow:** 40 mL/min
- **Air flow:** 400 mL/min

4.1.3. Installation set- up

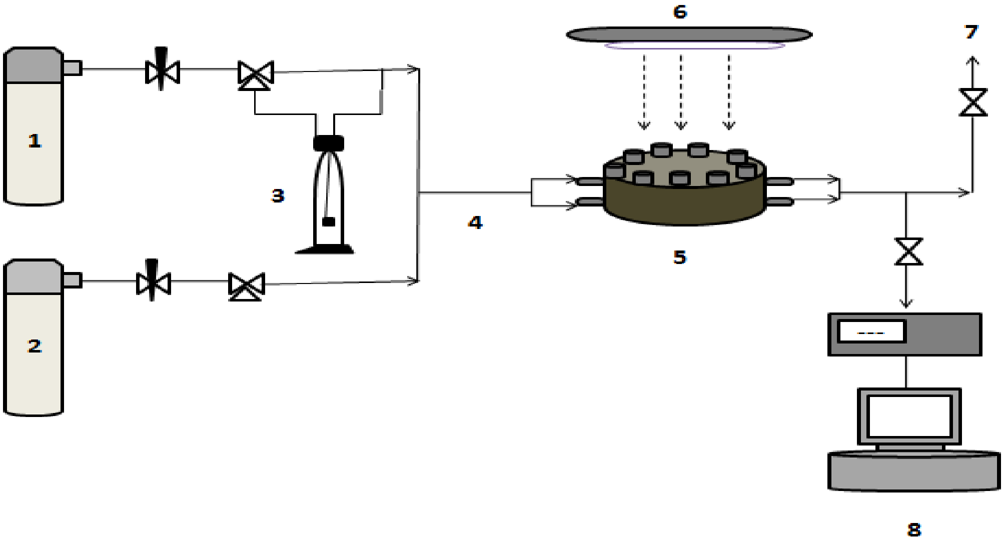


Figure 4.5. Installation diagram. 1) Synthetic air. 2) Toluene. 3) Humidifier. 4) Reactor inlet. 5) Reactor. 6) UV lamps. 7) Gas extraction. 8) Chromatographic analysis. [Source: own]

Gas supply to the installation is executed using two bottles: a synthetic dry air bottle and a toluene bottle. This last presents a concentration of 1,117 mg/m^3 –diluted in dry air-. A concentration of toluene required in the photoreactor is approximately 200 mg/m^3 (VLA: 192 mg/m^3, exposure 8 hours). It is needed a ratio of 5:1 (air: toluene). In Figures A.6, A.7 and A.8 of annex *A* it can see a photos of real installation.

Afetr the gas bottles there are two mass flowmeters. The air flowmeter has an operating range of 0-150 L/h ±1.5%. The toluene flowmeter has an operating range of 0-20 L/min ± 2%. Then, the airstream passes through a humidifier. The objective of humidifier is to provide the system with the desired moisture. According to Cámara best results were seen with 50% of humidity (Cámara, 2012).

Two flows are mixed before the photoreactor. Afterwards, the mixture in the photoreactor is contacted with the catalyst where radiation is received. The catalyst is supported on a rectangular piece of cement as it explained in section 4.1.2.1. The photoreactor used in this work presents a rectangular shape taking as a starting point ISO 22197-1 norm (International Standard ISO22197-1, 2007). In figure A.9 it shows a real photo of this photorecator and in Table A.VI it shows the main characteristics in annex *B*. The light source applied consists of four fluorescent tubes (Philips CLEO Compact) OF 15 W either one. The radiation emitted is UVA (300-400 nm) with a maximum intensity centred at 365 nm. To mesure radiation in the installation it used a photo-radiometer HD2102-1. The measurement range is $0.1 \cdot 10^{-3}$ – 2000 W/m^2. To simulate the maximum solar radiation in one day it set the radiation of each experiment is 25-30 W/m^2.

Gas samples are taken at the outlet of the reactor. Gas flow is passed at 200 mL/min through an activated carbon tube to ensure good adsorption of the toluene (Cámara, 2012). Sample flow is regulated by a sampling pump. Its model is SKC 224-44MTX. The main features of this sampling pump are preented in table A.VII in annex *C*. The sampling pump, as can see in Figure A.10 and A.11 in annex *C*, is connected in serie to a rotameter which allows measuring flow rates lower than 1L/min. Later, toluene in the activate carbon tube is desorbed in carbon disulfide (CS_2), as it explained in section 4.1.2.3. Finally, the sample is analyzed in a gas chromatograph equipped with a flame ionization detector (FID).

Fugues were analyzed at the beginning of work by means of detector of fugues in spray (Herraiz) supplied by Herraiz S.A.

4.2.RESULTS AND DISCUSSION

4.2.1. Experiments

Firstly, it was done the calibration curve. Carbon disulfide, as dissolvent, and liquid toluene were used. Different concentrations of toluene solutions were prepared from concentrated liquid toluene. Figure A.12 in annex *D* shows the calibration curve.

With the purpose to check that the experimental and analytical methods are correct, it was done a blank experiment using only toluene in the installation. It was used 0.5 L/min during 10 minutes - to ensure concentration of toluene is enough to be within the range of a calibration curve and to ensure the amonut of toluene is less than maximum amount that activated carbon can adsorb (max. 5.5 mg of toluene)- (INSHT, 2007). This experiment was done without radiation or catalyst. It was desorbed shaking the threaded tube during 30 minutes. The results were not satisfactory obtaining 1% of recovery. These results are presented in Figure A.13 in annex *E*. For this reason, it was changed the desorption procedure. New experiment as done with the same conditions as the previous experiment. But it was desorbed in Vortex during 10 minutes. The results were satisfactory obtaining 97% of recovery. Figure A.14 in annex *E* shows the chromatography. It was done two replicas to ensure the results are reliable obtaining a error percentage of ±1%.

At that time, other blanks and experiments were donde in various conditions to study the effect of different aspects in the photocatalytic process in gas phase (photolysis, adsorption, total flow rate effect, radiation effect and concentration of toluene effect). Different experiments are presented in Table A.VIII in annex *F*. All experiments were replicated twice. Mortar was made with 5% of TiO_2 in each experiment, where it was necessary, and new mortar was made for each experiment. Each time of experiment was calculated for not to exceed the maximum quantity of toluene that activated carbo can admit. Results were not satisfactory obtaining between 1-5% of recovery. That fact was made to think that it could be due to chromatograph which had been spoiled during 3 weeks. It turned to pass a patrons to ensure that the calibration curve presented the same results. Results displayed that the chromatograph was not the problem. Then, it was though if the problem could be the samples because they were in the fridge at 4 ºC for 3 weeks. Best procedure would be have the samples in the fridge during 1 day. For this reason, it was performed a experiment using 0.5 L/min of toluene during 10 minutes. It was desorbed in Vortex during 10 minutes and it was analyzed immediately. Results were not satisfactory obtaining 2% of recovery. This led to think that the problem was in desorption. Thus, different procedures of desorption were analyzed (ultrasound tip during 5, 10, 20 minutes and centrifuge during 10, 30 minutes). Results were not satisfactory obtaining between 1-5% of recovery again. In order to discard the desorption as source of problem, it was injected liquid toluene in the activated carbón tube and it was desorbed with different techniques studied. Results were satisfactory obtaining 99% ± 2% of recovery by means of ultrasound tip, Vortex and centrifugue during 10 minutes in each one of them.

Finally, it were checked the leakages. Intallation presented a lot of leakages. This fact could be because there had been an overpressure in the system. This could be one source of the problem of the installation.

4.2.2. Problems associated with the installation

As it has been seen in the previous section there are some problems related to the installation.

Fisrtly, it is important to choose the suitable material to get optimal results. For this reason, in the different connections are used Teflon and Tygon tubes. These are characterized as practically inert materials. Maybe some tube of Teflon (less inert tan Tygon) does not prevent the adsorption of toluene.

Secondly, many of connections are “fast connections” and this is problem in gas phase in order to the fugues. Also, valves and connections are not stainless steel which is important when it are used organic compounds.

Moreover, the installation presents a lot of fugues. If there are some fugues in the system, this fact could to vary the concentration of toluene and it could show different results tan exposed without photocatalytic proces.

Connection with activated carbón tube and installation tube is simple. It can be a source of loss of toluene.

Finally, there is no pressure gauge at the end of installation in which it could to know if there are some leakages at the reactor outlet.

4.2.3. Potential solutions

- To use Tygon tubes which are done inert material.
- To make minor connections as possible.
- To not use “fast connections”.
- To use valves and connections of stainless steel.
- To propose another connection system more complex between activated carbon tube and installation tube.

- To put a pressure gauge at the end of installation.

4.3.CONCLUSIONS

- The installation just as it is now does not serve to carry out different experiments to evaluate the effect of diverse variables.
- All material on the installation have to be inert and material of stainless steel.
- Activated carbon can adsorb toluene with an elevated recovery percentage.
- Desorption can be done with Vortex, ultrasound tip and centrifugue during 10 minutes in each of them. Worst results were obtained with another times of desorption.
- The chromatographic method for analyze toluene is reliable.
- Best results were achieved at the beginning of experiments with 97% of recovery of toluene in gas phase.
- According to previous studies the impregnation method presents low durability.
- The synergy of many factors affected the project (choice of compound, resources, installation, time and chromatograph).

4.4.RECOMMENDATIONS

- It would be necessary to change tube of all installation to Tygon tubes and all tubes should have the same diameter. Valves and connections should be change to valves and connections of stainless steel.
- It would be necessary to try different impregation techniques which have higher durability as the exposed in previous sections. In this project it had been though to develop a water-based paint. This technique colud be elaborate in University.
- Durability of the surface application methods should be analyzed. In order to observe the effects of environmental impact on the surface coatings should to place the samples outside to have weather exposure and temperatures ranging from 0 ºC to 37 ºC during 4 months (Shen *et al*, 2012).
- To evaluate the thickness of the catalyst layer is the same at the beginning and end of the experiment was designed to evaluate the thickness by X-ray diffraction. These analysis can be made in the scientific and technical cennter UB.
- Finally, it would be necessary to evaluate the mineralization. It had though to create a chromatographic method to detect CO_2.

5. LIQUID PHASE

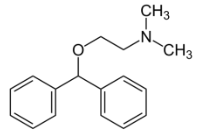
5.1.MATERIALS, ANALYTICAL METHODS AND PROCEDURES

5.1.1. Chemicals and reagents

Diphenhydramine hydrochloride

In this study, DPH was chosen as a model compound to represent micropollutant presence in water. The solution of 50 mg/L of DPH ($C_{17}H_{21}NO \cdot HCl$, HPLC grade, purity ≥98% from Sigma-Aldrich) was prepared using deionized water. CAS No. 147-24-0. This high concentration (50 mg/L) was selected to assure accurate measurements of concentrations and to follow TOC. Moreover, this concentration was chosen to represent the conditions of wastewater coming from some pharmaceutical industries (Pupo *et al.*, 2005 & Kuhn *et al.*, 2004). Main characteristics of DPH are shown in Table 5.IX and in Figure A.15 of annex *G* it can see the ultraviolet spectrum of DPH.

Table 5.IX. Physical and chemical characteristics of DPH.

Diphenhydramine hydrocloride	
Molecular weight	291.81 (g/mol)
Formula	$C_{17}H_{21}NO \cdot HCl$
Molecular structure	
Log K_{ow}	3.27
Log K_{oc}	3.33 to pH 5.5
pKa	8.98

Other chemicals and reagents

Table 5.X. Chemical properties of all other reactives used in this work.

Name	CAS No.	Formula	Supplied by	Purity (%)	Used in/as
Hydrogen peroxide	7722-84-1	H_2O_2	Merck	30 w/w	Photocatalytic experiments
Titanium dioxide P-25	13463-67-7	TiO_2	Sigma-Aldrich	>85	Catalyst

Name	**CAS No.**	**Formula**	**Supplied by**	**Purity (%)**	**Used in/as**
Bisulfite	7631-90-5	$NaHSO_3$	Panreac	-	Stop the reaction with peroxide to TOC
Methanol	67-56-1	CH_3OH	Panreac	>99.9%	Stop the reaction with peroxide to HPLC
Acetonitrile	75-05-8	CH_3CN	Fischer-Chemical	99.8%	HPLC analysis
Orthophosporic acid	7664-38-2	H_3PO_4	Panreac Quimica	85%	HPLC analysis

Heterogeneous photocatalysis was performed using TiO_2 P-25 (EvoniK, Germany).

5.1.2. Analytical methods

5.1.2.1.Determination of DPH concentration

DPH concentration was monitored by HPLC from Waters using a SEA18 Teknokroma column (250 x 4.6 mm i.d.; 5µm particle size) and a Waters 996 photodiode array detector. The mobile phase was composed by water (pH 3) and acetonitrile (70:30), injected with a flow-rate of 0.85 mL/min. DPH concentration was followed at UV maximum absorbance (220 nm).

5.1.2.2.Determination of TOC

TOC was analyzed with a Shimadzu TOC-VCNS analyzer equipped with an automatic system sample ASI-V.

5.1.2.3.Determination of H_2O_2 concentration

H_2O_2 consumption was followed using the metavanadate spectrophotometric method at 450 nm (De la Cruz, *et al*., 2013).

5.1.2.4.Determination of intermediates

For the intermediates identification, samples were analyzed by the electrospray ionization/mass spectrometry using an electrospray (ion spray) ESI-MS and a LC/MSD-TOF (Agilent Technologies) mass spectrometer.

5.1.3. Experimental devices

5.1.3.1.Artificial irradiation: UVC reactor

The experiments with UVC lamps were performed in a thermostatic Pyrex-jacketed 2 L vessel (inner diameter 11 cm, height 23 cm), equipped with three low pressure mercury lamps (Phillips TUV 8W, G8T5) located at the center of reactor. Lamps emit monochromatic radiation (254 nm). The radiation inside the photoreactor was assessed by uranyl oxalate actinometry (Kuhn *et al*., 2004) and the obtained value was 8.01 J/s at 254 nm. A solution of DPH (50 mg/L) was introduced in the reactor with TiO_2 (0.4 g/L), and immediately the lamps were switched on. Next H_2O_2 (150 mg/L) was added depending on the experiment to be carried out. Magnetic stirring was used to ensure a good mixing. The temperature of the solution was maintained constant at 25 ºC by the jacket connected to an ultra-thermostatic bath. In Figure A.16 in annex *H* it can see the diagram of installation.

5.1.3.2.Artificial irradiation: Black Blue Lamps (BLB) reactor

BLB reactor consists on a 2 L Pyrex-jacketed thermostatic vessel (inner diameter 11 cm, height 23 cm), equipped with three 8W BLB lamps (Philips TL 8W-08 FAM) located at the center of reactor. The lamps emit radiation between 350 and 400 nm, with a maximum at 365 nm. The radiation entering to the photoreactor was 1.97 J/s, measured by o-nitrobenzaldehyde actinometry (Kuhn *et al*., 2004). The used actinometry changes according to the wavelength range of lamp emission. The tank was fed with DPH solution (50 mg/L) and TiO_2 (0.4 g/L). Next H_2O_2 (150 mg/L) was added depending on the experiment to be carried out. The solution was maintained at constant temperature (25 ºC) by controlling the jacket temperature with an ultra-thermostatic bath. In Figure A.17 in annex *H* it can see the diagram of installation.

5.1.3.3.Artificial solar irradiation: Solarbox (SB)

A Solarbox (CO.FO.ME.GRA, 220V, 50 Hz) was used with a Xenon lamp (Phillips 1kW), located at the top of the device. The irradiation entering the photoreactor was 3.59 J/s measured also by o-nitrobenzaldehyde actinometry (Kuhn *et al.*, 2004). The tubular photoreactor (24 cm length, 2.11 cm diameter, Duran glass material) was placed at the bottom of the Solarbox on the axis of a parabolic mirror made of reflective aluminum. A filter cutting off wavelengths under 280 nm was placed between the lamp and the reactor. The DPH solution (50 mg/L) was prepared in a batch jacketed feeding tank (total volume 1L), connected to an ultra-thermostatic bath (HaaKe K10) to assure constant temperature during the process. Next H_2O_2 (15 or 150 mg/L) and TiO_2 (0.05, 0.1, 0.4 g/L) were added depending on the experiment to be carried out. The solution to be treated was pumped to solarbox by peristaltic pump (Ecoline VC-280 II, Ismatec) from the feeding tank with a flow-rate of 0.71 L/min. All connections employed were made of Teflon to avoid losses. In Figure A.18 in annex *H* it can see the diagram of installation.

5.1.3.4.Solar irradiation: CPC reactor

Photocatalytic experiments were also carried out in a solar pilot plant based on compound parabolic collectors (CPC), at the University of Barcelona. The CPC consists in a module, 41º inclined, with a mirror made of polished aluminum, with 6 parallel tubular quartz reactors (length 56 cm, inner diameter 1.75 cm, wall thickness 0.15 cm). The total volume irradiated was 0.95 L. The total mirror´s area for solar irradiation capture-reflection was 0.228 m^2. Experiments were done between 12:00 and 18:00 hours in summer and temperature was 30 ± 5 ºC. The exposure time was enough to reach the total hydrogen peroxide consumption. The aqueous suspension of DPH was pumped, with a peristaltic pump with a flow-rate 2.6 L/min, from the stirred (RW 16 basic agitator IKA) reservoir tank (5 L) to irradiated quartz tubes and continuously recirculated. Solar irradiation was measured by a spectroradiometer Bentham DMc300. The reservoir tank was fed with DPH solution (50 mg/L) and 0.4 g/L of TiO_2. Next H_2O_2 (150 mg/L) was added depending on the experiment to be carried out. In Figure A.19 in annex *H* it can see the diagram of installation.

5.2.RESULTS AND DISCUSSION

DPH degradation by photocatalysis was evaluated during one hour, in each experimental device, using different concentrations of H_2O_2 (15 and 150 mg/L) and

TiO_2 (0.05, 0.1 and 0.4 g/L). These TiO_2 and H_2O_2 concentrations can be broadly found in literature and they were also selected based on the previous group experience (Romero *et al*., 2011; Romero *et al*., 2013; Romero *et al*., 2015; Romero *et al*., 2016).

In this section, degradation and mineralization results are shown with respect to the accumulated energy (Q, kJ/L) (Eq. 2).

$$Q = \sum_{i=0}^{n} \frac{I \Delta t_i}{V} \qquad \text{(Eq.2)}$$

Where I is the incident photon flow (kJ/s), Δti is the time interval (s) and V is the volume of the treated solution (L).

Preliminary tests were performed to study the DPH adsorption onto the catalyst. A two-parameter isotherm model (Langmuir isotherm) was tested in the fitting of adsorption data (Eq. 3).

$$qe = \frac{q_m K_a C_e}{1 + K_a C_e} \qquad \text{(Eq.3)}$$

Where q_e (mol/g) is the DPH amount adsorbed on the catalyst, C_e (mg/L) is the DPH concentration in solution after adsorption, K_a is the Langmuir adsorption equilibrium constant (0.017 L/mol) and q_m represents the maximum monolayer adsorption capacity (0.048 mol/g). These low values of K_a and qm show that adsorption does not play an important role. In Figure A.20 of annex *I* it can see the adsorption isotherm of DPH on TiO_2.

Moreover, it was evaluated the temperature influence, 1 L of DPH solution with a concentration of 200 mg/L was placed in the stirred tank and heated at 20, 40, 60 and 80 °C. Degradation and/or mineralization were not observed at any tested temperature.

5.2.1. Photolysis

To evaluate DPH degradation by photolysis, experiments were carried out with 50 mg/L of DPH in the different reactors without catalyst. The influence of photolysis on DPH degradation and mineralization is low in SB, CPC and BLB (2.45, 1.38 and 4.66%, respectively). Only UVC light (31.48% of DPH removal in 60 min) is powerful enough to break the DPH bonds, because UVC covers the range of light absorption of DPH (λmax at 220 nm). Moreover, photolysis did not promote relevant mineralization (max. 4.66% for BLB). In Table 5.XI values of photolysis are summarized.

Table 5.XI. Percentage of photolysis under differet light sources

Experimental device	% DPH conversión at 60 min
SB	2.45
CPC	1.38
BLB	4.66
UVC	31.48

5.2.2. Photocatalysis

5.2.2.1.Effect of concentration catalyst

DPH degradation by photocatalysis was evaluated during one hour, in SB experimental device, using different concentrations of TiO_2 (0.05, 0.1 and 0.4 g/L). In Figure 5.21 the percentages of DPH conversion and TOC removal at 60 minutes using different TiO_2 load are presented.

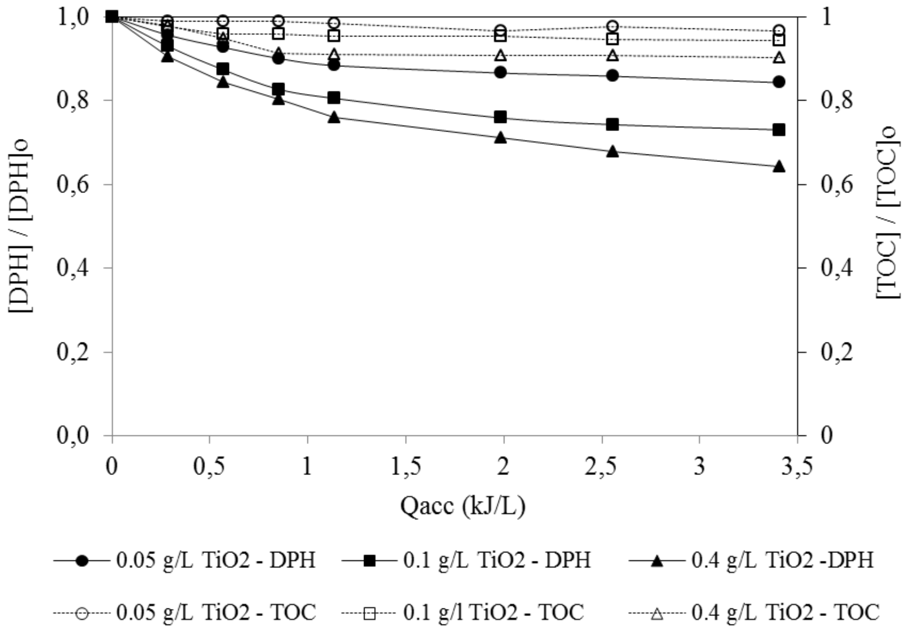


Figure 5.21. DPH conversion and TOC removal in SB reactor for different TiO_2 load.

DPH elimination at 60 minutes (Q: 3.41 kJ/L) was 35.7% (for 0.4 g/L TiO_2), 27% (for 0.1 g/L TiO_2) and 15.8% (for 0.05 g/L TiO_2). This is explained by the fact that having more catalyst particles in a specific volume, more light is absorbed and more electron-hole pairs are generated. Therefore, the reaction rate is faster. Moreover, having higher concentrations of catalyst, higher photocatalytic surface is avalaible and more molecules of DPH can be adsorbed. TOC removal is low and catalyst concentration does not present significant influence. Although high catalyst load improves DPH conversion, with concentrations higher than 0.4 g/L TiO_2, catalyst settling was observed in the reactor, which could increase radiation scattering, decreasing the reaction rate (Pastrana-Martínez *et al.*, 2012).

5.2.2.2.Influence of hydrogen peroxide

The effect of H_2O_2 addition was evaluated with 0.4 g/L of catalyst in SB 15 or 150 mg/L of H_2O_2 were added to 50 mg/L DPH solution directly in the feeding tank. The highest degradation of DPH was obtained with 150 mg/L of H_2O_2 (62.6%). The joint presence of UV, H_2O_2 and TiO_2 improves DPH degradation, because peroxide acts as additional source of hydroxyl radicals, improving the overall efficiency. Figure 5.22 shows the results of DPH conversion and mineralization vs. accumulated energy (Q, kJ/L) for three different H_2O_2 concentrations.

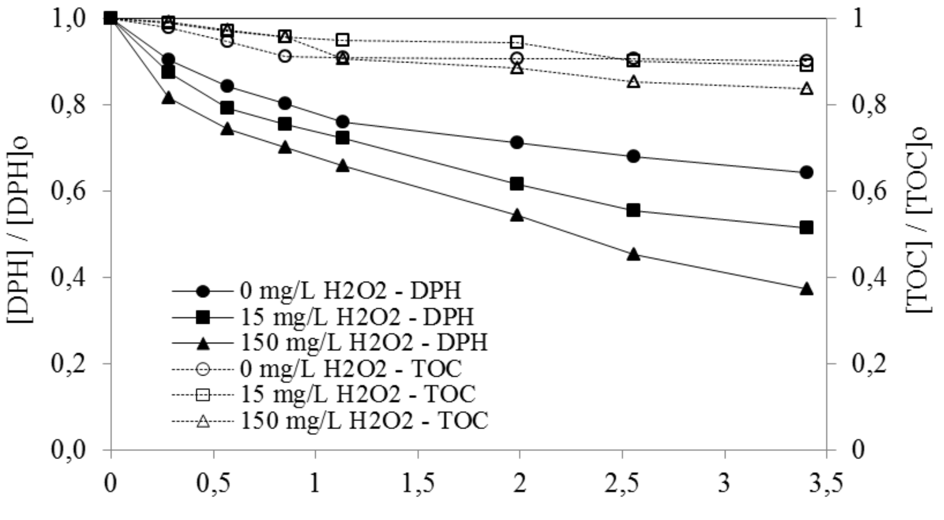


Figure 5.22. DPH conversion and TOC removal in SB reactor for different H_2O_2 concentration at 60 min. $[TiO_2]$= 0.4 g/L.

It is noted that with the addition of H_2O_2 DPH conversion is higher and this conversion is bigger when concentration of H_2O_2 is higher too. The percentage increase without H_2O_2 and 150 mg/L H_2O_2 is 43% approximately. It is a notable percentage. But this quantity of peroxide (150 mg/L) is very high. Peroxide can act as “scavenger”. That can to react with HO· decreasing its concentration in the solution. Therefore, there is less HO· to react with pollutants.

5.2.2.3.Comparison of photocatalyisis in SB, BLB, UVC and CPC reactors

DPH conversion and TOC removal were evaluated in four different experimental devices: SB, BLB, UVC and CPC. Experimental conditions were the same in all installations (50 mg/L DPH, 0.4 g/L of TiO_2 and two concentrations of H_2O_2 - 0 mg/L and 150 mg/L -). Differences were only related to the geometry of the reactors and type and amount of radiation. Table 5.XII shows the energy required to remove 1 mg of DPH in four devices (0.4 g/L TiO_2; 0 mg/L H_2O_2).

Table 5.XII. Energy required to remove 1 mg of DPH in four devices.

Device	Q (kJ/L) at 60 min	Energy / DPH removed (kJ/mg)at 60 min
BLB	3.81	0.12
UVC	10.8	0.34
SB	3.41	0.10
CPC	2.28	0.26

SB shows the best results in the range of wavelengths considered. The required energy for DPH removal is higher in CPC than SB. A likely explanation for these results can be related to the fact that the radiation field is defined by the radiation arriving at the photoreactor but also by the wavelength spectrum. In this way, wavelength spectrum is not the same for the solar light and for the Xe lamp (SB), which could explain the different behavior observed in CPC and SB. UVC presents the worst results in this range of wavelengths due to that device uses a powerful radiation.

As to DPH conversion and TOC removal the results are presented in Table 5. XIII. The reaction kinetics are presented too. These kinetics are pseudo-first order and were obtained from the slopes –ln $[DPH]/[DPH]_0$ vs. time of radiation at 60 min.

Table 5.XIII. DPH and TOC removal by photocatalysis for the four different devices at 60 min and consants kinetics.

Device	**H_2O_2 (mg/L)**	**TiO_2 (g/L)**	**% DPH conversion at 60 min**	**% TOC removal at 60 min**	**$k \cdot 10^{-3}$ (h^{-1})**
BLB	0	0.4	30.80	7.42	6.34
BLB	150	0.4	36.05	9.90	6.60
UVC	0	0.4	31.70	8.71	6.36
UVC	150	0.4	100.00	28.58	31.35
SB	0	0.4	35.70	9.80	6.57
SB	15	0.4	44.51	10.09	11.02
SB	150	0.4	62.60	11.94	15.05
CPC	0	0.4	8.77	1.58	1.96
CPC	150	0.4	53.89	12.51	2.98

BLB and UVC present similar performances removing DPH without H_2O_2 (30.80% and 31.70%, respectively). Although the UVC lamps used are monochromatic (maximum at 254 nm) TiO_2 generally does not absorb at this wavelength, 31.7% of DPH conversion was obtained due to photolysis and photocatalysis. In BLB and UVC reactors, the radiation absorption by the solution is favored by the geometry of the systems, because the lamps are located at the center of the reactor. SB presents the best results removing DPH without H_2O_2 (35.70%). TiO_2 absorb radiation between 300-400 nm and lamps used in SB emit from 290 nm. TiO_2 can be activated. As CPC presents the worst results removing DPH (8.77%). These differences are explained due to wavelength spectrum is not the same for the solar light and for the Xe lamp (SB). CPC requires more time of experiment for degradate the same percentage as the SB. Afetr 360 minutes (Q: 36 kJ/L) DPH conversion was 49.2%. It can be related to the richness of Xe lamp in the UV wavelength range useful for TiO_2 absorption.

As seen in Table 5.XIII, the addition of a source of $OH^{\cdot}$ radicals, as H_2O_2, improves the DPH conversión in each device. UVC presents the best results removing DPH with 150 mg/L of H_2O_2 (100%). As it stated above TiO_2 does not absorb at 254 nm. Total conversión of DPH is due to the joint of photolysis and UV/H_2O_2. SB presents good results removing DPH obtaining a value of 62.60% with 150 mg/L H_2O_2. This value is due to the richness of Xe lamp in the UV wavelength range for TiO_2 absorption and the addition of a source of OH· radicals in the system. CPC presents a good results too (53.89%). In this case BLB displays the worst results for DPH conversión (36.05%).

TOC removal without H_2O_2 is similar in BLB, UVC and SB devices (7.42%, 8.71% and 9.80%). In CPC TOC removal is very low (1.58%). But its DPH conversión is very low too. Again, these values are consistent with the avarage wavelength in each device and TiO_2 absorption wavelength range. Like DPH conversión the addition of a source of OH· radicals, as H_2O_2, improves the TOC removal in each device. BLB, UVC, SB and CPC present results of 9.90%, 28.58%, 11.94% and 12.51%, respectively with 150 mg/L H_2O_2.

Concerning the reaction kinetics, results fit better regarding accumulated energy instead of irradiation time, because, if only time is considered, the radiation entering the reactors is omitted, which can lead to a misinterpretation of the results. As it observes in Table 5.XIII.the kinetics constants in BLB, UVC and SB are similars without H_2O_2 (6.34 h^{-1}, 6.36 h^{-1} and 6.57 h^{-1}, respectively). CPC presents the worst results about kinetic constant obtainig a value of 1.96 h^{-1}. Again, the addition of a source of OH· radicals, increases the kinetics constants in each device. BLB, UVC, SB and CPC present results of 6.60 h^{-1}, 31.35 h^{-1}, 15.05 h^{-1} and 2.98 h^{-1}, respectively with 150 mg/L H_2O_2. UVC shows the best results removing total DPH at 30 minutes.

5.2.2.4.Intermediates and degradation pathways

Identification of intermediates was performed with samples taken at 120 min of irradiation in all the devices, with 50 mg/L of DPH and 0.4 g/L of TiO_2. The intermediates identified are shown in Table A.XIV in annex *J*.

According to the intermediates found and their proposed structures, several degradation pathways can be proposed (Figure A.23) in annex *J*.

In SB reactor due to OH· generation by TiO2 photoabsorption, it is logical to expect the addition of OH· on the aromatic ring (Menachery *et al.*, 2015) leading to the formation of DPH-274. Moreover, the hydroxycyclohexadienyl form of DPH-274 could be attacked by OH· forming a compound with a trihydroxyl (DPH-290) (Menachery *et al.*, 2016). In all the photoreactors studied, the photocatalytic process lets to the formation of m/z 183 and m/z 90 (DPH-90). This could be by the benzylic dissociation via proton transfer within an intermediate ion-neutral complex (DPH-272) (Menachery *et al.*, 2015). Meanwhile, DPH-272 could be formed from DPH-256 by the H-abstraction from the carbon group of the alkylamine and a hydroxylation of the ending carbon of the chain. Moreover the dissociation of oxygen from hydroxyl group of the ether group of DPH-90 may generate the DPH-72 compound. In SB and BLB devices, the hydroxyl addition on alkylamine chain of DPH- 272 can lead to m/z 167 (DPH-167) and m/z 88 (DPH-88) fragments via proton transfer within an intermediate ion-neutral complex (Menachery *et al.*, 2015). The mechanism leading to the formation of DPH-194 compound is initiated by the attack of OH· on the orto position of DPH-256 followed by the elimination of a phenol and the subsequent oxidation (Menachery *et al.*, 2016).

5.3.ECONOMICAL CONSIDERATION

As previously stated, in this study different energetic radiation were used to evaluate their contribution to DPH removal. To assess the suitability of these methods for real applications, cost estimation was carried out in order to compare them from an economic point of view. The calculation was based in the work of Bolton (Bolton *et al.*, 2001) with which is possible to normalize the efficiency of the AOPs. Thus, the electrical energy per order of magnitude (EEO) was calculated taking into account electricity costs of irradiation, mixing, and chemicals, all of them normalized to the reactor volume. The number of orders of magnitude was calculated from the percentage of DPH degradation. Finally, technical-scale commercial prices were taken for chemical reagents used and converted to energy values of Catalonia (Spain) in 2016 (0.149 €·kWh^{-1}).

Table A.XV. in annex *K* shows the conversion prices of chemicals and reagents to energy values. Table A.XVI. in the same annex shows the energy requirements of the experiments performed in different experimental devices.

It is observed that UVC reactor (0.4 g/L of TiO_2 and 150 mg/L of H_2O_2) shows the best results (4,354.07 Wh (L·order)$^{-1}$) due to this experiment presents total DPH remove. This value could be lower because total DPH was removed at 30 minutes. At 60 minutes had H_2O_2 yet. CPC (0.4 g/L of TiO_2) presents the worst results (48,500.01 Wh (L·order)$^{-1}$). It have to take into account that radiation is free because is solar radiation. But are required more hours for degradate the same percentage of DPH.

5.4.CONCLUSIONS

- All experimental devices studied (UVC, BLB, SB and CPC) may be use for DPH degradation.
- No absorption of DPH occurs on the surface of TiO_2. Termodegradation not been observed. In this way all degradation of DPH is due to advanced oxidation process.
- Photolysis was negligible in SB, BLB and CPC (2.45%, 4.66% and 1.38%, respectively). Only UVC light (31.48%) is powerful enough to break the DPH bonds. Photolysis did not promote relevant mineralization (max. 4.66% for BLB).
- Concentration of catalyst affects to DPH degradation. Best results are presented with 0.4 g/L of TiO_2 (35.70% in SB).
- SB shows the best results in the range of wavelengths considered without peroxide (0.10 kJ/mg at 60 minutes). UVC presents the worst results in this range of wavelengths without peroxide due to that device uses a powerful radiation (0.34 kJ/mg at 60 minutes).
- SB shows the best results removing DPH without H_2O_2 than the other devices. Obtaining a removal value of 35.70% at 60 minutes.
- UVC presents the best results removing DPH with 150 mg/L of H_2O_2 (100%). But total conversión of DPH is due to the joint of photolysis, photocatalysis and UV/H_2O_2. However, SB presents good results removing DPH obtaining a value of 62.60% with 150 mg/L H_2O_2.
- The addition of a source of $OH^{\cdot}$ radicals, as H_2O_2, improves the degradation of DPH in each device. Moreover, best results are shown with 150 mg/L H_2O_2 than with 15 mg/L of H_2O_2.
- The addition of a source of $OH^{\cdot}$ radicals, as H_2O_2, improves the TOC removal in each device. But this value is very low in all experiments.
- The kinetics constants are similar in UVC, BLB and SB without H_2O_2 (6.36 h^{-1}, 6.34 h^{-1} and 6.57 h^{-1}, respectively). CPC presents a low kinetic constant both with H_2O_2 and without it (1.96 h^{-1} and 2.98 h^{-1}). The addition of a source of $OH^{\cdot}$ radicals, as H_2O_2, improves the velocity of degradation in each device.
- The intermediates obtained in the photocatalytic treatment of DPH, without hydrogen peroxide, show that hydroxyl radicals mostly attack the aromatic ring

only if TiO_2 is photoactivated. The H-abstraction from the carbon group of the alkylamine chain is the most probably mechanism of the degradation in the other cases.

- As to economical consideration it is observed that UVC reactor (0.4 g/L of TiO_2 and 150 mg/L of H_2O_2) shows the best results (4,354.07 Wh $(L·order)^{-1}$). CPC (0.4 g/L of TiO_2) presents the worst results (48,500.01 Wh $(L·order)^{-1}$). It have to take into account that radiation is free because is solar radiation. But are required more hours for degradate the same percentage of DPH.

5.5.RECOMMENDATIONS

- It would be necessary to carry out experiments with other concentration of H_2O_2 for to evaluate the optimal dose of this reagent and to evaluate its scavenger effect.
- As to CPC experiments should be performed on days with similar radiation in order to make more precises comparisions.
- Regarding the project in general, experiments could be replicated thrice in order to have more reliable results and to calculate the error.
- It would be necessary to follow other parameters such as COD (Chemical Oxygen Demand) BOD (Biological Oxygen Demand) and toxicity to complement the performance of these techniques.
- To perform a study of environmental impact in order to establish a comparison both economic and environmental referring to efficiency of advanced oxidation processes.
- It would be advisable to study the degradation of DPH in real waters to determine if DPH degradation follows the same trends.
- To complement the study of photocatalysis would be interesting to investigate the same experiments with other catalysts to carry out comparisons and trying to improve the process.
- It would be very advisable to carry out a study of intermediate compounds where there is the addition of H_2O_2.

6. LITERATURE

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7. ANNEXES

ANNEX A: Installation set-up

Figure A.6. Installation set-up

Figure A.7. Installation set-up

Figure A.8. Sampling pump with activated carbon tube

ANNEX B: Characteristics of photo-reactor

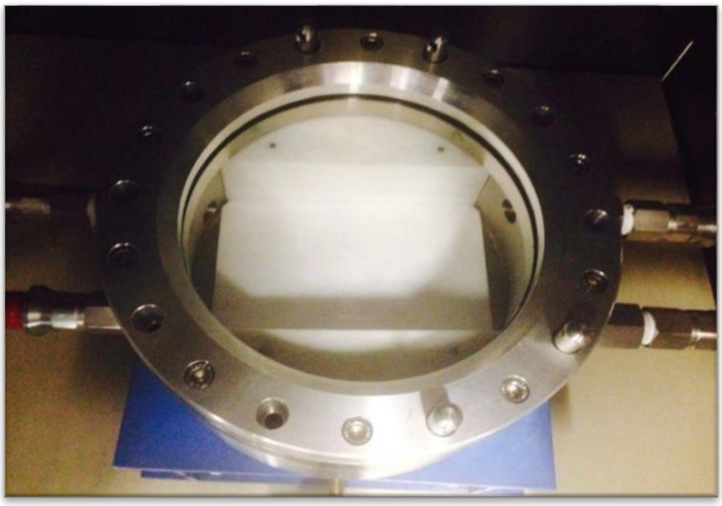


Figure A.9. Photoreactor

Table A.VI. Characteristics of photoreactor.

Photoreactor	
Internal diameter	16 cm
External diameter	4.6 cm
Volume of photoreactor	0.64 L
Glass	Borosilicate of 5 mm of thickness

ANNEX C: Characteristics of the sampling pump

Table A.VII. Main features of sampling pump.

Sampling pump	
Operation range	5-4,000 ml/min. An adapter is required to work in conditions 5-500 ml/min.
Flow control	±5%
Flow switch	0.5-5.5 L/min
Temperature of operation	-20 ºC to 40 ºC
Moisture of operation	0 to 95% RH

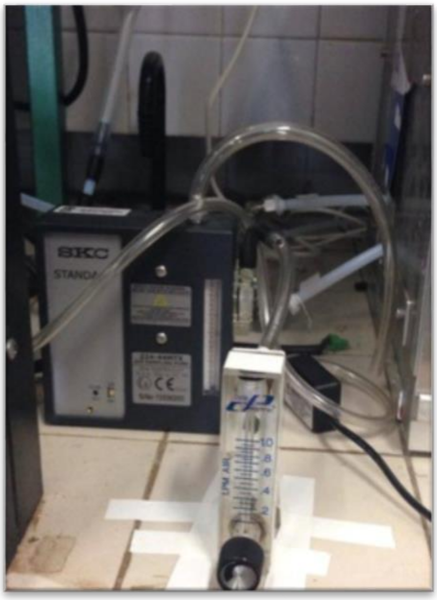


Figure A.10. Sampling pump with rotameter

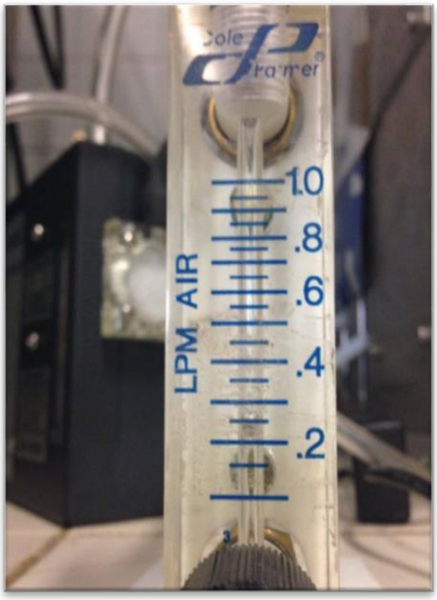


Figure A.11. Rotameter (Flow rates until 1L/min).

ANNEX D: Calibration curve of toluene

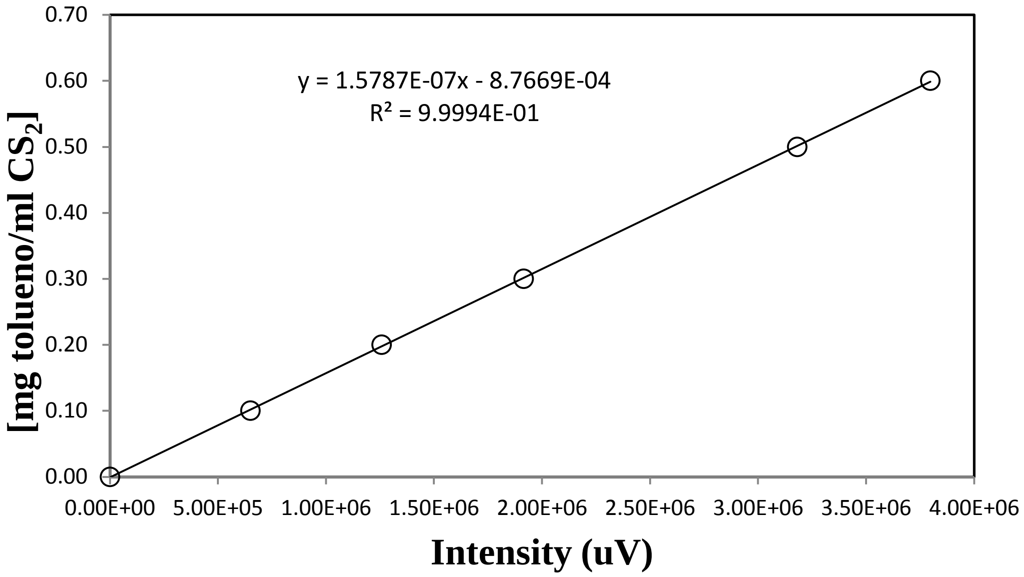


Figure A.12. Calibration curve of toluene

ANNEX E: Chromatographs of toluene

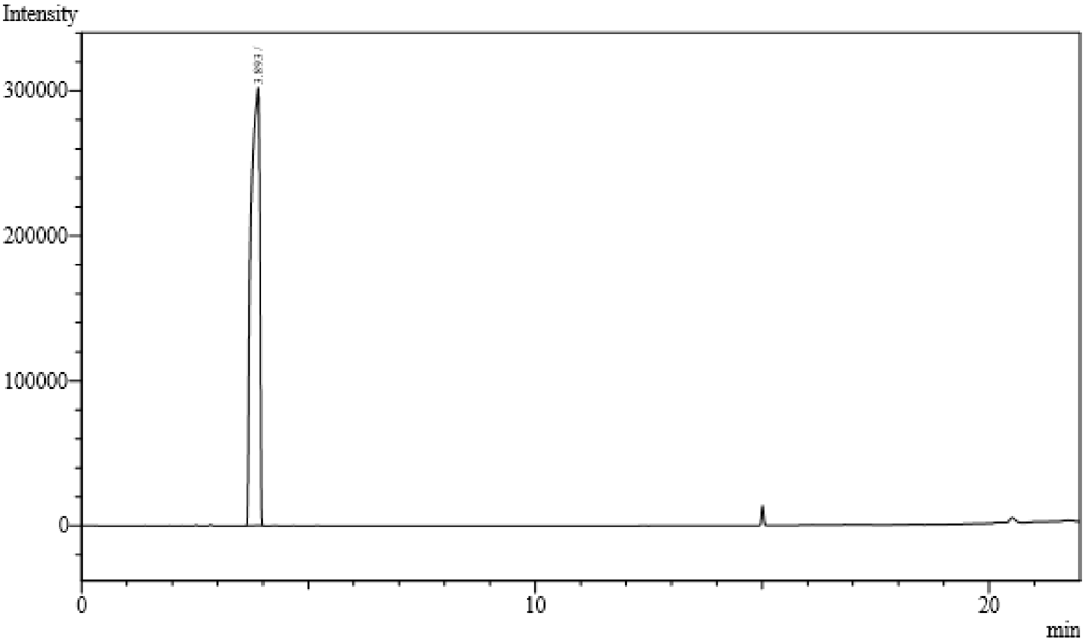


Figure A.13. Chromatography of toluene [Flow rate of toluene: 0.5 L/min; Time: 10 minutes]. (1% of recovery).

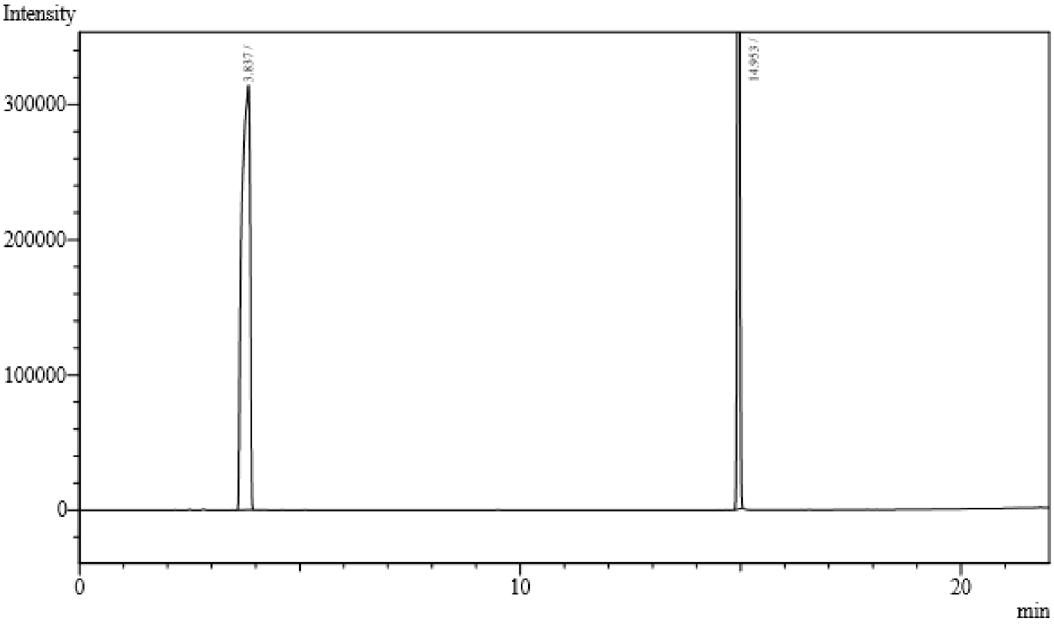


Figure A.14. Chromatography of toluene [Flow rate of toluene: 0.5 L/min; Time: 10 minutes]. (97% of recovery).

ANNEX F: Experiments performed in gas phase

Table A.VIII. Different experiments perforormed in gas phase

Experiment	Flow of toluene [L/min]	Flow of air [L/h]	Total flow [L/min]	Time of experiment [min]	Radiation [W/m^2]	Moisture [%]	Catalyst [TiO_2]
Adsorption	0.50	-	0.50	10	-	-	√
Photolysis	0.50	-	0.50	10	28.43	-	-
200 mg/m^3 toluene	0.40	96.00	2.00	12	15.00	49	√
200 mg/m^3 toluene	0.40	96.00	2.00	12	28.20	51	√
200 mg/m^3 toluene	0.20	48.00	1.00	24	25.60	57	√
200 mg/m^3 toluene	0.10	24.00	0.50	48	25.73	47	√
100 mg/m^3 toluene	0.20	108.00	2.00	20	27.59	52	√
100 mg/m^3 toluene	0.10	54.00	1.00	30	26.20	48	√
50 mg/m^3 toluene	0.10	114.00	2.00	30	28.50	53	√

ANNEX G: Characteristics of diphenhydramine hydroclhoride

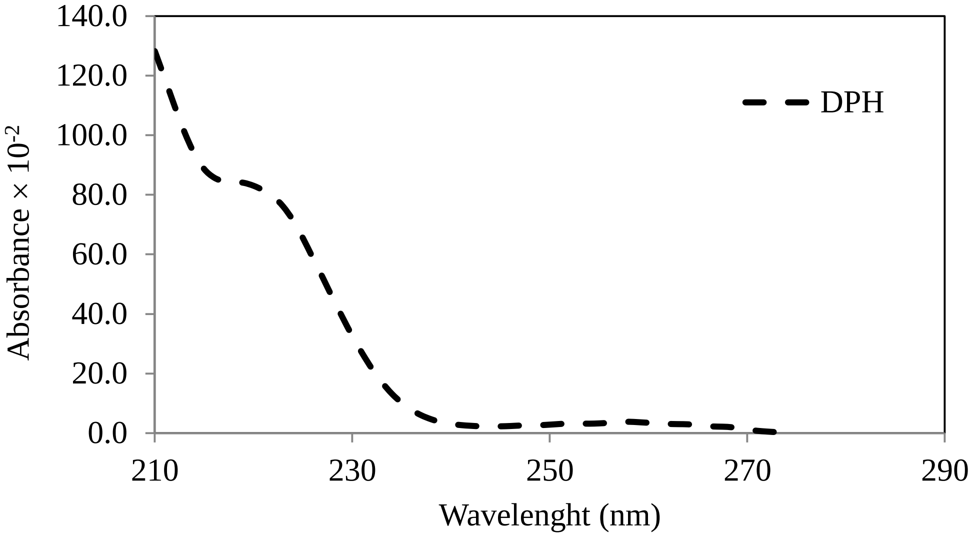


Figure A.15. Ultraviolet spectrum of DPH. It presents the absorbance peak at a wavelenght of 200 nm.

ANNEX H: Experimental devices in liquid phase

Figure A.16. UVC reactor [Source: Romero, 2015].

Figure A.17. BLB reactor [Source: Romero, 2015].

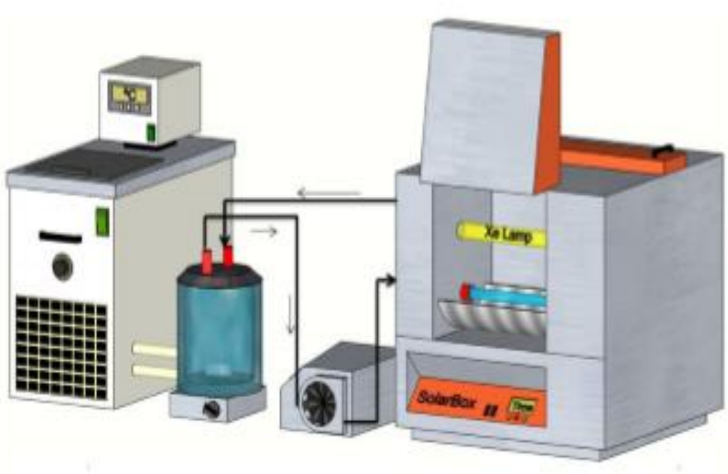


Figure A.18. Solarbox device [Source: Romero, 2015].

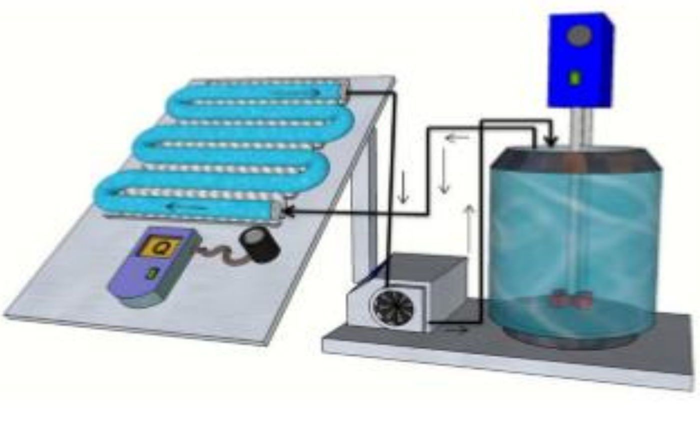


Figure A.19. CPC device [Source: Romero, 2015].

ANNEX I: Adsorption of DPH on TiO_2

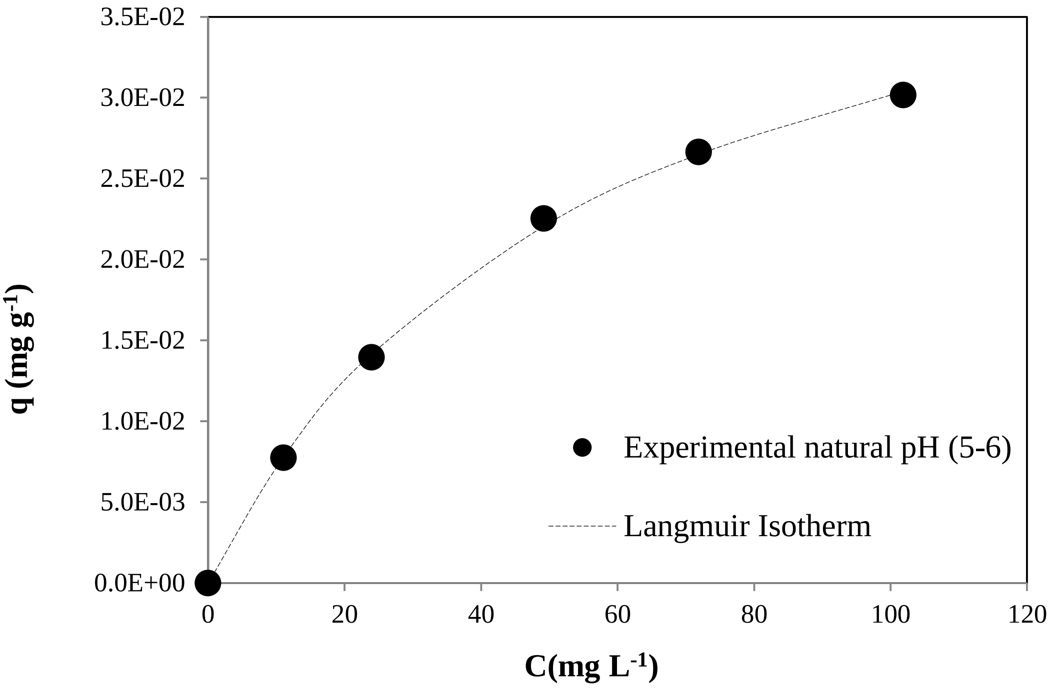


Figure A.20. Adsorption isotherm of DPH on TiO_2.

ANNEX J: Intermediates and degradation pathways

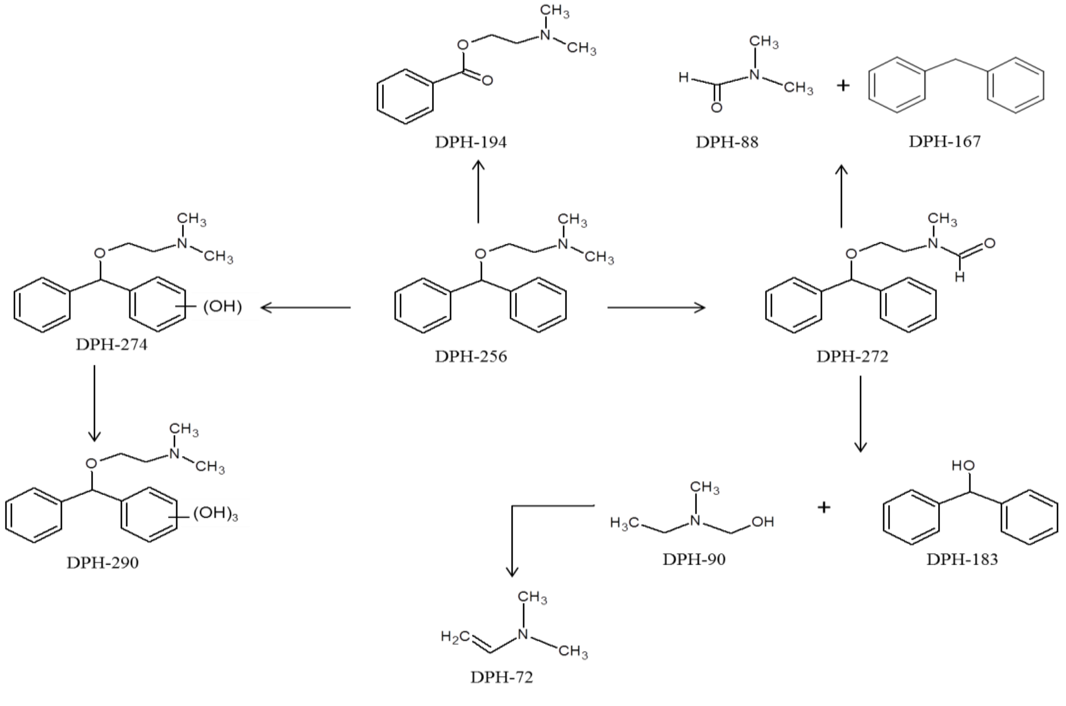
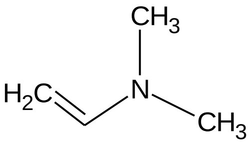
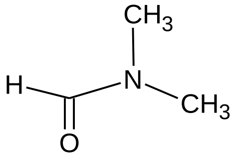
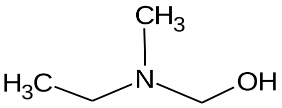
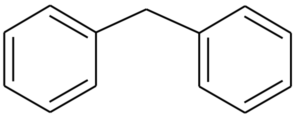
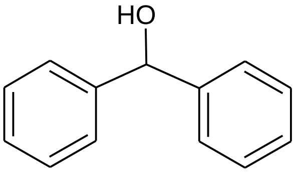
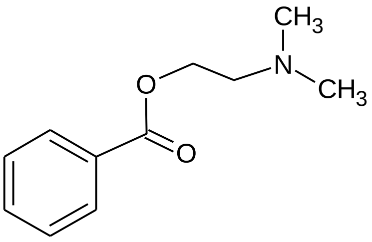
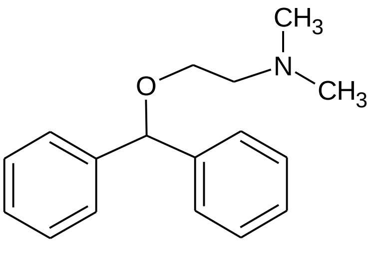
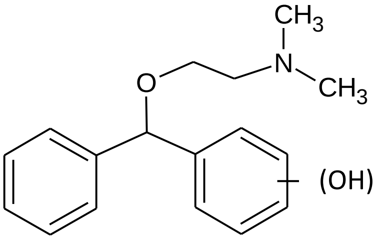
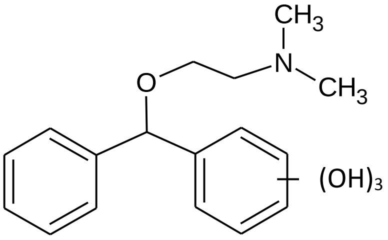


Figure A.23. Proposed DPH degradation pathways for photocatalytic process.

Table A. XIV. DPH and its main intermediates detected by LC/MS analysis in photodegradation experiments.

m /z **(Da)**	**Elemental composition**	**Proposed structure (Label)**	**Light Source**		
			UVC	**BLB**	**SB**
72	$C_4H_{10}N$	 DPH-72		√	√
88	$C_4H_{10}NO$	 DPH-88		√	√
90	$C_4H_{12}NO$	 DPH-90	√	√	√
167	$C_{13}H_{11}$	 DPH-167		√	√
183	$C_{13}H_{12}O$	 DPH-183	√	√	√
194	$C_{11}H_{16}NO_2$	 DPH-194	√	√	√
256	$C_{17}H_{22}NO$	 DPH-256	√	√	√

m /z **(Da)**	**Elemental composition**	**Proposed structure (Label)**	**Light Source**		
			UVC	**BLB**	**SB**
274	$C_{17}H_{20}NO_2$	 DPH-274			√
290	$C_{17}H_{22}NO_3$	 DPH-290			√

ANNEX K: Economical consideration

Table A.XV. Conversion prices of chemicals and reagents to energy values.

Reagents	**Company**	**Art. no.**	**Volume [L]**	**%**	**ρ [g·ml^{-1}]**	**Price [€]**	**[kg]**	**[€·(kWh)$^{-1}$]**	**[€·kg^{-1}]**	**[Wh· g^{-1}]**
H_2O_2	Merck	1.410.761.211	1	30	1.11	21.25	0.3	0.15	70.83	510.84
TiO_2	Sigma-Aldrich	718467	-	99	-	144.00	0.1	0.15	1,454.54	10,490.16

Table A. XVI. Energy requirements of the experiments performed in different experimental devices.

Treatments	**Time [s]**	**OM [-]**	**$E_{E,\,mix}$ [Wh L^{-1}]**	**$E_{E,pro}$ [Wh L^{-1}]**	**$E_{E,chem}$ [Wh L^{-1}]**	**$E_{E,tot}$ [Wh L^{-1}]**	**$E_{EO,rx}$ [Wh(L·order)$^{-1}$]**	**$E_{EO,tot}$ [Wh (L·order)$^{-1}$]**
SB [0,05 g·L^{-1} TiO$_2$]	3600	0.16	15	1000	529.80	1,544.80	9,706.89	9,802.07
SB [0,1 g·L^{-1} TiO$_2$]	3600	0.27	15	1000	1,059.61	2,074.61	7,619.72	7,675.22
SB [0,4 g·L^{-1} TiO$_2$]	3600	0.36	15	1000	4,238.45	5,253.45	14,673.53	14,715.54
SB [0,4 g·L^{-1} TiO$_2$ - 15 mg/L H$_2$O$_2$]	3600	0.48	15	1000	4,246.11	5,261.11	10,832.36	10,863.33
SB [0,4 g·L^{-1} TiO$_2$ - 150 mg/L H$_2$O$_2$]	3600	0.63	15	1000	4,315.07	5,330.07	8,490.54	8,514.50
BLB [0,4 g·L^{-1} TiO$_2$]	3600	0.33	15	24	4,238.45	4,277.45	13,123.30	40,404.27
BLB [0,4 g·L^{-1} TiO$_2$ - 150 mg/L H$_2$O$_2$]	3600	0.36	15	24	4,315.07	4,354.07	12,032.95	12,074.54
UV-C [0,4 g·L^{-1} TiO$_2$]	3600	0.22	15	24	4,238.45	4,277.45	19,687.99	19,757.27
UV-C [0,4 g·L^{-1} TiO$_2$ - 150 mg/L H$_2$O$_2$]	3600	1	15	24	4,315.07	4,354.07	4,339.07	4,354.07
CPC [0,4 g·L^{-1} TiO$_2$]	3600	0.09	15	-	4,238.45	4,253.45	48,328.97	48,500.01
CPC [0,4 g·L^{-1} TiO$_2$] /- 150 mg/L H$_2$O$_2$]	3600	0,54	15	-	4,315.07	4,330.07	8,007.19	8,035.03

Symbology used

ρ [g mL^{-1}]	Density
OM[-]	Magnitude order = ([C_i]-[C_t])/[C_i]
E_E, mix[Wh L-^{1}]	Electric power for mixing
E_E, pro[Wh L-^{1}]	Electric power for irradiatio
E_E, chem[Wh L^{-1}]	Cost of reagents become to energy
E_E, tot[Wh L^{-1}]	Total electric power
E_{EO}, rx[Wh (L·order)$^{-1}$]	Electric power for irradiation per magnitude order
E_{EO}, tot[Wh (L·order)$^{-1}$]	Total electric power per magnitude order