Dr. Jaume Giménez Farreras Dra. Pilar Marco Buj Departamento de Ingeniería Química y Química Analítica



# **Treball Final de Grau**

Tiapride drug treatment by Advanced Oxidation Processes Tratamiento del fármaco Tiaprida mediante Procesos de Oxidación Avanzada

Adrián Marí Espinosa

June 2017



Aquesta obra esta subjecta a la llicència de: Reconeixement-NoComercial-SenseObraDerivada



http://creativecommons.org/licenses/by-ncnd/3.0/es/

A mis padres.

# CONTENTS

รเ	JMMARY	i
RESUMEN		iii
1.	INTRODUCTION	1
	1.1. PHARMACEUTICAL COMPOUNDS	1
	1.1.1. Toxic effects	2
	1.1.2. Tiapride	3
	1.2. ADVANCED OXIDATION PROCESSES	3
	1.2.1. Mechanism of action	3
	1.2.2. Benefits and drawbacks	4
	1.2.3. AOP techniques	4
	1.2.3.1. Direct photolysis	5
	1.2.3.2. UV, hydrogen peroxide	5
	1.2.3.3. Fenton	5
	1.2.3.4. Photo-Fenton	6
	1.2.3.5. Heterogeneous photocatalysis	7
2.	OBJECTIVES	9
3.	MATERIALS AND METHODS	11
	3.1. REAGENTS	11
	3.2. ANALYTICAL METHODS	12
	3.2.1. pH measurement	12
	3.2.2. Determination of hydrogen peroxide	12

3.2.3. Determination of iron (II) and total iron	13
3.2.4. Determination of Tiapride concentration	13
3.2.5. Determination of total organic carbon	14
3.2.6. Determination of toxicity	14
3.3. EXPERIMENTAL DEVICES	14
3.3.1. BLB reactor	14
3.3.2. Solarbox reactor	15
3.4. EXPERIMENTAL PROCEDURE	16
4. RESULTS AND DISCUSSION	19
4.1. DESIGN OF EXPERIMENTS	19
4.2. BEZOYA MINERAL WATER CARACTERIZATION	21
4.3. DIRECT PHOTOLYSIS	22
4.4. EXPERIMENTS WITH IRON (II)	23
4.5. EXPERIMENTS WITH HYDROGEN PEROXIDE	24
4.6. FENTON	25
4.7. PHOTO-FENTON	25
4.7.1. Comparison between Fenton and photo-Fenton processes	27
4.7.2. Study of the effect of iron (II) in photo-Fenton process	28
4.7.3. Study of the effect of $H_2O_2$ in photo-Fenton process	29
4.8. HETEROGENEOUS PHOTOCATALYSIS	30
4.8.1. Study of the light action in heterogeneous photocatalysis proc with $\text{TiO}_2$	ess 31
5. CONCLUSIONS	33
REFERENCES AND NOTES	35
ACRONYMS	37

# APPENDICES

# APPENDIX 1: CONCENTRATIONS, DEGRADATION AND MINERALIZATION DURING EACH EXPERIENCE AT DIFFERENT TIMES 41

# SUMMARY

In recent years, it has been observed the appearance of a great amount of organic compounds in wastewaters, rivers and other surface flows. This compounds are pesticides or biocides, hygienic and personal care products, surfactants, antiseptics, flame retardants, disinfection subproducts, gasoline additives and even drugs. These compounds are known as emerging pollutants.

Emerging pollutants tend to present a high molecular weight, an elevated persistence and a high toxicity, in addition they are not regulated by law. Moreover, in most cases, it is not known the risk they exert on the human health and on the environment. Furthermore, in the wastewater treatment plants (WWTPs), which work through biological treatments, it is not possible to remove them completely due to their high stability.

Advanced Oxidation Processes (AOPs) are techniques developed in the last decades able to remove or increase the biodegradability of such compounds so that the effectiveness of biological treatments is augmented. These techniques are based on the formation of radicals with elevated oxidation power, such as hydroxyl radicals (HO•), capable of removing and mineralizing the pollutant molecules.

In this work, the degradation and the mineralization of the pharmaceutical compound Tiapride, a neuroleptic used to treat mental illness, has been studied through Photolysis, Fenton and Photo-Fenton techniques in reactors with BLB (Black Light Blue) lamps and Heterogeneous Photocatalysis in a Solarbox reactor. Moreover, it has also been studied the interaction of the compound with Fe<sup>2+</sup> ions and hydrogen peroxide in absence and presence of UV light, and with titanium oxide (IV) in absence of radiation.

Photo-Fenton has been the Advanced Oxidation Process that achieved the best results. A 98.7% of degradation and a 44.4% of mineralization was obtained using concentrations of 100 ppm of  $H_2O_2$ , 10 ppm of  $Fe^{2+}$  and 50 ppm of Tiapridre.

**Keywords**: Tiapride, Photolysis, Fenton, Photo-Fenton, Heterogeneous Photocatalysis, emerging pollutant, degradation, mineralization.

# RESUMEN

Estos últimos años se ha observado la aparición de una gran variedad de compuestos orgánicos en aguas residuales, ríos y otras corrientes superficiales. Estos compuestos son pesticidas o plaguicidas, fármacos, productos de higiene personal y belleza, surfactantes, antisépticos, retardantes de llama, subproductos de desinfección, aditivos de la gasolina e incluso drogas de abuso. Son conocidos como contaminantes emergentes.

Los contaminantes emergentes acostubran a tener un elevado peso molecular y son altamente persistentes y de elevada toxicidad, además de no estar regulados por la ley. A todo esto hay que añadir, en muchos casos, el desconocimiento acerca de los riesgos que representan para la salud humana y el medioambiente. Además de todo ello, en las estaciones depuradoras de aguas residuales (EDAR), que funcionan mediante tratamientos biológicos, no es posible eliminarlos por completo a causa de su elevada estabilidad.

Los Procesos de Oxidación Avanzada (AOPs) son técnicas desarrolladas en las últimas décadas capaces de eliminar este tipo de compuestos o aumentar su biodegradabilidad para incrementar la eficacia del tratamiento biológico. Estas técnicas se basan en la formación de radicales de un elevado poder oxidante, como los radicales hidroxilo (HO•), capaces de eliminar y mineralizar las moléculas de contaminante.

En este trabajo, la degradación y mineralización del fármaco Tiaprida, un neuroléptico utilizado en el tratamiento de enfermedades mentales, ha sido estudiada mediante técnicas de Fotólisis, Fenton y Foto-Fenton en un reactor con lámparas BLB (Black Light Blue), y Fotocatálisis Heterogénea en un reactor Solarbox. Además se han estudiado las interacciones del compuesto con iones Fe<sup>2+</sup> y peróxido de hidrógeno en ausencia y presencia de luz UV, y con óxido de titanio (IV) en ausencia de radicación.

Foto-Fenton ha sido el Proceso de Oxidación Avanzada con el que se han obtenido mejores resultados. Se obtuvo un 98,7% de degradación y un 44,4% de mineralización utilizando concentraciones de 100 ppm de  $H_2O_2$ , 10 ppm de  $Fe^{2+}$  y 50 ppm de Tiaprida.

**Palabras clave**: Tiaprida, Fotólosis, Fenton, Foto-Fenton, Fotocatálisis Heterogénea, contaminante emergente, degradación, mineralización.

# **1. INTRODUCTION**

Without water, most of living organisms would not exist. Its presence for life is essential because it is a very important factor for the development of biological processes. In human society, it plays a very importante role, being used for personal and household cleaning, for cooking and for consumption. In addition, in the industry it is used as reagent and solvent for many processes.

Hazardous organic waste, widely spread in water by industrial, domestic and military sources, is an emerging issue. The increase of world population and the development of the industry has led to an increase in the use and demand of water putting at risk its quantity and quality. In the last years, it has been observed the appearence of a great and diverse amount of organic compounds in wastewaters, rivers and other surface flows due to this use. These compounds (emergint contaminants) are not regultad by law due their low concentration, but their effects in human health and environment are not known.<sup>1</sup> All beauty products, cleaning products, medicinies as well as industrial waste end up depositing in the water causing a high risk for human health and ecosystems.

This is a very serious problem, life is not concived without water. That is why a serie of methods are being developed in order to clean the water of pollutants aiming not to compromise the survival of future generations.<sup>2</sup>

In this work, the decomposition of pharmaceutical compound Tiapride will be carried out using a few techniques of Advanced Oxidation Processes.

## 1.1. PHARMACEUTICAL COMPOUNDS

As known, a pharmaceutical compound is a bioactive molecule capable of interacting with protein macromolecules, mainly located in the membrane, cytoplasm or nucleus of the cell, giving raise to an action with evident response. On the other hand, a medicament is the pharmaceutical

compound after being conditioned. The objective of conditioning the pharmaceutical compounds is to obtain the maximum therapeutic benefit and the minimal side effects.

In *Table 1*, there is a list with some types of pharmaceutical compounds and the type of treatment they perform.

Categories	Treatment	
Analgesic	Against pain	
Antibiotic	Against bacterial infections	
Antidepressant	Against depression	
Antipyretic	Against fever	
Antypsychotic	Against psychosis or other mental or emotional procedures	
Cytostatic	To disrupt cell division, useful for cancer treatment	

Table 1. Different categories of drugs and their utility

#### 1.1.1. Toxic effects

Between 50 and 90% of medicines are excreted through the urine into the sewers. This residues are the main threat to aquatic life and water. Due to the non-existence of 100% effective elimination methods, these compounds become food for fishes, molluscs and other types of aquatic life when water is returned to aqueous effluents, producing effects like problems in the reproduction or reducing the defenses of their immunologic system.

Pharmaceuticals present a great diversity of problems depending on the category and on the pharmaceutic in particular.

In humans, antibiotics are quite dangerous, not only because they can cause alterations in the intestinal flora, but because resistant bacteria that are immune to the drug may appear. Moreover, anticarcinogenics are mutagenic and toxic for reproduction, or hormones, such as estrogens, can affect human development.

In addition, pharmaceuticals are commonly very persistent compounds and intoxication is not just produced for use or consume water, eat contaminated fishes or molluscs is another way to get intoxicated.

#### 1.1.2. Tiapride

In this work, the treated pharmaceutical will be the Tiapride (see estructure in *Figure 1*). It is an atypical neuroleptic which shows selectivity for D2 and D3 dopaminergic receptors. Its clinical use is directed to diseases such as severe agression and behaviour disorders, dysphoria, Huntington's disease or Tourette's Syndrome.



Figure 1. Molecular estructure of Tiapride

## 1.2. ADVANCED OXIDATION PROCESSES

Emerging pollutants, such as pharmaceuticals, can be persistent, toxic and hardly biodegradable. It is needed a strong photochemical potential to carry out their decomposition. Advanced Oxidation Processes include different treatments able to eliminate these organic compounds in water and wastewaters. These treatments are based on the formation of highly reactive radicals, such as hydroxil radicals (HO•), capable of removing a wide range of contaminants that can not be degraded by biological processes.<sup>3</sup>

#### 1.2.1. Mechanism of action

These techniques show a common mechanism of action. First of all, it is necessary the formation of strong oxidants. As commented before, hydroxil radical is the one with the highest oxidizing potential (2.8 V), greater than other known oxidant species as ozone (2.7 V), hydrogen peroxide (1.78 V) or chlorine dioxide (1.56 V). Then, the reaction of these oxidants ocurrs with the contaminants that are in the water forming reaction intermediates. It is important to form a sufficient amount of oxidants in order to obtain a good degradation of the pollutant. Meanwhile, the oxidants react with the intermediates as well, carrying out the mineralization, which ends with the contaminants decomposed in inorganic salts, water and carbon dioxide. Unfortunately, the degradation and mineralization of many compounds does not result quickly, and sometimes can be formed intermediates more toxic than the starting compounds.

In urban wastewater treatments, AOPs are commonly applied after biological treatment with the aim of eliminating recalcitrant compounds and improving water quality. Nevertherless, in industrial wastewater treatments, AOPs are used before the biological treatment. The reason is that biodegradability is increased and the microorganisms responsible of the biological degradation perform their function more efficiently.

#### 1.2.2. Benefits and drawbacks

The main adventages of these treatments are that the organic compounds are destroyed without pollution transfer into another phase and innocuous and non-toxic reagents are used. These techniques are also very effective in the remotion of a lot of organic pollutants and some toxic metals. They are easy to install and can be adapted on a small scale for developing countries as well. On the other hand, the main disadventages are the elevated cost due to the high cost of operation (chemical compounds and/or energy). Another drawback could be the high toxicity of some reaction intermediates formed. In addition, it is a technology which requires much research and is not fully developed yet.<sup>4</sup>

#### 1.2.3. AOP techniques

It is possible to name different AOP technologies depending on the working conditions. It is possible the presence or absence of light, the use or not of different catalysts or the presence of other factors such as current or ultrasounds.

In *Table 2* it is shown some AOP techniques classified according to the presence or absence of irradiation.<sup>4</sup>

Irradiation	Technique	
	Ozone (O <sub>3</sub> )	
	Fenton (Fe <sup>2+</sup> , H <sub>2</sub> O <sub>2</sub> )	
Dark AOP's	Electrolysis (electrodes, current)	
	Sonolysis (ultrasounds)	
	Photolysis (UV, H <sub>2</sub> O <sub>2</sub> )	
Light driven AOPs	Photocatalysis (light, catalyst)	
	Photo-Fenton (UV, Fe <sup>2+</sup> , H <sub>2</sub> O <sub>2</sub> )	

#### 1.2.3.1. Direct photolysis

Direct photolysis is not considered an AOP, but it is convenient to name it in order to do the comparison with hydrogen peroxide and UV radiation process.

It consists in increasing the reactivity of the species due to the irradiation of light that brings them to their excitate state.<sup>2</sup> It is important to note that the range of wavelenghts to which the compound is irradiated must be close to its maximum absorption range. Otherwise, the radiation will not affect the compound, which will remain in its ground state.

#### 1.2.3.2. UV, hydrogen peroxide

In order to improve the efficiency of direct photolysis, hydrogen peroxide can be added. The effect of this method is based on two principles, the first one is the direct conversion due to UV radiation, as in direct photolysis, and the second one is the conversion due to the hydroxil radicals, formed from the absorption of UV radiation by hydrogen peroxide, as it is shown in the next scheme:<sup>5</sup>

 $H_2O_2 + hv \rightarrow 2 HO \bullet$ 

As commented in photolysis, for the formation of a high amount of hydroxil radicals, it is necessary to irradiate hydrogen peroxide molecules in its maximum range of absorption, which is around 240 nm. Moreover, to avoid the scavenger effect, which is produced by secondary reactions which reduce the effectiveness, hydrogen peroxide concentration must be maintended within limits.

#### 1.2.3.3. Fenton

In Fenton process, hydrogen peroxide and iron are used as reactants. Unlike photo-Fenton process, no radiation is used. Despite this, it is a very effective method.

Hydroxyl radicals formation is led by the following reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^-$$

As can be seen, the catalyst is consumed in the production of the oxidant. However, it is possible to regenerate the catalyst, but consuming hydrogen peroxide molecules. In the recovery reaction, hydroperoxil radicals (HO<sub>2</sub>•) are formed, but its reduction potential (1.70 V) is not comparable to the hydroxil radicals.<sup>6</sup>

 $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 \bullet + H^+$ 

The kinetics of both reactions shows that the reaction rate of the catalyst is higher than its regeneration even when the system is practically composed of iron (III). Studies show that typical  $H_2O_2$ :Fe<sup>2+</sup> ratios are 5-10:1 wt/wt.

In terms of pH, the optimum is around 3, because at more basic pH mediums the hydrated ferrous ions are transformed into a coloidal ferric species (even can precipitate). In this form, iron catalytically decomposes the  $H_2O_2$  into oxygen and water, without forming hydroxyl radicals and producing a decrease in the efficiency. It is important that temperature does not exceed 40-50°C. If temperatures are higher, hydrogen peroxide decomposes into water and oxygen, reducing efficiency as well. The recommended temperature is set between 20-30°C for economic and safety reasons, in addition to the aforementioned.<sup>7, 8</sup>

Finally, it should be noted that Fenton process has a large number of advantages. On the one hand, hydrogen peroxide is easy to handle and iron is quite economical and non-toxic under the operating concentrations, besides no chlorinated compounds are formed as in others AOPs. Furthermore, the design of discontinuous reactors is very simple as well. On the other hand, and in contrast, it is required the continuous addition of reagents, increasing the cost of operation.

#### 1.2.3.4. Photo-Fenton

Unlike the Fenton process, in photo-Fenton process light is added. Therefore, a serie of reactions appear, increasing the efficiency for two reasons:<sup>9</sup>

- 1- As commented in photolysis, it is possible to form hydroxil radicals with the only action of light, as long as the wavelenght of the radiation is close to the absorption range of hydrogen peroxide, in addition to the direct decomposition of Tiapride.
- 2- In contradistinction to the Fenton process, the regeneration of catalyst does not require the consumption of hydrogen peroxide. Moreover, it is possible to generate hydroxil radicals in the catalyst recovery.

In the following scheme (*Figure 2*), it is shown the mechanism with the corresponding reactions:



Figure 2. Photo-Fenton reactions scheme

For the same reasons as in the Fenton process, it is necessary to control the pH and the temperature, but it is also important to control the wavelenght of the radiation. In cases where the radiation does not give the expected effectiveness, chelators with the ability to absorb in a wide range of wavelengths can be added, such as resorcinol or EDTA.

#### 1.2.3.5. Heterogeneous photocatalysis with titanium dioxide

Heterogeneous photocatalysis is a photochemical reaction, produced on the surface of a semiconductor that acts as a catalyst, such as TiO<sub>2</sub>.

Its operation is based in photoexcitation. Titanium dioxide is activated when it absorsb radiation with a wavelength smaller than 387 nm ( $\lambda$  < 387 nm). When this occurs, an electron of the valence band jumps to the conduction band generating a hole in the valence band.<sup>10</sup>

Electrons in the conduction band can react with molecular oxygen to form superoxide radicals.

$$O_2 + TiO_2(e_{cb}) \rightarrow O_2 + TiO_2$$

In the holes formed in the valence band, water molecules and hydroxide ions can be trapped, forming hydroxyl radicals, which will produce the oxidation of the pollutant.

$$H_2O + TiO_2(h^+{}_{vb}) \rightarrow OH^\bullet + H^+ + TiO_2$$
  
OH<sup>-</sup> + TiO<sub>2</sub>(h<sup>+</sup><sub>vb</sub>) → OH• + TiO<sub>2</sub>

In the following figure (Figure 3), the process is shown schematically:



Figure 3. Heterogeneous photocatalysis scheme

# **2. OBJECTIVES**

The main objective of this work is to study the effectiveness of Photolysis, Fenton and Photo-Fenton, using a BLB reactor, and Heterogeneous Photocatalysis, in a Solarbox, in the decomposition of Tiapride in mineral water solutions.

To achieve this objective, the degradation and the mineralization of Tiapride compound in different conditions were studied to know the influence of different variables. The toxicity is also analyzed in the process where better results were obtained.

Finally, the different techniques are compared in order to know which of them give the best results in the decontamination of the water.

# **3. MATERIALS AND METHODS**

# 3.1. REAGENTS

The following reagents were used:

Name	Formula	Company	Purity (%)
Tiapride hydrochloride	C15H24O4SHCI	Sigma-Aldrich	>99
Hydrogen peroxide	$H_2O_2$	Panreac	30
Iron (II) sulphate 7- hydrate	FeSO4·7H2O	Panreac	99
Titanium dioxide Degussa P-25	TiO <sub>2</sub>	Evonik Industries	70% anatase, 30% rutile
Sulphuric acid	$H_2SO_4$	Panreac	95-98
Sodium Hydrogen Sulphite	NaHSO₃	Panreac	40
Ammonium meta- Vanadate	NH <sub>4</sub> VO <sub>3</sub>	Panreac	>99
1,10-Phenantroline 1- hydrate	$C_{12}H_8N_2\cdot H_2O$	Sigma-Aldrich	>99
Ammonium Acetate	CH <sub>3</sub> COONH <sub>4</sub>	Panreac	>99
Acetic Acid glacial	CH₃COOH	Panreac	>99
L(+)-Ascorbic acid	$C_6H_8O_6$	Panreac	>99

## Table 3. Information about the reagents used

#### 3.2. ANALYTICAL METHODS

The following methods and measurements were used:

#### 3.2.1.pH measurement

The determination of pH was done with pH meter CRISON GLP 22. Consists in the measurement of the potential which is developed through a thin glass membrane that separate two solutions with different proton concentration, so it is necessary to know the sensitivity and the selectivity of the glass membrane in front of pH. For this reason, calibration was required every day with 4.0 and 7.0 pH buffers to ensure the accuracy.

#### 3.2.2. Determination of hydrogen peroxide

Hydrogen peroxide was determinated according *Simple and fast spectrophotometric determination of*  $H_2O_2$  *in photo-Fenton reaction using metavanadate* (R. F. Nogueira et al. 2005)<sup>11</sup>. This method consists in the reaction of  $H_2O_2$  with ammonium metavanadate in acidic medium, which results in the formation of a red-orange peroxovanadium cation, with maximum absorbance at 450 nm (*Figure 4*), following the next reaction scheme:

$$VO_3^- + 4H^+ + H_2O_2 \rightarrow VO_2^{3+} + 3H_2O_2$$

To measure the absorbance of peroxovanadium cation at 450 nm wavelength, Hach Lange DR 6000 spectrophotometer was used.



Figure 4. Hydrogen peroxide and vanadate absorbances

#### 3.2.3. Determination of iron (II) and total iron

Iron (II) was determinated according *Colormetric determination of iron in water with o-phenantroline* (D. H. Caldwell et al. 1946)<sup>12</sup>. The method is based on the reaction between o-phenantroline and ferrous iron to form a red-orange highly colored ferrous o-phenantroline complex (*Figure 5*) which is quantitatively proportional to the amount of iron present in the sample and with maximum absorbance at 510 nm. Sodium acetate buffer was added to adjust 4.0 pH.

L(+)-Ascorbic acid was used to reduce all ferric iron that remains in the sample in order to obtain the total iron concentration. Ferric iron was calculated by the difference between total iron and ferrous iron.

To measure the absorbance of ferrous o-phenantroline complex at 510 nm wavelength, Hach Lange DR 6000 spectrophotometer was used.



Figure 5. Iron (II) and o-phenantroline scheme reaction

#### 3.2.4. Determination of Tiapride concentration

Tiapride concentration was determinated through HPLC 1200 Infinity Series with the conditions indicated in *Table 4*. Samples were filtered using 0.45  $\mu$ m nylon filters, and in experiments where hydrogen peroxide was used, it is necessary to add sodium hydrogen sulphite to stop the reaction.

All the information is processed by Empower Pro software 2002.

HPLC set up		
Mobile phase	80% water, 20% acetonitrile	
Flow-rate	0.8 mL/min	
Detection	287.4 nm between 4.2-4.4 min, using a Water 996 photodiode array detector	

#### 3.2.5. Determination of total organic carbon

Total organic carbon was analyzed using Shimadzu TOC-V CNS instrument, where the samples are introduced into a combustion chamber with oxygen at 500°C. Organic compounds are decomposed to carbon dioxide (and water), and measuring the amount formed, it is possible to calculate the mineralization obtained.

#### 3.2.6. Determination of toxicity

Toxicity is measured from the loss of bioluminiscence of *vibrio fischeri* bacteria after 15 minutes in contact with samples of the contaminant before and after the degradation was carried out. It consists in obtaining the EC<sub>50</sub>, which is the concentration of a substance that causes a defined magnitude of response in the 50% of population in a given system. The results are calculated using the following equation:

Equitox/m<sup>3</sup> = 100/EC<sub>50</sub>

# 3.3. EXPERIMENTAL DEVICES

The following reactors were used:

## 3.3.1.BLB reactor

Consists of a BLB (Blacklight Blue lamps) reactor (see scheme in *Figure 6*) connected to a thermostatic bath with water. Water circulates through the jacket surrounding the reactor. Furthermore, it is located above a magnetic stirrer (AGMATIC – E, P SELECTA ®) with different stirring powers, allowing the homogenization of the reaction system. All charasteristics of the vessel and lamps are shown in *Table 5* and *Table 6*, respectively.

Vessel properties		
Volume	2 L	
Inner diameter	11 cm	
Height	23 cm	

Table 5. BLB reactor	vessel	properties
----------------------	--------	------------

Lamps properties			
Number of lamps	3		
Power	8W		
ID	Philips TL 8 W-08 FAM		
Radiation range	350-400 nm		
Maximum radiation	365 nm		

## Table 6. BLB reactor vessel properties



Figure 6. BLB reactor scheme

#### 3.3.2. Solarbox reactor

In the Solarbox (see scheme in *Figure 7*), the tubular photoreactor is located at the bottom of the device in the axis of a parabolic mirror. The solution to be treated is prepared in a 1 L jacketed vessel (feeding tank) connected to a thermostatic bath with water. Water circulates through the jacket surrounding the reactor. The solution is continuously agitated by a magnetic stirrer and pumped to the tubular photoreactor, being recirculated to the feeding tank.

Device	ID	
Solarbox	Solarbox Co.Fo.Me.Gra, 220 V, 50 Hz	
Stirrer	RCT basic, IKA® WERKE	
Pump	Peristaltic pump Ecoline VC-280II, Ismatec	
Lamp	Philips XOP 15-OF 1CT, Xenon, 1 kW	

Table 7. Solarbox devices

Table 8. Tubular reactor properties				
Tubular reactor properties				
Volume	0.078 L			
Inner diameter	2.11 cm			
Length	24 cm			

Photon flow was measured with *o-Nitrobenzaldehyde actinometry* (Kuhn et al. 2004; De la Cruz et al. 2013)<sup>13, 14</sup>, being 2.98 µEinstein L<sup>-1</sup> s<sup>-1</sup>.



Figure 7. Solarbox reactor scheme

# 3.4. EXPERIMENTAL PROCEDURE

First of all, a 50 ppm solution of Tiapride is prepared in a volume of 1 L for Heterogeneous Photocatalysis and 2 L for the rest of experiences, adjusting to the reactor capacity. Then, in experiments where acid medium is required, Fenton and photo-Fenton, pH is set to 2.7-2.8 using a concentrated solution of sulfuric acid.

In experiments where radiation is needed, lamps must be turned on 30 minutes before, to ensure that at the starting of the experience they are emitting light at their maximum emission range and have reached the steady state.

It is always necessary to turn the thermostat on and keep the temperature at 25°C (in the thermostatic bath), in adition to adjust the magnetic stirrer to the same power for all experiments.

Once everything is prepared, the solution is introduced into the vessel and the rest of the reactants are added in the case they are necessary. Next, the lamps are adjusted to the reactor, which is closed and secured with a metal clasp. Then, the timer is started. Sample times are shown in *Table 9*.

Time (min)	Tiapride	H <sub>2</sub> O <sub>2</sub>	Iron	TOC	Toxicity
0	х	х	х	х	х
2.5	х	х	х	х	
5	Х	x	х		
7.5	Х	x	х		
10	Х	х	х		
15	Х	x	х		
20	Х	x	х		
30	X	Х	X		
45	Х	x	х	x	
60	х	х	х	х	х

Table 9. Experiment sample times

Samples taken on time 0 only contain Tiapride while in the rest of the times, all the other reagents required are present. All samples are filtered through 0.45  $\mu$ m filters before performing the analysis.

Finally, the whole experimental device must be washed several times with water and sulfuric acid. Samples that cannot be analyzed instantaneously are stored in the refrigerator until then.

# 4. RESULTS AND DISCUSSION

## 4.1. DESIGN OF EXPERIMENTS

The study of the decomposition of Tiapride drug in aqueous mineral matrix was performed through the advanced oxidation techniques and with the conditions shown in *Table 10*.

Table 10. Act a configues with respective conditions of pir and reagents used					
Technique	рН	Reactants			
Photolysis	Natural	-			
UV, H <sub>2</sub> O <sub>2</sub>	Natural	H <sub>2</sub> O <sub>2</sub>			
Fenton	2.8	H <sub>2</sub> O <sub>2</sub> , Fe <sup>2+</sup>			
Photo-Fenton	2.8	H <sub>2</sub> O <sub>2</sub> , Fe <sup>2+</sup>			
Heterogeneous photocatalysis	Natural	TiO <sub>2</sub>			

Table 10. AOPs techniques with respective conditions of pH and reagents used

The parameters that remained constant throughout all experiments were the temperature, the agitation, the Tiapride concentration and the reaction time. Therefore, experiments were carried out under equal conditions and it is possible to perform the analysis of the results and the comparison between differents AOPs in an appropriate way. These parameters are indicated in *Table 11*.

Table 11. Parameters that remained constant with their respective values

Variables to	o control
Temperature	20-30 °C
Tiapride concentration	50 mg/L
Agitation	500-600 W
Reaction time	60 minutes

As a result, 12 experiments were designed to perform the study. The variables used were the type of light, the pH and the concentration of reagents. The following table (*Table 12*) shows each experiment an the conditions used.

Experiments	рН	Reactor	Light	H <sub>2</sub> O <sub>2</sub> (ppm)	Fe <sup>2+</sup> (ppm)	TiO₂ (g/L)	Degrad. (%)	Mineral. (%)
Experiment 1	Natural	BLB	Yes	-	-	-	6.7	0
Experiment 2	Natural	BLB	No	-	10	-	0	0
Experiment 3	Natural	BLB	Yes	-	10	-	5.9	0
Experiment 4	Natural	BLB	No	150	-	-	0	0
Experiment 5	Natural	BLB	Yes	150	-	-	12.9	1.7
Experiment 6	2.8	BLB	No	100	10	-	97.8	22.1
Experiment 7	2.8	BLB	Yes	25	2.5	-	88.5	19.3
Experiment 8	2.8	BLB	Yes	25	10	-	94.2	19.7
Experiment 9	2.8	BLB	Yes	100	2.5	-	90.4	14.8
Experiment 10	2.8	BLB	Yes	100	10	-	98.6	44.4
Experiment 11	Natural	SB	No	-	-	0.4	4.2	0
Experiment 12	Natural	SB	Yes	-	-	0.4	12.5	2.6

Table 12. Experiments designed with their respective reactor, light, pH, reagents concentration and degradation and mineralization obtained

In the following pages, the individual analysis of each experience and the relevant comparisons between them will be carried out.

# 4.2. BEZOYA MINERAL WATER CHARACTERIZATION

The characterization of the mineral water used as matrix of the solution (agua mineral Bezoya, © 2016 Calidad Pascual, S.A.U) was performed with different devices, such as pH meter CRISON GLP 22, Shimadzu TOC-V CNS, spectrophotometer Hach Lange 2500 and turbidimeter Hach 2100P. The results obtained are indicated in *Table 13*.

Bezoya mineral water characterization				
TOC	0.000 mg/L			
NPOC	0.583 mg/L			
IC	2.577 mg/L			
TN	1.226 mg/L			
COD unfiltered water	37.91 mg O <sub>2</sub> /L			
COD filtered water	2.63 mg O <sub>2</sub> /L			
UV	0.033			
Suspended solids	0.005 mg/L			
Voltatile solids	0.000 mg/L			
Total solids	0.127 mg/L			
Cl-	0.87 mg/L			
Na⁺	2.55 mg/L			
Ca <sup>2+</sup>	2.73 mg/L			
Mg <sup>2+</sup>	0.39 mg/L			
Turbidimetry	0.76 NTU			
рН	5.6			

Table 13. Agua mineral Bezoya characterization

It has been decided to perform the decomposition of Tiapride in a mineral water matrix due to the apparition, in the last years, of emergint pollutants in springs of potable water.<sup>15</sup> However, these contaminants are in low concentrations, but it is necessary to carry out the decomposition in order to improve the water quality.

# 4.3. DIRECT PHOTOLYSIS

The first technique tested was direct photolysis. The experiment was carried out in the BLB reactor in presence of light. No additional reagents were used.

The progress of the drug concentration in 60 minutes of irradiation is shown in Figure 8.



Figure 8. Tiapride concentration in front of time in direct photolysis experiment

Observing these results, it can be concluded that the degradation obtained by direct photolysis was very low (6.9%). Accordingly, TOC results showed that there was no mineralization.

The reason is that BLB lamps emit radiation in a wavelength of 365 nm and the maximum absorption wavelenght of Tiapride is at 217 nm. The absorption curve of Tiapride, at natural pH, it is shown in *Figure 9*.



Figure 9. Absorption spectrum of Tiapride

Tiapride absorption range is between 190-300 nm, clearly out of BLB lamps range emission. For reactors with emission wavelengths closer to the absorption range of the compound, such as UV-C reactors, higher degradation would be expected.

# 4.4. EXPERIMENTS WITH IRON (II)

In the next experiments, the effects of the catalyst on the compound were tested in presence and absence of light and without oxidant action. Experiments were performed in natural pH and in the BLB reactor as well.

When only iron (II) was use, without light, Tiapride concentration remained constant during all the experience, which means there is no decomposition.

With iron (II) and light, the degradation obtained (5.9%) was very close to the direct photolysis experiment. In addition, no mineralization was obtained.

Therefore, it can be concluded that the individual action of the catalyst without the presence of the oxidant is not enough to carry out the degradation of the compound.

# 4.5. EXPERIMENTS WITH HYDROGEN PEROXIDE

In order to determine the interaction between hydrogen peroxide and Tiapride in absence of catalyst and in absence and presence of light, two experiments were performed in the BLB reactor.

On the one hand, in the case where hydrogen peroxide in absence of light was used to carry out the decomposition of the compound, there was neither degradation nor mineralization of the contaminant.

On the other hand, when light was added, there was 12.9% of Tiapride degradation and 1.7% of mineralization.

Comparig the results obtained in the experiments of direct photolysis and hydrogen peroxide with light, slighter degradation is observed in the latter, although in both cases it is not very high.

As it was discussed previously in the theoretical introduction, on the oxidation technique with UV and hydrogen peroxide (*section 1.2.3.2.*), it is possible to produce hydroxyl radicals from the irradiation of hydrogen peroxide molecules.

It is true that in absence of light and catalyst, the presence of hydrogen peroxide is not enough to carry out the decomposition of Tiapride, but when light is added, degradation ocurrs due to the direct photolysis of the compound and the formation of oxidizing hydroxyl radicals by the photolysis of hydrogen peroxide.

The reason why degradation is greatest than in direct photolysis when hydrogen peroxide is added, is that hydroxil radicals are also generated. Even so, if the maximum absorption wavelenght of hydrogen peroxide (*Figure 4*) is analyzed, it is note that it is far from the emission range of the BLB lamps, such as Tiapride. As it was commented in direct photolysis, a greater efficiency would be expected for reactors with emission wavelengths between 210-250 nm, because both compounds would be subjected to a higher excitation.

To study the effectivenes of the Fenton process in the decomposition of the compound, an experiment was carried out in the BLB reactor with the following conditions:

Table 14. Fenton experiment conditions					
Experiment pH Tiapride (ppm) Light H <sub>2</sub> O <sub>2</sub> (ppm) Fe <sup>2+</sup> (p					
6	2.8	50	No	100	10

A very high degradation was obtained (97,8%), but the mineraliation was a bit low (22.1%).

These results will be compared with those obtained from the photo-Fenton process with the same concentration of pollutant and reagents (*section 4.7.1*.).

# 4.7. PHOTO-FENTON

In order to determine the effect of the irradiation and the concentration of iron (II) and hydrogen peroxide in this process, the experiments which conditions are indicated in *Table 15* were performed in the BLB reactor

Experiment	рН	Tiapride (ppm)	Light	H <sub>2</sub> O <sub>2</sub> (ppm)	Fe <sup>2+</sup> (ppm)
7	2.8	50	UV	25	2.5
8	2.8	50	UV	25	10
9	2.8	50	UV	100	2.5
10	2.8	50	UV	100	10

Table 15. Photo-Fenton experiments conditions

Figure 10 shows the progress of the degradation of the compound after one hour of reaction.



(a) Indicated ratios correspond to the concentration (ppm) of hydrogen peroxide and iron (II) respectively

Figure 10. Progress of Tiapride degradation in front of the reaction time

The degradation and the mineralization for these experiments are shown below:

Experiment	H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> ratio	H2O2 (ppm)	Fe²+ (ppm)	Degradation	Mineralization
7	25:2.5	1.5	1.2	88.5%	19.3%
8	25:10	0.15	9.2	94.2%	19.7%
9	100:2.5	19.7	0.6	90.4%	14.8%
10	100:10	6.6	2.4	98.6%	44.4%

Table 16. Summary of the results obtained in photo-Fenton experiments after 60 minutes of irradiation.

#### 4.7.1. Comparison between Fenton and photo-Fenton techniques

The results obtained in the *Experiment* 6 and in the *Experiment* 10 show a similar degradation for both techniques, slightly higher for the photo-Fenton process (98.6% vs. 97.8%). However, the mineralization was higher for the photo-Fenton process (44.4% vs. 22.1%).

The main reason, and the only difference between both processes, is the presence of irradiation. As commented in the introduction, UV light increases the performance because it decomposes the pollutant directly and it generates hydroxil radicals from the hydrogen peroxide molecules. In addition, iron (III) becomes to iron (II), creating hydroxil radicals as well, even though the radiation is not in the desired ranges.

These causes were demonstrated by monitoring the iron (II) and the hydrogen peroxide concentration during the experiments.

If iron (II) concentration after 30 minutes of reaction is compared in both experiments, it is appreciated a deficiency of the catalyst in the Fenton experiment when the reaction is in progress. The consumption of Fe<sup>2+</sup> is clearly greater than its regeneration. In Fenton process, the regeneration is carried out only from the reaction of iron Fe<sup>3+</sup> with hydrogen peroxide. In the Photo-Fenton process, this reaction also occurs, but there is also regeneration from the reaction between Fe<sup>3+</sup>, irradiation and water.

Iron (II) concentration (ppm)					
Time (min)	Fenton	Photo-Fenton			
0	10.1 ppm	9.9 ppm			
30	0.5 ppm	2.7 ppm			

Table 17. Comparison of Fe<sup>2+</sup> concentration in Fenton and photo-Fenton processes

In the determination of the consumption of hydrogen peroxide at the end of the experiments (*Table 18*), it was demonstrated that in the photo-Fenton process there was a higher use of the oxidant than in the Fenton process.

	proceede					
Hydrogen peroxide concentration (ppm)						
Time (min)	Fenton	Photo-Fenton				
0	100 ppm	100 ppm				
60	14.5 ppm	6.6 ppm				

Table 18. Hydrogen peroxide concentration at the end of the Fenton and the photo-Fenton processes

In the Fenton process, the hydrogen peroxide consumption occurs by the reaction with iron (II), to form the hydroxyl radicals, and with iron (III), to regenerate the catalyst. Nevertheless, in the photo-Fenton process, in addition to these commented reactions, the consumption is also produced from the photolysis of the oxidant by the action of UV light, generating more hydroxil radicals and improving the results.

#### 4.7.2. Study of the effect of iron (II) in photo-Fenton process

Analyzing the results obtained in the *Experiment* 9 and in the *Experiment* 10 (*Table* 17), it was demonstrated that, for the same initial oxidant concentration, an increase in the initial catalyst concentration improves the process efficiency.

Even so, increasing concentrations for better results is not as simple and trivial as it seems. In the introducton, it was mentioned that catalyst and oxidant ratios between 5-10:1 wt/wt are recomendable (*section 1.2.3.3.*). As it is shown in *Figure 10*, the degradation achieved in 15 minutes of reaction is very different for both experiments, the slope for the 100:10 oxidant/catalyst ratio is clearly higher than for the 100:2.5 ratio. The reason is very simple, in the initial minutes of reaction, the catalyst is saturated as Fe<sup>3+</sup> due to the oxidation of Fe<sup>2+</sup>, which is limiting the reaction, for 100:2.5 ratio experiment. When this occurs, the efficiency of the process is affected because side reactions appear, such as the reaction between hydrogen peroxide with hydroxyl radicals, forming water and perhydroxyl radicals, with lower oxydizing power.

$$H_2O_2 + OH \rightarrow H_2O + OOH \rightarrow$$

It is true that the degradation of the drug is quite fast and practically complete for this process, but it is important to respect the reagents ratios in order to avoid the side reactions, because the decomposition will be carried out in less time. The same conclusions can be reached when the *Experiment* 7 (25 ppm H<sub>2</sub>O<sub>2</sub>:2.5 ppm Fe<sup>2+</sup>) and the *Experiment* 8 (25 ppm H<sub>2</sub>O<sub>2</sub>:10 ppm Fe<sup>2+</sup>) are analyzed.

#### 4.7.3. Study of the effect of H<sub>2</sub>O<sub>2</sub> in photo-Fenton process

Hydrogen peroxide influence in photo-Fenton process was performed from the comparison between the *Experiment 8* and the *Experiment 10* (*Figure 10* and *Table 16*). It was demonstrated that an increase in the initial concentration of the oxidant, for the same concentration of catalyst, improves the process efficiency.

Degradation obtained in photo-Fenton process increased slightly when higher concentration of hydrogen peroxide was used. However, the highest difference is observed in the mineralization. Attending to the progress of the degradation of the compound during time (*Figure 10*), and monitoring the hydrogen peroxide concentrations throughout the reaction for each experiment, it is possible to find the reasons that explain this fact.

First of all, the difference between the slopes in the initial minutes, greater for the experiment with a ratio of 25:10, is due to the fact that in the first instants, the reaction occurs very quickly, producing the oxidation of the catalyst. Therefore, in the experiment where a higher concentration of hydrogen peroxide was used (100:10), there was a mild saturation of the catalyst, while in the other experience (25:10) there is more free iron (II). Nowithstanding, hydrogen peroxide is a reagent that is consumed. If we compare the concentrations of the oxidant in both experiments, it is observed that in 30 minutes of practice, hydrogen peroxide has almost fully reacted for the 25:10 experience.

Hydrogen peroxide concentration (ppm)						
Time (min)	Photo-Fenton 25:10	Photo-Fenton 100:10				
0	25 ppm	100 ppm				
15	3.7 ppm	67.9 ppm				
30	0.8 ppm	45.4 ppm				
60	0.15 ppm	6.6 ppm				

Table 19. Comparison of oxidant concentration in photo-Fenton process for different initial concentrations of oxidant

As shown in *Table 19*, the amount of oxidant at 15 minutes of reaction, for the experiment with 25:10 ratio, is quite low. If we compare it with the progress of the degradation shown in *Figure 10*, we can see that, at this time (15 minutes), it is just when the degradation is almost stopped, remaining practically constant during the last 45 minutes. The degradation and mineralization of the compound can be carried out by this process, but if elevated degradation and mineralization results are desired, a higher concentration of the oxidant is required. Once these low levels are reached, it is possible to continue the decomposition but with lower efficiency. In the absence of hydrogen peroxide, the only possible reaction is the direct photolysis of the pollutant, and it was demonstrated that in the BLB reactor it is not carried out effectively (*section 4.3.*). For this reason, better results were reached with 100:10 ratio, the oxidant concentration was sufficient to carry out the decomposition during the whole hour of experiment.

## 4.8. HETEROGENEOUS PHOTOCATALYSIS WITH TITANIUM DIOXIDE

In the study of the heterogeneous photocatalysis technique, two experiments were carried out in the Solarbox reactor, in the absence and presence of light, with the same concentration of titanium oxide (IV).

Experiment	рН	Tiapride (ppm)	Light	TiO₂ (g/L)
Experiment 11	Natural	50	No	0.4
Experiment 12	Natural	50	Xe lamp	0.4

Table 20. Heterogeneous photocatalysis experiment conditions

Using  $TiO_2$  without light, very low degradation was observed (4.2%), and there was no mineralization. The individual action of the titanium dioxide was not enough to effect the degradation of the compound.

When light is used with TiO<sub>2</sub>, the degradation was low (12.5%), but slightly higher than in the previous case. There was low mineralization as well (2.6%).

#### 4.8.1. Study of the light action in heterogeneous photocatalysis with TiO<sub>2</sub>

The difference between the performances obtained, despite being very low, is found in the presence of light. In the experiment where there was no light, the decomposition could have been effected by the adsorption of the pollutant molecules on the surface of the titanium dioxide, exciting them and carrying out the decomposition.

In the experiment where light was added, the decomposition is carried out by the action of the electron-hole pair produced by the radiation (*section 1.2.3.5.*), which results in this slight increase in the performance.

Finally, it should be noted that the reactant solution presented some turbidity. This generates a shielding of the light, reducing the radiation that reaches the catalyst particles. This is, in addition to the low adsorption of Tiapride in titanium dioxide surface, another reason that explains the low yield obtained.

# 5. CONCLUSIONS

- Direct photolysis with BLB lamps is not a suitable technique for the Tiapride treatment, because very low degradation and mineralization were reached. The addition of hydrogen peroxide slightly improves the effectiveness of the process but the improvement in the Tiapride degradation and mineralization is really small.
- Fenton and photo-Fenton are suitable techniques to carry out the decomposition of Tiapride.

 In Fenton process, using 100 ppm of hydrogen peroxide and 10 ppm of iron (II), 97.8% of degradation and 22.1% of mineralization were achieved.

- In photo-Fenton process, using 100 ppm of hydrogen peroxide and 10 ppm of iron (II), 98.4% of degradation and 44.4% of mineralization were achieved.
- H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> mass ratios higher than 10 can reduce the efficiency of photo-Fenton process.
- Photocatalysis with TiO<sub>2</sub> gives poor results in the treatment and only 12.5% of degradation and 2.6% of mineralization were achieved.

# **REFERENCES AND NOTES**

- Mastroianni, N.; López, M.; Barceló, D.; Emerging organic contaminants in aquatic environments: stateof-the-art and recent scientific contributions, *Contributions to Science*, 2010, 6, 2, 193–197.
- Palit, S.; Future vision of advanced oxidation process and its immediate efficacy-a deep, insightful comprehension and a far-reaching review, *International Letters of Chemistry, Physics and Astronomy*, 2011, 33, 136-145.
- Mota, A.; Albuquerque, L.; Beltrame, L.; Chiavone-Filho, O.; Machulek Jr., A.; Nascimento, C.; Advanced Oxidation Processes and their application in the petroleum industry: A review, *Brazilian journal of petroleum and gas*, **2008**, 2, 3, 122-142.
- Sandip, S.; Ruparelia, J. P.; Patel, M.; A general review on advanced oxidation processes for waste water treatment. *Paper presented at the Institute of Technology*, Nirma University, Ahmedabad, 2011, 382–481.
- 5. Legrini, O.; Oliveros, E.; Braun, A. M.; Photochemical Processes for Water Treatment, *Chem. Rev.*, **1993**, *93*, 671-698.
- Pawar, P.; Gawande, S.; An overview of the Fenton Process for Industrial Wastewater, IOSR Journal of Mechanical and Civil Engineering, 2015, 127-136.
- Jung, Y.; Taik, W.; Park, J.; Kim, Y.; Effect of pH on Fenton and Fenton-like oxidation, *Environmental Technology*, 2009, 30, 2, 183-190.
- Khamaruddin, P.; Azmi, M.; Aziz A.; Using Fenton's Reagents for the Degradation of Diisopropanolamine: Effect of Temperature and pH, *International Conference on Environment and Industrial Innovation*, 2011, 12, 12-17.
- Machulek, A.; Quina, F.; Gozzi, F.; Silva, V.; Friedrich, L.; Moraes, J.; Fundamental Mechanistic Studies of the Photo-Fenton Reaction for the Degradation of Organic Pollutants, Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update, Dr. Tomasz Puzyn (Ed.), *InTech*, Brazil, **2012**, 273-276.
- Gilmour, C; Water Treatment Using Advanced Oxidation Processes: Application Perspectives, *The University of Western Ontario*, Ontario, 2012, 5-13.
- Nogueira, R. F.; Oliveira, M. C.; Paterlini, W. C.; Simple and fast spectrophotometric determination of H<sub>2</sub>O<sub>2</sub> in photo-Fenton reactions using metavanadate, *Talanta*, **2005**, 66, 1, 86-91.
- Caldwell, D. H.; Adams, R. B.; Colorimetric determination of iron in water with o-phenanthroline. *Journal American Water Works Association*, **1946**, 38, 727.
- Kuhn, H. J.; Braslavsky, S.E.; Schmidt, R.; Chemical actinometry (IUPAC Technical Report), Pure Appl Chem, 2013, 76, 2105–2146.
- De la Cruz, N.; Romero, V.; Dantas, R. F.; Marco P.; Bayarri B.; Giménez J.; Esplugas, S.; o-Nitrobenzaldehyde actinometry in the presence of suspended TiO<sub>2</sub> for photocatalytic reactors. *Catal Today*, **2013**, 209, 209–214.
- Janet, M.; Soto, A; Usma, I.; Gutierrez, O.; Contaminantes emergentes en aguas, efectos y posibles tratamientos, *Producción + Limpia*, **2015**, 7, 2, 56-57.

# ACRONYMS

- (AOP) Advanced Oxidation Processes
- (BOD<sub>5</sub>) Biochemical Oxigen Demand
- (BLB) Blacklight Blue
- (COD) Chemical Oxigen Demand
- (EC<sub>50</sub>) Half Massive Efective Concentration
- (IC) Inorganic Carbon
- (NPOC) Non-Purgable Organic Carbon
- (SB) Solarbox
- (SUVA) Aromaticity and Specific Ultraviolet Absorbance
- (TN) Total Nitrogen
- (TOC) Total Organic Carbon
- (WWTP) Waste Water Treatment Plant

#### 39

# **APPENDICES**

# APPENDIX 1: CONCENTRATIONS, DEGRADATION AND MINERALIZATION DURING EACH EXPERIENCE AT DIFFERENT TIMES

## Interaction between light and Tiapride

Experiment 1. Direct photolysis results

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	52.1	32.43	0.00%	0.00%
2.5	51.9	-	0.43%	-
5	51.5	-	1.12%	-
7.5	51.4	-	1.41%	-
10	51.1	-	1.95%	-
15	50.7	-	2.77%	-
20	50.4	-	3.34%	-
30	49.9	-	4.37%	-
45	49.5	-	5.00%	-
60	48.6	33.21	6.69%	0.00%

## Table 21. Direct photolysis results

# Interaction betweern iron (II) and Tiapride

Experiment 2. Interaction between iron (II) and Tiapride without light results

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	53.8	31.26	0.00%	0.00%
2.5	53.9	-	0.00%	-
5	52.7	-	1.97%	-
7.5	52.8	-	1.80%	-
10	53.5	-	0.49%	-
15	53.7	-	0.08%	-
20	53.2	-	1.03%	-
30	53.5	-	0.49%	-
45	52.5	-	2.41%	-
60	52.6	33.61	2.27%	0.00%

Table 22. Iron (II) without light results

## Experiment 3. Interaction between iron (II) and Tiapride with light results

#### Table 23. Iron (II) with light results

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	52.1	33.01	0.00%	0.00%
2.5	50.5	-	3.21%	-
5	50.1	-	3.92%	-
7.5	49.9	-	4.27%	-
10	50.1	-	3.84%	-
15	50.3	-	3.49%	-
20	49.5	-	5.09%	-
30	49.9	-	4.24%	-
45	49.8	-	4.44%	-
60	49.1	34.14	5.90%	0.00%

# Interaction betweern hydrogen peroxide and Tiapride

Experiment 4. Interaction between hydrogen peroxide in absence of light results

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	49.4	32.34	0.00%	0.00%
2.5	49.5	-	0.00%	-
5	48.6	-	1.68%	-
7.5	49.4	-	0.08%	-
10	49.3	-	0.16%	-
15	48.2	-	2.56%	-
20	49.5	-	0.00%	-
30	49.6	-	0.00%	-
45	49.9	-	0.00%	-
60	49.5	32.31	0.00%	0.09%

Table 24. Hydrogen peroxide without light results

## Experiment 5. Interaction between hydrogen peroxide in presence of light results

Table 25. Hydrogen peroxide with light results
--

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	51.3	29.96	0.00%	0.00%
2.5	49.8	-	2.84%	-
5	47.8	-	6.85%	-
10	46.8	-	8.80%	-
20	45.8	-	10.66%	-
40	43.9	-	14.47%	-
60	44.7	29.44	12.90%	1.74%

# Fenton

Experiment 6. 100:10 Fenton results

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	49.2	30.01	0.00%	0.00%
2.5	7.6	-	84.46%	-
5	4.5	-	90.93%	-
7.5	2.8	-	94.27%	-
10	2.8	-	94.35%	-
15	2.6	-	94.63%	-
20	2.0	-	95.97%	-
30	1.7	-	96.45%	-
45	1.4	-	97.16%	-
60	1.1	23.39	97.80%	22.06%

Table 26. 100:10 Fenton results

# **Photo-Fenton**

Experiment 7. 25 ppm of hydrogen peroxide and 2.5 ppm of iron (II) results

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	50.0	28.18	0.00%	0.00%
2.5	28.1	24.90	43.79%	11.64%
5	26.6	-	46.86%	-
7.5	21.1	-	57.75%	-
10	18.0	-	64.06%	-
15	17.3	-	65.49%	-
20	11.4	-	77.31%	-
30	9.2	-	81.57%	-
45	8.9	24.07	82.26%	14.58%
60	5.7	22.73	88.51%	19.34%

Table 27. 25:2.5 photo-Fenton results

Experiment 8. 25 ppm of hydrogen peroxide and 10 ppm of iron (II) results

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	47.9	37.87	0.00%	0.00%
2.5	12.6	33.81	73.73%	10.72%
5	9.9	-	79.36%	-
7.5	4.7	-	90.16%	-
10	4.0	-	91.64%	-
15	3.9	-	91.83%	-
20	3.4	-	92.81%	-
30	3.2	-	93.40%	-
45	2.9	30.99	94.05%	18.17%
60	2.8	30.43	94.24%	19.65%

Table 28. 25:10 photo-Fenton results

Experiment 9. 100 ppm of hydrogen peroxide and 2.5 ppm of iron (II) results

Table 29. 100:2.5 photo-Fenton results

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	49.0	40.90	0.00%	0.00%
2.5	33.1	38.23	32.45%	6.53%
5	30.0	-	38.81%	-
7.5	28.8	-	41.29%	-
10	26.7	-	45.62%	-
15	23.7	-	51.70%	-
20	20.2	-	58.72%	-
30	13.3	-	72.79%	-
45	6.6	34.49	86.58%	15.67%
60	4.7	34.84	90.42%	14.82%

Experiment 10.	. 100 ppm of hydrogen	peroxide and 10 p	opm of iron (II) results

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	51.9	30.51	0.00%	0.00%
2.5	35.0	26.85	32.66%	12.00%
5	17.6	-	66.09%	-
7.5	10.9	-	79.07%	-
10	8.5	-	83.70%	-
15	1.9	-	96.31%	-
20	1.0	-	98.08%	-
30	1.8	-	96.58%	-
45	1.3	18.63	97.46%	38.94%
60	0.7	16.98	98.62%	44.35%

# Table 30, 100:10 photo-Fenton results

# **Heterogeneous Photocatalysis**

Experiment 11. TiO<sub>2</sub> without light action results

Table 31	. TiO2 withou	t light results
----------	---------------	-----------------

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	47.0	33.82	0.00%	0.00%
2.5	47.0	-	0.12%	-
5	45.8	-	2.54%	-
7.5	45.2	-	3.84%	-
10	44.9	-	4.52%	-
15	45.0	-	4.39%	-
20	45.0	-	4.36%	-
30	45.3	-	3.71%	-
45	44.6	-	5.12%	-
60	45.1	35.94	4.18%	0.00%

## Experiment 12. TiO<sub>2</sub> with light action results

Time (min)	Concentration (ppm)	TOC (ppm)	Degradation	Mineralization
0	52.2	33.82	0.00%	0.00%
2.5	47.1	-	9.86%	-
5	47.3	-	9.38%	-
7.5	46.1	-	11.62%	-
10	46.6	-	10.78%	-
15	46.5	-	10.89%	-
20	46.7	-	10.49%	-
30	45.5	-	12.77%	-
45	46.0	-	11.79%	-
60	45.7	32.94	12.51%	2.60%

## Table 32. TiO2 with light results