

Removal of propranolol in MilliQ water and wastewater by photo-Fenton process including experimental desingn

MASTER FINAL PROJECT



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Abstract

The water pollution has been increasing along time, being this big problem that threatens the environment. Emerging contaminants (ECs) such as pharmaceuticals present a peculiar problem because conventional water treatment plants in many cases cannot completely remove them and can cause a large environmental impact. Therefore, it is necessary to use alternative treatments such as advanced oxidation processes (POAs) that are based on the production of reactive species (especially the hydroxyl radical $\text{OH}\cdot$) to degrade or transform chemical pollutants. The aim of this study was to investigate the effect of advanced oxidation processes photo-Fenton on the removal to pharmaceutical pollutant: propranolol hydrochloride (PROP). Has been selected this emerging contaminant β -blocker because it is highly prescribed to treat arterial hypertension, irregular heart rhythm, certain types of tremors and migraine. PROP removal was studied in a reactor with artificial light (black light blue and UVC) by photolysis and photo-Fenton. All experiments were carried out with 50 mg/L of initial PROP in Milli-Q water and real water, at the same $\text{pH}=2.8$ and at different concentrations of reagents iron (II) (Fe^{2+} , 5 ppm and 10 ppm) and ratio $\text{Fe}^{+2}/\text{H}_2\text{O}_2$, 0.1 and 0.4.

The results show that after 60 minutes of treatment PROP removal was high in all of the experiments (>50%). The UVC reactor shows the best results, however this fact is due to the contribution of photolysis added to the UV/H₂O₂ process since the regeneration of iron doesn't occur correctly in the UVC, so the photofenton process isn't given correctly.

It is decided to apply an experimental design and thus from the results will be obtained a simple mathematical model that relates the response to the experimental conditions. Thus it was determined which variables are the most influential in the degradation of PROP.

Finally a study was made to see the economic viability of each experimental condition, obtaining the efficiencies of each one of them to be able to compare them.

Keywords: Emerging pollutants, advanced oxidation processes, photo-Fenton, propranolol, experimental design

Notation

AOPs	Advanced Oxidation Processes
BLB	Black Blue Lamp
ECs	Emerging contaminants
Fe⁺²	Iron (II)
Fe⁺³	Iron (III)
COD	Chemical Oxygen Demand
H₂O₂	Hydrogen peroxide
OH·	Hydroxyl radical
ppm	Part per million
ppb	Part per billion
PROP	Propranolol
R	Ratio
TOC	Total Organic Carbon
UVC	Ultraviolet radiation shortwave
WWTP	Waste Water Treatment Plant

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1. Introduction

1.1 Water pollution

Increasingly, human activities and lifestyles of developed countries are jeopardizing the viability of ecosystems, due to the contaminants generation. Additionally to the global water scarcity, the release of pollutants with potential to harm both humans and the environment into water bodies is the biggest threat to the world's freshwater supplies.

Effluent of municipal wastewater treatment plants is considered a good source of water for potential reuse. However the water should be free of emerging contaminants [1].

Environmental Engineering a possible contribution to facing the problem of water scarcity is the implementation of adequate treatment able to reduce the impact on the water system and eventually make possible the reutilization of treated water.

1.1.1 Emerging contaminants

The so-called emerging contaminants (ECs) (cleaning products, cosmetics, pharmaceuticals, etc.) are a significant concern today. Currently, these contaminants are only present in minute concentrations (ppm or ppb) in the aquatic systems.

Spain is ranked as one of the world's largest consumer of pharmaceuticals [2]. These compounds are also recalcitrant and present properties of bioaccumulation in the environment [3].

The most common treatment techniques (especially biological treatments) used for removing contaminants contained in wastewaters are not useful for the degradation of emerging contaminants. This fact, coupled with the increasing demands on water quality imposed by the European Union through the Water Framework Directive (2000/60/CE), (it's last modification is DOUE 292 de 10/11/2015 [18]) make necessary to use alternative techniques that enable the degradation and destruction of the emerging contaminants, achieving, if possible, their mineralization. This is where the Advanced Oxidation Processes (AOPs) come into play. AOPs are environmental friendly methods based on in situ production of hydroxyl radical ($\text{OH}\cdot$) as main oxidant.

1.1.2 Propranolol

British scientist James W. Black developed Propranolol (PROP) in the 1960s. Propranolol is a medication of the beta blocker type. It is used to treat high blood pressure, a number of types of irregular heart rate, thyrotoxicosis, capillary haemangiomas, performance anxiety, and essential tremors. It is used to prevent migraine headaches, and to prevent further heart problems in those with angina or previous heart attacks [4].

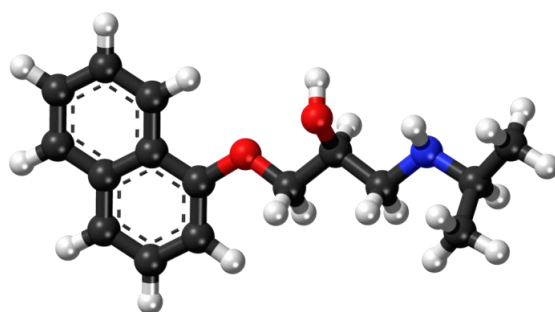


Fig. 1.I. Molecular structure of propranolol [Source: Wikipedia][4].

1.2 Advanced Oxidation Processes (AOPs)

AOPs are based on formation of $\text{OH}\cdot$, which can degrade different pollutants.

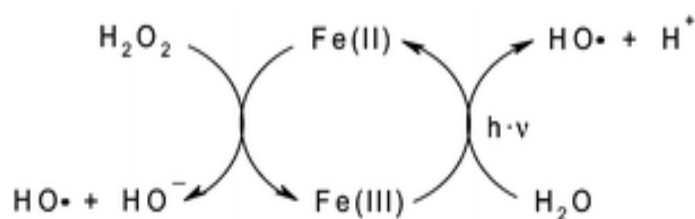
AOPs rely the high reactivity of $\text{OH}\cdot$ to drive oxidation processes and to achieve complete degradation and full mineralization of several organic pollutants [5]. $\text{OH}\cdot$ is among all oxidant species the second most reactive after fluoride ($E^\circ=2.80\text{ V}$) and being non-selective it can attack almost any organic compound.

1.2.1 Photo-Fenton

In this way, photo-Fenton is one of the most applied AOPs based on the joint action of iron and light.

This process consists in the addition of iron salts in the presence of hydrogen peroxide (H_2O_2), for the formation of $\text{OH}\cdot$ radicals. The most influential variables in technique are concentration of H_2O_2 and Fe^{+2} , temperature, pH, reaction time and nature of the contaminants under study. Very acid or alkaline pH conditions result in a decrease in the degradation rate of contaminants [6].

In photo-Fenton the use of UV-Vis radiation increases the oxidation power mainly by photo-reduction of Fe^{+3} to Fe^{+2} which produces more hydroxyl radicals and in this way a cycle is established in the Fenton reagent and the hydroxyl radicals are produced by the oxidation of organic compounds [7].



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.

Over the last fifteen years, pharmaceuticals have received increasing attention as potential bioactive chemicals in the environment [8]. They are considered as emerging pollutants in water bodies because they still remain unregulated or are currently undergoing a regularization process, although the directives and legal frameworks are not set-up yet. Pharmaceuticals are continuously introduced into the environment and are prevalent at small concentrations which can affect water quality and potentially impact drinking water supplies, ecosystem and human health [9][10].

The technologies currently used for degradation of these compounds are presenting 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.

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 [11]. In this study, PROP was chosen as a model compound to represent micropollutant in synthetic water. The following variables will be assessed: PROP degradation, Total Organic Carbon (TOC) reduction and Chemical Oxygen Demand (COD) reduction.

3. Objectives

3.1 General objective

The main objective of this project is to evaluate the degradation of the PROP in the liquid phase by means of photo-Fenton process at acid pH.

3.2 Specific goals:

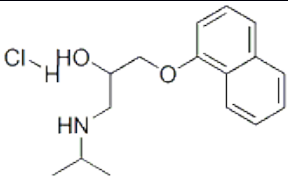
- To study the abatement of PROP in Milli-Q water and real waters coming from the secondary effluents of Gavà Waste Water Treatment Plant (WWTP) using photo-Fenton treatment at acid pH.
- Know the behaviour of the drug to be degraded by photolysis direct artificial light (UV).
- To compare results from BLB and UVC reactors.
- Evaluate the optimal doses of different chemical reagents (Fe^{2+} , H_2O_2) processes corresponding to the degradation of PROP.
- Evaluate the toxicity of the water before and after the process.
- To describe the experimental design.

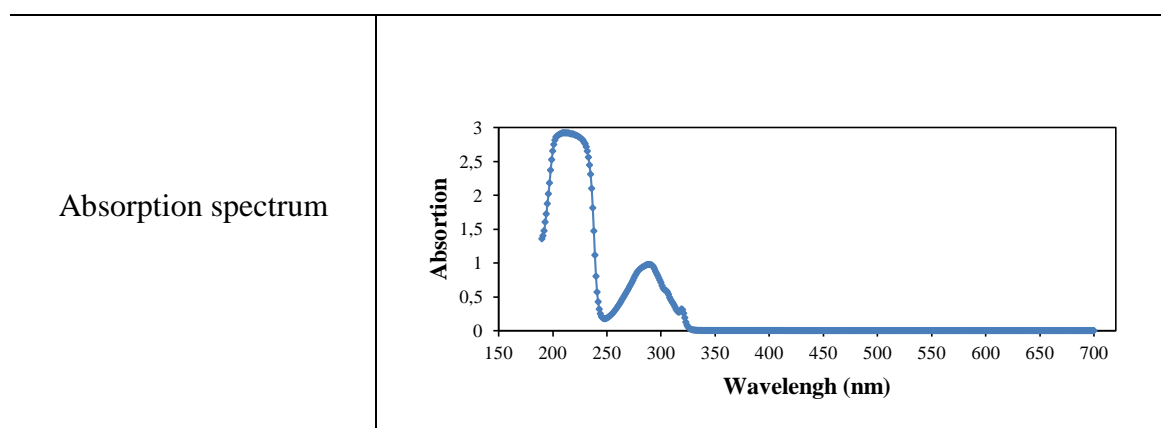
4. Materials and methods

4.1 Chemicals and reagents

Propranolol hydrochloride was purchased from Sigma-Aldrich Chemical Co.

Table 4.I. Chemical properties of PROP [12]

Formula	$\text{C}_{16}\text{H}_{21}\text{NO}_2 \cdot \text{HCl}$
Molecular structure	
Molecular weight (g/mol)	295.8
pK_a (25°C)	9.5
Melting point (°C)	163 – 164



4.1.2 Other chemical and reagents

Table 4.II. Chemical properties of all other reagents used in this work [13].

Name	CAS No.	Formula	Supplied by	Purity (%)	Used in/for
Acetonitrile	75-05-8	CH ₃ CN	Fischer Chemical	99.80	HPLC analysis
Ascorbic acid	50-81-7	C ₆ H ₈ O ₆	Panreac	99	Fe ⁺² determination
1,10-phenantroline	66-71-7	C ₁₂ H ₈ N ₂	Sigma Aldrich	99	Fe ⁺² determination
Hydrogen peroxide	7722-84-1	H ₂ O ₂	Merck	30 w/w	Photo-Fenton
Iron (II) sulphate heptahydrate	7782-63-0	(FeSO ₄ ·7H ₂ O)	Panreac	30	Photo-Fenton
Liver bovine catalase	9001-05-2	H ₂ O ₂ :H ₂ O ₂	Sigma Aldrich	-	To avoid further reactions
Ammonium metavanadate	7803-56-6	NH ₄ VO ₃	Sigma Aldrich	99	H ₂ O ₂ determination
Methanol	67-56-1	CH ₃ OH	Panreac	99.90	Stop the reaction with peroxide to HPLC
Orthophosphoric acid	7664-38-2	H ₃ PO ₄	Panreac Quimica	85	HPLC analysis
Sodium bisulphite	7631-90-5	NaHSO ₃	Panreac	40	Stop the reaction with peroxide to TOC
Sulfuric acid	7664-93-998	H ₂ SO ₄	Panreac	98	For initial pH value adjustment

4.2 Analytical methods

4.2.1 High Performance Liquid Chromatograph

PROP concentration was monitored by High Performance Liquid Chromatograph: HPLC from waters by Agilent Technologies 1260 infinity. PROP concentration was followed at UV maximum absorbance (289 nm).

The mobile phase was composed by water, orthophosphoric acid (pH 3) and acetonitrile (70:30), injected 10 μ L of sample with a flow-rate of 0.80 mL/min

4.2.2 Dissolved iron measurement

The iron content was determined according to the 1,10-phenantroline standardized procedure (ISO 6332) (International Organization for Standardization 1988). Ferrous iron Fe^{+2} forms a red colored complex with 1.10-phenantroline. The absorption of this complex measured at 510 nm, by spectrophotometer Hach Lange DR 3900, is proportional to ferrous iron concentration. Total iron can be measured after ferric iron Fe^{+3} reduction with ascorbic acid to ferrous iron Fe^{+2} . Consequently, ferric iron concentration Fe^{+3} can be eventually calculated as the difference between total iron and ferrous iron [11].

4.2.3 Determination of hydrogen peroxide consumption

Hydrogen peroxide determination was followed through metavanadate spectrophotometric procedure [14] in order to know H_2O_2 consumption during photodegradation reactions. The procedure is based on the reaction of H_2O_2 with ammonium metavanadate in acidic medium, which results in the formation of a red-orange color peroxovanadium cation, with maximum absorbance at 450 nm. The measurement was carried out by means of a spectrophotometer Hach Lange DR 3900 [11].

4.2.4 Determination of Chemical Oxygen Demand (COD)

COD analysis give and indirect measure of the organic compounds contained in the water sample. The test determines the amount of oxygen required to oxidize organic matter of a solution by means of strong oxidant agents. These tests were carried out following the Standard Method 5220 D: closed reflux and colorimetric method. The method consists of heating at high temperature (150°C) a known volume of sample with an excess of potassium dichromate the presence of sulphuric acid (H_2SO_4) over a period of 2 hours in a hermetically sealed glass tube. The dichromate was in excess, and thus, the organic matter was oxidized and dichromate was reduced to Cr^{3+} . Furthermore, to avoid possible interference of chloride in the sample, silver sulphate was also added. The residual chrome IV was then colorimetrically measured in a spectrophotometer (Hach Lange DR 2500) at 420 nm.

The samples were taken at initial time and 60 minutes.

4.2.5 Total Organic Carbon (TOC)

TOC determination was performed with a Shimadzu 5055 TOC-VCSN analyzer by means of catalytic combustion at 680 °C according to Standard Method 5220D procedures. The device was equipped with an ASI-V Autosampler.

4.2 Experimental devices

4.2.1 Artificial irradiation: Black Light Blue lamps (BLB) reactor

UVA Photo-Fenton-like experiments were carried out in a 2L Pyrex jacketed stirred vessel (inner diameter 11 cm, height 23 cm), equipped with three black-light blue lamps (Philips TL 8W, 08 FAM) wrapped in three Duran glass tubes. The lamps were axially arranged to the reactor and the emitted radiation was between 350 and 400 nm and maximum at 365 nm. During the runs, the temperature was kept at 25.0 ± 0.8 °C with a thermostatic bath (Haake C-40) by circulating the water through the jacket around the

reactor. Good mixing was provided using a magnetic stirrer. When hydrogen peroxide was added, UVA lamps were switched on. In Figure 2 is shown a schematic design of the UVA Photo-device [11].

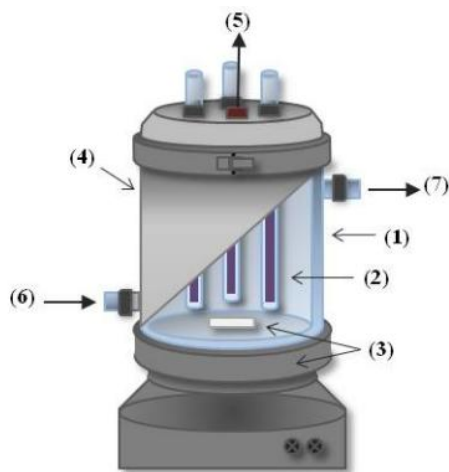


Fig. 4.II. BLB reactor. (1) 2L jacketed reactor, (2) Black light Blue Lamps, (3) Magnetic stirrer, (4) Alumina foil, (5) Sampling orifice, (6) Thermostatic bath (IN) and (7) Thermostatic bath (OUT)[11]

4.2.2 Artificial irradiation: UVC reactor

UVC light was supplied in a photochemical reactor quite similar to the previous but with different lamps. Thus, three fluorescent lamps (Philips TUV 8W, G8T5) wrapped in three quartz tubes, located at the center of the reactor, with emitted radiation between 200 and 280 nm, with a maximum of 254 nm were used. When hydrogen peroxide was added, UVC lamps were switched on. In Figure 3 is shown a schematic design of the UVA Photo-device [11].

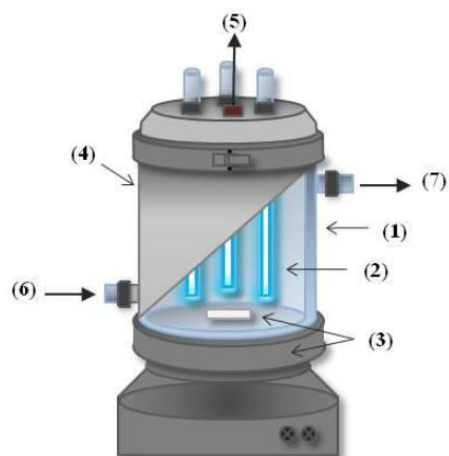


Fig. 4.III. UVC reactor. (1) 2L jacketed reactor, (2) Black light Blue Lamps, (3) Magnetic stirrer, (4) Alumina foil, (5) Sampling orifice, (6) Thermostatic bath (IN) and (7) Thermostatic bath (OUT) [11]

5. Results and discussion

The experiments will be carried out at acid pH = 2.8. Different concentrations of hydrogen peroxide and iron will be tested (5 - 10 mg/L of Fe²⁺ and 12.5 - 25 - 50 - 100 mg/L of H₂O₂). Always the samples filtered through a 0.45 µm disc filter before analysis. All experiments were done in duplicate.

In this work will kept the concentration of PROP (50 mg/L), temperature (25 °C) and pH (2.8) constants and will sought to develop a simple linear model with interactions. A full factorial design of experiments will employ to initiate a deeper investigation of the efficiency of photo-Fenton reaction against PROP degradation.

The experimental design corresponds to a factorial design 2⁴, therefore four factors of two levels each: type of water (Milli-Q water or real water), type of light (BLB or UVC), optimal concentration of iron (5 or 10 mg/L) and finally the Fe²⁺ / H₂O₂ ratio (R) (0.1 or 0.4). This ratios have been chosen by review the bibliography [15][16]. Annex I shows the experimental design table.

The actual water used came from WWTP Gavà, and was collected at the end of the biological treatment with MBR (Membrane BioReactor), this water was characterized and its results can be consulted in the annex VII.

To evaluate the effectiveness of the process, the following control variables were chosen: PROP, Fe²⁺ and H₂O₂ concentration, TOC, COD and toxicity. PROP degradation was evaluated during one hour. Annex I shows the experimental design table.

In this section, the results are shown as degradation and mineralization rates concerning the accumulated energy (Q_{acc}, kJ/L) achieved during experiments for each experimental device (Eq. (1)) where I is the incident photonflow (kJ/s) assessed by actinometry, t_i is the time (s) and V (L) is the volume of the treated solution [15]. In appendix II shows the calibration curve of propranolol used.

$$Q = \sum_{i=0}^n \frac{I \cdot \Delta t_i}{V} \quad (1)$$

5.2 Photolysis

When it's studying a AOPs, is very important to be able to separate the influence of photolysis. To evaluate the degradation of PROP in the process without oxidizing reagent.

Table 5.III. PROP degradation and TOC removal at 60 min in photolysis with MQ.

Experimental device	% PROP conversion	% TOC removal
BLB	5.12	2.57
UVC	26.71	4.20

The influence of photolysis on PROP degradation and mineralization is low in BLB reactor. Only UVC light (26.71% of PROP removal in 60 min) is powerful enough to

break the PROP bonds, because UVC covers the range of light absorption of PROP. Moreover, photolysis did not promote relevant mineralization.

5.3 BLB reactor and Milli-Q water

Table 5.IV. PROP degradation, COD and TOC removal at 60 min in BLB reactor with Milli-Q.

Experimental device	Ratio	% PROP conversion	% COD removal	% TOC removal
10/100	0.1	99.09±0.09	64.97±2.87	60.51±3.84
10/25	0.4	94.15±0.53	53.27±2.13	21.93±2.50
5/50	0.1	76.70±1.77	27.09±1.30	19.68±3.97
5/12.5	0.4	72.23±0.26	25.89±2.39	10.65±0.65

In Figure 5.IV. and 5.V. shows the percentages of PROP degradation and TOC removal at 60 minutes, using different ratios are presented vs. accumulated energy (kJ/L), in BLB reactor with MQ.

The highest degradation of PROP was obtained with 10 mg/L of Fe^{2+} and a ratio of 0.1 (99%) that coincides and the highest TOC removal rate (61%) and was obtained when H_2O_2 was used the maximum concentration. The values of COD removal with 10 mg/L of Fe^{2+} show that the state of oxidation of organic matter has decreased significantly. At the moment in BLB reactor the most important parameter is iron concentration as with 10 mg/L when observed the best conversions. Hydrogen peroxide acts as additional source of $\text{OH}\cdot$, improving PROP degradation.

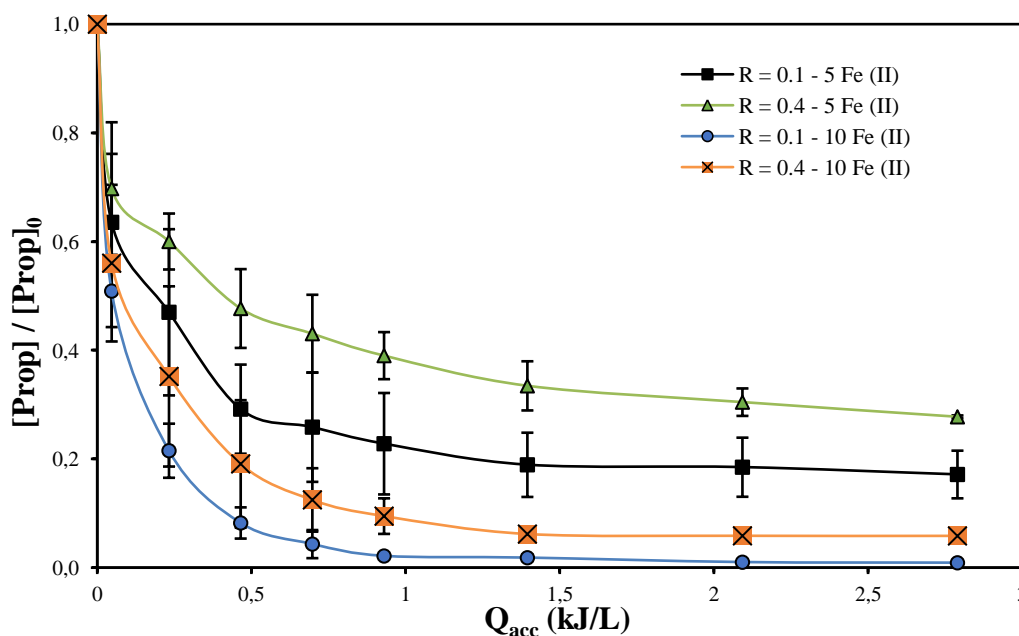


Figure 5.IV. PROP degradation at 60 min in BLB reactor with Milli-Q.

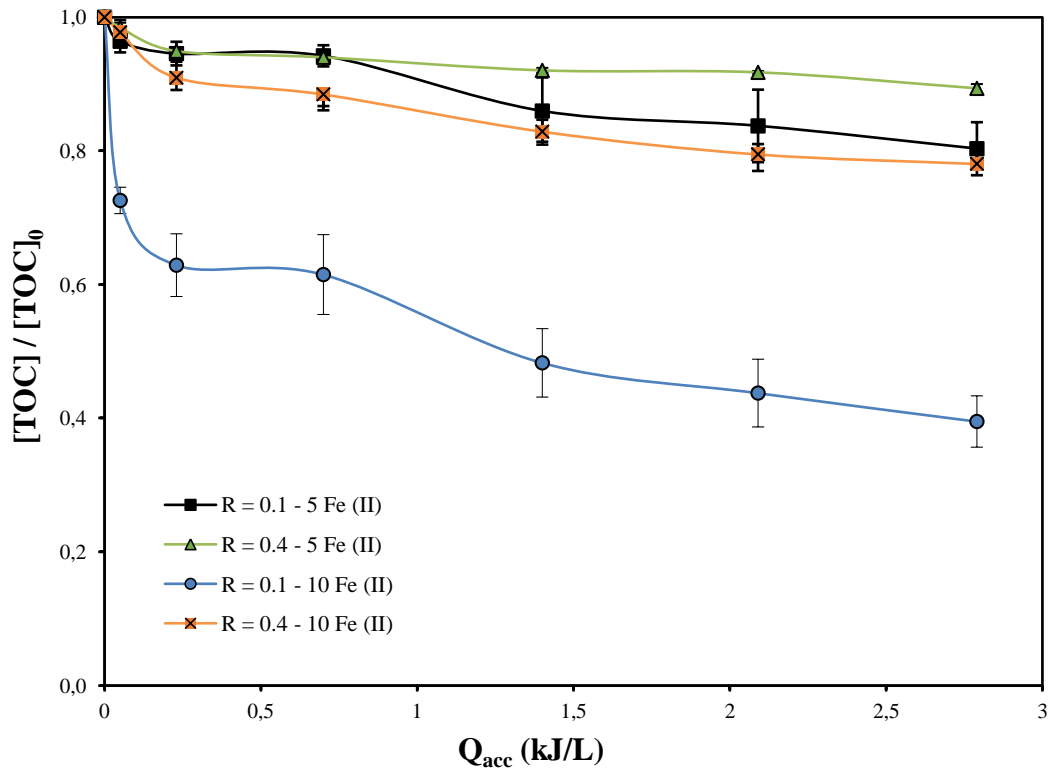


Figure 5.V. TOC removal at 60 min in BLB reactor with Milli-Q.

5.4 BLB reactor and real water

Table 5.V. PROP degradation, COD and TOC removal at 60 min in BLB reactor with real water.

Experimental device	Ratio	% PROP conversion	% COD removal	% TOC removal
10/100	0.1	97.02±1.84	94.81±1.51	39.21±3.45
5/50	0.1	90.94±0.030	69.34±3.58	12.26±0.41
10/25	0.4	90.89±3.78	81.25±2.75	7.95±0.79
5/10	0.4	51.56±3.31	62.04±3.88	8.60±0.63

In Figure 5.VI. and 5.VII. shows the percentages of PROP degradation and TOC removal at 60 minutes, using different ratios are presented vs. accumulated energy (kJ/L), in BLB reactor with real water.

The highest degradation of PROP was obtained with 10 mg/L of Fe²⁺ and a ratio of 0.1 (97%) that coincides and the highest TOC removal rate (39%) and was obtained when H₂O₂ was used the maximum concentration. The values of COD removal with 10 mg/L of Fe²⁺ show that the state of oxidation of organic matter has decreased.

When use the real water in BLB reactor the most important parameter is ratio Fe²⁺/H₂O₂ as with 0.1 when observed the best conversions.

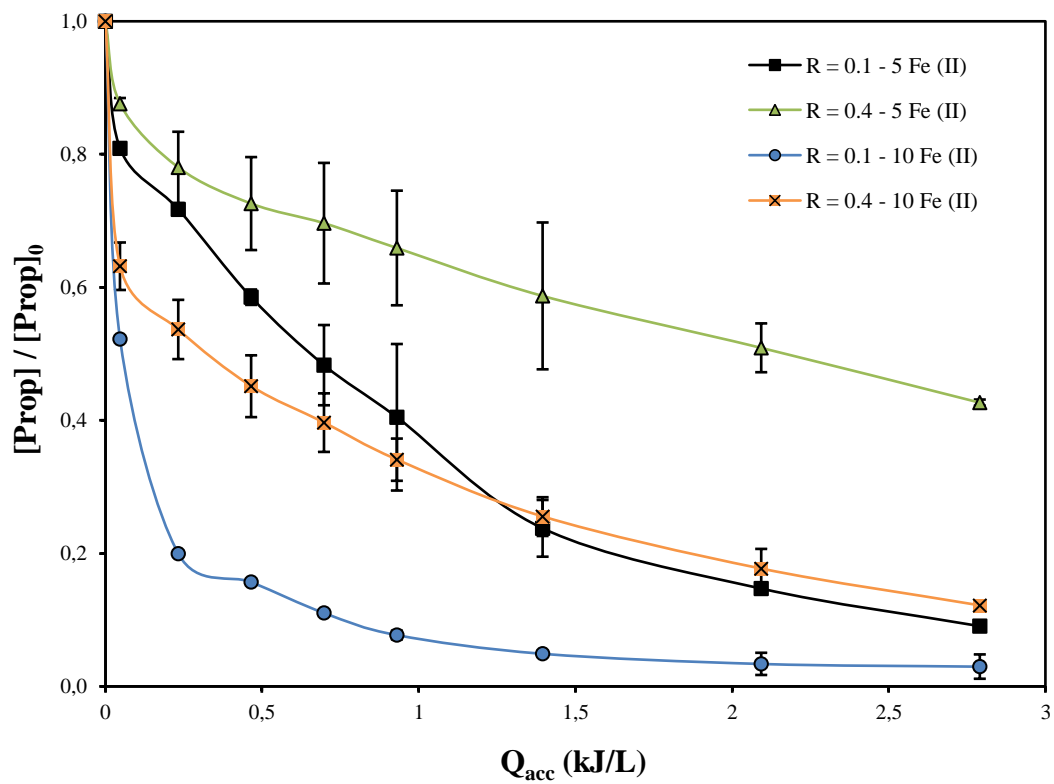


Figure 5.VI. PROP degradation at 60 min in BLB reactor with real water.

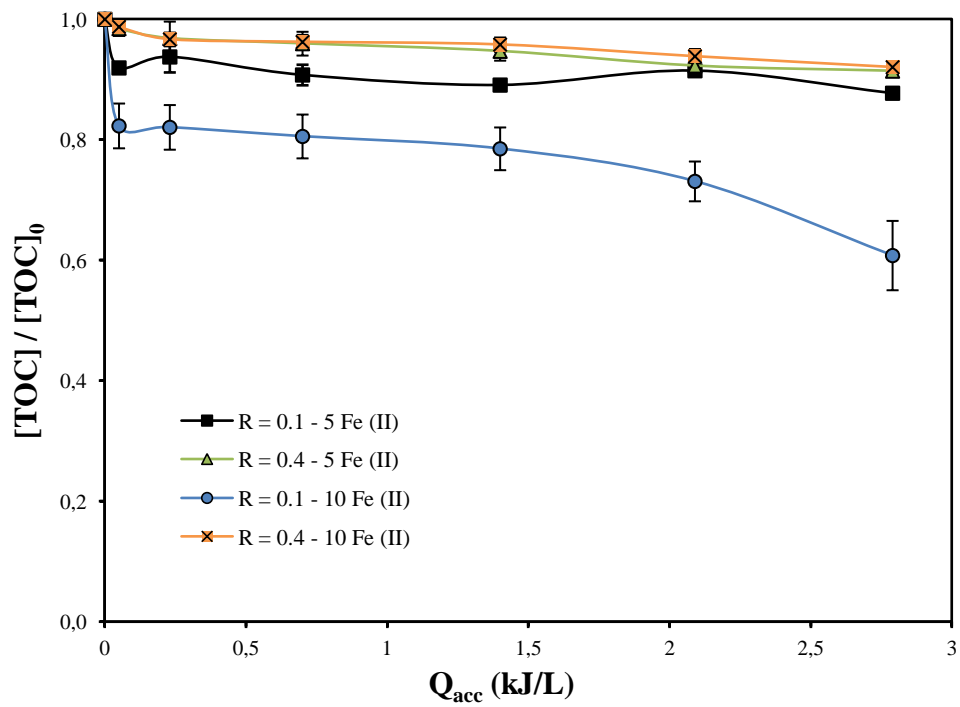


Figure 5.VII. TOC removal at 60 min in BLB reactor with real water

5.5 UVC reactor and Milli-Q water

Table 5.VI. PROP degradation, COD and TOC removal at 60 min in UVC reactor with Milli-Q.

Experimental device	Ratio	% PROP conversion	% COD removal	% TOC removal
10/100	0.1	97.52±0.31	87.43±2.02	50.00±1.29
5/50	0.1	96.00±0.25	82.73±1.28	29.51±1.45
10/25	0.4	93.68±0.88	74.84±1.46	31.20±1.80
5/12.5	0.4	82.54±0.70	63.35±2.12	11.86±0.51

In Figure 5.VIII and 5.IX shows the percentages of PROP degradation and TOC removal at 60 minutes, using different ratios are presented vs. accumulated energy (kJ/L), in UVC reactor with Milli-Q.

The highest degradation of PROP was obtained with 10 mg/L of Fe^{2+} and a ratio of 0.1 (98%) that coincides and the highest TOC removal rate (50%) and was obtained when H_2O_2 was used the maximum concentration. But all experimental devices showed that UVC reactor is suitable for conversion and removal of PROP, but this is due to the high amount of photolysis, however, also influences the process $\text{UV}/\text{H}_2\text{O}_2$. This is deduced since we know that in iron don't absorb radiation at 245 nm, therefore the iron isn't regenerating to Fe^{+2} and hydrogen peroxide acts as additional source of hydroxyl radicals, improving PROP degradation.

In agreement with the values of degradation of COD removal show that the state of oxidation of organic matter has decreased considerably.

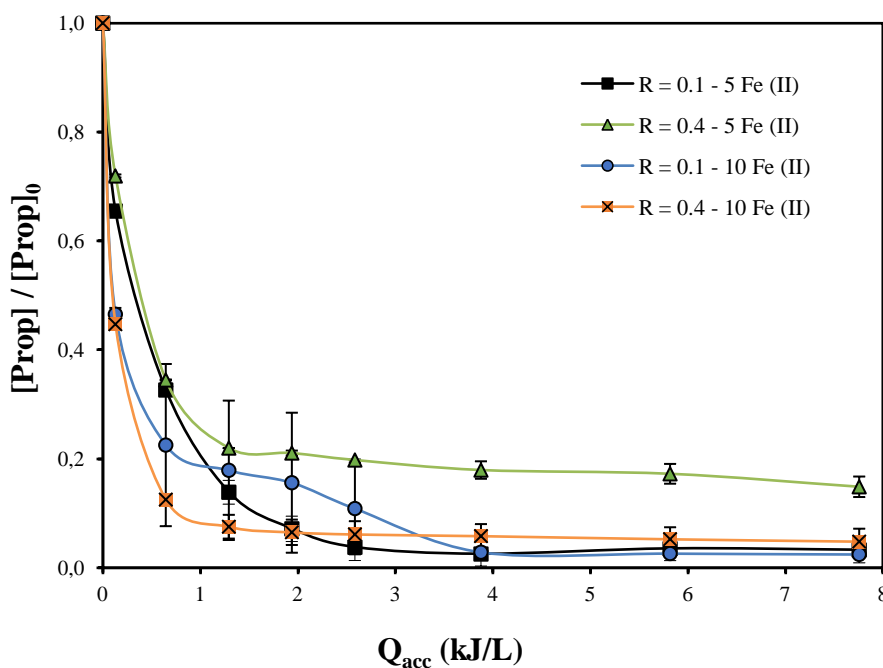


Figure 5.VIII. PROP degradation at 60 min in UVC with Milli-Q.

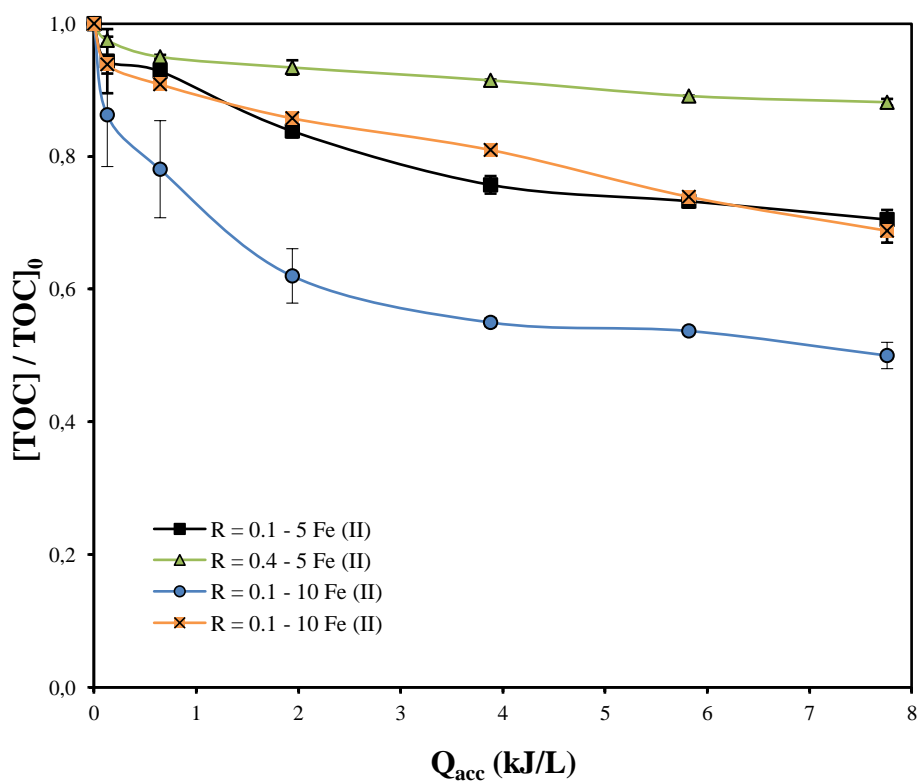


Figure 5.IX. TOC removal at 60 min in UVC with Milli-Q.

5.6 UVC reactor and real water

Table 5.VII. PROP degradation, COD and TOC removal at 60 min in UVC reactor with real water.

Experimental device	Ratio	% PROP conversion	% COD removal	% TOC removal
10/100	0.1	97.70±0.49	97.12±3.51	47.27±0.77
5/50	0.1	96.34±0.83	88.19±2.14	20.39±1.81
10/25	0.4	94.09±1.29	85.70±3.20	23.65±2.62
5/12.5	0.4	92.72±1.61	69.53±1.39	9.27±0.13

In Figure 5.X. and 5.XII shows the percentages of PROP degradation and TOC removal at 60 minutes, using different ratios are presented vs. accumulated energy (kJ/L), in UVC reactor with real water.

The highest degradation of PROP was obtained with 10 mg/L of Fe²⁺ and a ratio of 0.1 (97%) that coincides and the highest TOC removal rate (47%) and was obtained when H₂O₂ was used the maximum concentration. But all experimental devices showed that UVC reactor is suitable for conversion and removal of PROP, but this is due to the high amount of photolysis, however, also influences the process UV/H₂O₂. In agreement with the values of degradation of COD removal show that the state of oxidation of organic matter has decreased almost totally.

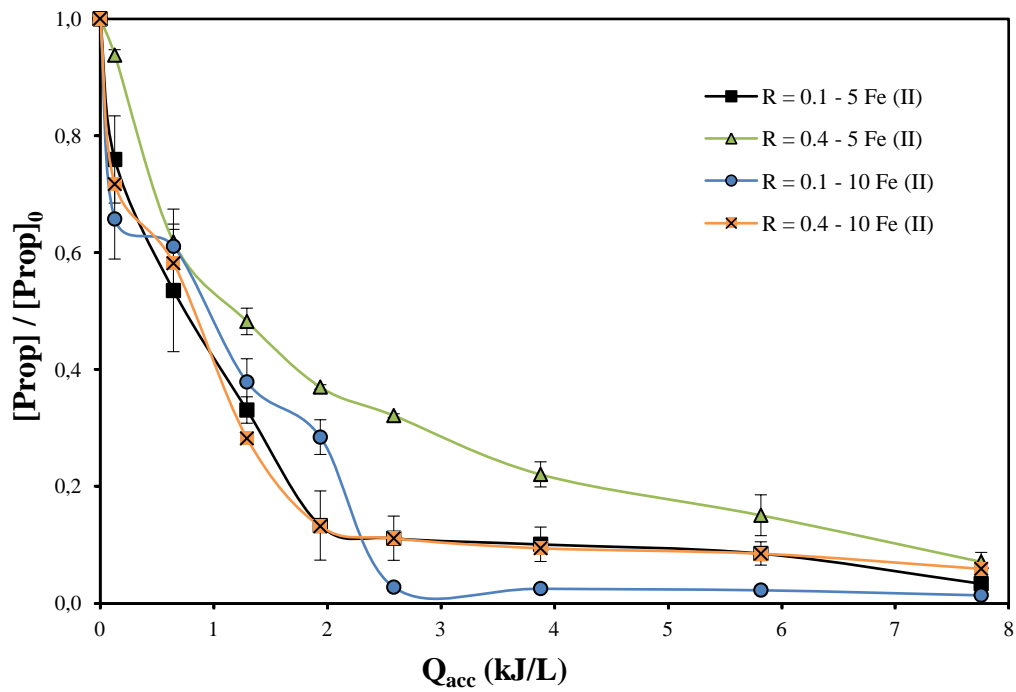


Figure 5.X. PROP degradation at 60 min in UVC with real water.

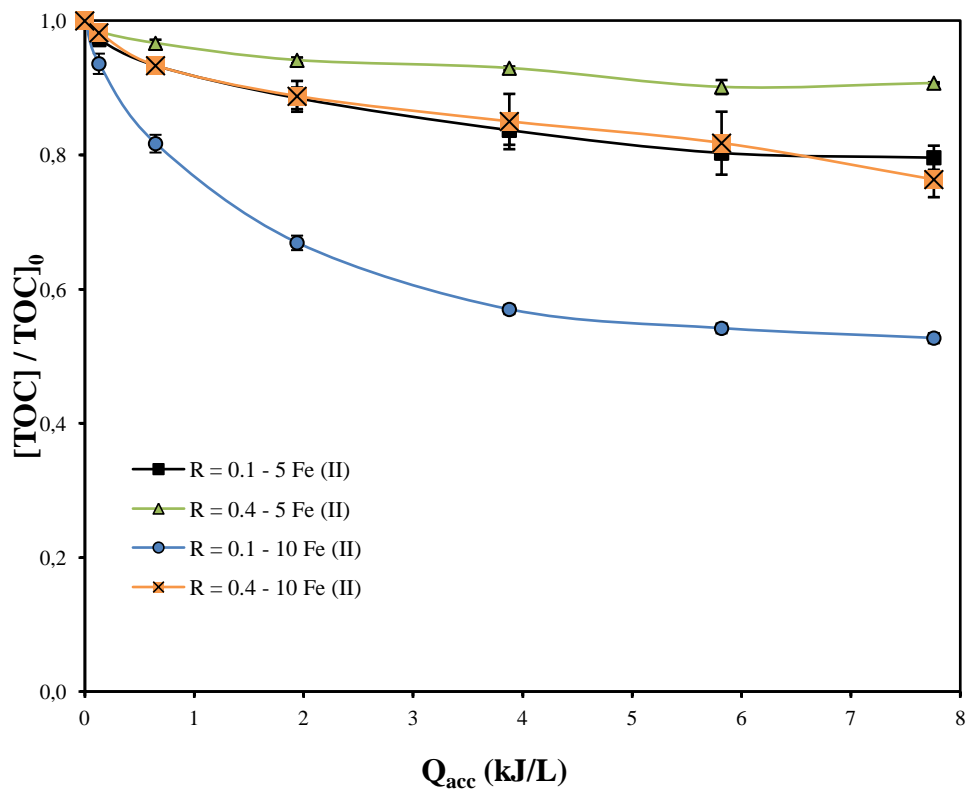


Figure 5.XI. TOC removal at 60 min in UVC with real water.

5.7 Toxicity

Regarding to hazardousness of treated solutions, toxicity (*Vibrio fisheri*) was assessed for the different experimental conditions in all devices. The result are expressed in Half maximum effective concentration (EC_{50}), is the concentration of a compound at which 50% of its maximum response is observed. Initial and final toxicity values were relatively high: EC_{50} : >100 mg/L. For treated solutions by means of the different experimental conditions in all devices, there were no changes in toxicity. With these EC_{50} values and, according to the toxicity classification established in Directive 93/67EEC (very toxic to aquatic organisms: 0.1-1 mg/L, toxic: 1-10 mg/L, harmful: 10-100 mg/L, non-toxic >100 mg/L), PROP would be considered as non-toxic to aquatic organisms and neither its intermediates [21].

5.8 Experimental design

It is decided to apply an experimental design and thus from the results will be obtained a simple mathematical model that relates the response to the experimental conditions, requiring a total of sixteen experiments and their respective replicas, in order to evaluate the main effects and interactions of the parameters involved in the degradation of PROP.

The 2^n factorial designs are the simplest possible design, requiring a number of experiments equal to 2^n , where n is the number of variables under study. In these designs each variable has two levels, coded as -1 and +1, and the variables can be either quantitative [19] (e.g., % PROP conversion and iron) or qualitative (e.g., type of water and light). The evaluation factor (dependent variable) is % PROP conversion.

Here, the concentration and the constant temperature are maintained and we seek to develop a linear model with interactions. This means that the factorial design is suitable for estimating the interactions between variables (i.e., the difference in changing variable 1 when variable 2 is at its higher level or at its lower level, and so on).

The mathematical model is therefore the following:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4$$

The model developed included design factors: light type, water type, Fe^{+2} concentration and iron Fe^{+2}/H_2O_2 ratio. The two parameters: Fe^{+2} and ratio indirectly reveal some economic aspect of the process, where smaller quantities of residual peroxide are present and less iron has, avoiding excessive and unnecessary addition of reactants and thus contributing to lower treatment costs [16].

In appendix A.III shows the nomenclature study variables in the factorial design chosen, and the appendix A.IV shows the full factorial design of experiments set-up.

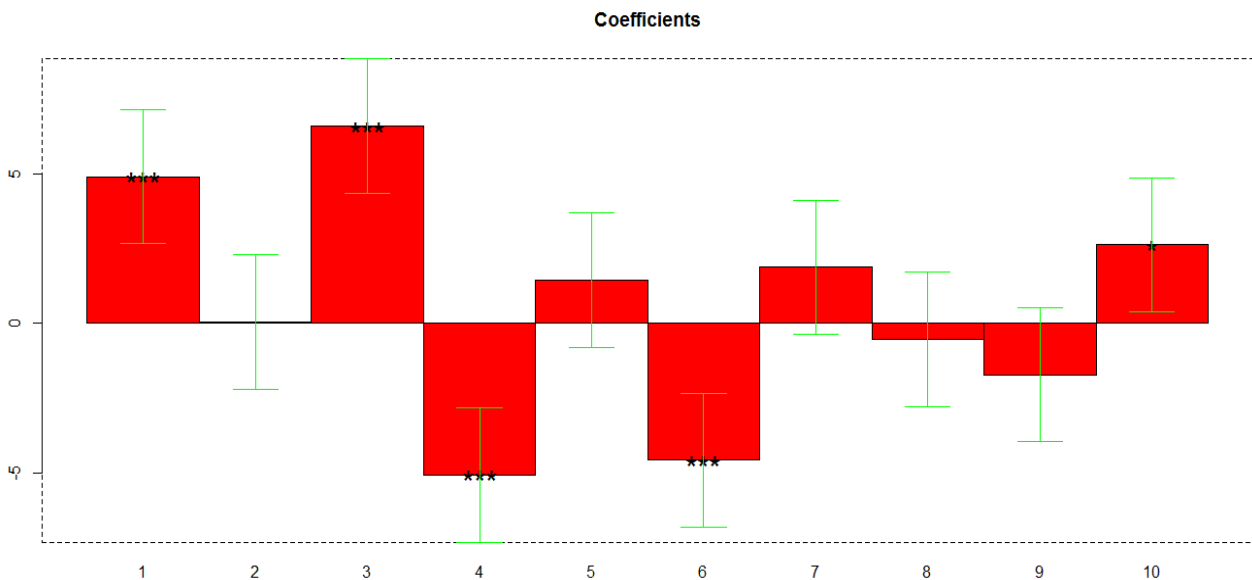
5.8.1 Modelling

The significance of the coefficients can be estimated (the level of significance is indicated according to the usual convention: * = $p < 0.05$, ** = $p < 0.01$, *** = $p <$

0.001). An easier way to look at the coefficients and at their relative magnitude is the bar plot reported in Figure 5.XII. and shows a graphical representation of the coefficients of the models of the response of the design. The mathematical model obtained is shown below:

$$Y = 89.02 - 4.89X_1 - 0.041X_2 + 6.59X_3 - 5.07X_4 + 1.44X_1X_2 - 4.57X_1X_3 + 1.87X_{14} - 0.54X_2X_3 - 1.72X_2X_4 + 2.62X_3X_4$$

Figure 5.XII. Plot of the coefficients of the model. The brackets correspond to the confidence intervals at $p = 0.05$; the stars indicate the significance of the coefficient.



The statistical treatment allows to draw conclusions about which variables are the most important in the process, and to ensure it with a high level of confidence.

In this case the variables that if they are significant are type of light and concentration of faith. And the significant interactions are: type of light, type of water and ratio.

The most significant relationships in the propranolol conversion that observed were:

- **X₁**: type of light, there is a positive relationship, which favors the degradation option being more effective with UVC.
- **X₂**: type of water: there is no significant relationship.
- **X₃**: Fe⁺² concentration, which favors the degradation option being more effective with 10 ppm de Fe²⁺.
- **X₄**: ratio , there is a negative relationship, means that the best results was obtained when the ratio is 0.1
- **X₁-X₃**: the interaction with type of light and Fe⁺², are negative because always increase the iron concentration goes better in BLB in comparison with UVC.

- **X₃-X₄**: the interaction with Fe⁺² and ratio are negative, although it must be taken into account that the measure has a high standard of error. The ratio effect is higher with higher concentrations of iron.

One more comment. The above example is not an optimization. Probably, if more experiments were done with more experimental designs, better results could have been obtained. The immediate objective was to find the optimum and find a commercially valid solution, and the factorial design, allowed to obtain very valuable information with a very limited experimental effort [19].

6. Economical consideration

As previously stated, in this study different energetic radiation were used to evaluate their contribution to PROP 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 is based on the conversion of the energy consumption of the necessary equipment into monetary cost. To this amount is added the cost of the reagents: iron and hydrogen peroxide all of them normalized to the reactor volume. For this section it is assumed that the cost of analysis reagents are constant. The number of orders of magnitude was calculated from the ppm degradations of PROP.

Finally, technical-scale commercial prices were taken for chemical reagents used and converted to energy values of Catalonia (Spain) in 2017 (0.15 €/kWh) [20].

In annex A.V shows the prices of reagents. Table A.VI. in the same annex shows the energy requirements of the experiments performed in different experimental devices and their prices. In this case the energy cost is equal, as much for BLB as for UVC. Therefore, in this section the cost difference will be given only by the type of water used, since the use of Milli-Q must be added. Although in this case it is imperceptible, since the used volume is of 2L and the difference in the final price of the energetic cost is of 0.01. The result is expressed as €/ppm converted to be able to compare the efficiencies of each case.

Table 6.VIII. Efficiency of each experiment expressed in €/ppm converted.

Experimental device	BLB MQ	UVC MQ	BLB real water	UVC real water
5/10	0.066	0.051	0.080	0.069
5/50	0.19	0.16	0.17	0.17
10/25	0.090	0.096	0.091	0.094
10/100	0.31	0.30	0.30	0.35

6.1 Economical conclusions

- There were no significant differences in cost depending on the reactor used.
- The most economical treatment of all performed is: UVC Milli-Q, 5 ppm Fe⁺² and ratio of 0.4 with a cost of 0.051 €/ppm converted
- The most economical treatment of all the facts in which the photo-Fenton treatment is given correctly is BLB Milli-Q, 5 ppm Fe⁺² and ratio of 0.4 with a cost of 0.066 €/ppm converted.
- The most expensive reagent is peroxide, so if we use more it will make the process more expensive.

6.2 Recommendations

The most economical treatment is BLB Milli-Q, 5 ppm Fe + 2 and ratio of 0.4, but this one has a degradation of 72%.

Which is why we recommend BLB Milli-Q treatment, 10 ppm Fe + 2 and ratio of 0.4 That although it has a slightly higher cost 0.09 €/ppm its degradation amounts to 94%.

7. Conclusions

It can be concluded that PROP degradation, TOC and COD removal via photo-Fenton are highly dependent on iron concentrations and ratio used.

7.1 BLB reactor:

- Photolysis are negligible in BLB reactor.
- The results show that higher concentrations of Fe⁺² lead to better degradation rates. When the Fe⁺² concentration the same as the maximum values are found in those cases in which concentration of H₂O₂ is higher.
- The experiments indicated that the most effective strategy for the degradation and mineralization of PRO by photo-Fenton in were obtained at 10 mg/L of Fe²⁺ and a ratio of 0.1.

7.2 UVC reactor:

- Photolysis are very important in UVC reactor.
- The results show that higher concentrations of H₂O₂ lead to better degradation rates.
- The experiments indicated that the most effective strategy for the degradation and mineralization of PRO by photo-Fenton in Milli-Q water were obtained in BLB reactors because in UVC reactor there is a high amount of photolysis, however, also influences the process UV/H₂O₂, therefore the photo-Fenton process is not being given correctly.

7.3 Experimental design

The most significant variables in the propranolol conversion that observed were:

- Reactor: the most effective is UVC
- Iron concentration: the degradation option being more effective with 10 ppm de Fe²⁺.
- Ratio: that the best results was obtained when the ratio is 0.1.

8. Literature

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10. Annexes

Table A. I. Experimental design table

Light sources	Type of water	Ratio [Fe ²⁺ /H ₂ O ₂]	[Fe ²⁺] mg/L
BLB	MilliQ	0.1	5
BLB	MilliQ	0.1	10
BLB	MilliQ	0.4	5
BLB	MilliQ	0.4	10
UVC	MilliQ	0.1	5
UVC	MilliQ	0.1	10
UVC	MilliQ	0.4	5
BLB	Real water	0.1	5
BLB	Real water	0.1	10
BLB	Real water	0.4	5
BLB	Real water	0.4	10
UVC	Real water	0.1	5
UVC	Real water	0.1	10
UVC	Real water	0.4	5
UVC	Real water	0.4	10

Table A. II. Calibration curve of propanolol

patr3 (ppm)

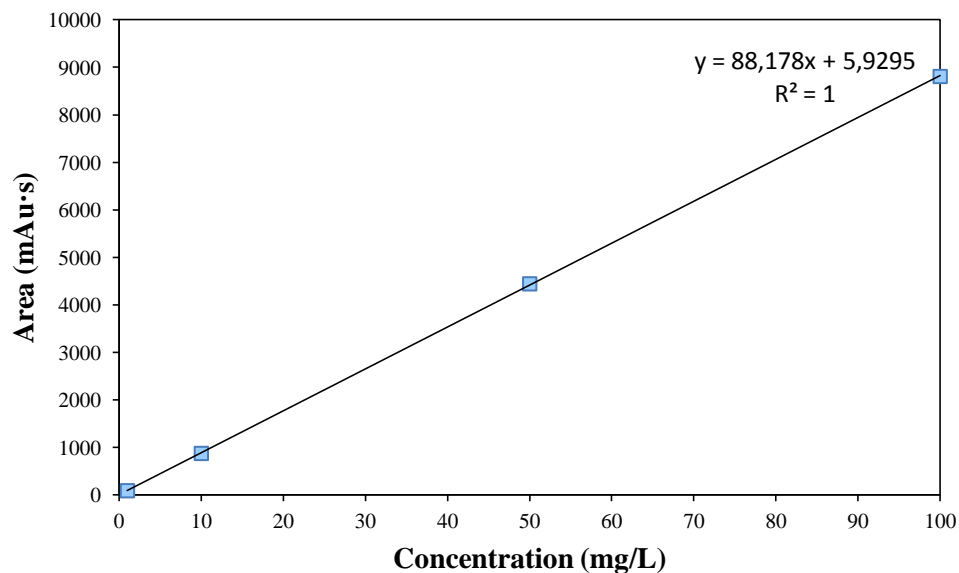


Table A. III. Nomenclature the study variables in the factorial design

	-	+
X₁	BLB	UVC
X₂	MQ	Real
X₃	5	10
X₄	0.1	0.4

Table A. IV. The experimental matrix of the 2⁴ factorial design. (Y = % PROP conversion)

X₁	X₂	X₃	X₄	Y
-1	-1	-1	-1	78.46
-1	-1	-1	-1	74.93
1	-1	-1	-1	95.75
1	-1	-1	-1	96.25
-1	1	-1	-1	90.91
-1	1	-1	-1	91.97
1	1	-1	-1	97.17
1	1	-1	-1	95.51
-1	-1	1	-1	99.00
-1	-1	1	-1	99.18
1	-1	1	-1	97.83
1	-1	1	-1	97.21
-1	1	1	-1	98.86
-1	1	1	-1	95.18
1	1	1	-1	98.19
1	1	1	-1	99.00
-1	-1	-1	1	72.40
-1	-1	-1	1	71.97
1	-1	-1	1	81.84
1	-1	-1	1	83.23
-1	1	-1	1	56.87
-1	1	-1	1	46.25
1	1	-1	1	94.33
1	1	-1	1	91.15
-1	-1	1	1	93.62
-1	-1	1	1	94.67
1	-1	1	1	94.55
1	-1	1	1	92.80
-1	1	1	1	87.11
-1	1	1	1	94.67
1	1	1	1	95.38
1	1	1	1	92.46

Table A.V. Prices of reagents

H₂O₂ (ppm)	H₂O₂ (mL)	Cost 1L (€/L)	Real cost (€)
10	0.067	21.25	1.42
25	0.17	21.25	3.54
50	0.34	21.25	7.08
100	0.67	21.25	14.17
Fe (ppm)	Fe (g)	Cost (€/kg)	Real cost(€)
5	0.050	26.38	0.0013
10	0.10	26.38	0.026

Table A.VI. Requirements of the experiments performed in different experimental devices and your prices.

Equipment	Time use equipment (h/exp)	Power (W)	Consumption (kWh)	Cost (€)	Consumption (%)
Lamp (24 W)	1.00	0.024	0.024	0.0035	0.37
Thermostatic bath (240 W)	1.00	0.24	0.24	0.035	3.68
Magnetic stirrer (1-5 W)	1.00	0.0025	0.0025	0.00037	0.038
HPLC (8 min/sample)	1.20	2.00	2.40	0.35	36.77
TOC (15 min/sample)	1.75	2.20	3.85	0.57	59.00
Water desionization device	0.10	0.10	0.010	0.0015	0.15
		Total	6.53	0.96	

Table A.VII. Real water characterization

Real water	
Alkalinity (mg CaCO ₃ /L)	346,19
pH	7,76
DQO total (mgO ₂ /L)	12,38
DQO soluble (mg O ₂ /L)	1,29
DQO particulada (mgO ₂ /L)	11,09
Turbidity (NTU)	0,85
DBO (mgO ₂ /L)	1,4
DOC (mgO ₂ /L)	15,33
TN (mgN/L)	3,68
SUVA	0,18
ST (g/L)	2,36
STF (g/L)	0,61
STV (g/L)	1,75
SST (g/L)	0,014
SSF (g/L)	0,012
SSV (g/L)	0,002
SDT (g/L)	2,34
SDF (g/L)	0,59
SDV (g/L)	1,75