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The role of the wastewater matrix in the degradation of Metoprolol by photo-Fenton process at circumneutral pH

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Index

Chapter I: Introduction

1. Introduction	1
1.1 Actual water situation	1
1.2 Water treatment: Gavà i Viladecans wastewater treatment plant.....	2
1.3 Emerging contaminants	4
1.3.1 Beta blockers: Metoprolol	4
1.4 Advanced oxidation processes.....	5
1.4.1 Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$)	5
1.4.2 Conventional photo-Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$)	5
1.4.3 Photo-Fenton at circumneutral pH ($\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$)	5
1.5 Legal framework of water	6

Chapter II: Objectives and experimental setup

2. Objectives	7
3. Material and methods	7
3.1 Samples preparation	9
3.2 Experimental devices.....	10

Chapter III: Results and discussion

4. Previous experiments.....	12
4.1 Thermo-degradation and photolysis	12
4.2 Characterization of mineral water and wastewater.....	12
4.3 Selection of chelating agent.....	12
4.4 Interaction between iron, hydrogen peroxide and chelating agent.....	14
5. Photo-Fenton experiments	15
5.1 Mineral water.....	15
5.1.1 MET degradation	15
5.1.2 TOC, COD, and SUVA reduction	17
5.1.3 Toxicity.....	17
5.2 MBR wastewater	18
5.2.1 MET degradation	18
5.2.2 TOC and COD reduction	20
5.2.3 Toxicity.....	20
6. Preliminary cost analysis	21
7. Conclusions	24
8. Future work	24
Bibliography	25
Annex	28

List of figures

Figure 1: Projected water scarcity in 2025. Source IWMI, 2013	1
Figure 2: Water exploitation index (%) around year 2030 in Europe. Source: EEA, 2012	2
Figure 3: Integral water cycle	2
Figure 4: Scheme of water line treatment: pretreatment (represented in blue colour), physical-chemical treatment (represented in orange colour) and biological treatment (represented in green colour) of Gavà WWTP. (Adapted from l'Àrea Metropolitana de Barcelona, EDAR de Gavà i Viladecans).....	3
Figure 5: MET structure	4
Figure 6: HPLC 1260 from Waters	8
Figure 7: TOC-VCNS analyzer Shimadzu	8
Figure 8: Spectrophotometer Hach Lange DR 3900	9
Figure 9: Iron vials	9
Figure 10: Spectrophotometer Hach Lange DR 6000	9
Figure 11: COD vials.....	9
Figure 12: BLB device	10
Figure 13: CPC device.....	11
Figure 14: MET degradation under conditions of 2.5 mg/L Fe^{2+} and different H_2O_2 concentrations in mineral water.....	15
Figure 15: MET degradation under conditions of 5.0 mg/L Fe^{2+} and different H_2O_2 concentrations in mineral water.....	15
Figure 16: MET degradation under conditions of 10.0 mg/L Fe^{2+} and different H_2O_2 concentrations in mineral water.....	16
Figure 17: MET degradation under conditions of 2.5 mg/L Fe^{2+} and different H_2O_2 concentrations in MBR wastewater.....	18
Figure 18: MET degradation under conditions of 5.0 mg/L Fe^{2+} and different H_2O_2 concentrations in MBR wastewater.....	18
Figure 19: Comparison of MET degradation in BLB and CPC reactor under conditions of 5.0 mg/L Fe^{2+} and 150 mg/L H_2O_2 in MBR wastewater	19
Figure 20: Conversion of area measured in HPLC to MET concentration	28

List of tables

Table I. Reactives used in the experimental work.....	8
Table II. Technical characteristics of the BLB reactor.....	10
Table III. Technical characteristics of the CPC reactor.....	11
Table IV. Mineral water and MBR wastewater characterization results.....	12
Table V. Chelating agents assessed and their stability constant with Fe ²⁺ in mineral water and the respective result: “x” if iron precipitates, “√” if iron keeps in solution .	13
Table VI. Chelating agents assessed and their stability constant with Fe ²⁺ in real wastewater and the respective result: “x” if iron precipitates, “√” if iron keeps in solution	13
Table VII. Summary of the obtained results using different chelating agents in MBR wastewater	14
Table VIII. Different Fe ²⁺ :EDDS ratios tested in MBR wastewater.....	14
Table IX. Summary table of the parameters evaluated in the experiments with mineral water	16
Table X. Evolution of toxicity under the different experimental conditions with mineral water	17
Table XI. Summary table of the parameters evaluated in the experiments with MBR wastewater	19
Table XII. Evolution of toxicity under the different experimental conditions with MBR wastewater	20
Table XIII. Economic requirements of photo-Fenton carried out in different experimental conditions.....	22
Table XIV. Contribution of energy and reagents cost in total cost (%).....	23
Table XV. Conversion of reagents quantity to economic values	23
Table XVI. Quantity of reagent used	23

Abbreviations and acronyms

AOPs	Advanced oxidation processes
BLB	Black light blue
CLRTAP	Convention on Long-range Transboundary Air Pollution
COD	Chemical oxygen demand
CPC	Compound parabolic collector
E°	Redox potential
ECs	Emerging contaminants
EC ₅₀	Effective concentration
EDDS	Ethylenediamine-N,N'-disuccinic acid
EDTA	Ethylenediaminetetraacetic acid
EE, bath	Electric power of thermostatic bath
EE, HPLC	Electric power of HPLC device
EE, irr	Electrical power of irradiation
EE, str	Electric power of magnetic stirrer
EE, TOC	Electric power of TOC device
EE, tot	Total electrical power
EEA	European Environment Agency
Fe	Iron
FOG	Fats oils and greases
FSCS	Ferrous sulphate chelate solution
HPLC	High performance liquid chromatography
H ₂ O ₂	Hydrogen peroxide
<i>hν</i>	Radiation
IC	Inorganic carbon
IFAS	Integrated fixed film activated sludge
IPs	Intermediate products
ISO	International Organization for Standardization

IWMI	International Water Management Institute
MBR	Membrane bioreactor system
MET	Metoprolol
nm	Nanometer
NOM	Natural organic matter
NPOC	Non-purgable organic carbon
NTA	Nitrilotriacetic acid
OH·	Hydroxyl radical
POPs	Persistent organic pollutants
ppm	Parts per million
ppb	Parts per billion
PPCPs	Personal care products
Qacc	Accumulated energy
rpm	Revolutions per minute
SUVA	Specific UV absorption
TN	Total nitrogen
TOC	Total organic carbon
UV	Ultraviolet light
WFD	Water Framework Directive
WEI	Water exploitation index
WWTP	Waste water treatment plant
λ	Wavelength
μm	Micrometers

Abstract

Increasingly, human activities and lifestyles of developed countries are jeopardizing the viability of ecosystems, especially with the expansion of the chemical industry and the production of so-called emerging contaminants, including cleaning products, cosmetics, pharmaceuticals etc. Metoprolol (MET) is a type of beta-blocking drug increasingly consumed in Spain. Although these contaminants are only present in minute concentrations (ppm or ppb) they could seriously affect aquatic ecosystems if they are not removed from the wastewater.

The most common treatment techniques used for removing contaminants in wastewaters have no influence on the degradation of emerging contaminants. This, coupled with the increasing demands on water quality imposed by the Water Framework Directive (2000/60/CE) makes necessary to use alternative techniques that enable the degradation of the contaminants. This is where the advanced oxidation processes (AOPs) come into play.

In this project the photo-Fenton process has been applied to degrade MET, added to mineral water and wastewater from membrane bioreactor system (MBR) treatment from Gavà wastewater treatment plant (WWTP). The optimal pH of this process is 2.8 but in this project the experiments will be assessed at circumneutral pH to improve the process to all levels, not only industrial. In order to maintain the iron in solution different chelating agents have been assessed. Different concentrations of hydrogen peroxide and iron have been tested (25, 150 mg/L H₂O₂ and 2.5, 5.0 and 10.0 mg/L Fe²⁺). All experiments were carried out in the period of 60 minutes and the following variables were assessed: MET degradation, total organic carbon (TOC) and chemical oxygen demand (COD) reduction, specific UV absorption (SUVA) and toxicity.

It has been proved that MET does not suffer photolysis. In mineral water ethylenediaminetetraacetic acid (EDTA) has acted as a chelating agent. The highest MET degradation and COD, SUVA and toxicity reduction in mineral water were obtained for the highest concentrations of iron and hydrogen peroxide (Fe²⁺:H₂O₂ 10:150) with a values of 100%, 45.4%, 54.8%, 91.9% respectively. This is because the increase in the H₂O₂ dose enhances the reaction rate due to higher OH· production. Regarding the reduction of TOC it was highest under the conditions Fe²⁺:H₂O₂ 5:150.

Wastewater from MBR treatment was also investigated. The method applied in mineral water does not work so EDTA had to be changed by ethylenediamine-N,N'-disuccinic acid (EDDS). No significant differences in MET degradation have been observed when different concentrations of iron and hydrogen peroxide were assessed. The highest COD reduction was obtained for the highest concentrations of iron and hydrogen peroxide (Fe²⁺:H₂O₂ 5:150) with a value of 46.8%. Higher toxicity reduction was achieved when the concentration of iron was the lowest (2.5 mg/L) with a value of 90.4%. Regarding TOC reduction, it was highest when hydrogen peroxide concentration was highest (150 mg/L). In order to compare the efficiency of the process under sunlight conditions an experiment was carried out in a compound parabolic collector (CPC) reactor.

Keywords: photo-Fenton, circumneutral pH, MET, EDTA, EDDS.

Chapter I: Introduction

1. Introduction

1.1 Actual water situation

According to the Water Framework Directive (WFD) 2000/60/EC: "Water is not a commercial product like any other but, rather, a heritage which must be protected, defended and treated as such", because water is essential for life and living matter includes very high percentages of it in its composition. Currently the water supply to meet the daily needs of a person (ranges between 50-100 L/(habitant · day), (Human Development Report, 2006) is being increasingly compromised in some parts of the world. According to the International Water Management Institute (IWMI) it is expected that by 2025 the world water scarcity will be a serious problem for the countries of the southern hemisphere and a not severe problem for the countries of the northern hemisphere, Spain is classified as "Little or no water scarcity" (*Figure 1*). The IWMI classify the countries in six groups.

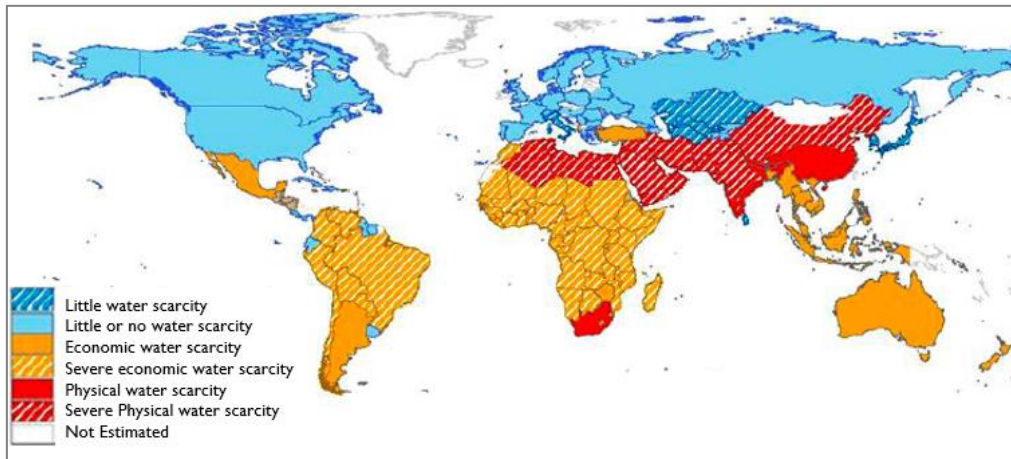


Figure 1: Projected water scarcity in 2025. Source: IWMI, 2013.

According to the information shown in *Figure 1*, although it is a prediction, it seems that countries in the northern hemisphere should not dedicate much effort in finding new sources of water. This is in contrast to the data obtained by the European Environment Agency (EEA) leading to conclusions such as: "While water is abundant in Europe, water scarcity and droughts continue to affect some water basins in particular seasons. The Mediterranean region and most of the densely populated river basins in different parts of Europe are hot spots for water stress conditions" (Use of freshwater resources, EEA, 2016). One way to distinguish sensitive countries from water shortage is by calculating the water exploitation index (WEI), which is obtained by dividing the total water abstraction by the long term annual average resource of freshwater. The warning threshold, which distinguishes a non-stressed region from a water scarce region, is around 20% (EEA, 2011). This is reflected in *Figure 2*.

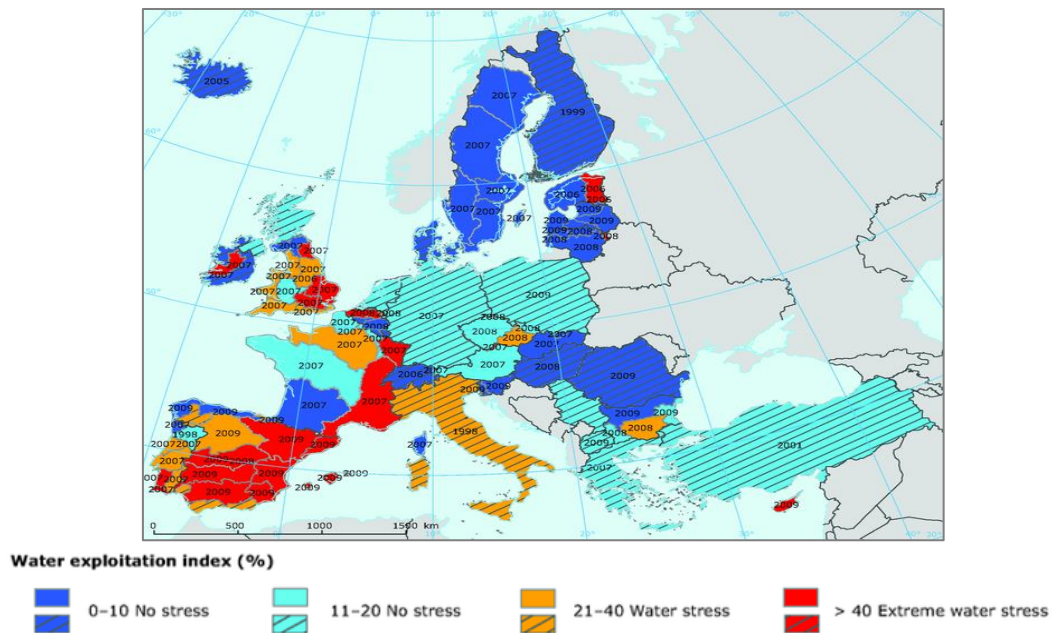


Figure 2: Water exploitation index (%) around year 2030 in Europe. Source: EEA, 2012.

According to the EEA in the year 2030 it is predicted that different European countries are considered to have severe water stress, Spain is one of them. Because of that it is necessary to make an effort to get a better water quality and look for another water sources.

The main objective of wastewater reclamation and reuse projects is to produce water of sufficient quality for all non-potable uses (uses that do not require drinking water quality standards) such as agricultural and landscape irrigation, environmental applications (surface water replenishment, and groundwater recharge), etc. The use of reclaimed water for these applications would save significant volumes of freshwater that would otherwise be wasted. In *Figure 3* is shown the reuse water cycle.

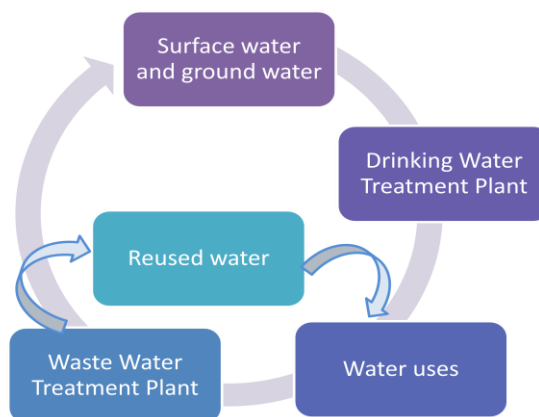


Figure 3: Integral water cycle

1.2 Water treatment: Gavà i Viladecans wastewater treatment plant

Gavà wastewater treatment plant (WWTP) purifies urban and industrial wastewater and also rainwater from Gavà, Sant Boi de Llobregat, Sant Climent de Llobregat and Sitges.

The main objectives of the sewage plant are the elimination of: solid waste, sand, fats, oils and foams, organic matter, nutrients and surfactants.

In order to carry out this purpose, the WWTP has a set of processes: pretreatment, physical-chemical treatment and biological treatment (See *Figure 4*).

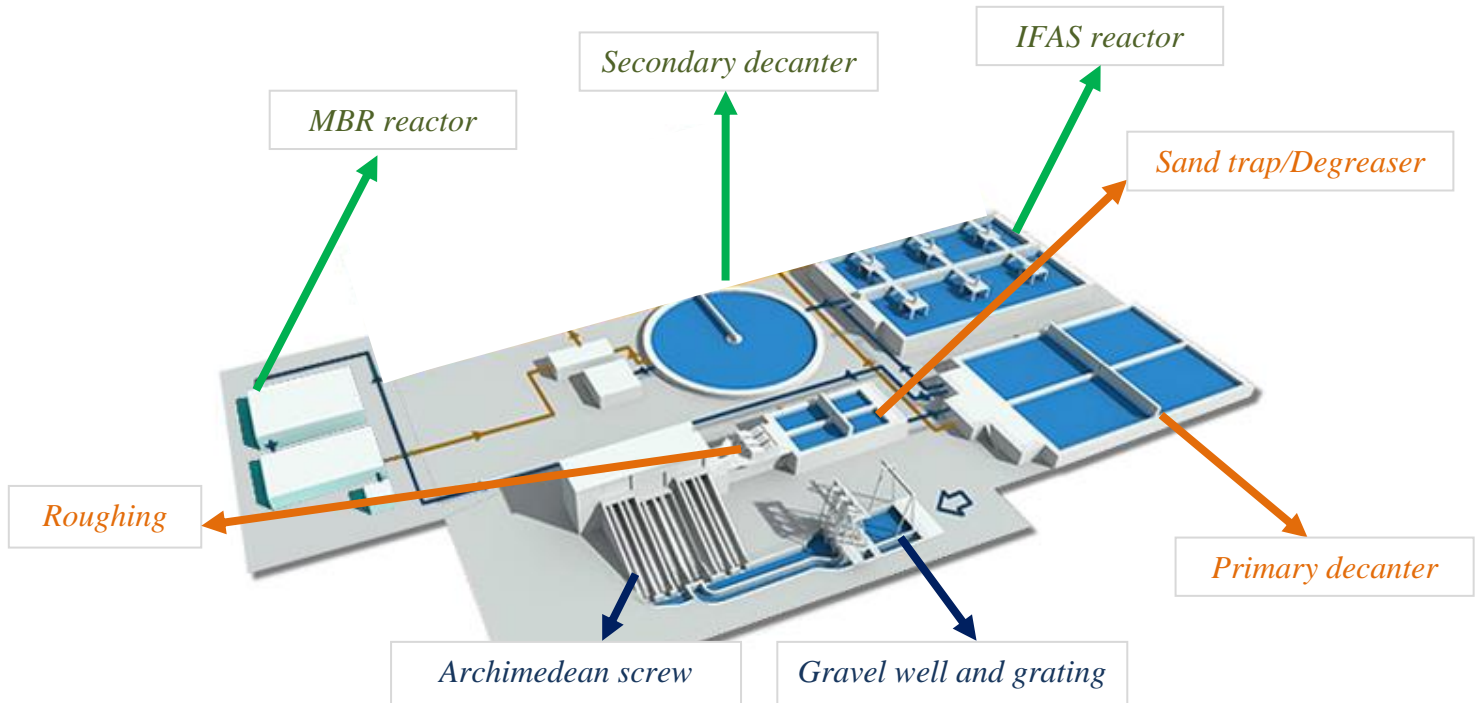


Figure 4: Scheme of water line treatment: pretreatment (represented in blue colour), physical-chemical treatment (represented in orange colour) and biological treatment (represented in green colour) of Gavà WWTP. (Adapted from l'Àrea Metropolitana de Barcelona, EDAR de Gavà i Viladecans)

The studied water was taken from the secondary decanter after the biological treatment. This treatment aims to eliminate organic matter and dissolved nutrients through the action of microorganisms and chemical additives in the case of phosphorus. In Gavà WWTP the water is distributed equally in two different treatments: integrated fixed film activated sludge (IFAS) line, and membrane bioreactor system (MBR) line.

- IFAS: Water from the primary decanter is passed through a configuration of anoxic-aerobic reactors. This treatment differs by incorporating mobile media in the aerobic reactor that allow the growth of biofilm, increasing the efficiency of the process.
- MBR: The other part of the water that is not treated in the IFAS line is passed through an MBR reactor where ultrafiltration (passage light of $0.04 \mu\text{m}$) is carried out. The water that reaches this line comes directly from the pretreatment.

After this biological treatment, water coming from IFAS treatment is poured into the environment. In the case of MBR, disinfection is applied and after that water can be reused.

Almost in all the experimental work MBR wastewater was used. Regarding water from IFAS treatment, only the optimal ratio of Fe^{2+} :EDDS has been determined due to time constraint.

1.3 Emerging contaminants

The following contaminants are present in water:

- Suspended matter
- Fats, oils and greases (FOG)
- Natural organic matter (NOM)
- Microorganisms
- Pharmaceuticals and personal care products (PPCPs)
- Others: pesticides, flame retardants, fuel additives...

The vast majority of compounds present in these two last points are recognised as emerging contaminants (ECs). The WWTP are not designed for these types of pollutants, thus they can remain almost totally at the effluent of the WWTP.

ECs can be broadly defined as a group of organic pollutants that were previously undetected or had not been considered as a risk (Polar, 2007). A wide range of compounds are considered to be relevant ECs, such as: detergents, personal care products, drugs, flame retardants, antiseptics, fragrances, industrial additives, steroids and hormones, amongst others. They have been detected in ranges varying from ppm to ppb (Polar, 2007) in effluents of municipal WWTP, rivers, aquifers and even in drinking water (Ioannou, et al., 2011; Muñoz, et al., 2009; Yu, et al., 2006). Many of these ECs raise considerable toxicological and public concern (Ioannou et al., 2011; Rivas, et al., 2010) because, many of them are omnipresent and persistent and have high biological activity which, associated with a persistent toxic character, implies a potential impact on aquatic species even at low concentrations.

1.3.1 Beta blockers: Metoprolol

Beta blockers are a type of pharmaceuticals used to treat a variety of cardiovascular diseases, such as hypertension, coronary artery disease, and arrhythmias (Benner, et al., 2009) by blocking the action of epinephrine and norepinephrine on the β -adrenergic receptors in the body, primarily in the heart.

Metoprolol (MET) is a beta blocker highly prescribed in our country. Around 10% of the applied MET dose is excreted unchanged. This added to its low biodegradability makes it present in WWTP influents at concentrations varying from 0.6 to 2.0 $\mu\text{g/L}$ (Bendz, et al., 2005; Gros et al., 2006; Romero, et al., 2013; Ternes et al., 2003; Vieno et al., 2007a and Vieno et al., 2007b).

Several researches have demonstrated that MET shows slow direct photo-transformation and/or hydrolysis. (Liu, et al., 2009; Píram, et al., 2008; Rivas et al., 2010; Romero et al., 2013).

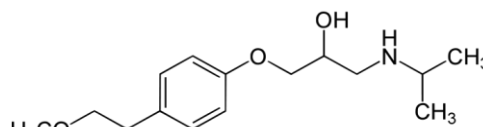


Figure 5: MET structure

The half-life of MET under solar light has been reported to be several hundreds of hours (Alder, et al., 2010; Rivas et al., 2010) due to its recalcitrant nature.

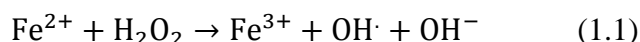
In this context, advanced oxidation processes (AOPs) appear as a good alternative to upgrade existing treatments for its degradation due to their versatility and ability to increase biodegradability.

1.4 Advanced oxidation processes

Advanced oxidation processes are a set of techniques that, using different agents, produce hydroxyl radicals (OH[•]). Due to its high oxidative capacity, these processes can chemically oxidize recalcitrant compounds present in aqueous effluents.

1.4.1 Fenton (H₂O₂/Fe²⁺)

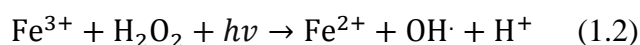
For over a century, H.J. Fenton, reported on the oxidative power that has hydrogen peroxide with certain organic molecules when iron salts were used as a catalyst. Later, it was discovered that this was due to the generation of OH[•] (*E*^o 2.80 V) according to the following reaction (Walling, 1975):



This reaction is spontaneous and it can be produced without light. In the presence of H₂O₂ and at pH ≤ 3, the reaction system is autocatalytic, because Fe³⁺ reacts with H₂O₂ giving Fe²⁺, which can be generated at a slow rate (K= 0.001-0.02 M⁻¹s⁻¹) (Litter and Quici, 2010). This reaction shows that iron acts as a catalyst and hydrogen peroxide as an oxidant.

1.4.2 Conventional photo-Fenton (H₂O₂/Fe²⁺/UV)

Fenton reaction (1.1) is the most applied for recalcitrant compounds removing, due to its simplicity. The worst drawback of this process is that it produces waste sludge of iron. To avoid this, photo-Fenton process has been developed for the reduction of Fe³⁺ to Fe²⁺, which reduces the amount of sludge formed (Voogelpohl, 2007). Photo-Fenton improves the degradation rate of organic pollutants with the addition of UV/visible light (λ= 300-420 nm) due to the generation of OH[•] during the regeneration of Fe²⁺ (1.2).



1.4.3 Photo-Fenton at circumneutral pH (H₂O₂/Fe²⁺/UV)

To increase photo-Fenton efficiency, the pH should be set at around 2.8, and then it has to be increased to neutral afterwards for water disposal (Pignatello, et al., 2007). This pH-conditioning increases the process cost and water salinity, so there is a strong interest in working at circumneutral pH to avoid it (Sánchez Pérez et al., 2013). However, at neutral pH, iron precipitates and then reaction ceases and consequently the degradation of MET (De la Obra, et al., 2017). In order to avoid the aforementioned it is required that iron remains dissolved. The main strategy consists of adding a chelating agent to able to form stable complexes with iron under the given conditions.

Several complexing agents have been tested such as oxalate, citrate, ethylenediaminetetraacetic acid (EDTA) and ethylenediamine-N,N'-disuccinic acid (EDDS) (Tang and Liu, 2016). The inconvenience of the use of chelating agents

consists of preparing an acidic solution to achieve complete dissolution in order to form a complex with the iron. In this project different chelating agents will be studied with the aim of finding one which can be dissolved at neutral pH.

1.5 Legal framework of water

European level

- Directive 2000/60/EC of the European Parliament and of the Council, of 23 October 2000, establishing a framework for the Community action in the field of water policy. To protect our water resources and the water environment since 2000 the WFD has been in place as the main European legislation. It requires managing the water so that its quality and quantity does not affect the ecological services of any specific water body.

The European Parliament and the Council shall adopt specific measures against pollution of water by individual pollutants or groups of pollutants presenting a significant risk to or via the aquatic environment, including such risks to waters used for the abstraction of drinking water (European Commission, 2000).

- Directive 91/271/CEE, concerning urban wastewater treatment. (European Commission, 1991).

In the EU, the commitments made under both the Stockholm Convention and the Convention on Long-range Transboundary Air Pollution (CLRTAP) persistent organic pollutants (POPs) protocol are translated into directly applicable law by the POPs Regulation.

- Regulation (EC) No 850/2004 of the European Parliament and of the Council of 29 April 2004 on persistent organic pollutants and amending Directive 79/117/EEC (European Commission, 2004).

Spanish level

- Real Decreto Ley 11/1995, de 28 de diciembre, por el que se establecen las normas aplicables al tratamiento de las aguas residuales urbanas. Desarrollado por el Real Decreto 509/1996, de 15 de marzo (Spanish Government, 1996).

- Real Decreto Legislativo 1/2001, de 20 de Julio, por el que se aprueba el texto refundido de la Ley de Aguas (Spanish Government, 2001).

- Real Decreto 1620/2007, de 7 de diciembre, por el que se establece el régimen jurídico de la reutilización de las aguas depuradas. (Spanish Government, 2007).

- Real Decreto 817/2015, de 11 de septiembre, por el que se establecen los criterios de seguimiento y evaluación del estado de las aguas superficiales y las normas de calidad ambiental. Modifica el Real Decreto 509/1996. (Spanish Government, 2015).

Catalonian level

- Decret Legislatiu 3/2003, de 4 de novembre, pel qual s'aprova el text refós de la legislació en matèria d'aigües de Catalunya. (Catalonia Government, 2003).

- Decret 130/2003, de 13 de maig, pel qual s'aprova el Reglament dels serveis públics de sanejament DOGC núm. 3894, 29.05.2003. (Catalonia Government, 2004).

Chapter II: Objectives and experimental setup

2. Objectives

General objective

- Check degradation of MET by photo-Fenton process at circumneutral pH in different water matrix.

Mineral water

- Check degradation of MET in mineral water under circumneutral pH conditions.
- Find a viable method to accomplish the elimination of MET in real waters through photo-Fenton process at circumneutral pH conditions.
- Achieve optimal conditions for the degradation of the pollutant.
- Investigate different chelating agents in order to optimise the process under neutral pH conditions.
- Check the process feasibility with iron concentrations lower than those stipulated by law.

Gavà wastewater

- Check degradation of MET in real water under circumneutral pH conditions.
- Verify that the viable method in mineral water is feasible in real water.
- Achieve optimal conditions for the degradation of the pollutant.
- Investigate different chelating agents in order to optimise the process under neutral conditions.

3. Material and methods

The initial solution has been prepared at a concentration of 50 mg/L of MET Tartrate salt. This high value was selected because it is the real concentration that can come from some industries (Romero, et al., 2016). MET concentration was monitored by HPLC 1260 from Waters using a Teknokroma column, and 80 Hz UV detector (*Figure 6*). The mobile phase was composed of water (pH 3) and acetonitrile (80:20), injected with a flow-rate of 0.85 ml/min. MET concentration was followed at UV maximum absorbance (221.9 nm). TOC was analyzed with a Shimadzu TOC-VCNS analyzer (*Figure 7*). To determine chemical oxygen demand (COD), the Standard Methods 5220D procedure was followed, using a spectrophotometer Hach Lange DR 3900 (*Figure 8*) at 420 nm. H₂O₂ consumption was followed using the metavanadate spectrophotometric method at 450 nm. The Fe²⁺ content was determined by o-phenanthroline standardized procedure (ISO 6332). The specific ultraviolet absorbance (SUVA) was measured using a spectrophotometer Hach Lange DR 6000 (*Figure 10*) at 254 nm. For the toxicity assessment, the bioassay Microtox was used, where the inhibition of *Vibrio fischeri* bioluminescence at 30 minutes of incubation was determined. All the reactivities used are shown in *Table I*.

Table I. Reactives used in the experimental work

Reactive	Nomenclature	Provider	Purity (%)
Iron sulphate hepta-hydrate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Panreac	99
Hydrogen peroxide	H_2O_2	Panreac	30
Sodium bisulphate	NaHSO_3	Panreac	40
Methanol	CH_3OH	Panreac	90
Phenanthroline	$\text{C}_{12}\text{H}_8\text{N}_2$	-	-
Ammonium vanadate	NH_4VO_3	-	-
Sodium hydroxide	NaOH	Panreac	98
Catalasa	$\text{H}_2\text{O}_2:\text{H}_2\text{O}_2$ oxidoreductase	Sigma-Aldrich	-
Sulfuric acid	H_2SO_4	Panreac	98
Ethanol	$\text{C}_2\text{H}_6\text{O}$	Panreac	96
Ascorbic acid	$\text{C}_6\text{H}_8\text{O}_6$	Panreac	-
EDTA	$\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$	Panreac	99
EDDS	$\text{C}_{10}\text{H}_{13}\text{N}_2\text{Na}_3\text{O}_8$	Sigma-Aldrich	35
NTA	$\text{C}_6\text{H}_9\text{NO}_6$	Panreac	99
Humic acid	-	Sigma-Aldrich	-
FSCS	$\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Sigma-Aldrich	100



Figure 6: HPLC 1260 from Waters



Figure 7: TOC-VCNS analyzer Shimadzu



Figure 8: Spectrophotometer Hach Lange DR 3900



Figure 9: Iron vials



Figure 10: Spectrophotometer Hach Lange DR 6000



Figure 11: COD vials

3.1 Samples preparation

Mineral water

The aqueous solution of 50 mg/L of MET has been dissolved in mineral water 24 hours prior to the experiment. The EDTA followed the same process but in other recipient. Then, iron was added (Fe^{2+} :EDTA 1:1.5) to the EDTA solution and after 15 minutes of stirring it was then placed in the reactor. Thermostatic bath and black lamps blue (BLB) were switched on 20 minutes previous to the experiment in order to maintain the experimental conditions (temperature and emitted radiation). The hydrogen peroxide was added and the lamps were switched on immediately. During the experiments, the MET degradation, TOC, COD, SUVA and toxicity reduction, hydrogen peroxide, Fe^{2+} and total Fe concentration and pH were measured.

Gavà wastewater

The aqueous solution of 50 mg/L of MET has been dissolved in wastewater from MBR treatment 24 hours prior to the experiment. The EDDS was dissolved in other recipient before the experiment. Then, iron was added (Fe^{2+} :EDDS 1:7) to the EDDS solution and after 15 minutes of stirring it was then placed in the reactor. The rest of the process was the same as for mineral water.

3.2 Experimental devices

Experiments were carried out in a BLB reactor (*Figure 12*), which is a 2 L Pyrex-jacketed thermostatic vessel (inner diameter 11 cm, height 23 cm), equipped with three 8W BLB lamps (Philips TL 8W-08 FAM) located at the center of the reactor. Magnetic stirring was used to ensure good mixing. The temperature of the solution was maintained constant at 25°C with the recirculated water by the jacket connected to an ultra-thermostatic bath.

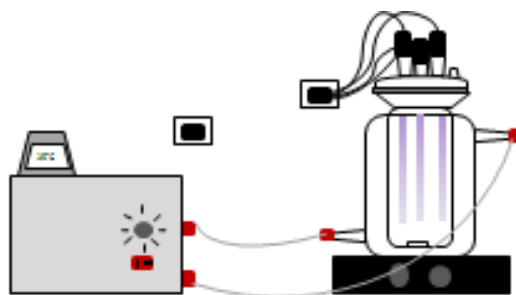


Figure 12: BLB device

Table II. Technical characteristics of the BLB reactor

BLB reactor	
Light source	Philips TL 8W-08 FAM
Lamps number	3
Photon flux ($\mu\text{Einstein/s}$)	6.0 (290-400 nm)
Total volume of suspension (L)	2
Temperature ($^{\circ}\text{C}$)	20-25

With the aim of comparing the degradation of MET under sunlight conditions an experiment was also carried out in a solar pilot plant: compound parabolic collector (CPC) (*Figure 13*). The exposure time was 1 hour, from 13:00 to 14:00 h. CPC reactor consists of a module, 41° inclined and made of polished aluminum, with 6 parallel tubular quartz reactors. MET solution was continuously pumped with a peristaltic pump from the stirred reservoir tank (10 L) to irradiated quartz tubes and continuously recirculated. The radiation arriving to CPC reactor was determined by a spectroradiometer Bentham DMc300. The data were integrated from 290 to 400 nm (UVB and UVA). Samples were collected from the reservoir tank.

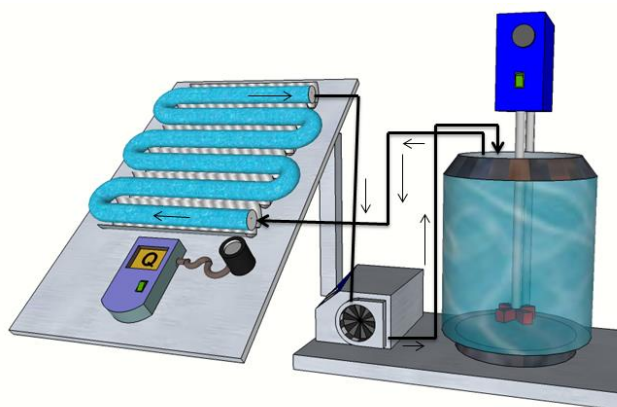


Figure 13: CPC device

Table III. Technical characteristics of the CPC reactor

CPC reactor	
Collector material	All-reflective mirrors
Mirror's area (m ²)	0.228
Light source	Solar light
Photoreactor number	6
Photon flux	Depending on the day (290-400 nm)
Total volume of suspension (L)	5
Temperature (°C)	30±5
Volumetric flow rate (L/min)	2.6
Inclination	(Latitude 41°28', Longitude 2°06')

Chapter III: Results and discussion

4. Previous experiments

4.1 Thermo-degradation and photolysis

Some preliminary assays were done to assure possible MET degradation not referable to photo-Fenton process. Thus, MET degradation only in the presence of light was investigated and photolysis resulted insignificant. Thermo-degradation was also assessed in the range of 20-80 °C. In all cases MET transformation and TOC reduction were negligible.

4.2 Characterization of mineral water and wastewater

Before performing the experiments with real water, mineral water was tested. This water was chosen due to its low ion count in order to avoid the complex formation with iron. Once completed all the experimental work with mineral water, wastewater was assessed. Before carrying out the experimentation, water was characterised. See *Table IV* for results.

Table IV. Mineral water and MBR wastewater characterization results

<i>Parameter</i>	<i>Mineral water</i>	<i>MBR wastewater</i>
TOC (mg/L)	0.00	78.33
NPOC (mg/L)	0.58	-
IC (mg/L)	2.58	-
TN (mg/L)	1.23	3.68
COD unfiltered water (mg O₂/L)	1.08	12.38
COD filtered water (mg O₂/L)	0.54	1.29
Alkalinity (mg CaCO₃)	-	346.19
UV	0.033	0.177
Suspended solids (mg/L)	0.005	0.014
Volatile solids (mg/L)	0.000	1.750
Total solids (mg/L)	0.127	2.356
Cl⁻ (mg/L)	0.87	32.41
Na⁺ (mg/L)	2.55	611.46
Ca²⁺ (mg/L)	2.73	99.34
Mg²⁺ (mg/L)	0.39	57.96
Turbidimetry (NTU)	0.76	0.85
pH	5.6	7.8

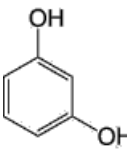
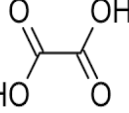
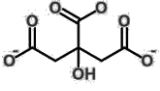
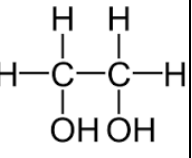
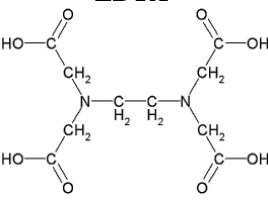
4.3 Selection of chelating agent

Mineral water

In order to make the procedure at circumneutral pH, different chelating agents were assessed to find one which can form stable complexes with iron. A bibliographic study was carried out to find chelating agents that could work. EDTA was the only one that

managed to keep iron in solution when mineral water was assessed. See *table V* (Furia, 1973; Kolodynska, 2011) for results.

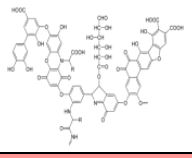
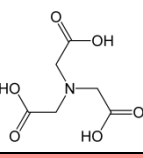
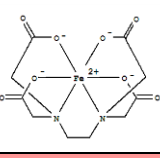
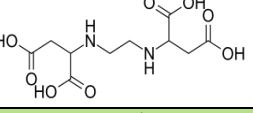
Table V. Chelating agents assessed and their stability constant with Fe^{2+} in mineral water and the respective result: “x” if iron precipitates, “✓” if iron keeps in solution

Chelating agent	Resorcinol 	Oxalic acid 	Citrate 	Etilenglycol 	EDTA 
Result	x	x	x	x	✓
log K_{M-L}	-	4.7	-	-	14.3

MBR wastewater

For real water EDTA was tested but it was not able to keep iron dissolved. Different ratios Fe^{2+} :EDTA were assessed (1:5, 1:7, 1:10). However the chelating agent was not able to form stable complexes with iron. In addition, EDTA is highly biorecalcitrant, and it has been classified as a persistent pollutant (Yuan and Van Briesen, 2006). Then, other chelating agents were assessed: humic acids, nitrilotriacetic acid (NTA) and EDDS. On the other hand, a prepared ferrous sulphate chelate solution (FSCS) composed by $FeSO_4 \cdot 7H_2O$ and EDTA (Fe^{2+} :EDTA 1.00:1.35) was also tested. All of them have been selected based on previous group experience, their metal complexing properties and bibliographic references (Papoutsakis et al., 2015; De Luca, et al., 2014; Clarizia et al., 2017). Different ratios were also tested for each one. See *Table VI* (Furia, 1973; Kolodynska, 2011) for results.

Table VI. Chelating agents assessed and their stability constant with Fe^{2+} in real wastewater and the respective result: “x” if iron precipitates, “✓” if iron keeps in solution

Chelating agent	Humic acids 	NTA 	FSCS 	EDDS 
Result	x	x	x	✓
log K_{M-L}	-	8.3	-	22.0

Humic acids were discarded due to the fact that they gave turbidity and color to the solution reducing the efficiency of the process.

In order to verify that iron remains in solution when the chelating agent was added, different experiments were carried out. In all cases, 2 L solution was prepared without the pollutant and placed in the BLB reactor. After lamps were switched on, samples were taken every 10 minutes, during a 60 minute period to verify the presence of Fe^{2+} in solution. Regarding NTA, it was able to maintain iron dissolved when the ratio Fe^{2+} :NTA was 1:5, but the regeneration of Fe^{2+} from Fe^{3+} ceased to exist, so photo-Fenton process did not occur. When FSCS was tested, iron precipitated, so it was also

discarded. Finally, EDDS was capable of holding iron dissolved and able to regenerate Fe^{2+} from Fe^{3+} . In addition, EDDS is biodegradable and considered environmentally safe (Rastogi, Al-Abed, Dionysiou, 2009; Papoutsakis et al., 2015).

Table VII. Summary of the obtained results using different chelating agents in MBR wastewater

Chelating agent	NTA	FSCS	EDDS
Fe^{2+} dissolved	✓	✗	✓
Fe^{2+} regenerated	✗	-	✓

4.4 Interaction between iron, hydrogen peroxide and chelating agent

Mineral water

Three different amounts of Fe^{2+} were used: 2.5 mg/L, 5.0 mg/L or 10.0 mg/L and two different H_2O_2 concentrations: 25 mg/L or 150 mg/L. These Fe^{2+} and H_2O_2 concentrations can be broadly found in literature and they were also selected based on the previous group experience. Further, the maximum 10.0 mg/L Fe^{2+} was selected due to the positive effect on the reaction kinetics. In addition, it is the limit value allowed in the discharge of municipal water according to the Decret 130/2003 (Catalonia Government, 2004). In order to reduce the amount of iron released to the water 5.0 mg/L was also assessed.

The addition of the chelating agent was investigated in order to find the optimal ratio. Different ratios Fe^{2+} :EDTA were tested (1:3, 1.0:1.5, 1:1). For the ratio 1:3 and 1.0:1.5 iron remained dissolved but the ratio 1:1 was not enough to maintain the iron in solution and it precipitated, so the optimal ratio was Fe^{2+} :EDTA 1.0:1.5.

Gavà wastewater

Two different amounts of Fe^{2+} were used: 2.5 mg/L or 5.0 mg/L and two different H_2O_2 concentrations: 25 mg/L or 150 mg/L. According to results obtained with mineral water, it was not necessary to test 10.0 mg/L of iron.

The addition of EDDS was also investigated in wastewater from MBR treatment to find the optimal ratio. In this case six ratios were assessed. See *Table VIII* for results.

Table VIII. Different Fe^{2+} :EDDS ratios tested in MBR wastewater

Ratio (Fe^{2+} :EDDS)	1.00:0.35	1.00:1.75	1.0:3.5	1.00:5.25	1.0:6.3	1:7
Result	Iron precipitation	Iron precipitation	Iron precipitation	Iron precipitation	Iron keeps dissolved	Iron keeps dissolved

Although ratio 1.0:6.3 was capable of maintaining iron in solution, ratio 1:7 was selected because the regeneration of Fe^{2+} from Fe^{3+} was faster, and in consequence the efficiency of the process was greater.

When wastewater from IFAS treatment was tested, the optimal ratio of chelating agent was higher, Fe^{2+} :EDDS 1.0:11.2, this could be due to a possible higher concentration of ions.

5. Photo-Fenton experiments

5.1 Mineral water

5.1.1 MET degradation

Figures 14, 15 and 16 show the MET degradation at different concentrations of iron (2.5, 5.0 and 10.0 mg/L) and hydrogen peroxide (25, 150 mg/L). These experiments were carried out with mineral water and in presence of EDTA to keep iron in solution.

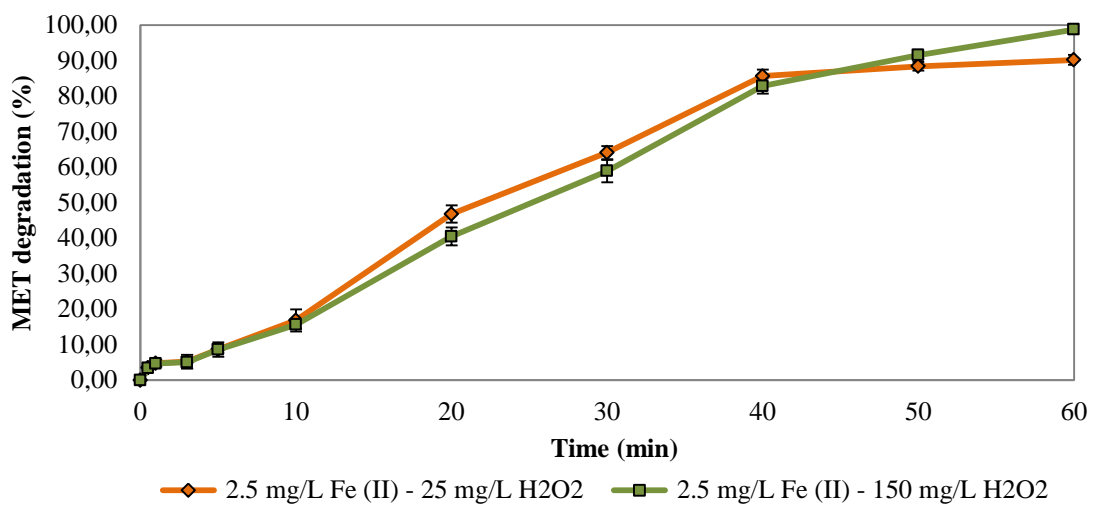


Figure 14: MET degradation under conditions of 2.5 mg/L Fe^{2+} and different H_2O_2 concentrations in mineral water

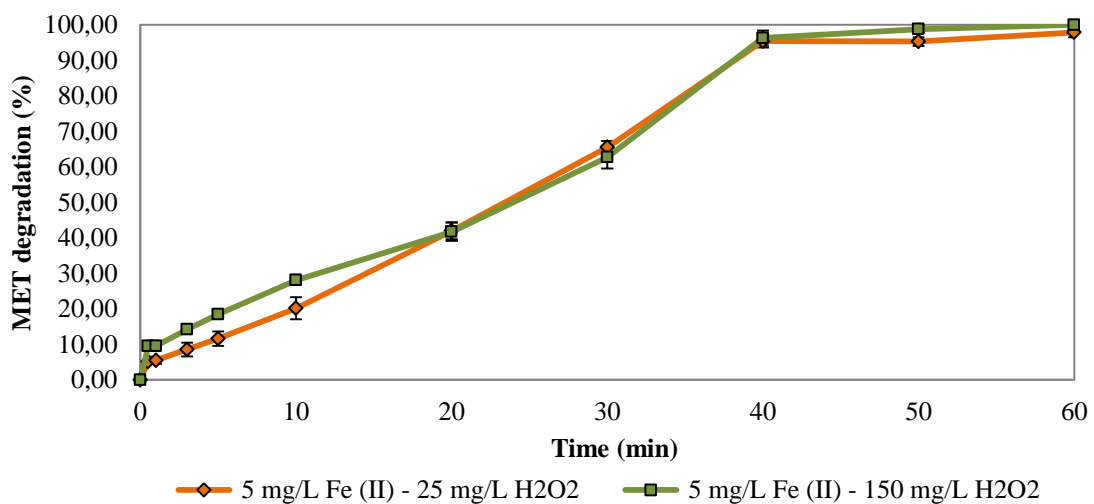


Figure 15: MET degradation under conditions of 5.0 mg/L Fe^{2+} and different H_2O_2 concentrations in mineral water

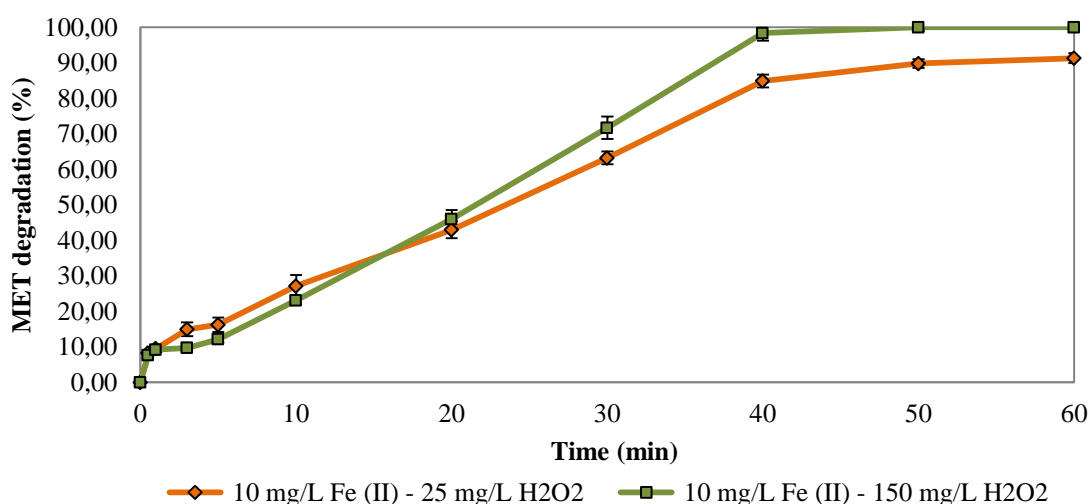


Figure 16: MET degradation under conditions of 10.0 mg/L Fe²⁺ and different H₂O₂ concentrations in mineral water

Table IX. Summary table of the parameters evaluated in the experiments with mineral water

Experiment	MET degradation (%)	TOC reduction (%)	COD reduction (%)	SUVA reduction (%)
2.5 mg/L Fe ²⁺ - 25 mg/L H ₂ O ₂	90.23 ± 1.39	16.45 ± 1.64	23.27 ± 3.43	35.52 ± 1.57
2.5 mg/L Fe ²⁺ - 150 mg/L H ₂ O ₂	98.80 ± 1.20	45.39 ± 1.48	40.47 ± 1.56	44.09 ± 2.00
5.0 mg/L Fe ²⁺ - 25 mg/L H ₂ O ₂	97.90 ± 1.39	16.09 ± 1.64	28.30 ± 3.43	4.35 ± 1.57
5.0 mg/L Fe ²⁺ - 150 mg/L H ₂ O ₂	100.00 ± 1.20	53.11 ± 1.48	45.42 ± 1.56	43.30 ± 2.00
10.0 mg/L Fe ²⁺ - 25 mg/L H ₂ O ₂	91.33 ± 1.39	11.76 ± 1.64	26.49 ± 3.43	48.17 ± 1.57
10.0 mg/L Fe ²⁺ - 150 mg/L H ₂ O ₂	100.00 ± 1.20	53.68 ± 1.48	45.35 ± 1.56	54.78 ± 2.00

As shown on *Table IX*, when a higher concentration of oxidant was assessed (150 mg/L) better results were achieved, reaching 100% of MET degradation, except for 2.5 mg/L Fe²⁺ (98.80% ± 1.20). This could be due to the higher generation of OH· and therefore a higher reaction rate. Iron has a direct influence on the rate of MET degradation so the greater the concentration of iron the quicker the elimination of the pharmaceutical. At 50 minutes, with 150 mg/L H₂O₂, the following results were obtained, 93.52% ± 1.93, 98.79% ± 1.03, 100% ± 0.82 for 2.5, 5.0 and 10.0 mg/L of iron. Although current legislation permits a maximum tipping of 10.0 mg/L of iron such concentration seems to be unnecessary, because with 5.0 mg/L Fe²⁺ the results were more than satisfactory, reaching a total degradation at 60 minutes or almost (when 25 mg/L of hydrogen peroxide was assessed). This is an important fact because legislation is becoming ever more demanding.

5.1.2 TOC, COD, and SUVA reduction

Concerning TOC reduction, *Table IX* shows that once again better results were achieved with higher concentrations of iron and hydrogen peroxide. Thus, as the growth of H₂O₂ concentration increased greater percentages of mineralization were achieved. The total conversion of organic carbon to CO₂ was not reached in any case, so MET degraded generating intermediate products (IPs). It is important to evaluate the toxicity of these IPs in order to determine the viability of the process at real scale.

The COD informs us about the necessity of oxygen that water should contain for oxidize the chemically oxidizable matter present in it. A total oxidation consists of transforming MET into CO₂, thus eliminating it from the water. Similar to TOC reduction, the highest concentration of hydrogen peroxide drives to the highest COD reduction. In this case the concentration of iron had no effect. Again, the increase in the generation of hydroxyl radicals when H₂O₂ concentration increases, can explain the highest oxidation.

The SUVA indicates the presence of aromatic compounds in water. When the concentration of catalyst and oxidant increase the content of aromatic compounds decreases, except when the conditions were Fe²⁺:H₂O₂ 5.0:25.

Although the best results were achieved when 10.0 mg/L of iron were assessed, the difference with the values obtained with 5.0 mg/L does not seem to be significant except for the content of aromatics in water, which acquires more quality when the concentration of catalyst was the highest.

5.1.3 Toxicity

Table X. Evolution of toxicity under the different experimental conditions with mineral water

Experiment	Initial toxicity (Equitox/m ³)	Final toxicity (Equitox/m ³)
2.5 mg/L Fe ²⁺ - 25 mg/L H ₂ O ₂	6.05	0.57
2.5 mg/L Fe ²⁺ - 150 mg/L H ₂ O ₂	6.05	0.52
5.0 mg/L Fe ²⁺ - 25 mg/L H ₂ O ₂	6.05	0.53
5.0 mg/L Fe ²⁺ - 150 mg/L H ₂ O ₂	6.05	0.50
10.0 mg/L Fe ²⁺ - 25 mg/L H ₂ O ₂	6.05	0.55
10.0 mg/L Fe ²⁺ - 150 mg/L H ₂ O ₂	6.05	0.49

According to AFNOR T90-301 standard, the results are expressed in “Equitox”, whereas the number of Equitox content per cubic meter of water is equal to the inverse of EC₅₀ expressed in percentage (5.1).

$$\text{Equitox}/\text{m}^3 = \left(\frac{1}{\text{EC}_{50}}\right) * 100 \quad (5.1)$$

The initial solution of 50 mg MET/L has an Equitox/m³ equal to 6.05. For the worse situation, after photo-Fenton treatment, toxicity has a value equal to 0.57 for the lowest concentration of iron and hydrogen peroxide. Toxicity decreases when the degradation of MET increases, thus, the best result is reached when the concentration of catalyst and oxidant are the highest but there are no large differences for the different experiments

carried out. In any case, a considerable decrease of toxicity can be observed in all of them.

5.2 MBR wastewater

5.2.1 MET degradation

Figures 17 and 18 show the MET degradation at different concentrations of iron (2.5, 5.0 mg/L) and hydrogen peroxide (25, 150 mg/L). These experiments were carried out with MBR wastewater and in presence of EDDS to keep iron in solution. Figure 19 shows the MET degradation in BLB reactor and in CPC reactor with 5.0 mg/L Fe^{2+} and 150 mg/L H_2O_2 .

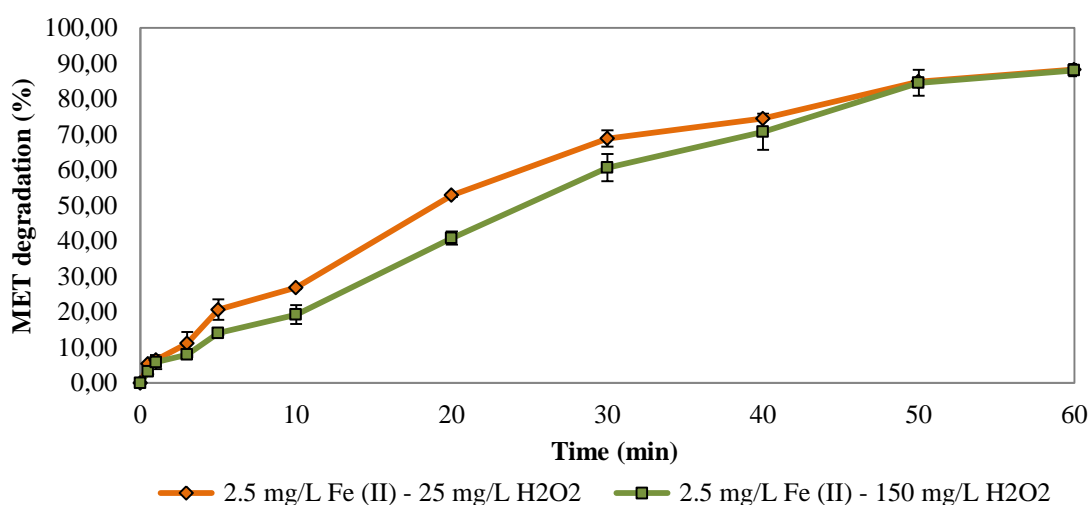


Figure 17: MET degradation under conditions of 2.5 mg/L Fe^{2+} and different H_2O_2 concentrations in MBR wastewater

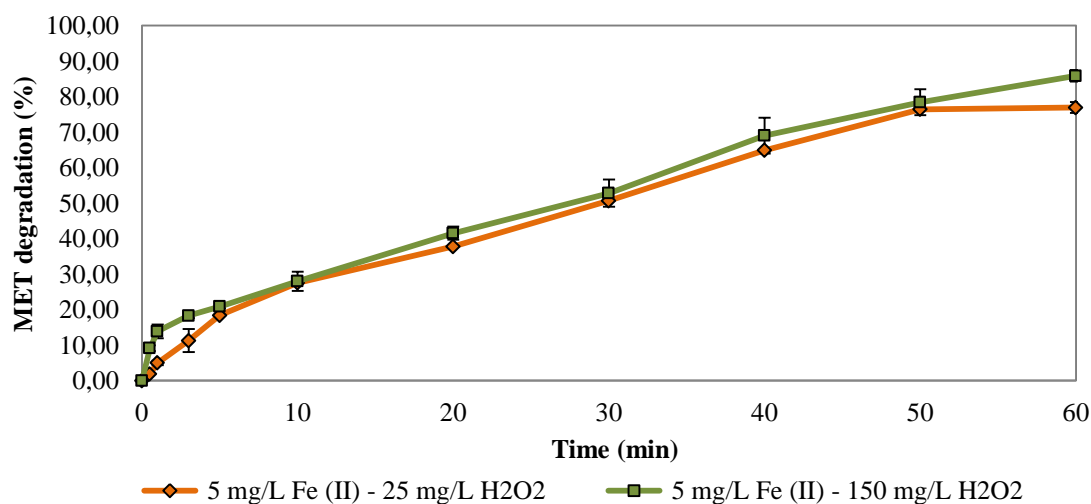


Figure 18: MET degradation under conditions of 5.0 mg/L Fe^{2+} and different H_2O_2 concentrations in MBR wastewater

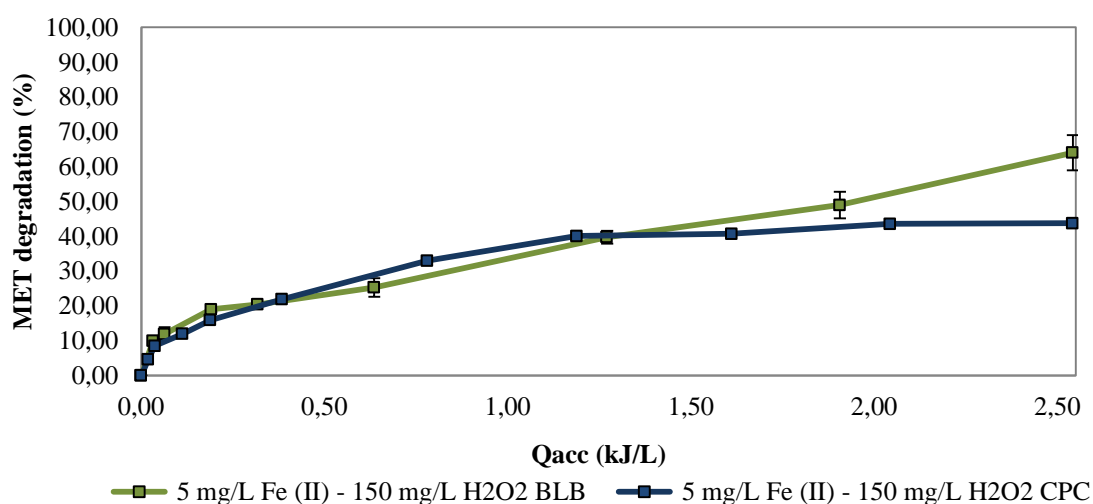


Figure 19: Comparison of MET degradation in BLB and CPC reactor under conditions of 5.0 mg/L Fe^{2+} and 150 mg/L H_2O_2 in MBR wastewater

Table XI. Summary table of the parameters evaluated in the experiments with MBR wastewater

BLB reactor			
Experiment	MET degradation (%)	TOC reduction (%)	COD reduction (%)
2.5 mg/L Fe^{2+} - 25 mg/L H_2O_2	88.30 ± 1.55	11.32 ± 0.47	22.68 ± 0.75
2.5 mg/L Fe^{2+} - 150 mg/L H_2O_2	88.07 ± 1.63	22.86 ± 0.70	41.54 ± 1.06
5.0 mg/L Fe^{2+} - 25 mg/L H_2O_2	76.94 ± 1.55	11.00 ± 0.47	20.41 ± 0.75
5.0 mg/L Fe^{2+} - 150 mg/L H_2O_2	85.87 ± 1.63	23.73 ± 0.70	46.76 ± 1.06
CPC reactor			
5.0 mg/L Fe^{2+} - 150 mg/L H_2O_2	43.75	22.45	45.58

As shown on *Table XI*, regarding MET degradation, there are no large differences comparing the different experimental conditions. Furthermore, better results were achieved with the lowest concentration of catalyst and oxidant. It could be due to the regeneration of Fe^{2+} , which occurs more slowly when the greatest concentration of iron was assessed and therefore reaction time decreases. On the other hand, when the highest concentration of iron (5.0 mg/L) and the lowest concentration of hydrogen peroxide (25 mg/L) were assessed (*Table XI* and *Figure 18*) it can be observed that the degradation was the lowest (76.94% ± 1.55). This may be because the hydrogen peroxide depleted at minute 50 and thus the production of hydroxyl radicals ceased. In no case the total elimination of the pollutant has been reached.

For CPC, MET degradation is going to be described in terms of accumulated energy (*Figure 19*) due to there is not a constant irradiation during the time. Thus, the use of the time as the calculation unit, could give rise to misinterpretation of results, because the differences in the incident radiation in the reactor during an experiment are not taken into account (Malato et al., 2009). Comparing MET degradation in these two different

reactors, it can be seen that there are large differences reaching higher elimination in the BLB reactor than with the CPC reactor. This can be due to the different spectrum of the irradiation used in each case (solar light in CPC and BLB in the other case) since solar light is rich in longer wavelengths and poor in UV. Actually, only around 20% of emitted photons are in the 300-400 nm stretch. The rest of photons are in the 400-500 nm part. Although light over 400 nm may be useful for photo-Fenton process, it is much less efficient.

5.2.2 TOC and COD reduction

As it can be observed in *Table XI*, higher mineralization was achieved when the highest concentration of hydrogen peroxide was assessed. In the case of experiments with real water, MET was not the only compound mineralized but also others present in the water. In addition there is a greater organic matter content than in the mineral water and that is why the percentages of TOC reduction are not so high. In no case the complete mineralization has been reached, and therefore IPs have been generated, so it is also of interest to assess toxicity.

Higher COD reduction was achieved when the concentration of oxidant was higher (150 mg/L) because this parameter expresses the amount of oxidized matter in water. In this case the values are so close to those obtained with mineral water. In no case a total oxidation has been achieved.

In the case of MBR wastewater, SUVA reduction could not be determined because the treated water acquired a yellowish color (not related to iron precipitation) at the end of the experiment which absorbs at a wavelength of 254 nm leading to erroneous values when samples were measured with the spectrophotometer.

5.2.3 Toxicity

Table XII. Evolution of toxicity under the different experimental conditions with MBR wastewater

BLB reactor		
Experiment	Initial toxicity (Equitox/m³)	Final toxicity (Equitox/m³)
2.5 mg/L Fe ²⁺ - 25 mg/L H ₂ O ₂	6.33	0.61
2.5 mg/L Fe ²⁺ - 150 mg/L H ₂ O ₂	6.33	0.61
5.0 mg/L Fe ²⁺ - 25 mg/L H ₂ O ₂	6.33	0.64
5.0 mg/L Fe ²⁺ - 150 mg/L H ₂ O ₂	6.33	0.62
CPC reactor		
5.0 mg/L Fe ²⁺ - 150 mg/L H ₂ O ₂	6.33	0.78

In this case, the initial solution has an Equitox/m³ equal to 6.33. In BLB experiments, toxicity decreases when the MET degradation increases, reaching a highest reduction when the concentration of iron was 2.5 mg/L. The lowest reduction corresponds to photo-Fenton treatment carried out in the CPC reactor with a value equal to 0.78 Equitox/m³ due to the low MET degradation achieved. As in the case of mineral water, toxicity has been considerably reduced.

6. Preliminary cost analysis

In this project, several experiments were carried out using the photo-Fenton process under different conditions. In order to assess the suitability of the process and different conditions for real applications, cost estimation has been conducted to compare them from an economic standpoint. The calculations take into account the energy cost (kWh) of the magnetic stirrer, BLB lamps, HPLC and TOC devices and the thermostatic bath. Regarding reagents, only Fe^{2+} , H_2O_2 , EDTA or EDDS (*Table XV* and *Table XVI*) have been taken into account since the amount of the other reagents remains constant independently of the experimental conditions.

To calculate the total energy cost (*Table XIII*) the following value has been used: 0.116 €/kWh obtained from the Spanish electricity grid. As for the calculation of the reagents cost the quantity of the product used in each experimental condition and the product price have been taken into account (*Table XV* and *Table XVI*). When both costs have been converted into monetary units (€) they have been added and subsequently divided by MET degradation reached in each experimental condition. This last value is calculated in order to compare the different experiments.

As shown on *Table XIII*, in the case of experiments carried out with mineral water, there are no significant differences from the economic point of view. In all cases the cost to degrade a ppm of MET are around 0.023-0.025 €. Regarding the experiments tested in MBR wastewater, differences were observed when different iron concentration was assessed achieving better results with the lowest iron concentration because higher degradation was reached.

Comparing all the experiments carried out, it can be observed that better results have been achieved with mineral water. This is because EDTA is more economical and it is used in smaller quantities than EDDS (*Table XV* and *Table XVI*). The most expensive process is the one that has been carried out in the CPC reactor, due to the low MET degradation (43.75%).

It can be observed in *Table XIV* that when the experiments were carried out with mineral water the greatest expense was due to energy use whereas when they were carried out with MBR wastewater the differences between energy and reagents costs have not been so clear. This again makes reference to the exposed in the previous paragraph, the EDDS is more expensive than EDTA.

Table XIII. Economic requirements of photo-Fenton process carried out in different experimental conditions

Experiment	MET degradation (mg/L)	$E_{E, str}$ (kWh)	$E_{E, irr}$ (kWh)	$E_{E, HPLC}$ (kWh)	$E_{E, TOC}$ (kWh)	$E_{E, bath}$ (kWh)	$E_{E, tot}$ (kWh)	Energy price (€/kWh)	Total energy cost (€)	Reagents cost (€)	Total cost (€)	Total cost/MET degradation (€/ppm)
Mineral water												
2.5 mg/L Fe ²⁺ -25 mg/L H ₂ O ₂	45.11	0.0025	0.024	5.208	4.034	0.24	9.508	0.116	1.103	0.005	1.108	0.025
2.5 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	49.40	0.0025	0.024	5.208	4.034	0.24	9.508	0.116	1.103	0.023	1.126	0.023
5.0 mg/L Fe ²⁺ -25 mg/L H ₂ O ₂	48.95	0.0025	0.024	5.208	4.034	0.24	9.508	0.116	1.103	0.007	1.109	0.023
5.0 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	50.00	0.0025	0.024	5.208	4.034	0.24	9.508	0.116	1.103	0.024	1.127	0.023
10.0 mg/L Fe ²⁺ -25 mg/L H ₂ O ₂	45.66	0.0025	0.024	5.208	4.034	0.24	9.508	0.116	1.103	0.009	1.112	0.024
10.0 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	50.00	0.0025	0.024	5.208	4.034	0.24	9.508	0.116	1.103	0.027	1.130	0.023
Water from MBR treatment												
BLB												
2.5 mg/L Fe ²⁺ -25 mg/L H ₂ O ₂	44.45	0.0025	0.024	5.208	4.034	0.24	9.508	0.116	1.103	0.683	1.786	0.040
2.5 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	44.05	0.0025	0.024	5.208	4.034	0.24	9.508	0.116	1.103	0.701	1.804	0.041
5.0 mg/L Fe ²⁺ -25 mg/L H ₂ O ₂	38.47	0.0025	0.024	5.208	4.034	0.24	9.508	0.116	1.103	1.363	2.466	0.064
5.0 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	42.93	0.0025	0.024	5.208	4.034	0.24	9.508	0.116	1.103	1.380	2.483	0.058
CPC												
5.0 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	21.87	0.0025	0.000	5.208	4.034	0.00	9.244	0.116	1.072	1.380	2.453	0.112

$E_{E, str}$: Electric power of magnetic stirrer

$E_{E, irr}$: Electrical power of irradiation

$E_{E, HPLC}$: Electric power of HPLC device

$E_{E, TOC}$: Electric power of TOC device

$E_{E, bath}$: Electric power of thermostatic bath

$E_{E, tot}$: Total electrical power

Table XIV. Contribution of energy and reagents cost in total cost (%)

Experiment	Total cost (€)	Total energy cost (€)	Reagents cost (€)	Energy cost (%)	Reagents cost (%)
Mineral water					
2.5 mg/L Fe ²⁺ -25 mg/L H ₂ O ₂	1.108	1.103	0.005	99.5	0.5
2.5 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	1.126	1.103	0.023	98.0	2.0
5.0 mg/L Fe ²⁺ -25 mg/L H ₂ O ₂	1.109	1.103	0.007	99.4	0.6
5.0 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	1.127	1.103	0.024	97.9	2.1
10.0 mg/L Fe ²⁺ -25 mg/L H ₂ O ₂	1.112	1.103	0.009	99.2	0.8
10.0 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	1.130	1.103	0.027	97.6	2.4
Water from MBR treatment					
BLB					
2.5 mg/L Fe ²⁺ -25 mg/L H ₂ O ₂	1.786	1.103	0.683	61.7	38.3
2.5 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	1.804	1.103	0.701	61.7	38.9
5.0 mg/L Fe ²⁺ -25 mg/L H ₂ O ₂	2.466	1.103	1.363	44.7	55.3
5.0 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	2.483	1.103	1.380	44.4	55.6
CPC					
5.0 mg/L Fe ²⁺ -150 mg/L H ₂ O ₂	2.453	1.072	1.380	43.7	56.3

Table XV. Conversion of reagents quantity to economic values

Reagent	Volume (L)	Weight (kg)	Density (g/ml)	Price (€)	Price/weight (€/kg)
H ₂ O ₂	1.0	-	1.11	21.25	19.32
FeSO ₄ ·7H ₂ O	-	1.0	-	26.38	26.38
EDTA	-	0.5	-	107.00	214.00
EDDS	0.1	-	1.24	73.80	595.16

Table XVI. Quantity of reagent used

Reagent	Quantity (ml)		Quantity (g)		
H ₂ O ₂ concentration (ppm)	25	150	-	-	-
H ₂ O ₂	0.17	1.00	-	-	-
Fe ²⁺ concentration (ppm)	-	-	2.5	5.0	10.0
FeSO ₄ ·7H ₂ O	-	-	0.0248	0.0498	0.9953
Fe ²⁺ concentration (ppm)	-	-	2.5	5.0	10.0
EDTA	-	-	0.0375	0.0750	0.1500
Fe ²⁺ concentration (ppm)	2.5	5.0	-	-	-
EDDS	0.92	1.84	-	-	-

7. Conclusions

- MET degradation under conditions of circumneutral pH is feasible.
- Depending on water matrix, the chelating agent changes as well as the optimal ratio with iron.
- In mineral water, iron has been maintained complexed with EDTA and therefore, available to carrying out the photo-Fenton process at neutral pH.
- In real water, EDTA did not maintain iron dissolved so the process was carried out with another chelating agent, EDDS.
- In mineral water, results obtained with 5.0 mg/L Fe²⁺ are very close to these ones obtained with 10.0 mg/L. Thus, it is not necessary to work on the border of the legal threshold (10.0 mg/L).
- The best results in MET degradation when mineral water was used were reached under maximum concentrations of catalyst and oxidant, respectively: 10.0 mg/L Fe²⁺ and 150 mg/L H₂O₂.
- There have been no significant differences in the degradation of MET in real water when different concentrations of iron and hydrogen peroxide were assessed.
- In both cases, a higher concentration of oxidant higher has led to a higher reduction of TOC and COD.
- The greater the MET degradation, the greater the reduction of toxicity.
- The process carried out with lamps is much more efficient than that carried out with solar radiation.

8. Future work

Once it has been established that it is possible to carry out the degradation of MET in real water at circumneutral pH, it should be investigated whether this method is applicable to water from different WWTP and even wastewater from hospitals and pharmaceutical industries due to its high content in this type of pollutants. On the other hand, it could be interesting to know how the water cations, amongst them Fe²⁺, affect the process yield and the biodegradability of the EDDS-cation complex.

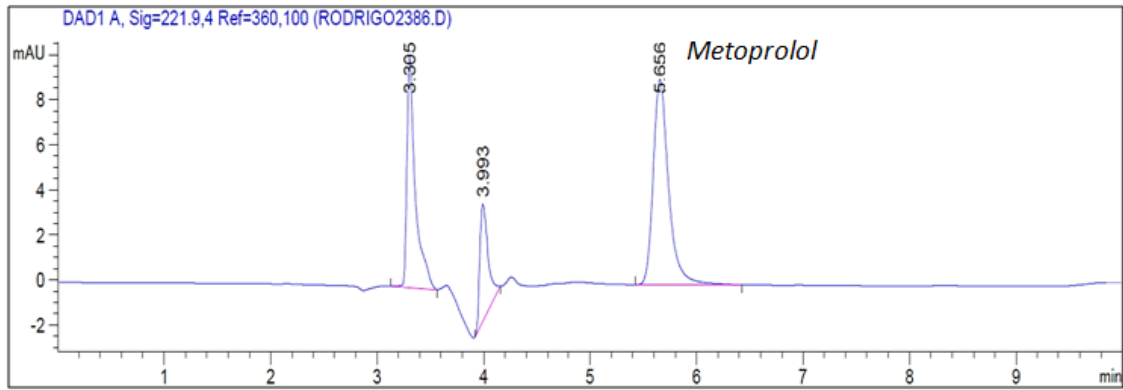
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Annex



Signal 1: DAD1 A, Sig=221.9,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.305	BB	0.0780	56.48086	10.30138	32.0689
2	3.993	BB	0.0839	27.69420	5.21714	15.7243
3	5.656	BB	0.1537	91.94831	9.11488	52.2068

Calibration curve: $y = 0.0182x + 0.1233$

$$[\text{MET}] = 0.0182 \cdot 91.95 + 0.1233 = 1.80 \text{ mg/L}$$

Figure 20: Conversion of area measured in HPLC to MET concentration

