

UNIVERSIDADE FEDERAL DE MINAS GERAIS
PROGRAMA DE PÓS-GRADUAÇÃO EM SANEAMENTO,
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**DEGRADATION OF CONTAMINANTS OF
EMERGING CONCERN IN DIFFERENT
MATRICES BY ADVANCED OXIDATION
PROCESSES: EVOLUTION OF TOXICITY AND
DISINFECTION**

Maria Clara Vieira Martins Starling

Belo Horizonte
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Degradation Of Contaminants Of Emerging Concern in Different Matrices By
Advanced Oxidation Processes: Evolution Of Toxicity And Disinfection

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RESUMO

O consumo crescente de fármacos, produtos de cuidado pessoal, agrotóxicos e outros químicos pela sociedade moderna levou à ocorrência generalizada dessas substâncias no meio ambiente. A detecção desses compostos no ambiente é recente e foi possibilitada pelo desenvolvimento de técnicas avançadas de cromatografia analítica. Desse modo, eles foram denominados “Contaminantes de Preocupação Emergente” (do inglês: CEC). CEC ocorrem em concentrações reduzidas (ng a $\mu\text{g L}^{-1}$) em águas superficiais e águas residuárias e têm sido associados à toxicidade aguda e crônica, seleção de genes de resistência, mutagenicidade e distúrbios endócrinos. Logo, é necessário que tecnologias efetivas de tratamento sejam implementadas para a remoção de CEC presentes em águas residuárias e superficiais. Nesse contexto, os objetivos desse estudo foram (i) avaliar a aplicabilidade dos sistemas de UV-C/ H_2O_2 e UV-C/ $\text{S}_2\text{O}_8^{2-}$ na remoção de losartan potássio (LP), furosemida (FRSM), cafeína (CAF) e carbendazim (CBZ) em água pura e superficial, (ii) investigar a eficiência do foto-Fenton solar tradicional (sol/ferro/ H_2O_2) e do foto-Fenton solar modificado (sol/ferro/ $\text{S}_2\text{O}_8^{2-}$) em pH neutro para a remoção desses CEC em efluente de estação de tratamento de esgoto, e (i ii) avaliar preliminarmente o custo dos tratamentos. Ademais, os impactos dos tratamentos na toxicidade e desinfecção foram avaliados. Esse é o primeiro estudo a propor a aplicação do sistema sol/ferro/ $\text{S}_2\text{O}_8^{2-}$ em pH neutro. A revisão de literatura indicou que melhorias nas condições de saneamento básico devem ser impostas antes que limites sejam estabelecidos para a remoção de CEC. Os resultados obtidos nesse trabalho indicaram que mais de 90% de todos os compostos alvo foram removidos em água pura e superficial por UV-C/ H_2O_2 e UV-C/ $\text{S}_2\text{O}_8^{2-}$. UV-C/ $\text{S}_2\text{O}_8^{2-}$ atingiu maior mineralização para a CAF e o CBZ e foi mais estável na presença de constituintes da água superficial. Entretanto, a toxicidade gerada durante a degradação do LP por UV-C/ $\text{S}_2\text{O}_8^{2-}$ não foi eliminada após o tratamento. O foto-Fenton solar tradicional (55 mg L^{-1} de Fe + 50 mg L^{-1} de H_2O_2) em pH neutro removeu mais de 80% do total de CEC e o pH se manteve constante durante o tratamento. Porém, o sistema sol/ferro/ $\text{S}_2\text{O}_8^{2-}$ ($27,5 \text{ mg L}^{-1}$ de Fe e $282,2 \text{ mg L}^{-1}$ de $\text{S}_2\text{O}_8^{2-}$) atingiu 60% de remoção de CEC devido à falta de ferro no sistema. Ambos os processos conduzidos em um reator do tipo carrossel em pH neutro removeram 50% do total de CEC, sendo que nenhum dos tratamentos gerou toxicidade aguda. Além disso, o sistema sol/ferro/ $\text{S}_2\text{O}_8^{2-}$ foi mais eficaz na remoção dos CEC e na inativação de *E coli*. A análise de custo realizada para ambos os processos de foto-Fenton revelaram a competitividade desses tratamentos frente a outras tecnologias avançadas.

Palavras-chave: micropoluentes, toxicidade, processos oxidativos, tratamento fotoquímico, rendimento quântico

ABSTRACT

Increasing consumption of pharmaceuticals, personal care products, agrochemicals and other chemicals by modern society have led to the occurrence of chemical pollutants in the environment. Ubiquitous occurrence of these contaminants and the risks they represent could be detected after recent development of advanced chromatography techniques and ecotoxicological assays. Thus, these pollutants were nominated contaminants of emerging concern (CEC). CEC occur at reduced concentrations (ng to $\mu\text{g L}^{-1}$) in surface waters and wastewaters and are associated to acute and chronic toxicity, selection of resistant genes, mutagenicity, and endocrine disruption. Hence, it is necessary to establish effective treatment technologies to remove CEC present in treated wastewater and surface water. The aims of this study were (i) to evaluate the applicability of UV-C/ H_2O_2 and UV-C/ $\text{S}_2\text{O}_8^{2-}$ on the treatment of losartan potassium (LP), furosemide (FRSM), caffeine, CAF) and carbendazim, (CBZ) in water and surface water, (ii) to investigate the efficiency of traditional solar photo-Fenton (solar/iron/ H_2O_2) and solar photo-Fenton like (solar/iron/ $\text{S}_2\text{O}_8^{2-}$) at neutral pH on the removal of these CEC from municipal wastewater treatment plant effluent and (iii) to perform a preliminary cost-benefit analysis. In addition, the impact of these advanced oxidation processes (AOPs) on acute toxicity and disinfection were also evaluated. This is the first study to propose the use of the solar/iron/ $\text{S}_2\text{O}_8^{2-}$) at neutral pH. Literature review indicated that basic sanitation conditions must be improved prior to the imposition of standards related to CEC removal. Results indicated in this study indicated that UV-C/ H_2O_2 and UV-C/ $\text{S}_2\text{O}_8^{2-}$ reached more than 90% degradation of all target compounds in pure and surface water. UV-C/ $\text{S}_2\text{O}_8^{2-}$ reached higher mineralization than UV-C/ H_2O_2 for CBZ and CAF, and was more stable in the presence of surface water constituents. However, toxicity generated during the degradation of LP via UV-C/ $\text{S}_2\text{O}_8^{2-}$ was not removed after treatment. Traditional solar photo-Fenton (55 mg L^{-1} of iron + 50 mg L^{-1} of H_2O_2) conducted at neutral pH was able to remove more than 80% of total CEC concentration and no pH decay was observed. Yet, solar-photo-Fenton like (27.5 mg L^{-1} of iron + 282.2 mg L^{-1} of $\text{S}_2\text{O}_8^{2-}$) reached a maximum of 60% removal due to lack of iron in the system. Both processes performed in a Raceway Pond Reactor at neutral pH reached nearly 50% removal of target CEC and neither of them generated acute toxicity. Solar/iron/ $\text{S}_2\text{O}_8^{2-}$ was more effective on CEC removal and on *E.coli* inactivation. Finally, cost analysis indicated that proposed treatments are competitive compared to other advanced technologies applied for the treatment of CEC.

Keywords: micropollutants, toxicity, oxidation processes, photochemical treatment, quantum yield

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LIST OF ACRONYMS AND SYMBOLS

AC	Amortization cost
ANVISA	National Agency of Health Surveillance
AOP	Advanced Oxidation Processes
AS	Activated Sludge
BPA	Bisphenol A
CAF	Caffeine
CBZ	Carbendazim
CEC	Contaminants of Emerging Concern
COD	Chemical Oxygen Demand
CPC	Compound Parabolic Collector
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DW	Drinking water
E1	Estrone
E2	17 β -estradiol
ED	Endocrine disruptors
EE/O	Electrical Energy per order
EE2	17 α -ethinylestradiol
EU	European Union
FRSM	Furosemide
GW	Groundwater
HPLC	High Performance Liquid Chromatography
IC	Investment cost
LED	Light Emitting Diode
LP	Losartan Potassium
MWW	Urban Wastewaters
MWWTP	Municipal Wastewater Treatment Plant
NOM	Natural organic matter
OP	Operational costs
PAH	Polycyclic Aromatic Compounds
PPCP	Pharmaceuticals and Personal Care Products
PS	Persulfate
RPR	Raceway Pond Reactor
SPE	Solid phase extraction
SW	Surface water
TC	Total Cost
TF	Trickling Filter
TOC	Total Organic Carbon
TP	Transformation Products
UASB	Upflow Anaerobic Sludge Blanket
USEPA	United States Environmental Protection Agency

WHO	World Health Organization
WTP	Water Treatment Plant
WW	Wastewater
WWTP	Wastewater Treatment Plant
YES	Yeast estrogenic screening test

1 CHAPTER I – INTRODUCTION, **RATIONALE AND GOALS**

1.1 INTRODUCTION

The development of the agrochemical, chemical, cosmetic and pharmaceutical industries contributed to the merge of a variety of products that are currently consumed on a daily basis by modern society. As these chemical substances are continuously consumed in our daily lives, these compounds are continuously discharged/ disposed of or end up in environmental compartments in urban and rural areas.

Agrochemicals applied to crops may run-off to surface water or infiltrate to soils, eventually reaching groundwater. Pharmaceutical drugs are taken by patients in excess doses and sequentially excreted by the body as original compounds or as metabolites and conjugates via urine and feces. In the sequence, these substances are directed to Municipal Wastewater Treatment Plants (MWWTP) (when existing) or disposed onto surface waters. Similarly, cosmetics and personal care products such as substances used in sunscreen, triclosan and caffeine also end up in sewage. In addition, chemicals used in the synthesis of plastics and petroleum or applied to furniture such as flame retardants, paints and bisphenol A may culminate in waters, sediment and soil.

Considering that MWWTP are not designed to remove these chemical compounds, which are mostly not biodegradable, these facilities have been pointed out as the main sources of chemical substances to the environment. Although these chemicals have been occurring in the environment for a few decades, attention to the ubiquitous presence and effects of these substances is recent, thus they are currently known as contaminants of emerging concern (CEC). In fact, the presence of CEC in municipal wastewater, surface water and other matrices (groundwater, rain water, ocean water, drinking water, sediments and soil) worldwide could only be determined after the development of advanced analytical chemistry techniques. This is because they occur in reduced concentrations ($\text{ng-}\mu\text{g.L}^{-1}$) in these

compartments and these matrices contain various other components that complicate the detection of these compounds.

Even in reduced concentrations, CEC have been associated to various toxic and physiological effects to aquatic fauna and human health such as: feminilization and masculinization, imposex, acute and chronic toxicity, mutagenicity, cytotoxicity, selection of resistant bacteria, obesity, and the development of tumors, respiratory diseases and diabetes in humans. As a consequence, scientific and legislative communities in developed countries are currently concerned about the continuous discharge of these pollutants to the environment and legal standards have been implemented to control the discharge of CEC.

In order to hinder environmental contamination by CEC and guarantee surface water quality and ecosystem integrity, it is important to implement tertiary treatment at MWWTP. This is also relevant in water treatment plants to assure the removal of CEC from drinking waters, thus preventing human health issues. Considering the variety of CEC present in sewage and surface water, Advanced Oxidation Processes (AOPs), such as UV-C and solar irradiated AOPs, are contemplated as some of the most appropriate technologies to be implemented as tertiary treatment for the removal of CEC due to their low selectivity. However, a few limitations with regard to oxidative radical quenching by matrix components and toxicity of transformation products formed during AOPs require further investigation.

Once analyses of CEC in real matrices are complex and costly, most studies that apply AOP for the degradation of CEC work with synthetic solutions in water rather than real samples. However, real matrices contain natural compounds (inorganic ions and natural organic matter) that consume oxidative radicals formed during AOP treatment, thus decreasing treatment efficiency when compared to tests performed in aqueous solutions. Therefore, these studies fail to reproduce the conditions that would be encountered in treatment plants. In addition, the

application of AOP in real scale is also limited due to costs associated to chemical reagents and electricity. Therefore, the development and testing of reactors and optimization of treatments for the application of low-cost and sustainable AOP, such as solar photo-Fenton are currently and intensively being investigated in developed countries. It is also important to perform research in this direction in developing countries, such as Brazil, so that the application of AOP for the removal of CEC becomes feasible in this country in the future.

In this context, the aim of this study was to review the literature regarding the occurrence, control and fate of emerging contaminants in different environmental compartments in Brazil and to investigate the degradation of selected target chemical compounds that are highly consumed in the country in different matrices: water, surface water and municipal wastewater via AOPs. Disinfection and removal of toxicity were also assessed during this study. After all, although Brazilian environmental legislation has not yet been updated to impose minimum percentage removal of CEC within MWWTP, this study will generate valuable information for when this time comes.

1.2 GOALS

1.2.1 Research aim

To investigate the degradation of selected CEC (caffeine, carbendazim, furosemide and losartan potassium) through advanced oxidation processes (UV-C/H₂O₂, UV-C/Persulfate, traditional and modified solar photo-Fenton) in different matrices: distilled water, surface water and MWWTP effluent, and to verify the impact of these processes on disinfection and toxicity removal.

1.2.2 Research objectives

- to review the literature regarding the occurrence, control and fate of contaminants of emerging concern in environmental compartments in Brazil in order to select a group of relevant CEC for the treatment via AOPs;
- to determine the quantum yield of each of the target compounds in pure water under UV-C irradiation in different pH;
- to verify the degradation of target compounds in water and surface water under UV-C_{254nm} and UV-C based AOPs (UV-C/H₂O₂ and UV-C/Persulfate);
- to investigate the evolution of acute toxicity during the proposed UV-C based AOPs;
- to identify the transformation products formed during UV-C based AOPs;
- to verify the degradation of target compounds in MWWTP effluent under solar irradiated processes (solar photo-Fenton and solar/iron/persulfate) at neutral pH,
- to evaluate disinfection and acute toxicity during solar photo-Fenton and solar/iron/persulfate;
- to perform a preliminary cost-benefit analysis for each of the proposed solar treatments.

1.3 RATIONALE

Currently, innumerable chemical compounds are consumed worldwide on a daily basis and continuously discharged onto surface water from MWWTP effluent, illegal sewage disposal, industries, and agricultural fields. Tackling the occurrence of these chemicals in the environment is a complex task, once compounds show different consumption patterns and physicochemical properties which dictate their fate in treatment facilities and in the environment. Therefore, it is important to adopt non-selective treatment solutions, which are able to degrade different classes of CEC, regardless of their physicochemical properties.

Advanced Oxidation Processes (AOPs) are suitable alternatives for this purpose and their application as tertiary treatment has been suggested by governmental authorities as effective solutions for preventing the disposal of CEC in surface waters (GIANNAKIS *et al.*, 2016).

Brazilian legislation has not yet been updated to include a minimum percentage removal of CEC in MWWTP. However, it is extremely important to conduct studies which aim at verifying the applicability of AOPs on the removal of chemicals that are highly consumed in the country in real wastewater. Considering all the existing AOPs, this study aimed at investigating the applicability of (i) UV-C irradiated processes for the removal of target CEC in pure water and surface water, and (ii) of traditional and modified solar photo-Fenton for CEC degradation in municipal wastewater treatment plant effluent. These AOPs were selected considering, respectively, that UV-C reactors are commonly applied in water treatment facilities for disinfection, and the solar potential available in Brazilian territory (MARCELINO *et al.*, 2015). Also, as sulfate radicals have been recognized as more stable in real matrices, the use of persulfate as an alternative oxidant was explored in all of these processes and compared to hydrogen peroxide. In view of the limitations related to the application of photo-Fenton in natural pH, different iron addition strategies were proposed in this study, not only for traditional solar-photo Fenton system (solar/Fe/H₂O₂), yet also for solar-photo-Fenton like (solar/Fe/persulfate). To date, this is the first work to apply intermittent iron addition strategy for this alternative system.

In addition, this study generated valuable data which is now available to guide decision makers on the implementation of proper tertiary treatment systems on the removal of CEC from surface waters and MWWTP effluent in Brazil when required. The quality of these data is acknowledged by the fact that experiments were performed in real matrices (surface water and MWWTP effluent) in addition to pure water, and best treatment conditions were tested in

semi-pilot scale. Furthermore, results obtained in this study not only account for the degradation of each compound, but also for disinfection and for the removal of toxicity obtained during the application of proposed treatments, thus contributing to a broader understanding of process effectiveness towards the maintenance of environmental integrity.

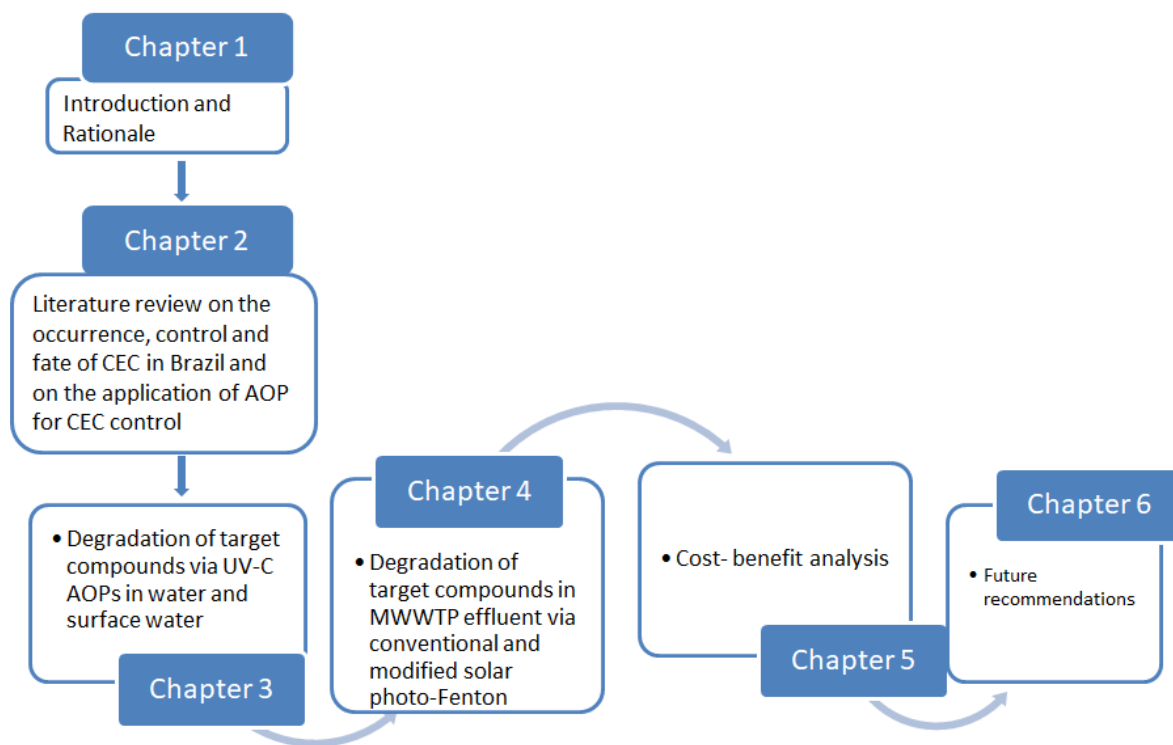
Moreover, target CEC explored in this work (caffeine, carbendazim, furosemide and losartan potassium) were carefully chosen according to their consumption level in the national territory and to represent different classes of CEC (pharmaceuticals, pesticides, pollution tracers). Their occurrence has been detected in surface waters in the country and worldwide. Moreover, apart from caffeine, which has been extensively studied by the scientific community due to its worldwide consumption, at least one of the proposed AOP has not yet been tested for the degradation of Losartan potassium (LP), Furosemide (FRSM) or Carbendazim (CBZ).

1.4 DOCUMENT STRUCTURE

In order to achieve all of the proposed objectives, this thesis was divided in five different chapters as represented in Figure 1.1. Chapter 1 is introductory and brings the rationale of this project. Chapter 2 brings the state of the art regarding contaminants of emerging concern and a literature review concerning the occurrence of these contaminants in Brazil and the application of hydroxyl and sulfate based AOP for the removal of emerging contaminants in different matrices, thus corresponding to the first objective. Chapters 3 and 4 explore the use of AOP to treat these compounds in water and wastewater. Chapter 3 analyses the degradation of target compounds via UV-C AOPs (UV-C/hydrogen peroxide and UV-C/persulfate) in water and surface water as stated in objective 2. Chapter 4 corresponds to the third specific objective and aims at the degradation of target compounds in real municipal wastewater via traditional (solar/iron/hydrogen peroxide) and modified solar photo-Fenton

(solar/iron/persulfate), thus exploring the use of persulfate as an oxidant in the solar photo-Fenton system. Chapter 5 brings a cost-benefit analysis of proposed treatments, as delineated in the last specific objective. Finally, Chapter 6 comprises future recommendations with regard to data generated during this work.

FIGURE 1. 1 – Structure of this thesis.



**2 CHAPTER II– STATE OF THE
ART ON THE OCCURRENCE
CONTROL AND FATE OF CECs
IN BRAZIL AND ON THE
APPLICATION OF AOPs ON
THE TREATMENT OF CECs**

2.1 INTRODUCTION

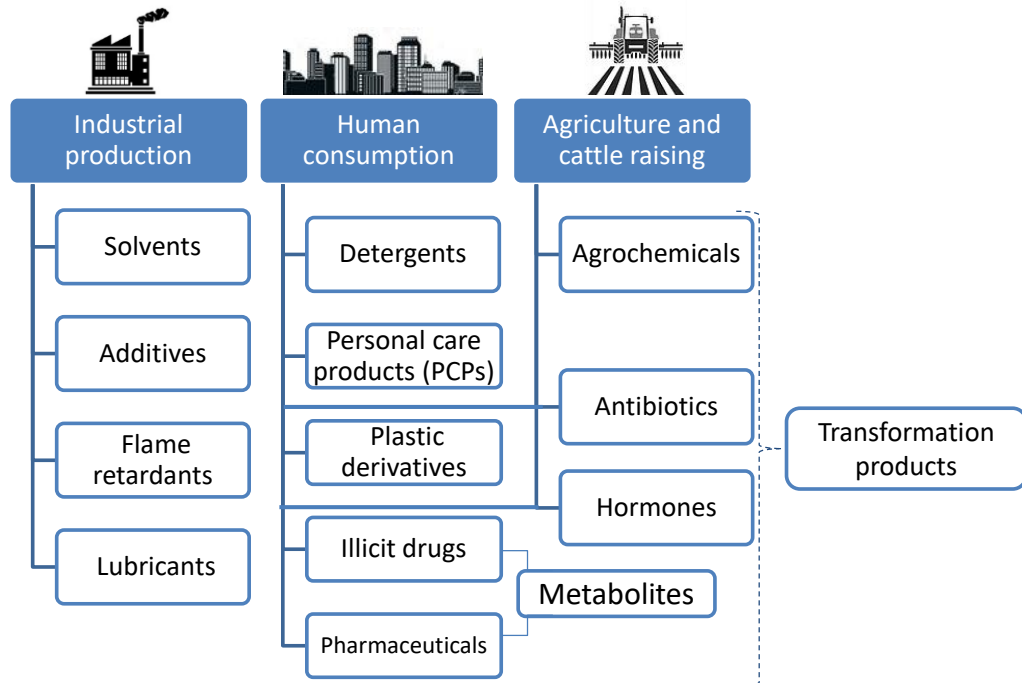
During the 20th century, population growth and the development of the agrochemical, chemical, cosmetic and pharmaceutical industries led to the synthesis and increased production of innumerable chemical compounds. These compounds are currently and continuously consumed and disposed of on a daily basis by millions of people worldwide (BAYER *et al.*, 2014). The improvement of analytical chemistry techniques allowed for the identification of these chemical compounds in reduced concentrations (μg to ng.L^{-1}) and in various and complex environmental matrices such as: soil, surface water and groundwater, sediment and atmosphere.

As a consequence, the ubiquitous occurrence of various chemical compounds - pharmaceutical and chemicals used in personal care products and industrial processes, illicit drugs, pesticides, endocrine disruptors, polycyclic aromatic compounds (PAH) - and their transformation products in the environment was revealed and became a topic of public concern (MALAJ *et al.*, 2014). These compounds are currently referred to as contaminants of emerging concern (CEC) by the scientific and legislative communities. Figure 2.1 illustrates the various classes of CEC that may be found in the environment and the sources to which they are associated.

Municipal wastewater (MWW) is one of the main point sources of CEC to the environment. Once consumed by population and collected in sewer lines, CEC flow to municipal wastewater treatment plants (MWWTP) which are not usually designed to remove them (BRACK *et al.*, 2015; RIBEIRO *et al.*, 2015). Therefore, when MWWTP effluent is discharged onto surface water, CEC flow along river streams. From surface water, CEC may volatilize, suffer photolysis, leach to groundwater or remain adsorbed on soil and sediment, depending on their physicochemical properties (JIN & PELDSZUS, 2012). Illegal disposal of

non-treated sewage and improper disposition of expired medication/cosmetics on toilets or landfills may also be a source of CEC to surface and groundwater (LUBICK, 2010).

FIGURE 2. 1 - - Classes of CEC and the sources to which they are associated.



In agricultural regions, run-off of pharmaceuticals used for veterinary purposes in feedlots and leakage of agrochemicals from crop fields may easily reach soil and surface water (BRAMBILLA & TESTA, 2014; MALAJ *et al.*, 2014). Pesticides, may also leach to groundwater depending on soil properties and aquifer depth, and their occurrence in groundwater in Europe is remarkable (LOOS *et al.*, 2010). Climatic conditions also play an important role on pesticide dispersion once it influences biodegradation and volatilization rates (LAABS, V. *et al.*, 2002). In addition, agricultural fires release polycyclic aromatic hydrocarbons (PAHs) to the atmosphere from where they may reach surface water and sediments. PAHs may also be introduced to the environment through non-treated wastewater or from forest fires, cooking, fossil fuel combustion reactions, and industrial processes (MEANS *et al.*, 1980). Also used in chemical industries, phthalates are additives applied to

plastics, carpets, pharmaceutical pills and toys. If disposed on soil, phthalates may reach surface water and coastal waters near urban areas (VRIJHEID *et al.*, 2016).

The fate of each CEC in the environment is dictated by its physicochemical properties and its interaction with the environmental matrix in which it has entered. Once a CEC, its metabolite or transformation product reaches an environmental compartment, it may undergo various phenomena such as sorption, dilution, hydrolysis, photolysis, biodegradation, volatilization, oxidation or complexation (MOMPELAT *et al.*, 2009). Each of these phenomena will lead to degradation, transformation or persistence of the compound in the environment. Therefore, CECs are often found in reduced concentrations (ng to $\mu\text{g}\cdot\text{L}^{-1}$) in environmental matrices.

Although CEC are currently present in attenuated concentrations in rivers and streams, groundwater and soils, they do represent a threat to ecosystem integrity (DAMIÀ BARCELÓ, 2008). Owing to the advance of environmental ecotoxicology in the past decades, CEC have been associated to feminization (KIDD *et al.*, 2007) and behavioral changes in fish (HENRY & BLACK, 2008), imposex (TITLEY-O'NEAL *et al.*, 2011; CACCIATORE *et al.*, 2016), neurological, reproductive and immunological disturbance in animals (FOWLER *et al.*, 2012), cancers (BOLONG *et al.*, 2009), development of antibiotic resistant genes in bacteria (PRUDEN *et al.*, 2006), reduction of microinvertebrate diversity in rivers (MALAJ *et al.*, 2014), bird extinction (DAMIÀ BARCELÓ, 2008), among other ecotoxicological effects. Regarding human health, the consumption of CEC through contaminated air, water and food is associated to the development of obesity, heart diseases and diabetes type 2 (VRIJHEID *et al.*, 2016). Considering that they are often mixed in complex matrices in the environment, the toxicity of one CEC may be enhanced (synergism) or eliminated (antagonism) due the presence of other compounds (ALTENBURGER *et al.*, 2004). Moreover, hydrophobic compounds tend to bioaccumulate in the tissues of aquatic species, thus entering terrestrial

food chain, and from where humans may be exposed to high concentrations as a consumer (JOBLING *et al.*, 1998).

Considering that Brazil is a developing country where basic sanitation conditions are still inappropriate in most regions, and environmental legislation regarding domestic sewage and industrial wastewater disposal does not account for the occurrence and effects of CEC in the environment, the aim of this chapter was to review the literature with regard to the occurrence, control and fate of CECs in environmental compartments in the country (surface water, wastewater, groundwater, seawater sediments and soil). This is the first review on the subject and may be valuable for environmental authorities on the implementation of environmental regulation applying to CEC in the country.

2.2 METHODS

Searches performed during literature review used three different databases: Portal Capes, Science Direct (Elsevier®) and Google Academic, and were conducted from March 2016 to December 2017. In order to cover all of the different classes of CEC and various matrices or environmental compartments, a group of keywords were used for each search in these databases as shown in Table 2.1. The terms “emerging contaminants”, “micropollutants” and “contaminants of emerging concern” were all searched for since all of them give reference to CEC. The name of each class of CEC: “pharmaceuticals and personal care products”, “urban pollution tracers”, “endocrine disruptors (EDs)”, “illicit drugs”, “pesticides and agrochemicals”, “polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs)” were also during searches in order to filter articles by class. For some emerging contaminants, the name of the contaminant itself was used as a keyword due to their relevance, which is the case of caffeine and Bisphenol A. In addition, when there were two or more studies related to the same contaminant or group of contaminants, the study with more

citations was chosen. Finally, most of the works cited in this review are articles published in international journals and written in English, only a few exceptions were made for a few thesis of great relevance written in Portuguese and which did not generate any publication in English so far.

TABLE 2. 1 – Keywords used on the searches made during the literature review

Keywords		
1st term	2nd term	3rd term
Brazil	Emerging contaminants Micropollutants Contaminants of emerging concern	occurrence control fate
	Emerging contaminants Micropollutants Contaminants of emerging concern	surface water
	Emerging contaminants Micropollutants Contaminants of emerging concern	wastewater
	Emerging contaminants Micropollutants Contaminants of emerging concern	drinking water
	Emerging contaminants Micropollutants Contaminants of emerging concern	soil
	Emerging contaminants Micropollutants Contaminants of emerging concern	treatment
	CEC group*	surface water wastewater drinking water soil treatment control

*See Section 2.2 Methods, for exact words.

2.3 OCCURRENCE OF CEC IN ENVIRONMENTAL MATRICES IN BRAZIL

One of the first studies about the occurrence of CECs in water in Brazil investigated the presence of thirteen different pharmaceuticals of human and veterinary use (analgesics, lipid

regulators and anti-inflammatory drugs) in 17 major streams in the state of Rio de Janeiro. MWW, surface water, sewer, urban wastewater and drinking water samples were all analyzed (STUMPF *et al.*, 1999). Nine of the investigated compounds (clofibric acid, fenofibric acid, bezafibrate, gemfibrozil, ibuprofen, diclofenac, ketoprofen, indometacine, naproxen) were detected in MWWTP effluent, maximum concentrations corresponded to lipid regulator bezafibrate (1.2 mg.L^{-1}), clofibric acid (1.0 mg.L^{-1}), and indometacine (0.95 mg.L^{-1}). On the other hand, none of the pharmaceuticals were present in drinking water. For surface water and seawater, clofibric acid, diclofenac and naproxen were detected with high frequency (0.01 to $0.06 \text{ }\mu\text{g.L}^{-1}$). A list of recent studies (published in the last 10 years) concerning the occurrence of CECs from different classes in Brazil in various matrices is presented in Table 2.2.

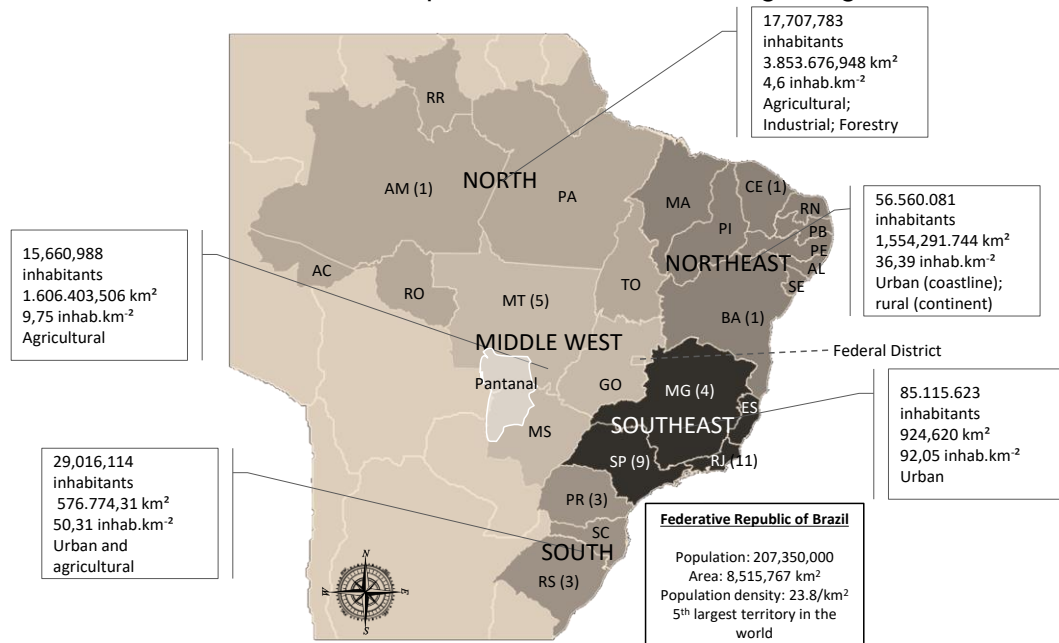
Most studies listed in Table 2.2 were conducted in the surroundings of São Paulo (SP) and Rio de Janeiro (RJ), the two biggest cities in Brazil, and mainly analyze the occurrence of pharmaceuticals and personal care products (PPCP) (FIGURE 2.1). These data could be valuable for other highly urbanized areas in the country, where pharmaceuticals and personal care products are also the main groups of chemicals consumed in a daily basis. However, Brazil is a large country and Brazilian regions show great variations related to climate, demographics, social conditions and economic activities (Figure 2.2). These factors play important roles on the chemical consumption pattern in each location. Therefore, data obtained in SP and RJ may not be representative for the entire nation.

TABLE 2. 2 - Studies on the occurrence of CEC in different environmental matrices in Brazil

CEC	Matrix	Location	Reference
Pharmaceuticals, Hormones, Triclosan	Surface water	Monjolinho River, SP	(CAMPANHA <i>et al.</i> , 2015)
Atrazine (ATZ) and transformation products	Surface water; spring water; drinking water and mineral water	Tibagi Basin, PR	(AMARAL <i>et al.</i> , 2014)
Caffeine, BPA, 4-octylphenol, cholesterol, estrone, 17 β -estradiol, 17 α -ethynylestradiol, and progesterone, coprostanol, stigmasterol and 4-nonylphenol	Drinking water	Campinas, SP	(SODRÉ <i>et al.</i> , 2010)
33 CECs including pharmaceuticals, cocaine and its main metabolite benzoylecognine	Ocean water	Santos Bay, SP	(PEREIRA <i>et al.</i> , 2016)
Erythromycin (antibiotic); diclofenac and ibuprofen (analgesics/anti-inflammatory); diazepam and carbamazepine (psychiatric drugs); atenolol (β -blocker); Tonalide, and galaxolide (fragrances). Caffeine.	Sediment samples	Todos os Santos Bay (BA)	(BERETTA <i>et al.</i> , 2014)
Pharmaceuticals: Amitriptyline; Carbamazepine; Carbamazepine-epoxide; Citalopram; Benzoylecognine; Diclofenac; Metoprolol; Propranolol; Sertraline. Cocaine and benzoylecognine.	Surface water	Rio Negro, Manaus, AM	(THOMAS <i>et al.</i> , 2014)
Estrogens and BPA	Surface water	Paraíba do Sul and Guandu Rivers, RJ	(DIAS <i>et al.</i> , 2015).
16 PAHs	Sediment samples	Iguaçu River, PR	(LEITE <i>et al.</i> , 2011)
Organochlorine pesticides (OCs) and PCBs	Sediments from mangrove areas	Guanabara Bay, RJ	(DE SOUZA <i>et al.</i> , 2008)
Bromazepam, lorazepam, carbamazepine, clonazepam and diazepam	Hospital wastewater	Santa Maria, RS	(DE ALMEIDA <i>et al.</i> , 2013)
Carbamazepine, diazepam and their metabolites	Hospital wastewater and surface water	Santa Maria, RS	(DE ALMEIDA <i>et al.</i> , 2015)
Acetaminophen, acetylsalicylic acid, diclofenac, ibuprofen, caffeine, 17 β -estradiol, estrone, progesterone, 17 α -ethynylestradiol, levonorgestrel, iethylphthalate, dibutylphthalate, 4-octylphenol, 4-nonylphenol, and BPA	Surface water	Atibaia River, SP	(MONTAGNER & JARDIM, 2011)
Triclosan and caffeine	Surface water	SP	(MONTAGNER <i>et al.</i> , 2014)

CEC	Matrix	Location	Reference
Antibiotics: Amoxicillin, ampicillin, cefalexin, ciprofloxacin, norfloxacin, sulfamethoxazole, tetracycline, and trimethoprim	Surface water	Atibaia River, SP	(LOCATELLI <i>et al.</i> , 2011)
OCs: α HCH (Hexachlorocyclohexane), β HCH, γ HCH, Heptaclor, Aldrin, Endrin, Dieldrin, DDE, DDT, α -Endosulfan, and β -Endosulfan	Sediment samples	Piracicaba River basin, SP	(SILVA <i>et al.</i> , 2008)
17 β -estradiol, 17 α -ethynylestradiol and 4-nonylphenol	Surface water and drinking water	MG	(MOREIRA <i>et al.</i> , 2009)
Acetylsalicylic acid, Acetaminophen, Azithromycin, Bezafibrate, Cimetidine, Ciprofloxacin, Clarithromycin, Diclofenac, Diltiazem, Gemfibrozil, Ibuprofen, Miconazole, Naproxen, Ranitidine, Sulfamethoxazole, Trimethoprim, Caffeine, Bisphenol-A, Bis-(2-ethylhexyl)phthalate, Diethylphthalate, 4-nonylphenol, 4-octylphenol, Estrone, 17 α -ethynylestradiol and 17 β -estradiol	Surface water	Rio Doce, MG	(RODRIGUES <i>et al.</i> , 2014)

FIGURE 2. 2 – Geographic map illustrating Brazilian regions and States, demographic data, and number of studies published in each state regarding CECs



(X) Number of studies published in each state concerning the occurrence and/or fate of CECs in the environment.

Furthermore, most studies published on the occurrence of PPCP in environmental compartments in Brazil target compounds which are intensively consumed in the developed regions of the world and for which analytical detection protocols are well established. According to a study carried out in Rio Negro (AM) (THOMAS et al., 2014) in a region which lacks sewage treatment system, the occurrence of some compounds such as diclofenac, carbamazepine and β -blockers were comparable to those found in European rivers which receive effluent from MWWTP, thus indicating differences in the consumption pattern of these target compounds in both regions. Therefore, assessing the occurrence of compounds which are highly consumed elsewhere may not reflect the real status of environmental contamination by CEC in Brazil, once consumption patterns, epidemiological context, regulation and prescription rules vary broadly among countries (LINDSTRÖM et al., 2002). Higher concentrations of acetyl salicylic acid and paracetamol were observed when compared to those detected for diclofenac in surface waters in the city of São Paulo. This may be attributed to the fact that paracetamol and acetyl salicylic acid are widely consumed in Brazil

as opposed to other drugs used for the same purpose in the EU, such as diclofenac which has recently been added to EU Directive as a priority substance (EU, 2013).

Anti-inflammatories (ibuprofen and diclofenac), anti-hypertensives (valsartan, losartan potassium, atenolol) and one analgesic (acetaminophen) were detected in coastal waters in Santos (SP) near a marine outfall. In this study, concentrations of diclofenac and β -blocker atenolol were lower than those usually detected for European coastal waters. In addition, atenolol occurred in lower concentrations in the Santos Bay when compared to other anti-hypertensive drugs such as sartans (PEREIRA *et al.*, 2016). Higher occurrence of sartans as opposed to β -blockers in Santos is probably due high consumption of sartans in Brazil (CFF, 2014).

Although there might be some discrepancies regarding the occurrence of pharmaceuticals in environmental compartments in different regions of the world, there are some chemicals which show widespread occurrence. These compounds are often called “tracers for MWW contamination” (PEREIRA *et al.*, 2016). Caffeine and Bisphenol A (BPA) are considered urban pollution tracers since their occurrence in streams near urban areas is extensively reported. These compounds have already been analyzed in surface water, drinking water, municipal wastewater and in wastewater from MWWTP in Brazil and their occurrence is similar to that observed in other continents (SODRÉ *et al.*, 2010; MONTAGNER & JARDIM, 2011; BERETTA *et al.*, 2014; MONTAGNER *et al.*, 2014; CAMPANHA *et al.*, 2015; DIAS *et al.*, 2015; PEREIRA *et al.*, 2016).

Another class of CEC that deserves attention is that of compounds that may be recognized by endocrine receptors present in mammalian cells: the endocrine disruptors (ED). The occurrence of endocrine disruptors has been intensively investigated in environmental

matrices due to their potential to cause disturbance to endocrine systems on humans and wildlife. Most of the studies concerning the occurrence of endocrine disruptors in Brazilian waters investigated the presence of natural estrone (E1), synthetic 17 β -estradiol (E2) and 17 α -ethinylestradiol (EE2), and bisphenol-A (BPA). Only a few studies considered other compounds (progesterone, levonorgestrel, coprostanol, cholesterol and stigmasterol). Stigamaesterol showed highest average concentration (0.34 $\mu\text{g.L}^{-1}$) in drinking water in Campinas, followed by cholesterol (0.27 $\mu\text{g.L}^{-1}$) and BPA (0.16 $\mu\text{g.L}^{-1}$) (SODRÉ *et al.*, 2010).

Besides natural and synthetic hormones, there are other chemicals such as pesticides, pharmaceuticals, and heavy metals (GIESY *et al.*, 2002) which also act as endocrine disruptors since they may as well be recognized by endocrine receptors in cells. Yet, their occurrence in the environment is rarely accounted for. Considering that endocrine disruptors occur in surface waters in reduced concentrations, sometimes lower than the analytical limits of quantification (LOQ) of chromatographic analysis, it is probably easier, less costly and time-consuming to monitor estrogenic activity of treated MWW instead of searching for each compound individually in the sample (MALAJ *et al.*, 2014). Bioassays, such as the Yeast Estrogenic Screening Test (YES), which estimates the effects caused by endocrine disruptors encountered in real samples (CAMPBELL *et al.*, 2006) may be used for this purpose. In order to properly prevent the contamination of surface waters by MWWTP effluent discharge and monitor illegal sewage disposal, it is strongly recommended to analyze treated wastewater and surface water for their estrogenic activity.

Regarding illicit drugs, only cocaine and its metabolite benzoylecognine were investigated for their occurrence in Brazilian surface water and municipal wastewater. The presence of this drug in surface water has been linked to “hot spots and hot moments” which may be defined as occasions in which the consumption of recreational illicit drugs increases (for example:

carnival, in Brazil, or sporting events throughout the world) (ROSI-MARSHALL et al., 2015). Cocaine and its metabolites have been proved to cause DNA damage and oxidative stress in zebra fish (PAROLINI & BINELLI, 2014), locomotion pattern alterations in crayfish (IMEH-NATHANIEL et al., 2017) and disturbance of reward system in invertebrates (ALCARO et al., 2011). Moreover, *D. melanogaster*, a proper representative of aquatic dipterans, shows multiple reflexive responses when exposed to cocaine, which is similar to human response (PAGÁN et al., 2013).

One of the studies performed on the occurrence of cocaine and benzoylecognine (cocaine metabolite) in Brazil was conducted in Santos Bay (SP), a region in which marine outfall discharges primarily treated MWW directly onto the sea (4.5 km from the coast). Samples were collected during carnival season, thus being representative of a “hot moment” for the consumption of this drug. The illicit drug and its metabolite were found in all of the samples, and their concentrations (12.6 to 537.9 ng.L⁻¹ for cocaine and 4.6 to 20.8 ng.L⁻¹ for benzoylecognine) were higher than those found for pharmaceuticals and caffeine in some sampling points (PEREIRA et al., 2016). Also, detected concentrations were superior to values found for the occurrence of these drugs in seawater elsewhere (KLOSTERHAUS et al., 2013). In a study conducted in the Rio Negro River Basin, near the city of Manaus (AM), cocaine and its metabolite concentrations were within the µg.L⁻¹ level, above the concentrations detected for pharmaceuticals, and in accordance with cocaine concentration found in freshwaters in Europe. The author suggested that cocaine and its metabolite could be used as markers for unplanned urbanization in the region (THOMAS et al., 2014).

Finally, the occurrence of pesticides was studied in different Brazilian watersheds, not only in surface water or drinking water, but also in sediments and aquatic biota. Organochlorines (OCs) are among the most investigated class of pesticides. Dichlorodiphenyltrichloroethane

(DDT) and its transformation products (DDE and DDD) were the subject of most studies due to their well-known toxicity and persistence in the environment, and intense former use of DDT in South America (WHO, 1979).

DDT was used as a pesticide worldwide and also for public health purposes in order to control diseases such as malaria and yellow fever. In Brazil, DDT use in agricultural crops was first banned in 1985. In the sequence (1998), its application for public health purposes was prohibited (RISSATO *et al.*, 2006). Finally, in 2009, DDT use was completely forbidden in the country. Most of the studies regarding the occurrence of OCs in Brazil, were performed some years after the partial ban on DDT. However, due to its low solubility, DDT persists in the environment in its original form or in the form of its metabolites (DDE and DDD) and may bioaccumulate (IWATA *et al.*, 1993), thus supporting the importance of investigating the occurrence of this compound even if its use is no longer allowed. DDT transformation to DDE occurs naturally in aerobic conditions and the occurrence of DDE levels higher than those of DDT indicates former contamination (MANIRAKIZA *et al.*, 2001).

Reduced concentrations of DDT and DDE were detected in sediments from Piracicaba River (SP) in a study conducted in 2008. However, in the same study, the occurrence of these compounds was also investigated in bivalve and fish species, and they were proven to occur in higher concentrations in aquatic organisms than in sediment samples (SILVA *et al.*, 2008). Similarly, DDT and total OCs concentrations in eggs from *C. granulata* in Guanabara Bay (RJ) (maximum of 80 ng.g⁻¹ and 668 ng.g⁻¹, respectively) were superior to the concentration of these compounds in sediments (maximum of 37 ng.g⁻¹ and 216 ng.g⁻¹, respectively) (DE SOUZA *et al.*, 2008).

Besides organochlorines, the occurrence of other pesticides was also investigated in Brazil. Atrazine, known as an endocrine disruptive and carcinogenic compound (ŠVORC *et al.*,

2013), was studied in the states of Paraná, Rio Grande do Sul and Rio de Janeiro. The pesticide was detected (average $0.231 \mu\text{g.L}^{-1}$) in surface waters from Paraíba do Sul river (Rio de Janeiro), near sugar-cane crops and power plants (AZEVEDO *et al.*, 2004). Neither atrazine nor its transformation products were found to occur in surface waters in Paraná (AMARAL *et al.*, 2014). In Rio Grande do Sul, it occurred in treated urban wastewater (92.3 ng.L^{-1}), yet it was not detected in surface waters, probably due to dilution (CALDAS *et al.*, 2013). However, in the same study, agrochemicals clomazone, diuron, epoxiconazole and tebuconazole were frequently detected in surface waters. These compounds were also detected in the ng.L^{-1} range in other regions of the world (STRUGER *et al.*, 2011; KÖCK-SCHULMEYER *et al.*, 2012; PAREJA *et al.*, 2012). Furthermore, in sediment samples collected in São Paulo, α HCH, aldrin, endrin, and endosulfan, dieldrin and heptachlor were among the most frequently detected pesticides (ARAÚJO *et al.*, 2006; SILVA *et al.*, 2008).

There are nearly 700 varieties of pesticides recognized by the EU (TOPPARI *et al.*, 1996), thus it is not possible to monitor the occurrence of all substances in use. Taking that Brazilian producers constitute the fifth largest market for pesticides consumption in the world, there is urgent need to keep track of the occurrence of the most consumed agrochemicals in our surface waters in order to assure water quality and public health safety (EVANGELOU *et al.*, 2016). Among all of the studies that investigate the occurrence of pesticides in environmental waters and sediments in Brazil, none of them refer to the occurrence of glyphosate, one of the most consumed agrochemicals in the country and which was classified as carcinogenic (WILLIAMS *et al.*, 2016).

2.4 CONTROL OF CEC IN BRAZIL

It is well known that most CECs are introduced to environmental compartments from MWW discharge since MWWTP are not specifically designed to remove these compounds (FATTA-

KASSINOS *et al.*, 2011). Therefore, understanding the fate of these compounds within treatment facilities may lead to the implementation of technologies which will enable CEC removal and prevent their disposal onto surface waters and contamination of drinking water and groundwater (OLIVEIRA *et al.*, 2012). The ability of different treatment methods to remove/degrade a pollutant from water or wastewater varies according to underlying removal mechanisms of each technology. In advanced oxidation processes (AOP), for example, the removal mechanism is the oxidation reaction between oxidative radicals, mainly hydroxyl radical (OH•), and organic compounds. Since OH• is non-selective, AOPs may lead to the oxidation of a variety of CECs present in MWWTP effluent (GIANNAKIS *et al.*, 2016). For other processes, certain properties of the CEC will dictate its susceptibility to treatment. Membrane filtration treatments, for example, are selective according to pollutant size, electrostatic repulsion and adsorption (JIN & PELDSZUS, 2012).

Brazilian legislation outlines 5 classes of surface water quality and the concentration of a few CEC, mainly agrochemicals, that must be assessed for proper classification of rivers and streams. These laws also determine that the discharge of wastewater must not deteriorate surface water quality. Therefore, MWWTP facilities should monitor these substances in surface water as routine operation procedures. Despite the standards imposed by national legislation, overall aims of MWWTP in Brazil are to remove mainly organic matter in order to preserve water quality in the receptor water body (BRASIL, 2005; 2011). Most of the existing plants in the national territory operate only up to secondary treatment stage and rely on biological treatment technologies such as: activated sludge (AS), anaerobic pond followed by facultative pond, Upflow Anaerobic Sludge Blanket (UASB) alone or followed by either polishing pond or trickling filter (TF), and aerated pond (OLIVEIRA & VON SPERLING, 2005). Whereas, the removal of CECs in these facilities is regarded as a future challenge for sewage treatment plants in the country (SPERLING, 2016).

A few studies have analyzed the removal of pharmaceuticals and endocrine disruptors within Brazilian MWWTP facilities (real and demo-scale). Table 2.3 shows the most recent works published on this subject. The removal of nine pharmaceuticals and/or endocrine disruptor compounds through UASB reactor alone was compared to that of UASB followed by submerged bed, polishing pond, and trickling filter. UASB alone was not able to remove target compounds, thus confirming the need for additional treatment stages. Additionally, the photolysis of some compounds contributed to higher removal rates, and hydrophobic compounds were more likely to be removed by sorption mechanisms (BRANDT *et al.*, 2013).

The fate of caffeine, E2, EE2, estrone and BPA were investigated in three different systems: activated sludge, UASB and stabilization lagoon. The three systems presented 99% removal for caffeine, BPA and estrone. In addition, sludge samples collected from each plant indicated higher efficiency of UASB reactors to remove hormones when compared to other technologies due to sorption of target compounds onto UASB sludge (FROEHNER *et al.*, 2011). When comparing activated sludge and trickling filter for the removal of different analgesics, lipid regulators and anti-inflammatories, Stumpf *et al.*, (1999) concluded that activated sludge was more efficient than trickling filter for the removal of target compounds presenting up to 83% decay. However, concentrations of bezafibrate and tolfenamic acid (veterinary drug) were still notable after treatment (mg L^{-1} range).

Most of the studies listed on Table 2.3 analyze the fate of a small list of pharmaceuticals and endocrine disrupting compounds within MWWTP in Brazil. However, the variety of compounds that may be present in real MWW is broader and more studies targeting different compounds should be performed in the country. For most part, studies show that high rate systems, such as activated sludge and UASB followed by disinfection or advanced treatment stages (UV-C, ozonation or chlorination) may be able to properly remove these few CEC.

TABLE 2. 3 - Studies on the control of CEC in MWWTP in Brazil

CEC	Matrix	Treatment	Results	Reference
Estrone, 17 β - estradiol, 17 α -ethynylestradiol, 17 β -estradiol 17-acetate	Municipal wastewater	Facultative pond followed by two maturation ponds, facultative pond alone, activated sludge + chlorination and UASB + chlorination	Higher removal rates (95%) for UASB and AS systems followed by chlorination. 54-79% removal for facultative lagoons.	(PESSOA <i>et al.</i> , 2014)
17b-estradiol (E2), 17a-ethinylestradiol (EE2), bisphenol A (BPA), nonylphenol (NP), Sulfamethoxazole (SMX), Thrimethropin (TRI), Bezafibrate (BZF), Diclofenace (DCF) and Miconazole (MCZ)	Municipal wastewater	UASB followed by: submerged bed, polishing ponds or trickling filters.	UASB system alone was not effective for the removal of NP, BPA, DCF, BZF, SMX, TRI, thus supporting the use of other treatments in the sequence.	(BRANDT <i>et al.</i> , 2013)
Caffeine, E2, EE2, estrone and BPA	Municipal wastewater and sludge from biological reactors	Activated sludge; UASB; stabilization lagoon	More than 56% for all of the studied plants. UASB treatment achieved higher average removal rates for all of the hormones. Hormone concentrations were higher in sludge samples taken from the UASB system.	(FROEHNER <i>et al.</i> , 2011)
Antibiotics: ciprofloxacin (CPF) ; clindamycin (CLM), sulfamethoxazole (SMX), trimetoprim (TMP). β -blocker: atenolol (ATL) and anti-inflammatory diclofenac (DCF)	Municipal wastewater secondary effluent	UASB and trickling filter followed by a UV-C reactor	CPF, DCF SMX and TMP were not further removed by UV-C irradiation, even at high doses. CLM and ATL concentrations were sensible to different UV-C irradiation doses.	(LOPES <i>et al.</i> , 2017)
4C-dicofol and its main metabolite dichlorobenzophenone	Municipal wastewater and biological sludge	Aerobic treatment and sludge anaerobic digestion	DCF was well converted to DBP, and 36% of DBP were converted to other products. 40% of the transformation products remained in sludge, indicating biodegradation rather than mineralization	(OLIVEIRA <i>et al.</i> , 2012)

CEC	Matrix	Treatment	Results	Reference
PPCP: Atenolol, Avobenzone, Benzophenone, Carbamazepine, Chlorpropamide, Diclofenac sodium, methybenzylidene camphor, Gemfibrozil, Furosemide, Glibenclamide, Mebendazole, Methylparaben, Nimesulide, Miconazole nitrate, Propylparaben, Triclocarban, Triclosan, Caffeine. Pesticides: Carbendazim, Carbofuran, Cyproconazole, Clomazone, Difenconazole, Diuron, Epoxiconazole, Fipronil, Imazapic, Imazethapyr, Iprodione, Irgarol, Malathion, Methalaxyl-M, Metsulfuron-methyl, Molinate, Penoxsulam, Pyrazosulfuron-ethyl, Pirimiphos-methyl, Propanil, Propiconazole, Quinclorac, Simazine, Tebuconazole, Tiabendazole, Trifloxystrobin	Drinking water	Conventional water treatment system: coagulation, flocculation, settling and filtration followed by chlorination.	Atrazine, Carbofuran, Clomazone, Diuron, Epoxiconazole, Irgarol, Mebendazole, Propilparabenand Tebuconazole were not removed during conventional treatment applied in the Water Treatment Plant.	(CALDAS <i>et al.</i> , 2013)

Multistage routes have been imposed by authorities in developed countries, mainly in Switzerland, where 80% of a list of priority CECs must be removed before discharge as of 2016 (GIANNAKIS *et al.*, 2016). However, in Brazil, sewage treatment is only available for 39% of generated MWW, thus, even if tertiary treatment is required in MWWTP, the disposal of untreated sewage in water receptors will continue to contribute to the disposal of CECs in surface waters (SPERLING, 2016).

When sanitary conditions are proper and surface waters used as sources of drinking water are well protected from illegal disposal of untreated MWW, concentration of CECs in drinking water should be reduced. Thus, human exposition to chemicals through potable water should be negligible when compared to other forms of exposure (food, daily products and air) (VANDENBERG *et al.*, 2007). This is probably one of the reasons for a reduced number of studies regarding the removal of CECs in WTP when compared to those assessing the occurrence of CEC in effluent from MWWTP. However, the risks of long term exposure to various combinations of compounds in low concentrations, as it occurs in drinking water, are still unknown. Therefore, it is important to generate information over the fate of CEC in water treatment plants so that potential risks to population health and safety may be promptly predicted and prevented (BERETTA *et al.*, 2014). Indeed, an incident regarding the presence of hepatotoxic cyanotoxin in a WTP in Caruaru, Brazil, in 1996, led to the death of 50 patients in a hemodialysis clinic (JOCHIMSEN *et al.*, 1998). In the sequence, water monitoring for the presence of cyanobacteria in surface water used for water supply became mandatory in Brazil. Later, the WHO adopted maximum permissible values for microcystin in water quality standards (WHO, 1998).

The occurrence of 18 PPCPs and 33 pesticides on the inlet and outlet of a WTP was assessed by Caldas *et al.*, (2013). Results indicated that a few compounds resist to the treatment

applied in conventional WTP and may show higher concentration in drinking water than that observed in surface water prior to treatment, which was the case for biocide tebuconazole, and pesticides carbofuran, atrazine and epoxiconzole.

The fate of 17 β -estradiol after direct and indirect ozonation was investigated with regard to estrogenic activity. YES test showed that only direct ozonation is able to deplete estrogenic activity, while transformation products formed after indirect ozonation still presented endocrine disrupting activity (BILA *et al.*, 2007). Meanwhile, estrogenic activity of E2, EE2 and BPA were above the acceptable levels after sand filtration and clarification stages in a WTP, thus indicating the persistence of endocrine disruptors in drinking water even after conventional treatment stages (DIAS *et al.*, 2015). In order to properly control these compounds in this WTP the author suggested the combination of low ozonation doses and chlorination. Similarly, prechlorination, flocculation–sedimentation and sand filtration were not able to eliminate 17 β -estradiol (E2), 17 α -ethynylestradiol (EE2) and 4- nonylphenol from SW. These results are alarming taking that human exposure to endocrine disruptors even when in very small concentrations may lead to reproductive disorders, which are sufficient to activate/deactivate physiological responses. Thus, emphasizing the importance of applying advanced treatment stages after conventional treatment routes in water treatment plants (COLBORN *et al.*, 1993; FOWLER *et al.*, 2012).

2.5 FATE OF CEC IN AGRICULTURAL AREAS

Once applied to agricultural crops or used in agricultural areas for veterinary purposes, CECs may undergo various phenomena: hydrolysis, photolysis, volatilization, complexation, oxidation, dilution, sorption, biodegradation or accumulation (MOMPELAT *et al.*, 2009). These phenomena contribute to the fate of each agrochemical in water, sediment and soil, thus influencing their degradation rate or persistence in the environment. The occurrence of each

of these phenomena will vary according to physicochemical properties of each compound, and to environmental conditions (solar irradiation, temperature, humidity, soil composition, dissolved oxygen content, etc) to which they are exposed (DORES, 2008).

While CECs consumed in urban areas are usually directed to and treated in MWWTP, and then discharged onto surface waters through point sources, monitoring the fate of agrochemicals and pesticides in rural areas is usually more complicated once they are applied directly on the field, thus being originated from diffuse sources. In order to enable environmental control of these substances and prevent disasters, an assessment of pesticide fate in water is mandatory before its sales are authorized. However, these tests are usually performed in fairly artificial scales which may hinder real contamination risks (CORREIA *et al.*, 2007; LAABS *et al.*, 2007). Therefore, performing several field monitoring campaigns for a long period of time is extremely necessary to obtain consistent data on the fate of pesticides in agricultural areas (SOARES *et al.*, 2017). Currently, computational modeling is a tool that assists researchers to understand and predict the fate of pesticides in soils while considering their physicochemical properties and soil characteristics, thus avoiding unnecessary costs related to sampling campaigns and analytical essays. However, no models are able to consider all of the numerous factors associated to pesticide leaching in its completeness due to the complexity of the system (PARAÍBA *et al.*, 2003; SOARES *et al.*, 2017).

Leaching of pesticides to surface waters and groundwater was intensively studied in field experiments performed in the temperate region. Although, these studies remain scarce in agricultural regions located in the tropics, especially when it comes to medium and long-term scales (LAABS, VOLKER *et al.*, 2002). Table 2.4 lists some studies conducted in tropical fields in Brazil regarding the fate of pesticides after they are applied to crops. It is known that higher temperatures observed in tropical soils favor microbial activity, leading to higher

TABLE 2. 4 – Studies published in international journals on the fate of agrochemicals applied in agricultural regions in Brazil

Agrochemical	Matrix	Location	Reference
Atrazine, chlorpyrifos, k-cyhalothrin, endosulfane a, metolachlor, monocrotofos, simazine, andtri-uraline	Soil	MT	(LAABS, V. <i>et al.</i> , 2002)
p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDT, p,p'-DDT, HCB, γ-HCH, Heptachlor, Heptachlorepoxide, α-Endosulfan, Aldrin, Dieldrin, Endrin	Sediments	Paraíba do Sul River, RJ	(TORRES <i>et al.</i> , 2002)
Acifluorfen, Alachlor, Ametryn, Atrazine, Carbaryl, Chlorimuron-ethyl, Chlorothalonil, Chlorpyrifos, Cyanazine,b-Cyfluthrin, λ -Cyhalothrin, Cypermethrin, 2,4-D, DDE, DDT, Deltamethrin, Desethylatrazine, Dimethoate, Ditalimfos, Diuron, Endosulfan, Endosulfan-sulfate, Fenitrothion, Glyphosate, α-HCH, Heptachlor, Lindane, Malathion, Methomyl, Methyl-parathion, Metolachlor, Metribuzin, Monocrotofos, Paraquatdichloride, Parathion, Permethrin, Profenofos, Quintozene, Simazine, Tebuconazole, Teflubenzuron, Terbutylazine, Triazofos, Trifluralin	Surface water, sediment and rain water	Pantanal, MT	(LAABS, VOLKER <i>et al.</i> , 2002)
Phenanthrene, Anthracene, Fluoranthene, Pyrene, Chrysene, Benzo[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenzo[ah]anthracene, Indeno[123cd]pyrene, Benzo[ghi]perylene, B[a]P/Phe	Sediments	Paraíba do Sul River, RJ	(AZEVEDO <i>et al.</i> , 2004)
Alachlor, atrazine, chlorpyrifos, endosulfan, metolachlor, profenofos, simazine, andtrifluralin	Surface water and sediment	MT	(LAABS <i>et al.</i> , 2007)
Atrazine	Soil	RJ	(CORREIA <i>et al.</i> , 2007)
Simazine, metribuzin, metolachlor, trifluralin, atrazine, and two metabolites of atrazine, deisopropylatrazine and deethylatrazine	Surface water and groundwater	MT	(DORES, 2008)
4C-dicofol and its main metabolite dichlorobenzophenone	Wastewater and sludge	RJ	(OLIVEIRA <i>et al.</i> , 2012)

biodegradation rates and attenuated leaching of pesticides to surface water and groundwater in these locations when compared temperate regions(WALKER & BARNES, 1981). On the other hand, high soil temperatures observed in the tropical zone also increases dispersion through volatilization, thus playing an ambiguous role (LAABS, VOLKER *et al.*, 2002).

Semi-field scale tests were conducted in order to understand the fate of eight pesticides in small and large water vs. water/sediment cosmos simulating the tropical region of Pantanal, Brazil. The author concluded that polar pesticides, such as atrazine, are more persistent in clear water ecosystems, while endosulfan and other non-polar compounds showed increased persistence in sediments due to adsorption (LAABS *et al.*, 2007). As according to the US Environmental Protection Agency (USEPA), the potential of a pesticide to become a water contaminant may be predicted by three main factors: sorption coefficient (K_{oc}), water solubility and half-life in soil (WAUCHOPE *et al.*, 2002). Due to its high solubility in water and low K_{oc} , carbofuran was detected in groundwater in a crop region in Brazil and other regions (LEANDRO *et al.*, 2008). In a study performed in Mato Grosso, five pesticides (simazine, metribuzin, metolachlor, trifluralin, atrazine) and two metabolites of atrazine were detected more frequently in groundwater samples when compared to surface water samples (DORES, 2008). Another study showed that Atrazine reached deep layers (50 cm) within two days of its application to soil, thus confirming the risk of groundwater contamination by this pesticide (CORREIA *et al.*, 2007).

In addition to run-off, humid deposition of pesticides on pristine waters and soil may occur after volatilization through rainfall. A study conducted in the Pantanal region monitored 29 pesticides and 3 metabolites. Pesticides were detected with higher frequency in rainwater (87%) when compared to samples taken in the other sources (68 and 62%, respectively).

Therefore, volatilization of pesticides in this area is more prominent than run-off and has a

higher contribution to surface water and groundwater contamination. According to the study, pesticides were transported up to 75 km in distance through the atmosphere. Endosulfan, alachlor, metolachlor, trifluralin, monocrotofos and profenofos were detected with high frequency in rainwater in the region and concentrations of pesticides in rainwater were similar to those found in Europe. In the end of the study, 2,800 kg of pesticides were deposited through rainwater during 3.5 months, thus reinforcing the importance of investigating this phenomenon in tropical regions, where it may be more relevant than in temperate regions (LAABS, VOLKER *et al.*, 2002). Finally, Pantanal is the world's largest tropical wetland area which harbors rich biodiversity and must be properly preserved. Taking that Brazil is one of the biggest consumers of pesticides worldwide, there is urgent need to account for the transportation and deposition of pesticides through volatilization and rainfall in the national territory, especially when determining natural resource protection areas near biodiversity sanctuaries such as Pantanal.

2.6 CEC SELECTED AS TARGET COMPOUNDS IN THIS STUDY

After this extensive literature review, four compounds were chosen as representatives of three different classes of CEC: pharmaceuticals and personal care products, urban pollution tracer and pesticides. This selection was based on the current and predicted consumption level of these compounds in the national territory as well as in other regions of the world and on their occurrence in the national territory. In addition, considering the apparatuses available for the detection and quantification of these compounds and the noteworthy amount of studies published on the control of CEC by advanced oxidation processes during the past years, physicochemical properties, analytical methodology used for identification and quantification and the number of studies related to the control of these compounds were also used criteria for selection. Each of the selected target compounds is presented in the sequence in items 2.6.1 to

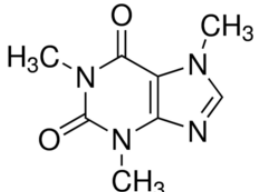
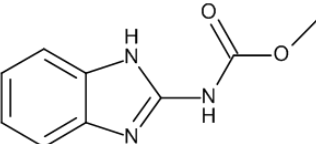
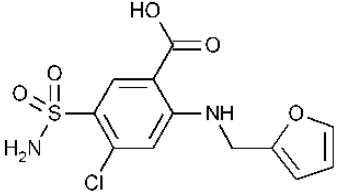
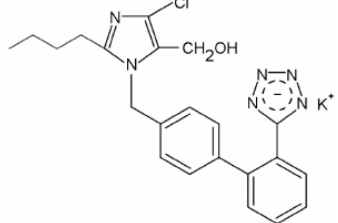
2.6.4 and Table 2.5 shows a detailed description of physicochemical properties inherent to each of them.

2.6.1 Caffeine (CAF)

As shown in Table 2.5, caffeine is very soluble in water and also resistant to direct photolysis under UV-C irradiation and direct sunlight due to its low absorption of irradiation and reduced molar absorption coefficient when compared to photo liable compounds such as methylene blue ($46,000 - 91,000 \text{ M cm}^{-1}$)(CHAN *et al.*, 2012) at 254 nm and at wavelengths above 290 nm, which correspond to the solar spectrum. In addition, as caffeine ionization constant (pka) is above 10.4 (Table 2.5), the molecule is not dissociated in natural waters and wastewaters as the pH of these matrixes usually fall between 6.5 and 7. Therefore, it behaves similarly with regard to light absorption in different pH ranges.

Mass balance studies revealed similarities between theoretically calculated anthropogenic input of caffeine and its concentrations in lakes in Switzerland, thus making it a promising indicator of sewage discharge and suitable urban pollution tracer. Biodegradation of caffeine is also reduced, although its rate may vary in temperate and tropical regions (BUERGE *et al.*, 2003). In addition, since caffeine is almost totally removed by different treatment technologies in MWWTP in Brazil, it may be used to indicate the discharge of untreated sewage (FROEHNER *et al.*, 2011). Caffeine occurred in 97% of samples collected during 16 months in different water bodies located in the state of São Paulo and higher concentrations were found in the dry season, thus confirming its relation to untreated sewage discharge (MONTAGNER *et al.*, 2014). It was also detected in 100% of sediment and surface water samples taken in coastal waters of Bahia de Todos os Santos and Santos Bay, respectively, where primarily treated UWW is disposed through marine outfall (BERETTA *et al.*, 2014; PEREIRA *et al.*, 2016). Drinking water sampled in the city of Campinas, showed caffeine

TABLE 2.5 - Chemical structure and physicochemical properties of selected target compounds

Compound	Abbreviation	Class	CAS number	Molecular formula	Molar Mass	Chemical structure	Solubility (water)	pKa	ϵ_{254}
Unit					g mol ⁻¹		mg L ⁻¹		M ⁻¹ cm ⁻¹ (pH 7)
Caffeine	CAF	methylxanthine	58-08-2	C ₈ H ₁₀ N ₄ O ₂	194.194		11.000 ¹	10.4 ⁴ Not observed ⁵	4,590
Carbendazim	CBZ	benimidazole	10605-21-7	C ₉ H ₉ N ₃ O ₂	191.19		8	4.2	3,310
Furosemide	FRSM	benzoic-sulfonamide-furan	54-31-9	C ₁₂ H ₁₁ ClN ₂ O ₅ S	330.739		11.8 ¹	3.9 ³	6,700
Losartan Potassium	LP	angiotensin type 1 receptor	11096-26-7	C ₂₂ H ₂₂ ClKN ₆ O	461.007		21.6 ¹	4.15 (basic). 14.27 (acidic) ²	11,772

¹VCCLAB. Virtual Computational Chemistry Laboratory. <http://www.vcclab.org>. 2005. ²<https://chemaxon.com/consultancy> ³ Khan SJ, Ongerth JE; Chemosphere 54:355-67 (2004) ⁴Dean, J. et al., 1999. ⁵

CARLSON et al., 2015.

concentrations between $0.22 \pm 0.06 \mu\text{g.L}^{-1}$ which is comparable to concentrations detected in treated WW in other regions. In the same study, caffeine concentrations in DW were, in some cases, higher than those found in SW, thus indicating the disposal of untreated sewage directly into water supply network (SODRÉ *et al.*, 2010).

2.6.2 Carbendazim (CBZ)

Carbendazim was the 15th most sold pesticide in Brazil in 2014 and it is currently used in various crops in the country (IBAMA, 2016). Although it presents reduced solubility in water (Table 2.5), CBZ was detected in low concentrations ($0.003\mu\text{g.L}^{-1}$ - $156\mu\text{g.L}^{-1}$) in surface water, ground water, effluents from MWWTP and even in drinking water in Brazil and worldwide (LOEWY *et al.*, 1999; BURKHARDT, 2007; MONTAGNER *et al.*, 2014). In addition, it is photo-stable under UV-C irradiation, which is confirmed by its low molar absorption coefficient reported at 254 nm (Table 2.5), which is similar to that of caffeine and very reduced when compared to photo-sensitive compounds such as dyes (CHAN *et al.*, 2012) and solar irradiation (DA COSTA *et al.*, 2018), thus being persistent in the environment. As its pka is equivalent to 4.2, it is expected to be in the dissociated state in natural waters, a state in which it is known to absorb more UV irradiation, thus being more reactive under irradiated processes (PANADÉS *et al.*, 2000). Carbendazim presents moderate toxicity, although it is confirmed to be mutagenic and to cause reproductive disturbance and acute and chronic toxicity to aquatic biota and it is not biodegradable (EU, 2008). Carbendazim is one of the compounds included in the drinking water standard in Brazil ($< 120 \mu\text{g.L}^{-1}$) which supports the search for tertiary treatments to degrade this fungicide (MS, 2011).

2.6.3 Furosemide (FRSM)

Furosemide (FRSM) is one of the most prescribed diuretics in the world (STUER-LAURIDSEN *et al.*, 2000). Diuretics are highly consumed in Brazil (GONÇALVES, 2013)

and are usually prescribed along with anti-hypertensive drugs for patients treating high blood-pressure. It is estimated that 1.5 billion people will suffer from hypertension by 2020 and the increase in the consumption and disposal of drugs related to this disease will also increase (WHO, 2013). In addition, diuretics are sold in high quantities in the “black market” in the country for weight-loss purposes, which hinders the estimation of real consumption numbers. Despite its reduced solubility in water (Table 2.5), FRSM was detected in 62% of the samples taken along Guanabara Bay (nearly 400 ng.L⁻¹) and in effluents from MWWTP in Rio de Janeiro (> 2000 ng.L⁻¹) (GONÇALVES, 2012). It was also detected in rivers in Spain (median concentrations 1000 ng.L⁻¹), mainly near MWWTP disposal locations (VALCÁRCEL *et al.*, 2011). The removal of Furosemide from MWWTP effluent is extremely important since it shows toxicity (ISIDORI *et al.*, 2006) and estrogenic activity. Furosemide showed maximum estrogenic response to YES test (EC₅₀ = 0.99 mg.L⁻¹) (ISIDORI *et al.*, 2009). Moreover, as predictable by the increased molar absorptivity presented by this compound at 254nm, it is highly photodegradable under UV-C irradiation and its photolysis product shows chronic toxicity and mutagenicity (ISIDORI *et al.*, 2007). As the pKa of FRSM is 3.9, it is in its dissociated state in natural waters, a state in which its molar absorptivity decays when compared to the neutral state which occurs when the pH is lower than 3.9 (MOORE & BURT, 1981). Therefore, FRSM treatment by irradiated processes at neutral pH must be investigated to assure treatment efficiency and toxicity removal.

2.6.4 Losartan Potassium (LP)

Losartan potassium (LP) is an anti-hypertensive which was one of the most sold pharmaceuticals in Brazil in 2014 (CFF, 2014). It is available to the population in a reduced price through the Popular Pharmacy program and its high consumption has been linked to population aging in Brazil. A study conducted in Belo Horizonte indicated that anti-

hypertensives, such as Losartan Potassium, correspond to 52% of total drug consumption by elder population in the city and predictions indicate an increase in this percentage, thus supporting the importance of studying the removal of Losartan Potassium from MWW and surface water via tertiary treatments (LOYOLA FILHO *et al.*, 2006; GONÇALVES, 2013). As LP shows considerable solubility (Table 2.5), it is expected to occur in surface waters after discharge. The occurrence of Losartan Potassium was detected in the Santos Bay (up to 32 ng.L⁻¹) and Guanabara Bay (up to 549 ng L⁻¹, 87% frequency of detection) (GONÇALVES, 2012; PEREIRA *et al.*, 2016). It has also been found in surface waters in India (2000 µg L⁻¹), in the Rhine river, and in MWW in Portugal (HEBERER, 2002; LARSSON *et al.*, 2007; SOUSA *et al.*, 2012). In addition, due to its high molar absorptivity at 254 nm (Table 2.5), which is above that presented for all of the other four compounds, LP is expected to undergo photolysis under UV-C irradiation, even though this has only been documented for the medical formulation of LP which contains other compounds that contributed to photolysis (SEBURG *et al.*, 2006) while no reports regarding the quantum yield of this compounds have yet been performed in pure solution. As according to the pKa reported for LP (Table 2.5), the molecule is in its dissociated form in natural waters, in which it may behave differently when concerning the absorption of irradiation and susceptibility to irradiated treatments when compared to acidic pH. Although, no previous reported on LP molar absorption shifts as according to pH have yet been reported. One of the most serious problems associated to the presence of Losartan Potassium in surface waters and MWW is that it may form cyanide (a toxic compound that threatens human health) if it reacts with sodium hypochlorite, a reagent which is commonly used for water purification and disinfection in treatment plants (ADACHI & OKANO, 2008). In addition, it has been tested positive for acute toxicity (BAYER *et al.*, 2014).

2.7 ENVIRONMENTAL LEGISLATION AND CEC

In the European Union water resources are shared amongst different countries through common rivers, thus legislation must be followed by all EU members. After Directive 2000/60/CE (EU, 2000), which aimed at protecting water resources and recovering water quality in European rivers, the European Parliament approved Decision 2455/2001/CE (EU, 2001) which was the pioneer legal document regarding this subject and listed 33 priority substances. Environmental quality standards (EQ) for each compound were established seven years later through Directive 2008/105/CE (EU, 2008). In the sequence, another list containing 15 other priority compounds was published and these chemicals have been monitored for their occurrence since 2011 (EU, 2011). EQ were established for 12 out of these 15 compounds (EU, 2013). In 2015, monitoring the occurrence and respecting EQ also became mandatory for 17 α -ethynilestradiol, 17 β -estradiol and Diclofenac (EU, 2015).

Meanwhile, in Switzerland, a recent amendment that requires a minimum removal of 80% for some priority compounds (amisulpride, carbamazepine, citalopram, clarithromycin, diclofenac, hydrochlorothiazide, metoprolol, venlafaxine, benzothiazole, candesartan, irbesartan and mecoprop) in MWWTP was recently approved (FOEN, 2014). It is important to notice that most of the compounds in the list made by the Swiss authorities are pharmaceuticals used mainly for the treatment of psychological disorders and diseases related to the cardiovascular system, and their consumption may be directly related to modern society life style and to the aging of population.

In the United States of America, each State is responsible for updating its legislation regarding surface water quality. However, the EPA is responsible for the nationwide drinking water quality standards. In 2009, the EPA announced primary standards for 88 items (microorganisms, disinfection by products, organic and inorganic compounds, among others)

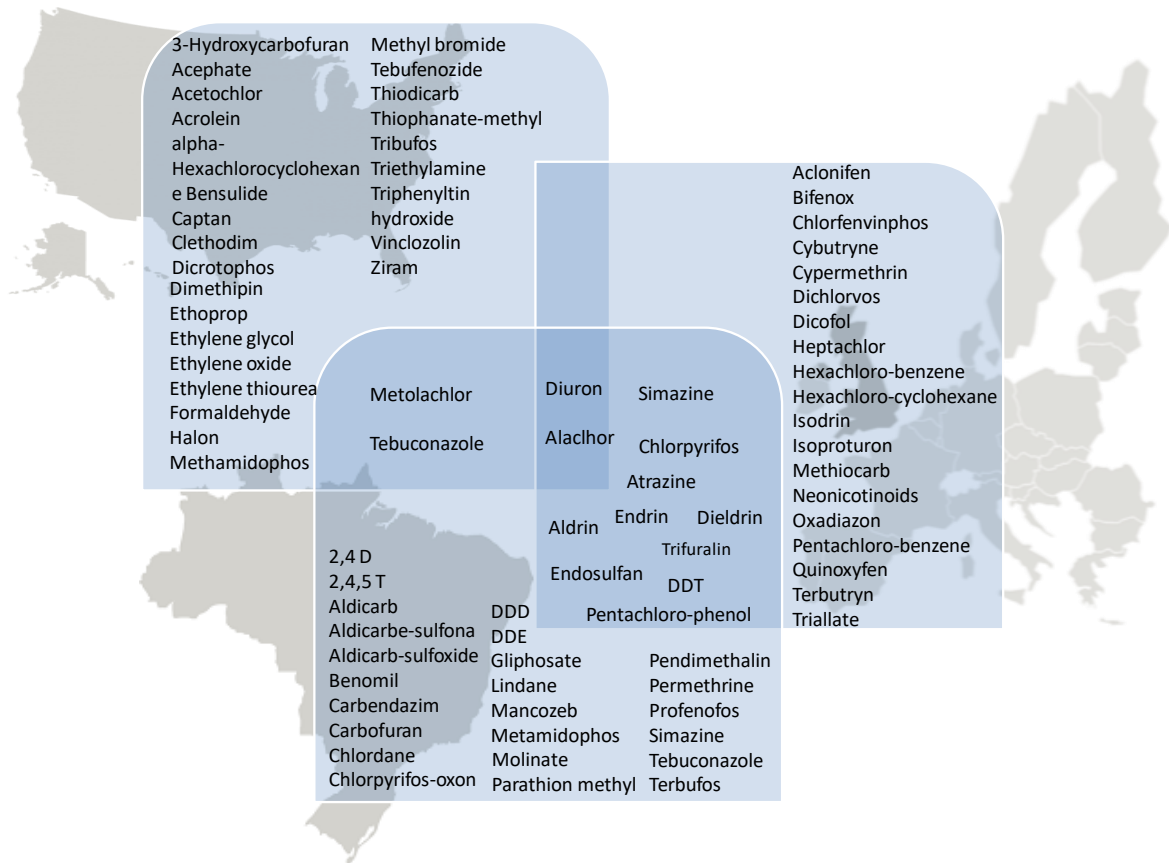
(EPA, 2009). Unregulated compounds must also be tracked in each state through the Unregulated Contaminant Monitoring Program. This program aims at tracking possible contaminants that may be present in drinking waters. As a consequence of the Unregulated Contaminant Monitoring Program, a Contaminant Candidate List (CCL), which includes compounds that may be harmful to human health, is published every five years. Since the first CCL, the number of target compounds has increased from 60 (CCL₁) to 112 (CCL₄) contaminants to include pesticides, pharmaceuticals, hormones, toxins and endocrine disrupting compounds (EPA, 2017). Each CCL is evaluated by the EPA and, if necessary, new primary standards are set. A recent study conducted in the lakes of Minnesota (MN), a leading state on water quality management in the USA, revealed the presence of many PPCP and chemicals in most of the lakes and showed that some compounds may be leading to genetic impacts on fish population (FERREY *et al.*, 2017). Impacts on the life-cycle of aquatic biota were also linked to the presence of various pharmaceuticals and personal care products and pesticides detected in surface water throughout the territory (BRADLEY *et al.*, 2017).

There is no specific national legislation that imposes the removal of CEC in MWWTP to prevent surface water contamination in Brazil. However, the legislation (CONAMA 430/2011)(BRASIL, 2011) states that the discharge of treated wastewater onto surface water must not deteriorate surface water quality leading to a change in class. This implies that MWWTP facilities should be attentive to the concentration of a few organic pollutants, mainly pesticides and hydrocarbons, that must be monitored in surface water for the classification of water bodies (BRASIL, 2005; 2011). Although, periodical monitoring performed by treatment plant facilities and environmental agencies occur mainly for organic matter and solids, while organic compounds are hardly ever monitored in the point of discharge of MWWTP effluent. This occurs because the removal of CEC at Brazilian

MWWTP is a challenge to be faced in the future considering lack of basic sanitation infrastructure in the country (SPERLING, 2016).

In addition, the Public Department of National Health (Ministério da Saúde) and the National Agency of Health Surveillance (ANVISA) have established maximum concentration levels for a few chemicals in water reservoirs used for drinking water supply, most of them are agrochemicals and/or their transformation products and cyanotoxins (MS, 2011). Agrochemicals monitored through Portaria 2914/2011 are listed in Figure 2.3 and compared to those monitored in the USA and in the EU. DDT and its derivatives, carbendazim, endosulfan, diuron, atrazine are some of these compounds. However, controlling the presence of these compounds in drinking water only does not lead to the protection of numerous species existing in various natural communities in Brazil which are rich on biodiversity, once CEC will continue to be disposed of in water bodies through the disposal of effluent from MWWTP. Therefore, it is important to increase inspection of discharged municipal and industrial wastewaters and to review the requirements related to treatment efficiency in MWWTP, as it was performed in Switzerland. Above all, considering that non-treated MWW and MWWTP effluent treated only up to the secondary stage (biological treatment) are some of the main sources of CEC to the environment, it is urgent to improve basic sanitation conditions, since only mere 38% of total MWW generated in Brazil is currently treated (SPERLING, 2016).

FIGURE 2.3 – Diagram showing pesticides for which monitoring is mandatory regulated in the USA, Brazil and/or in the EU



Regarding future inclusion of CEC to standards related to the control CEC in Brazil, which is the fifth largest country in the world, territory extension may be considered, simultaneously, as an obstacle and as an advantage. From the first perspective, the extension of the territory of a country reflects on the variety of ecosystems and resources that it may contain and, consequently, on the variety of activities (industrial, agriculture, human consumption) performed in each region. Thus, as different chemicals are used frequently, an extensive list of chemical products may occur in the environment and an increased number of analyses must be performed for the preliminary assessment of substances to be included in a “watch list”. Also, in a large territory, costs to perform regular monitoring analysis are increased, not to mention considerable need of technical apparatuses and specialized personnel. Instead of targeting a wide range of compounds which is more costly and time consuming, a different approach to lower costs could be performing ecotoxicological assays and searching for the

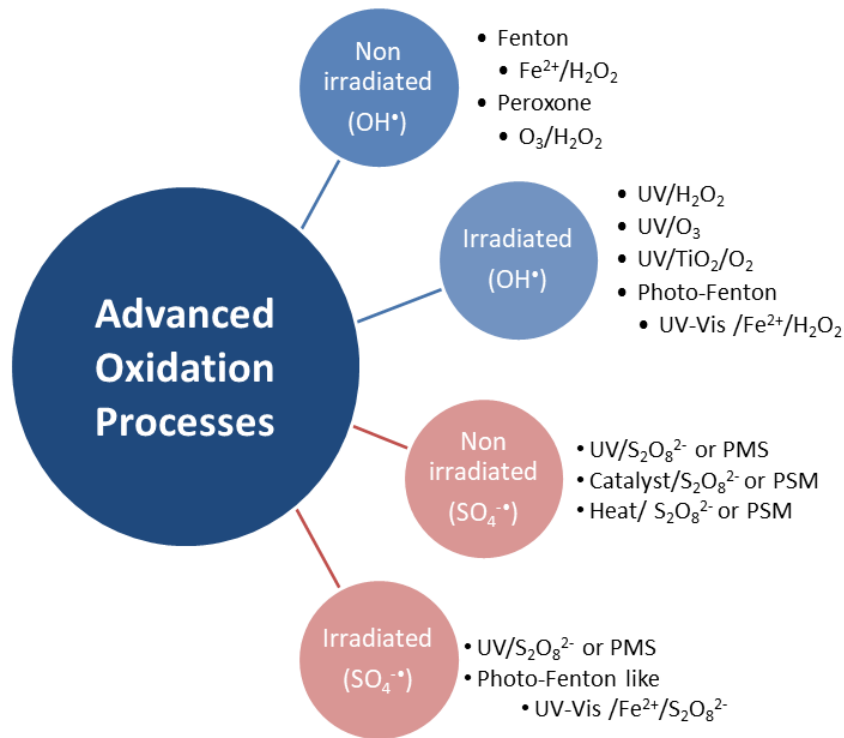
effects of CEC in samples and only for a few compounds used as indicators of contamination by CEC.

On the other hand, from the second perspective, territory extension may be considered an advantage for the management of CEC in water resources since water flows an extended distance (from springs to the ocean) only within the border of a single country where all of the states must comply with the national legislation. Therefore, in large countries, such as Brazil, surface and ground water quality will not be impacted by the activities performed in neighboring nations where environmental legislation regarding CEC may not be as strict or may not even exist. This is true for five of the eight main Brazilian watershed basins which do not cross the border of the national territory and this fact may facilitate the control of these compounds in the environment after national standards are imposed.

2.8 ADVANCED OXIDATION PROCESSES (AOPS) AND CEC

Advanced Oxidation Processes (AOP) have been pointed out as alternatives for the treatment of CEC from surface waters in WTP and from municipal wastewater in MWWTP (GIANNAKIS *et al.*, 2016). AOPs are conventionally characterized by the formation of non-selective and highly reactive radicals, mainly hydroxyl radicals (OH^\bullet ; $EH = 2.8 \text{ V}$), which oxidize matrix compounds, thus leading to the degradation of recalcitrant components. Different reagents and various combinations may be used for the formation of OH^\bullet (Figure 2.4). However, systems containing other types of free oxidative radicals may also be classified as AOPs, which is the case of sulfate radical ($\text{SO}_4^{\bullet-}$), for example (WACŁAWEK *et al.*, 2017). The study of AOP exploring $\text{SO}_4^{\bullet-}$ has increased abruptly in the past decades. Mechanisms involved in the formation of hydroxyl and sulfate radicals, – which were explored in Chapters 3 and 4 of this Thesis - and advantages and disadvantages pertaining to each of them are detailed in the following sections.

FIGURE 2. 4 – Non-irradiated and irradiated combinations used for the formation of hydroxyl radicals and sulfate radicals in AOP



2.8.1 Hydroxyl radical (HO•) based AOPs

Among all AOPs represented in Figure 2.4, UV-C/H₂O₂ is the most amply applied and reactors for the application of this process are commercially available in industrial scale worldwide (KRUITHOF *et al.*, 2007). In this process, H₂O₂ is cleaved into two hydroxyl radicals in the presence of UV-C light (254 nm) (Equation 2.1) (TARR, 2003). UV-C/H₂O₂ is considered a clean process once it does not generate sludge and the reagent tends to decompose (TARR, 2003). In addition, it is not necessary to adjust the pH, thus not requiring the use of chemical reagents for acidifying and neutralizing the wastewater after treatment. However, the use of an artificial light source increases treatment costs (MIRALLES-CUEVAS *et al.*, 2017).



As an alternative to UV-C/H₂O₂, UV-C irradiation may be replaced by iron salts which react with hydrogen peroxide as catalysts for the formation of HO[•]. This process is named Fenton (Fe²⁺/H₂O₂) in honor to the scientist that first described the reaction and is delineated by Equation 2.2 (TARR, 2003). In addition to the reaction of Fe²⁺ with H₂O₂, Equation 2.3, which represents the cycling of Fe³⁺ salts onto Fe²⁺, also occurs in this system, yet in a slow rate. Therefore, as Fe²⁺ is continuously consumed, reaction rate reduces with time, stagnating at a certain point (LITTER; CANDAL; MEICHTRY, 2013). The Fenton process is favorable once iron is not toxic and is one of the most abundant elements in the lithosphere, thus being inexpensive (PAPIĆ *et al.*, 2009).



Nevertheless, Fenton reaction requires acidic pH (≈3) once iron must be dissolved in the system to enable the reaction with H₂O₂. Therefore, two extra stages are necessary when this technology is applied: acidification of wastewater before treatment and neutralization prior to the discharge of treated wastewater onto surface water. As a consequence, operational requirements are more complex when compared to UV-C/H₂O₂, once chemical reagents (sodium hydroxide and hydrochloric acid) must be handled and applied by operators. In addition, during neutralization, iron precipitates generating a sludge, which must be disposed of subsequently (ROBINSON *et al.*, 2001).

When the Fenton process is submitted to UV-Vis irradiation, the process is called photo-Fenton and its effectiveness is enhanced. In this system, Fenton reactions represented by Equations 1.2 and 1.3 still occur. Indeed, Fe²⁺ cycling (Equation 2.3) is favored and occurs in

a higher rate, thus extending the reactivity of the system. In addition to Equations 2.2 and 2.3, photocatalytic reactions also occur during photo-Fenton (Equation 2.4). In these reactions, Fe(OH)^{2+} , the predominant species in the system at pH 3, absorbs light in the visible range (<540-580 nm) which results in supplementary pathways for the formation of hydroxyl radical and Fe^{2+} in the system. Hence, with extra pathways for the generation of $\text{HO}\cdot$ and Fe^{2+} , the effectiveness of photo-Fenton process is superior to that presented by UV-C/ H_2O_2 and the non-irradiated Fenton system (TARR, 2003).



Considering that Fe(OH)^{2+} absorbs light in the visible range, solar irradiation, which is composed of UV-A and UV-B (<5%, UV-B: 280-315 nm and UV-A: 315-400 nm) and, for the most part, visible irradiation (95% UV-Vis: > 400 nm) may be explored in the solar photo-Fenton system (PÉREZ *et al.*, 2002; CARRA, I. *et al.*, 2013). Electricity costs related to the application of solar photo-Fenton are reduced once the use of artificial light source is eliminated. The application of solar photo-Fenton is especially favorable in tropical countries, such as Brazil which gets high levels of solar irradiation throughout the whole year (MARCELINO *et al.*, 2015). However, this technology is still underexplored in the country.

In addition to solar irradiation, another alternative to reduce energy demand required in UV-C/ H_2O_2 and photo-Fenton systems is replacing mercury lamps (Hg) by LED (light-emitting diode) semiconductors (UV-C, UV-B or UV-A). Advantages of LED over conventional Hg lamps are detailed in Table 2.6. LED semiconductors present lower energy consumption and longer lifetime when compared to other sources once they convert less energy into heat (LI, 2016). It is estimated that LED semiconductors last up to ten times longer than conventional low pressure lamps (CARRA *et al.*, 2015). In addition, the disposal of LED semiconductors does not require special handling, which is the case for conventional mercury lamps. LED

may be applied as an alternative light source to solar reactors in cloudy days when solar irradiation is not sufficient to trigger reaction. However, environmental applications of LED light sources are still under development, and more studies for the development of efficient LED reactors are still needed, so that the application of this technology in real scale becomes feasible (CARRA *et al.*, 2015). These studies will also be helpful to reduce LED prices.

TABLE 2. 6 - Characteristics of conventional Hg lamp compared to LED lamp

Feature	Mercury lamp	Light-emitting diode semiconductors (LED)
Lifetime	500 – 2,000 hours	20,000 hours 1.2 – 3 years
Environmental features	Contains mercury so it must be properly disposed. Generates ozone.	Mercury and ozone free
Operation	Minutes are required for warm-up	Instant “on-of” no warm-up period needed
Energy demand	Only 3-5% is UV	30% power is UV
Footprint	Larger footprint	Compact, cool, modular and no special treatment or disposal is necessary
Pricing	Low	Costly, yet prices are declining

In order to avoid iron precipitation at higher pH (5-8) and increase the feasibility of Fenton and photo-Fenton processes, some studies have suggested the use of chelating agents (humic acid, citrate, oxalate, EDDS and EDTA) that complex with iron thus avoiding its precipitation in the system. When comparing the use of oxalate and EDDS as chelating agents for the degradation of CEC in secondary wastewater, Klammerth *et al.*, (2013) found that EDDS was the best alternative when compared to ferrioxalate since there was no pH decrease in the presence of EDDS. However, the use of these complexes not only increases the organic carbon content but it also elevates treatment costs. In addition, it is important to consider that these complexes may persist in the water and lead to heavy metal solubility and eutrophication in surface waters, not to mention unknown toxicity upon long-term exposure to these substances (CLARIZIA *et al.*, 2017). Therefore, the use of chelating agents is not

recommended when photo-Fenton is applied as tertiary treatment of wastewater (CARRA *et al.*, 2013).

After Rincón and Pulgarin (2006) launched the application of solar photo-Fenton in near neutral pH for water disinfection, research in this direction intensified, as shown in Table 2.7. At first Klammerth *et al.*(2010) and Bernabeu *et al.* (2012), studied the addition of small iron concentration (5 mg L^{-1}) in near neutral pH for the removal of CEC in distilled water and synthetic and real wastewater. Both of them concluded that carbonates present in real matrixes must be removed in order to limit hydroxyl radical quenching by these ions. Also, these authors had contradictory results with regard to the impact of humic acids in the system, which were favorable for the removal of small concentrations of CEC, yet unfavorable in higher concentrations of CEC.

Later, Carra *et al.*, (2013) proposed a strategy that enabled the application of solar photo-Fenton at mild pH as an alternative to the use of chelating agents for the removal of CEC in wastewater. This strategy consisted in the intermittent addition of iron ($5, 10$ or 20 mg.L^{-1}) to the reactor (every 5 min), so that it could be kept in solution. The approach led to total removal of pesticides from wastewater. In the sequence, the author published another study comparing continuous (1 or 5 mg.L^{-1} per min) and sequential (20 mg.L^{-1} 3 or 4 times leading to a total of 60 mg.L^{-1}) iron addition strategies (CARRA *et al.*, 2014). The continuous iron addition strategy was better than the sequential one, since iron was available in the system during the entire reaction. Once again, the authors concluded that the reaction is more efficient when in the absence of carbonates.

After these studies were published, other works have proved the strategy successful for the degradation of CEC, disinfection and toxicity removal. Freitas *et al.*, (2017), achieved 99% removal of micropollutants present in MWWTP effluent after 90 min of reaction conducted at

neutral pH (after the consumption of bicarbonates). Fe^{2+} was first added (20 mg.L^{-1}) to begin the reaction and two other additions were made after 5 and 15 min. Toxicity was also

TABLE 2.7 – Articles related to the application of solar photo-Fenton at near neutral pH using different strategies of iron addition

<i>Matrix</i>	<i>CEC</i>	<i>Iron strategy</i>	<i>Result</i>	<i>Reference</i>
Synthetic wastewater Simulated effluent MWWTP effluent	Acetaminophen, Antipyrine, Atrazine, Caffeine, Carbamazepine, Diclofenac, Flumequine, Hydroxybiphenyl, Ibuprofen, Isoproturon, Ketorolac, Ofloxacin, Progesterone, Sulfamethoxazole and Triclosan	Single (5 mg/L)	CECs at low concentrations ($\mu\text{g/L}$) were successfully degraded to negligible concentrations with solar photo-Fenton at low iron concentrations (5 mg/L) and low initial H_2O_2 (50 mg/L) concentrations without adjusting the pH. One limiting factor was the presence of CO_3^{2-} and HCO_3^- which are OH radical scavengers and must be removed prior reaction. In the beginning of photo-Fenton reaction, there is an increase in toxicity. Degradation is faster in real effluent than in synthetic effluent due to natural organic matter.	(KLAMERTH <i>et al.</i> , 2010)
Distilled water Tap water MWWTP effluent	Amoxicillin, acetaminophen, acetemiprid, caffeine, clofibric acid and carbamazepine	Single (5 mg/L)	Inorganic salts played an inhibitory role. Experiments performed with 10 $\mu\text{g/l}$ of each CEC had nearly complete removal of the CECs with neutral photo-Fenton after 120 min of irradiation; in this case, humic substances played a unfavorable role. Toxicity increased during treatment, but was removed towards the end of reaction.	(BERNABEU <i>et al.</i> , 2012)
Demineralized water Real wastewater	Oxamyl, methomyl, imidacloprid, dimethoate, pyrimethanil	Iron dosage scheme Total: 20, 40, 60, 70 or 80 mg/L. One single addition of 20 mg/L, (2x20 + 3x10 mg/L at 5, 15, 25 and 35 min)	<u>Dark Fenton (pH 2.8, Fe 20 mg/L)</u> : no mineralization and pesticides were removed in 45 min. <u>Traditional solar photo-Fenton (pH 2.8, Fe 20 mg/L)</u> : 80% mineralization, pesticides removed in 15 min. Dissolved iron decreased to 5 mg/L in the end. <u>Solar photo-Fenton (pH 7, 4 x 5 mg/L)</u> : partial removal of pesticides, no mineralization, dissolved Fe < 10 mg/L during the additions of Fe and below 5 after all additions were made. <u>Solar photo-Fenton (pH 7, 20-20-10-10-10 mg/L)</u> : pesticides totally removed after 25 min of reaction, 80% DOC removal, dissolved Fe > 20 mg/L during the reaction. The first Fe addition is crucial for iron concentration along the experiment	(CARRA <i>et al.</i> , 2013)

Matrix	CEC	Iron strategy/species	Result	Reference
Simulated municipal wastewater treatment plant	Acetamiprid, thiabendazole, imazalil	Sequential additions (every 5 min): 3x20 mg/L, 4x 20 mg/L (total 60 or 80 mg/L) Continuous: 1 mg/L per minor 5 mg/L per min (total 75 mg).	The best condition was the one in which 3 x 20 mg/L of Fe were added. In the presence of bicarbonates, pesticides were partially removed in 45 min. Bicarbonates impaired Fe cycling and dissolved Fe concentration rapidly falls to 1 mg/L. Some degradation takes place due to Fenton reaction. The process was faster when bicarbonates were removed from the matrix and all CECs were removed >95%. Iron was between 5-25 mg/L. Bicarbonates should be removed from the matrix to obtain CEC removal. In the CPC, for the sequential strategy w/out bicarbonates: 3x20 sequence, photo-Fenton was similar to Fenton. An extra addition of Fe was added (4 x 20) and degradation took place in 20 min, compare to 35 min for the Fenton. When 80 mg/L were added all at once, reaction was not as effective.	(CARRA <i>et al.</i> , 2014)
WWTP effluent	77 organic compounds (including caffeine)	3 x 20 mg Fe/L additions	99% removal of CEC was reached, yet some compounds were still present in the end (salicylic acid). 56% mineralization was achieved. Total coliforms and E.coli were removed bellow the detection limit in 90 min. After iron addition, it was hydrolyzed, as a consequence iron hydroxides precipitated and pH dropped. Although, after the third addition of Fe, its concentration stabilized at 9 mg/L. H ₂ O ₂ was totally consumed during the 90 min of reaction. D. magna inhibition decreased from 20% to 5% inhibition. A. fischeri showed no sensitivity to treatment before nor after treatment. There was no increase in toxicity for any of the organisms tested.	(FREITAS <i>et al.</i> , 2016)

removed during treatment. Rivas Ibáñez et al., (2017) also achieved micropollutant and toxicity and estrogenic activity removals via the sequential iron strategy at near neutral pH.

The non-selectivity and high reactivity of hydroxyl radicals formed in UV-C/H₂O₂, Fenton and photo-Fenton contribute to the effectiveness of AOP on the degradation of the various CEC that may be present in MWW. However, when it comes to real matrices that contain not only CEC but also other components such as inorganic ions (HCO₃⁻, Cl⁻, NO₃⁻, PO₄³⁻, SO₄²⁻) and natural organic matter (NOM), these species compete with recalcitrant compounds for hydroxyl radicals (MURUGANANDHAM *et al.*, 2014). Therefore, these matrix constituents are called radical scavengers as they compete for oxidative radicals, thus reducing the reaction rate and hindering the degradation of target compounds. As a consequence of the consumption of hydroxyl radicals by these scavengers, higher doses of reagent must be applied, thus increasing costs. Considering the removal of CEC by AOP, this is even more relevant since these compounds are 1000 to 100000 times less concentrated than matrix components (LIAN et al., 2017). The impact of these natural scavengers on the performance of oxidative radicals reinforces the need of performing research in real matrices (surface and municipal wastewater), once degradation rates in solutions made in pure water will always be higher than in the presence of these species. In addition, the search for alternative radicals showing lower reactivity and higher lifespan in natural matrices, such as sulfate radical, also became a topic of interest.

2.8.2 Sulfate radical (SO₄^{•-}) based AOPs

In order to overcome the effect of scavengers present in real matrices recent studies have searched for reactive yet selective radicals, which is the case of sulfate radical (SO₄^{•-}). Although still very reactive ($E_0 = 2.55 - 3.1$), SO₄^{•-} is more selective than HO[•] since it reacts with organic compounds mainly through one mechanism: electron transferring (LUTZE *et al.*,

2015). Therefore, it should be more resistant when exposed to natural *scavengers* present in real matrices (CHAWLA & FESSENDEN, 1975; BUXTON *et al.*, 1988; ANTONIOU & ANDERSEN, 2015; LUO *et al.*, 2015; ZHANG *et al.*, 2016). In a detailed review on the chemistry of persulfate in water, the author brings reaction rate constants between sulfate radical and natural scavengers when compared to those observed for hydroxyl radicals, as reproduced in Table 2.8 (WACLAWEK *et al.*, 2017). Since reaction rate constants are lower for sulfate radicals, higher stability of sulfate radicals in natural matrices is expected. Moreover, at neutral pH, sulfate radical presents a stronger reduction potential than that observed for HO• (ANIPSITAKIS & DIONYSIOU, 2004). This explains why SO₄^{-•} sometimes leads to higher degradation and mineralization of a few compounds when compared to HO• (ANIPSITAKIS & DIONYSIOU, 2004; DENG *et al.*, 2013; XIAO *et al.*, 2016; ZHANG *et al.*, 2016). Although, this is not an absolute rule once the degradation of each compound by these reagents depends strongly on individual chemical structure (YANG *et al.*, 2016; SERNA-GALVIS *et al.*, 2017).

TABLE 2.8 – Reaction rate constants reported in the literature for the reaction of sulfate and hydroxyl radicals with natural constituents of surface water and wastewaters

<i>Radical</i>	<i>Rate Constant (M⁻¹ s⁻¹)</i>				
	Cl ⁻	Br ⁻	HCO ₃ ⁻	CO ₃ ²⁻	Humic acid (NOM)
SO ₄ ^{-•}	1.3-6.6 x 10 ⁸	3.5 x 10 ⁹	2.6-9.1 x 10 ⁶	4.1 x 10 ⁶	6.8 x 10 ^{3*}
HO•	3.0-4.3 x 10 ⁹	1.9 x 10 ⁹	n x 10 ⁷	4 x 10 ⁸	1.4 x 10 ^{4*}

The generation of SO₄^{-•} may be achieved by using either peroxymonosulfate (PMS; H₂SO₅) or peroxydisulfate (PDS, S₂O₈²⁻) as reagents. Both, PMS and PDS may be activated by UV irradiation, heat, transition-metals, alkaline pH, electrolysis, nanocarbons and anionic organic compounds (LIAN *et al.*, 2017);WACLAWEK *et al.*, 2017). Similarly to hydrogen peroxide and as shown in Figure 2.4, H₂SO₅ and S₂O₈²⁻ are cleaved onto SO₄^{-•} when submitted to UV-C irradiation (Equation 2.5). For PDS, the quantum yield (ϕ) for this reaction at 254 nm is equivalent to 1.8 Einstein.mol⁻¹, while that for the cleavage of H₂O₂ is 1.0 (MARK *et al.*,

1990). Therefore, the rate of formation of $\text{SO}_4^{\bullet-}$ from PDS is higher than that of HO^{\bullet} formation from H_2O_2 under UV-C irradiation (254 nm). In addition, energy required to break $\text{S}_2\text{O}_8^{2-}$ into two $\text{SO}_4^{\bullet-}$ radicals ($140 \text{ kJ}\cdot\text{mol}^{-1}$) is lower than the amount which is necessary for the cleavage of H_2O_2 ($213 \text{ kJ}\cdot\text{mol}^{-1}$) into hydroxyl radicals (REINTS *et al.*, 2000).



The selection between PMS or PDS as reagents may be performed as according to the matrix where the technology will be applied and to the goal of each application. PMS is usually encountered in its most stable form as a white powdered potassium salt (KHSO_5) and is commonly applied in “in situ soil chemical oxidation” (ISCO) for the remediation of soil as a commercial product named Oxone®. However, the energy required to cleave PMS onto sulfate radical (377 kJ mol^{-1}) is greater than the energy that is necessary for the cleavage of PDS ($\text{S}_2\text{O}_8^{2-}$). In addition, the stability of persulfates in water is higher than that observed for PMS (WACLAWEK *et al.*, 2017). Therefore, PDS is usually more explored as a source of sulfate radicals for water and wastewater treatment, when compared to PMS.

As mentioned earlier, and similarly to hydroxyl radicals, $\text{SO}_4^{\bullet-}$ may also be generated in the presence of transition-metals. Although Ag was proved to be the most efficient transition metal for the activation of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), iron salts may also be used for this purpose (ANIPSITAKIS & DIONYSIOU, 2004). In this Fenton-like process, Fe^{2+} reacts with $\text{S}_2\text{O}_8^{2-}$ as according to Equation 2.6 ($k = 2 \times 10^1 \text{ M}\cdot\text{s}^{-1}$) (TRAVINA *et al.*, 1999). In order to achieve high degradation rates, Fe^{2+} concentration must be optimized due to the consumption of excess Fe^{2+} by sulfate radical with further generation of Fe^{3+} (Equation 2.7). Similarly to traditional solar photo-Fenton, this process must also be applied at pH 3, since this limitation is inherent to the chemical properties of iron which is a common reagent for both systems.



Table 2.9, brings a few recent studies performed using the Fe/PMS or Fe/PDS systems for the removal of CEC in distilled water, surface water and wastewater. As confirmed by Ahmed & Chiron (2014), Iron/PMS and Iron/PDS system may also be intensified when exposed to solar irradiation, as it occurs for the traditional Fenton system. In this case, reaction is enhanced due to concomitant occurrence of three mechanisms: (i) Fe^{2+} cycling in the presence of UV-Vis irradiation, (ii) cleavage of $\text{Fe}(\text{OH})^{2+}$ species in the system forming hydroxyl radicals simultaneously with sulfate radicals, and (iii) the cleavage of PDS after absorption of light at <310 nm. Therefore, sulfate and hydroxyl radicals act simultaneously in the system at pH 3. However, when compared to traditional photo-Fenton performed at pH 3, irradiated/Fe/PDS system is usually slower and requires a higher ratio of Fe/reagent to achieve the same efficiency reached by photo-Fenton reaction (WANG *et al.*, 2015). This may be a limitation considering that commercial prices of PDS are usually above that of H_2O_2 (WACLAWEK *et al.*, 2017). Slower reaction rates presented by solar/iron/PS were not observed in a study performed by Miralles-Cuevas *et al.*, (2017), who used lower Fe/PDS molar ratio for the solar/iron/PDS system when compared to the solar/iron/ H_2O_2 . However, cost-benefit analysis performed in this study indicated the treatment using H_2O_2 is more cost-effective than when PDS is applied.

As mentioned in Section 2.8.1, recent studies have focused on the application of different strategies to enable the traditional photo-Fenton reaction at near neutral pH, or at the pH of natural waters and wastewaters, such as the use of Fe-chelating agents or intermittent iron additions. However, to this date, there are no studies published on the use of these strategies to enable the application of irradiated and non-irradiated iron/PDS systems at natural pH. For

TABLE 2. 9 – Articles related to the application of irradiated Fe/PMS or Fe/PDS systems in different matrices

<i>Treatment</i>	<i>CEC</i>	<i>Matrix</i>	<i>Result</i>	<i>Reference</i>
solar/iron/PDS	Carbamazepine (CBZ)	Distilled water MWWTP effluent	Direct photolysis, solar/PDS and solar/Fe/PS removed 8%, 60% and 100% of CBZ, respectively. Optimum PS: Fe(II) ratio of 2:1. PS was activated by UV-Vis alone because it absorbs light at < 310 nm. Although, the activation of PS via Fe(II) is faster than that via Uv-Vis. OH [•] radicals were also formed during Fe(II) cycling from Fe(III).	(AHMED &CHIRON, 2014)
solar/iron/PMS solar/TiO2	Pesticides: bifenthrin, mesotrione and clothianidin) Pharmaceuticals: diclofenac, sulfamethoxazole, carbamazepine	MWWTP effluent	Except for CBZ, apparent kinetic rate constants were always 10 times higher in PMS/Fe(II)/UV-Vis than in TiO ₂ /UV-Vis system. More than 70% of TOC abatement in less than one hour. All compounds were totally eliminated within 30 min.	(AHMED <i>et al.</i> , 2014)
LED/Fe/H ₂ O ₂ LED/Fe/PS	Sulfamethazine	Water and simulated wastewater	Dark Fenton system achieved 79% removal within 30 min, while LED-Fenton reached 90%. The PDS system was slower with Fe/PS and LED/Fe/PS reaching 28% and 44% rates, respectively. While the photo-Fenton system had best results at 0.2: 1 Fe/oxidant ratio, and the system with PS at 1:5. The LED/Fe/PS system behaved similarly at pHs 2 to 5, while the system with H ₂ O ₂ was limited to pHs 3 and 4. The impact of Cl ⁻ and HCO ₃ ⁻ ions was higher on photo-Fenton rather than on the system with PDS. Results suggest different degradation pathways for each system.	(WANG <i>et al.</i> , 2015)
UV-C/H ₂ O ₂ , UV-C/PDS, solar/Fe/H ₂ O ₂ and solar/Fe/PDS	Antipyrine, caffeine, carbamazepine, ciprofloxacin and sulfamethoxazole	Simulated freshwater	Solar and UV-C processes promoted by H ₂ O ₂ are more cost-effective than when employing S ₂ O ₈ ²⁻ . After 3.2 kJ/L of UV-C alone, 67% of total CEC removal was achieved. While only 0.28 and 0.24 kJ/L were necessary for 90% removal via UV-C/H ₂ O ₂ and UV-C/PS. 2.64 and 2.54 kJ/L were necessary for 90% removal of CEC via solar/Fe/H ₂ O ₂ and solar/Fe/PDS, respectively.	(MIRALES-CUEVAS <i>et al.</i> , 2017)
solar/iron/PDS	Chloramenophenicol (CPA)	Deionized water and colloids (filtrate, permeate, wastewater)	Solar/iron/PDS system was more effective than Iron/PDS. 96% removal of CPA were achieved at pH 3 (PDS = .6 mM and Iron = 0.2 mM). Sulfate and hydroxyl radicals acted simultaneously in the system. At pH 7, removal rate was nearly 60%. Degradation of CAP was affected in the real matrix.	(NIE <i>et al.</i> , 2018)

instance, all studies listed Table 2.9 were conducted at pH 3 (WACLAWECK *et al.*, 2017). However, two of these studies have investigated the influence of pH treatment efficiency. During the treatment of antibiotic sulfamethazine, LED/Iron/PDS was more stable in different pH when compared to LED/Iron/H₂O₂, being similarly effective at pHs 2 to 5 when compared to pHs 3 and 4, only, for the traditional system (WANG *et al.*, 2015). In addition, the solar/Iron/PDS system reached up to 60% degradation of chloramphenicol at pH 7 with no use of any iron strategies, while removal at pH 3 reached > 95% removal (NIE *et al.*, 2018). The effectiveness of Fe/PDS processes at higher pH may be explained by the occurrence of secondary reactions of SO₄^{-•} with OH⁻ or H₂O (Equations 2.8 and 2.9) which generate hydroxyl radicals in the system, thus contributing to process efficiency. Even though the redox potential of hydroxyl radical is lower at higher pH, the simultaneous presence of both radicals may lead to a similar reactivity of that obtained in the acidic pH. In natural matrices, reactions represented in Equation 2.9, may occur at rate of 10¹ to 10² M⁻¹ s⁻¹. Therefore, it is recognized that in PMS or PDS systems, SO₄^{-•} prevail in acidic systems, while HO[•] is predominant in alkaline conditions. The equilibrium between both radicals is reached at pH 9 (FANG *et al.*, 2013).



Secondary reactions of sulfate radical with OH⁻ and water, is not the only context in which the formation of hydroxyl radicals may occur simultaneously with sulfate radicals. At pH 7 and in the presence of Cl⁻ ions, which occurs naturally in surface waters and wastewaters, SO₄^{-•} may react with Cl⁻, thus generating Cl[•]. As Cl[•] reacts with water H₂OCl[•] is formed and may deprotonate forming HOCl[•] and HO[•] (WACLAWEK *et al.*, 2017). Hence, the impact of chloride ions on Fe/PDS systems may be lighter than those observed for iron/H₂O₂ systems,

not only due to lower reactivity of $\text{SO}_4^{\bullet-}$ with this scavenger, yet also due to the formation of HO^{\bullet} in the system, thus contributing to continuous degradation of target compounds. This supports the need for research exploring irradiated and non-irradiated Fe/PMS and Fe/PDS systems in near neutral pH conditions since this system may be more feasible at these conditions.

2.8.3 Hydroxyl and sulfate radical based AOPs on the treatment of CEC

Among all of the possible combinations for the application of AOP, four different processes will be explored in the following chapters of this study for the removal of target CEC: (i) UV-C/ H_2O_2 , (ii) UV-C/ $\text{S}_2\text{O}_8^{2-}$, (iii) solar photo-Fenton (solar/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and (iv) solar photo-Fenton like (solar/ $\text{Fe}^{2+}/ \text{S}_2\text{O}_8^{2-}$). Table 2.10 shows some of the most recently published works using these treatments.

When comparing UV-C/ H_2O_2 and UV-C/PS for the degradation of fifteen different CEC in wastewater, Lian *et al.*, (2017), concluded that some compounds, such as Ibuprofen, Gemfibrozil, Tinidazole, Ornidazole and Ronidazole are better degraded by UV-C/ H_2O_2 when compared to UV-C/PS. On the other hand, the degradation of Propanolol, Naproxen, Atenolol and Metropolol, among others, was higher via UV-C/PS. Meanwhile, Carbamazepine, which is a highly photo-stable compound showed equal reactivity with both radicals. In the referred work, overall efficiency of UV-C/PS was higher than that obtained by UV-C/ H_2O_2 , probably because CEC react more selectively with $\text{SO}_4^{\bullet-}$. In order to explore the effectiveness of sulfate radical against antibiotics, the effect of $\text{SO}_4^{\bullet-}$ on the degradation of these compounds was assessed in distilled water and wastewater (SERNA-GALVIS *et al.*, 2017). The author concluded that the addition of $\text{S}_2\text{O}_8^{2-}$ to the system was particularly important to enhance the degradation rate of the antibiotics that presented reduced quantum yields.

TABLE 2. 10 - Recent works published on the application of AOP proposed to be used in this work for the treatment of CEC

AOP	Target CEC	Water matrix	Results	Reference
UV-C ₂₅₄ UV-C/PS	Antibiotics	Distilled water and simulated hospital WW	Photolysis of antibiotics differed as according to their quantum-yields. Adding PS to the medium improved the degradation of photo-stable compounds due to the formation of sulphate radicals. UV-C/PS was able to remove more than 90% of all antibiotics in simulated hospital WW.	(SERNA-GALVIS <i>et al.</i> , 2017)
UV-C/H ₂ O ₂ Fenton solar photo-Fenton	Venlafaxine (VLFX)	Pure water, synthetic and real UWW and human urine	UV-C based AOP were efficient on the removal of the antidepressant. Solar photolysis was limited to 12% for VLFX after 24h of exposure. Fenton results were optimum at pH 3 and when using Fe:H ₂ O ₂ ratio of 20:50, which increased VLFX biodegradability. 90% of CEC removal was obtained after hours of Fenton reaction. Whereas, in solar photo-Fenton, 90% removal was achieved in minutes. Degradation in urine was limited and dilution of urine prior to AOP treatment increased efficiency.	(GIANNAKIS <i>et al.</i> , 2017)
UV-C/H ₂ O ₂ UV-C/PS solar photo-Fenton solar/iron/PS	Antipyrine, caffeine, carbamazepine, ciprofloxacin and sulfamethoxazole	Simulated SW	All of the proposed processes were efficient to remove the target compounds (>90%). One of the advantages of UV system over solar systems is that it is efficient in neutral pH. Electricity costs related to UV-C artificial lamp has a big impact on UV-C process total cost. For solar AOP, the use of H ₂ O ₂ is more cost effective than applying PS.	(MIRALLES-CUEVAS <i>et al.</i> , 2017)
Solar-photo-Fenton	Carbamazepine, flumequine, ibuprofen, ofloxacin and sulfamethoxazole	MWWTP effluent	Solar photo-Fenton treatment performed with iron complexing agent in near neutral pH removed 90% of target CEC. Raceway Pond reactor (RPR) was more effective for the removal of pharmaceuticals when compared to Compound Parabolic Reactor (CPC).	(DE LA OBRA, PONCE-ROBLES, <i>et al.</i> , 2017)
Solar photo-Fenton	Acetamiprid (ACM) and 58 CEC present in real WW	Synthetic and real MWWTP effluent	RPR was operated in continuous flow and solar photo-Fenton was adequate to remove more than 90% of initial ACM. From the 58 pollutants identified in treated UWW, 46 were degraded below the limit of detection. For the remaining CEC, removal rates were higher than 70%. Both batch and continuous operation lead to more than 80% removal of CEC. Continuous treatment through solar photo-Fenton in the RPR was stable and not strongly dependent on incident irradiation.	ARZATE <i>et al.</i> , 2017

Similarly, the degradation of Velanfaxine was performed in pure water and two other matrices: synthetic MWW and in human urine, which are the main sources of this drug to sewage. Velanfaxine is an anti-depressant that is included to the list of 12 priority contaminants to be removed by a minimum of 80% in MWWTP in Switzerland. Photolysis, UV-C/H₂O₂, solar light, Fenton and solar photo-Fenton were tested for the degradation of this anti-depressant. While hours of non-irradiated Fenton reaction were necessary to achieve 90% degradation of Velanfaxine in pure water, photo-Fenton accomplished this degradation level in minutes. In MWW and human urine, which are two complex matrices, the degradation of the anti-depressant was influenced by matrix compounds such as natural organic matter and inorganic ions. In fact, the MWW effluent from moving bed bioreactor (MBBR) treatment showed lower interference on tested AOPs than effluents from activated sludge (AS) and coagulation-flocculation processes (GIANNAKIS *et al.*, 2017).

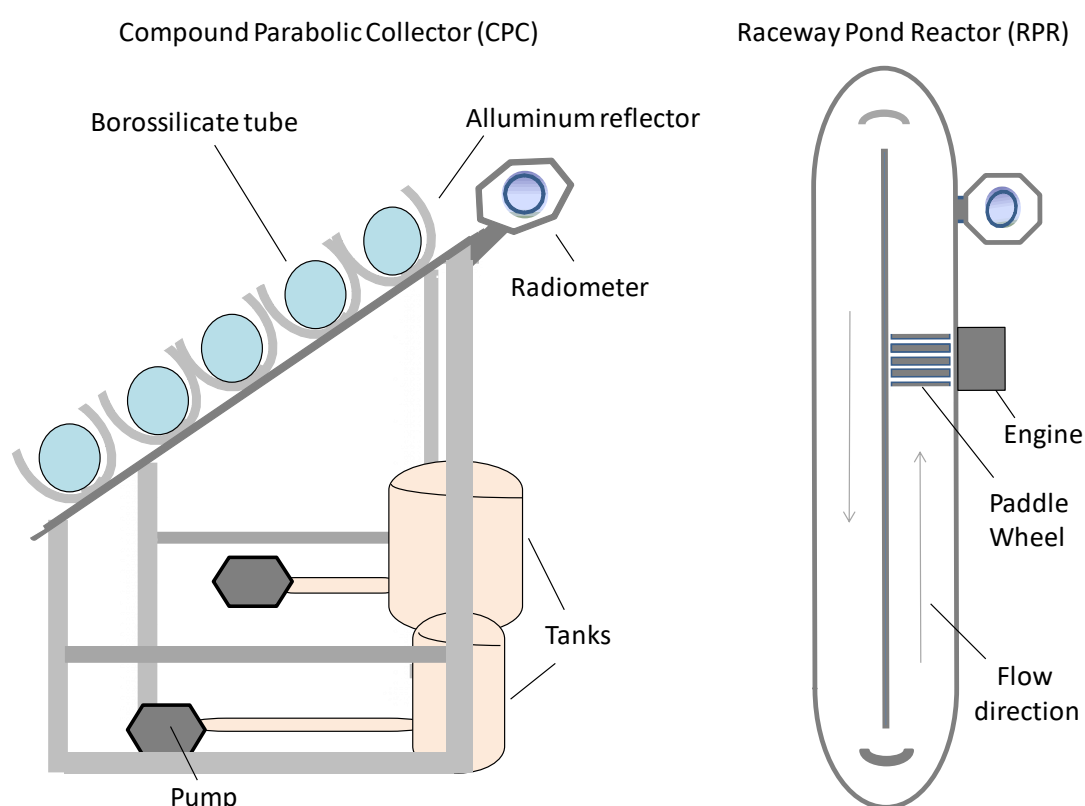
In order to properly assess the actual feasibility of applying these processes in treatment plants, it is important to conduct studies in real matrices and in large scale reactors (semi-pilot and pilot). This was the goal of a study conducted in Spain in which UV-C irradiated processes (UV-C/H₂O₂ and UV-C/PS) were compared to solar AOP (solar/Fe/ H₂O₂ and solar/Fe/ S₂O₈²⁻) for the degradation of antipyrine, caffeine, carbamazepine, ciprofloxacin and sulfamethoxazole in synthetic surface water. Nearly three minutes of reaction were necessary for 90% removal of CEC via UV-C/H₂O₂ and UV-C/PS (50 mg L⁻¹ of reagent). However, when the reagent concentration was reduced to 10 mg L⁻¹ the reaction via UV/PS was 2.5 times faster than UV-C/H₂O₂. With regard to solar processes conducted at acidic pH, CEC degradation was also superior to 90% for both solar/Fe/ H₂O₂ and solar/Fe/ S₂O₈²⁻ after nearly 3 kJ of accumulated irradiation per liter of synthetic surface water. Finally, the author concluded that treatments that apply H₂O₂ are more cost effective due to high cost of peroxydisulfate (MIRALLES-CUEVAS *et al.*, 2017).

In fact, the development of reactors for the application of solar treatments is a challenging task. In the 1990's, the Compound Parabolic Collector (CPC) reactor was developed for the application of solar photo-Fenton and photo-Fenton like processes mainly with the aim of treating effluents containing pollutants in high concentrations. In CPC, direct and diffuse incident solar beams are concentrated in the collectors within which the wastewater circulates (MALATO *et al.*, 2009) (Figure 2.5). However, when it comes to CECs, which occur in reduced concentrations in the environment, solar light concentration is not as determining for the success of the photo-Fenton process. Consequently, the research group from Almeria (Spain), a reference group on reactor design for the application of solar technology, proposed the use of the Raceway Pond reactor (RPR) which is also represented in Figure 1.6. RPR is a low cost reactor that has been proved successful for the removal of CEC from MWWTP effluent. While costs related to the CPC reactor reach 400 €·m⁻², the cost of RPR, a reactor that is built with cheap material, is estimated to be around 10 €·m⁻² (CARRA *et al.*, 2014; RIVAS *et al.*, 2015). Regarding energy power required for wastewater recirculation, CPC uptakes an average of 80 W·m⁻³ while RPR employs 4W·m⁻³.

The first study that proposed the use of RPR for the treatment of CEC as a tertiary treatment confirmed the applicability of this reactor for the degradation of pesticides acetamiprid and thiabendazole (100 µg·L⁻¹ of each) in water and synthetic secondary wastewater. Operational factors such as iron concentration and liquid depth were evaluated. The degradation of these pesticides in water was optimum when the RPR was operated at a liquid depths equivalent to 15 cm and 5.5 mg·L⁻¹ of iron. In these conditions, there was maximum absorption of photons by iron species, and more than 90% of pesticides were removed in a short reaction time (CARRA *et al.*, 2014). In MWW, RPR was also effective for the removal of pesticides, and no significant changes were observed on final removal rates due the presence of *scavenging* compounds. Although, the degradation of acetamiprid was faster in CPC, treatment capacity

of RPR ($48 \text{ mg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$, for 5.5 or $10 \text{ mg Fe}\cdot\text{L}^{-1}$) was greater than that obtained for CPC ($29 \text{ mg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$, for $5.5 \text{ mg Fe}\cdot\text{L}^{-1}$). Similar results were obtained in another study which explored the degradation of five CEC (carbamazepine, flumequine, ibuprofen, ofloxacin, and sulphamethoxazole) via near neutral solar photo-Fenton in CPC and RPR. The treatment efficiency in RPR was four times higher than that obtained in CPC (DE LA OBRA, PONCE-ROBLES, *et al.*, 2017). Thus, confirming the advantages of replacing CPC for RPR when aiming at tertiary treatment of contaminants of emerging concern.

FIGURE 2. 5 – Illustrative schemes of the CPC and RPR reactors used for solar AOPs



One of the limitations for the application of photo-Fenton in real scale in WTP and MWWTP is its execution at continuous flow. Arzate *et al.*, (2017) went a step further and investigated the continuous operation of RPR as tertiary treatment for the degradation of 58 CEC from MWWTP secondary effluent. Continuous solar photo-Fenton treatment in RPR was confirmed to be effective removing all of the 58 CEC from 79 to 89%. Despite the success

obtained via continuous operation, reaction was performed in acidic pH which increases operational complexity.

In addition to operation in continuous flow, the toxicity of transformation products formed during reaction is another concern regarding the dissemination of AOP as a tertiary treatment in MWWTP. Although the degradation by AOP tends to form carboxylic acids (MOREIRA *et al.*, 2009), CO₂ and water in ideal conditions, some studies have detected the increase in toxicity after the treatment by AOP (TROVÓ *et al.*, 2012; PUNZI *et al.*, 2015). Therefore, toxicity must be monitored during treatment, especially when concerning urban wastewater that will be disposed of in water bodies after treatment. A recent study assessed CEC elimination and toxicity removal of MWW effluent via near neutral photo-Fenton by adding iron in partial doses. Moreover, estrogenic activity, phytotoxicity and cytotoxicity were also assessed. The intermittent iron strategy was successful leading not only to CEC removal, but also to mineralization of real wastewater components (30% dissolved organic carbon removal). Phytotoxicity, cytotoxicity and estrogenic activity were also removed by solar photo-Fenton in neutral pH (RIVAS IBÁÑEZ *et al.*, 2017). Besides demonstrating the potential of applying solar photo-Fenton as tertiary treatment for water quality maintenance, the referred article also stresses the importance of conducting bioassays to complement analytical techniques once toxic/estrogenic compounds may be present in the wastewater below detection levels (MALAJ *et al.*, 2014).

Once the effectiveness of solar photo-Fenton on the removal of CEC has been established, it is important to consider the fact that solar light availability varies according to environmental and climatic conditions. Therefore, it is essential to develop a feasible and low cost alternative for days during which solar irradiation is insufficient to trigger reaction. Considering high energy uptake by conventional mercury lamps, the development of reactors for the application

of LED irradiated AOP has been tested by a few authors. As mentioned earlier, LED semiconductors may emit irradiation in various wavelengths (UV-C, UV-B and UV-A) thus enabling its use for photo-Fenton or modified photo-Fenton (LED/Fe²⁺/sulfate) reactions. In addition, they present long lifespan and low power consumption (DE LA OBRA, ESTEBAN GARCIA, *et al.*, 2017). An innovative system was recently proposed for the application of LED AOP (365 -270 nm) using TiO₂ as photocatalyst, and its efficiency was compared to that of usual LED reactor design (375 – 380 nm), and to that of a reactor that uses traditional Hg lamp for the degradation of a surfactant. As a result, the author found that the Hg reactor shows the best performance, while the new reactor is confirmed to be more effective than usual LED reactors (DOMINGUEZ *et al.*, 2016).

In another study three different UV-A LED lamps (365, 385 and 400 nm) were tested for the degradation of Acetamiprid, a recalcitrant pesticide, in simulated secondary effluent via LED photo-Fenton at acidic conditions. Due to higher absorbance of iron species at 365 nm, this was the most appropriate wavelength for the degradation of the target compound. However, 365 nm LED smiconductors showed higher energy consumption (DE LA OBRA, ESTEBAN GARCIA, *et al.*, 2017). The degradation of acetamiprid was also investigated through LED photo-Fenton, yet in acidic and natural pH. In order to enable reaction at natural pH, the addition of Fe²⁺ was performed intermittently. The degradation of the pesticide was tested using a LED lamp and a low pressure Hg lamp. Low pressure Hg lamp achieved complete acetamiprid removal with a H₂O₂:Fe ratio equivalent to 2:1 in acidic pH, while a ratio of 4:1 was necessary for the LED reactor to achieve the same efficiency. This probably happens because, while LED lamps irradiate at one wavelength only, Hg lamps also distribute light in other wavelengths which are absorbed by iron species. Although, when the same reactions were performed in natural pH, the performance of LED photo-Fenton reactor was comparable to that obtained via low pressure Hg lamp (CARRA *et al.*, 2015). These results confirm that it

is possible to apply LED as an alternative irradiation source for the degradation of CEC in water and wastewater, thus reducing costs.

2.9 CONCLUSION

The number of studies which analyze the occurrence of CEC in Brazil is still limited. Only a shortlist of target compounds has been investigated and studies are restricted to urbanized areas of the territory. Most studies were performed in the Southeast region of Brazil and monitor the occurrence of compounds which are frequently found in watersheds in Europe. Therefore, existing data is not representative for the national territory in its totality. Besides, it is important to generate official consumption data for PPCP and pesticides before launching an intensive monitoring program, so that future studies may focus on pollutants which are locally and intensively consumed, and not only on those for which analytical methodology is already established and for which occurrence was detected elsewhere.

Furthermore, only a few studies examine the bioaccumulation of these compounds on the tissues of aquatic species and/or acute and chronic impacts on their population. The investigation of the occurrence of CEC in both physical and biological matrices in Brazil should be performed in order to enable a holistic analysis of environmental contamination. Such analyses lead to proper assessments on the bioaccumulation of these compounds and provide the protection of aquatic species and human health.

Regarding the control of PPCP and other CEC in municipal wastewater treatment facilities in Brazil, studies show that conventional (up to secondary treatment stage) treatment plants, when existing, are not effective for the removal of these compounds. Recent results indicate persistent contamination of surface waters and reservoirs after treated wastewater disposal and also due illegal launching of untreated wastewater. Therefore, as an urgent priority, sanitation

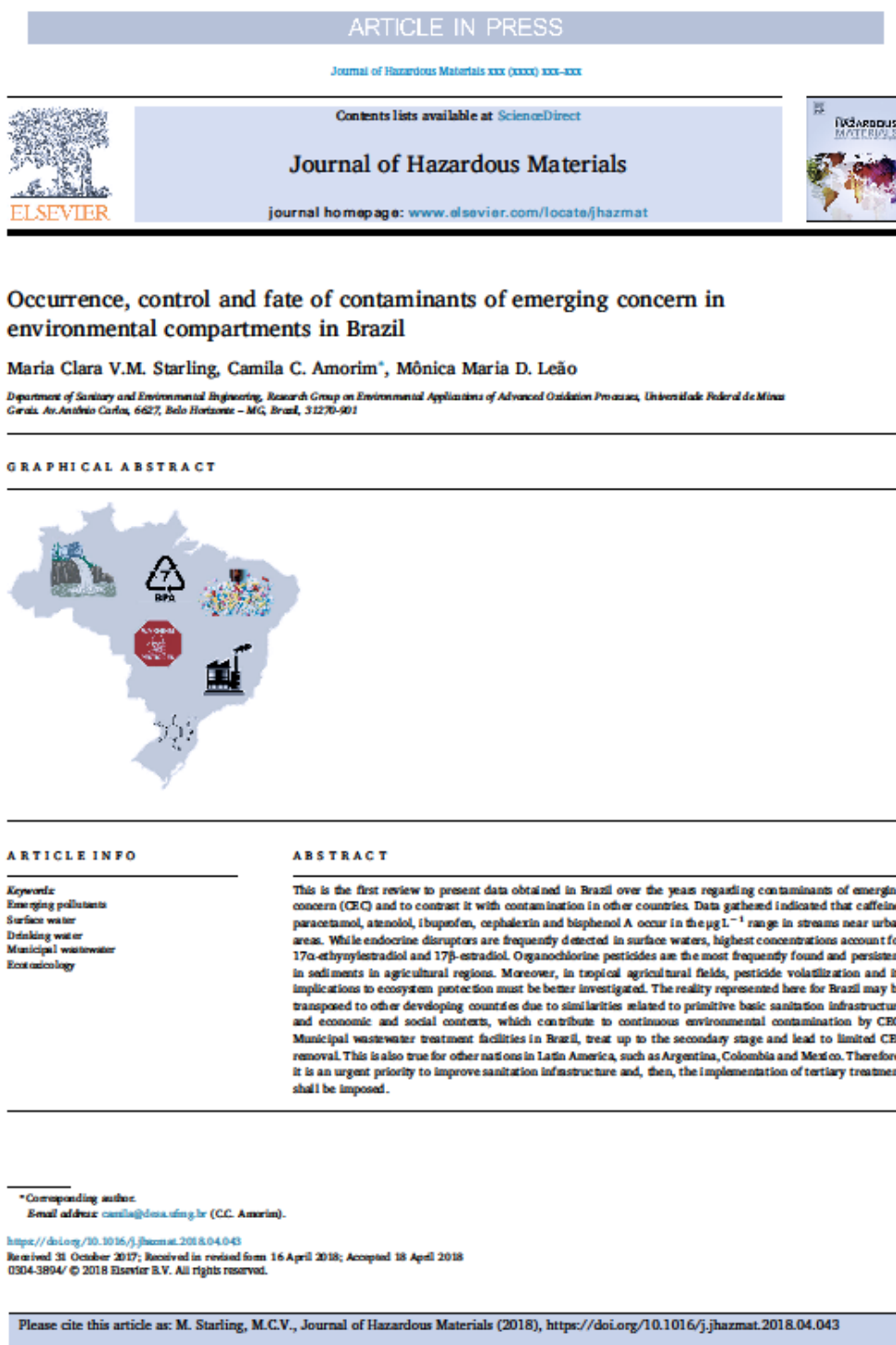
infrastructure must be improved in Brazil in order to prevent the disposal of these compounds directly into surface waters without treatment. As shown throughout the first part of this chapter, the reality represented here for the occurrence, control and fate of CEC in Brazil may be transposed to other developing countries due to similarities related to primitive basic sanitation infrastructure and economic and social contexts. This is true mainly for other nations in Latin America, such as Argentina, Colombia and Mexico. Only in the sequence, the implementation of tertiary treatment in MWWTP may be imposed. In agricultural areas, a closer look should be given at pesticide volatilization in tropical areas and its implications to ecosystem protection.

In Europe and in the United States, environmental legislation standards have already been updated to include a monitoring program for CEC and/or their removal in MWWTP. Although, Brazilian legislation has not yet been revised to include monitoring of CEC in surface waters. Revisions should also be performed on the standards regarding the disposal of treated wastewater, thus contributing to the maintenance of water quality and environmental integrity, so that ecosystem services may be preserved for future generations.

Finally, considering the effectiveness of AOP on the removal of emerging contaminants in real matrices, research and application of these technologies should be stimulated by governmental authorities in Brazil. This should be done mainly towards the most sustainable alternatives such as solar irradiated processes. This way, when time comes, these technologies may be installed in water and wastewater treatment facilities, by putting in practice the know-how and data generated by research groups and companies throughout the country.

2.10 ATTACHMENT

This first part of this review concerning the CECs in Brazil was published on April, 2018, in the Journal of Hazardous Materials (Elsevier®), as shown in this attachment (doi.org/10.1016/j.jhazmat.2018.04.043) (STARLING *et al.*, 2018).



3 CHAPTER III: TREATMENT OF TARGET CEC IN PURE WATER AND SURFACE WATER VIA UV- C AOPs

3.1 INTRODUCTION

In view of the effectiveness of UV-C irradiation (254nm) on the inactivation of pathogens, UV-C disinfection has been traditionally applied in water and wastewater treatment plants (HIJNEN *et al.*, 2006). Along with disinfection, UV-C irradiation may lead to the degradation of chemical compounds present in the matrix. The transformation of a chemical substance under UV-C irradiation alone may occur through direct or indirect photolysis. Direct photolysis takes place when the compound absorbs UV-C light directly, thus suffering degradation (LEGRINI *et al.*, 1993). Indirect photolysis may be triggered by a variety of mechanisms, such as the formation of organic reactive species during the irradiation of photosensitizers (CANONICA, 2007), or the generation of singlet or triplet oxygen species and other inorganic radicals formed during the UV-C irradiation of ionic species (FENG *et al.*, 2007; KALSOOM *et al.*, 2012).

As attention to the occurrence of contaminants of emerging concern (CEC) in drinking water, groundwater, surface water and wastewaters continuously increases, advanced oxidation processes (AOP) have been proved as robust alternatives for the degradation of CEC in these matrices (GIANNAKIS *et al.*, 2016). Considering that existing UV-C reactors may be easily converted into systems for the application of UV-C-based advanced oxidation processes (UV-C AOPs), the use of UV-C AOPs may be favored in the near future (HOKANSON *et al.*, 2016).

Among UV-C AOPs, UV-C/H₂O₂ is one of the most diffused processes as it is commercially applied in industries and treatment plant facilities (KRUITHOF *et al.*, 2007). In this process, hydrogen peroxide undergoes photolysis (UV_{254 nm}) and is cleaved onto two hydroxyl radicals (HO•). HO• present elevated redox potential ($E^0 = 1.8\text{--}2.7\text{ V}$), thus being very reactive and non-selective (TARR, 2003). The reaction of hydroxyl radicals with organic and inorganic

compounds may occur through three main mechanisms: (i) OH addition, (ii) hydrogen transfer and (iii) electron transfer which contribute to the degradation of organic compounds. In ideal conditions, complete mineralization of organic pollutants to CO₂ and H₂O may be achieved during reactions, and no sludge is formed during this process. In addition, UV/H₂O₂ does not require pH adjustment, thus simplifying operational requirements.

However, when it comes to real matrices that contain natural organic matter (NOM), inorganic ions (HCO₃⁻, Cl⁻, NO₃⁻, and SO₄²⁻) and dissolved oxygen (DO), UV-C/H₂O₂ reactions may be disturbed due to quenching of HO[•] by these compounds (MURUGANANDHAM *et al.*, 2014). Since HO[•] is a non-selective species, it reacts intensively with various chemical structures and this is considered one of the main drawbacks to be overcome by this technology. As an alternative, increased interest has been given lately to systems that explore strongly reactive yet selective radicals, such as sulfate radical (SO₄^{-•}).

The production of sulfate radicals may also be achieved under UV-C irradiation, in which peroxydisulphate (PDS, S₂O₈²⁻) or peroxymonosulphate (PMS, SO₅²⁻) are cleaved to produce SO₄^{-•} (MATTA *et al.*, 2011). Similarly to hydroxyl radical, SO₄^{-•} also presents high redox potential ($E^0 = 2.55 - 3.1$). Although, it acts only through electron transfer mechanism, thus making it more selective and resilient when in the presence of NOM and inorganic ions present in real matrices. Previous works have confirmed that UV/PS performance is not as disturbed by carbonate ions (HCO₃⁻) as UV-C/H₂O₂ performance, probably due to lower reaction constants of SO₄^{-•} radical with HCO₃⁻ ($k_{SO_4^{-\bullet}, HCO_3^-} = 2.8 \times 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$; $k_{HO^{\bullet}, HCO_3^-} = n \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$) (CHAWLA & FESSENDEN, 1975; BUXTON *et al.*, 1988; ANTONIOU & ANDERSEN, 2015; LUO *et al.*, 2015; ZHANG *et al.*, 2016; WACŁAWEK *et al.*, 2017).

Nevertheless, scavenging also occurs in UV-C/PS system. Cl⁻ was classified as the scavenger that shows higher effect upon SO₄^{-•} (FANG *et al.*, 2012; LUO *et al.*, 2015; YANG *et al.*,

2016). Reactions of Cl⁻ ions with HO[•] and SO₄^{•-} lead to the formation of “daughter radicals” such as Cl[•], ClOH^{•-}, Cl₂^{•-} which decrease degradation rates (ZHANG *et al.*, 2016). Additionally, these “daughter radicals” may be consumed by NOM in surface waters, thus, impairing the degradation of target compounds.

In this context, the goal of this chapter was to evaluate the performance of UV-C photolysis alone, UV-C/H₂O₂ and UV-C/PS on the degradation of four target CEC in pure water and surface water in order to simulate the treatment in water treatment plant. Although conditions depicted in pure water are not loyal to conditions existing in natural surface waters, these conditions were performed in order to enable the identification of transformation products formed during treatment, so that a degradation route could be proposed for each process.

CEC targeted in this study represent different classes of micropollutants and were chosen due to their environmental relevance. Losartan potassium (LP) and Furosemide (FRSM) represent pharmaceutical drugs. Table 3.1 shows the studies that were already conducted via AOP for the degradation of these compounds in water or surface water and results that were obtained. These compounds are widely prescribed and increasingly consumed by hypertensive patients worldwide and have been detected in environmental matrices in various locations (STUER-LAURIDSEN *et al.*, 2000; HEBERER, 2002; LARSSON *et al.*, 2007; GONÇALVES, 2012; SOUSA *et al.*, 2012; PEREIRA *et al.*, 2016). In addition, LP reacts with sodium hypochlorite forming cyanide (ADACHI & OKANO, 2008), and FRSM is known for its estrogenic potential and the formation of toxic byproducts after photolysis (ISIDORI *et al.*, 2007; ISIDORI *et al.*, 2009). Due to the potential use of caffeine (CAF) as an urban pollution tracer and its regular occurrence in surface waters and drinking waters, it was chosen to represent personal care products (SODRÉ *et al.*, 2010; FROEHNER *et al.*, 2011; MONTAGNER *et al.*, 2014). Finally, carbendazim (CBZ) represents the group of agrochemicals, since it has already

been detected in surface waters around the world and is known for its toxicity (LOEWY *et al.*, 1999; BURKHARDT, 2007; MONTAGNER *et al.*, 2014).

TABLE 3. 1 - Studies assessing the degradation of the target compounds in water and surface water mainly

Compound	Matrix	Treatment	Result	Reference
Caffeine	Pure water	UV-C/H ₂ O ₂ UV-C/K ₂ S ₂ O ₈	1,3,7 - thrimethyluric acid is formed during the oxidation with HO [•] . In the presence of sulphate radical, caffeine-8-phosphate radical was formed and degraded to 1,3,7 - thrimethyluric acid.	(P. TELO & J. S. C. VIEIRA, 1997)
	Pure water	UV-C/H ₂ O ₂ UV-C/TiO ₂ Fenton	Caffeine degradation via UV/TiO ₂ is achieved within 150 min with 13% of TOC removal and intermediates accumulate in the system. Similar results were obtained for the other processes. Dimethylparabanic acid (m/z 143) and di(N-hydroxymethyl)parabanic acid (m/z 175) were obtained as some of the transformation products.	(DALMÁZIO <i>et al.</i> , 2005)
	Pure water and real secondary effluent	UV-C UV-C/H ₂ O ₂ UV-C/PMS (under saturated air and oxygen environments)	Photolysis of caffeine increased under saturated oxygen conditions. Degradation kinetics was modified when caffeine was in the presence of other compounds due to synergist effects. Caffeine removal via photolysis in water is slightly higher than that obtained in effluent. Caffeine degradation is increased in the presence of hydroxyl and sulfate radicals in secondary effluent which obtained similar results.	(RIVAS <i>et al.</i> , 2011)
	Pure water	UV-C UV-C/H ₂ O ₂	UV direct photolysis for caffeine is negligible. The degradation rate of caffeine was increased 30 times in the presence of hydroxyl radicals. 154.4, 4.89 and 2.5 kJ.L ⁻¹ were necessary for 90% degradation of caffeine in the absence and presence of 25 and 50 mg.L ⁻¹ of H ₂ O ₂ , respectively.	(SHU <i>et al.</i> , 2013)
	Pure water	UV-C (low and medium pressure lamps)	No photolysis was observed for caffeine under low pressure lamp. Yet some photolysis was observed under medium pressure lamp, the photolysis rate was very low.	(CARLSON <i>et al.</i> , 2015)
	Pure water	Fe/sulphate	At a first stage caffeine was quickly removed, then the reaction rate stabilized. Caffeine degradation rate was higher when persulphate was activated by zero valent iron when compared to Fe ²⁺ . 10% TOC removal was achieved. Treated sample was not toxic.	(RODRIGUEZ <i>et al.</i> , 2017)

Compound	Matrix	Treatment	Result	Reference
	Pure water	UV-C (different concentrations of oxygen)	There was no photolysis of CBZ at pH 1 and degradation increases as pH increases due to lower instability of CBZ at higher pH. Even in the presence of oxygen, CBZ is very resistant to photolysis reinforcing the need of more oxidative methods.	(PANADÉS <i>et al.</i> , 2000)
	Pure water	UV-C	Photolysis of CBZ occurred at pH 5.5 and transformation product absorbed strongly at 254 nm. Aminobenzazole (m/z 113) is formed as a transformation product via photohydrolysis. Photolysis of aminobenzazole is 1.5 times higher than that of CBZ. Photodegradation of CBZ was increased in the presence of oxygen. The photoproducts obtained in this study indicate that degradation pathway occurs via different pathways.	(MAZELLIER <i>et al.</i> , 2002)
	Pure water	UV-C/H ₂ O ₂ (presence and absence of HCO ₃ ⁻)	CBZ reacted very quickly with hydroxyl radicals and totally removed. In the presence of HCO ₃ ⁻ , there was slower degradation of CBZ via UV/H ₂ O ₂ due to the quenching effect of this ion. The reaction of CBZ with carbonate radical formed in the system also contributes to the degradation of the fungicide.	(MAZELLIER <i>et al.</i> , 2003)
Carbendazim	Pure water	UV-C/TiO ₂	90% of fungicide degradation were achieved under UV/TiO ₂ in 75 min. While CBZ concentration was already very low after 45 min, it took more than 60 minutes for proper toxicity removal.	(SAIEN & KHEZRIANJOO, 2008)
	Pure water and surface water (lake and river), groundwater, drinking water	UV-C/TiO ₂	Faster degradation of CBZ occurred in pure water and was followed by: groundwater, lake water, drinking water and river water due to the presence of scavengers in natural matrices.	(G. MUHAMAD <i>et al.</i> , 2011)
	Drinking water	UV-C/H ₂ O ₂ (pilot plant)	Degradation of CBZ was between 30-50%.	(LEKKERKERKER-TEUNISSEN <i>et al.</i> , 2013)
	Pure water	UV-C/H ₂ O ₂ UV-Vis/H ₂ O ₂ Fenton photo-Fenton Solar photo-Fenton	96% removal of CBZ and toxicity removal was achieved under UV/H ₂ O ₂ and UV-Vis. Non-irradiated Fenton was also effective when higher doses of reagent were used. Solar photo-Fenton performed in RPR achieved 95% removal in 15 minutes.	COSTA, 2017

Compound	Matrix	Treatment	Result	Reference
Furosemide	Pure water	Artificial light Sun light	In pH 8-10, no degradation of FRSM was observed under artificial laboratory light. However, in acidic conditions, fast photolytic degradation took place. No degradation took place under sunlight. The neutral (unionized molecule) form of FRSM is the most liable form of the compound. Dechlorination is the main mechanism taking place during photolysis.	(BUNDGAARD <i>et al.</i> , 1988)
	Pure water, surface water and tap water	UV-C UV/H ₂ O ₂	The reaction rate of FRSM with hydroxyl radical was estimated to be 1.1×10^{10} in pure water. The degradation via UV/H ₂ O ₂ was slower in natural water when compared to pure water. While, photolysis rate was higher in natural waters due to the presence of nitrogen and other ions that contributed to the formation of oxidative radicals under UV irradiation.	(WOLS <i>et al.</i> , 2013)
	Pure water, surface water and tap water	UV-C/H ₂ O ₂	The degradation of FRSM by photolysis only was similar to that obtained in the presence of hydroxyl radical due to high UV light absorption by this compound. FRSM showed high reaction rate with carbonate radicals because it contains an aniline group.	(WOLS <i>et al.</i> , 2014b)
	Surface water	UV-Vis	FRSM was degraded up to the limit of detection after one hour of exposition to the Xe lamp, when only the transformation products remained in solution. The main transformation product was derived from dechlorination of FRSM molecule (m/z 311).	(JAKIMSKA <i>et al.</i> , 2014)
	Water-acetonitrile solution	Fluorescent lamp	Photodegradation of FRSM led to a change in solution color from translucent to yellow. FRSM in water-acetonitrile mixture (1 : 1) underwent hydrolysis and substitution of the Cl moiety with OH, and reacted with acetonitrile.	(KATSURA <i>et al.</i> , 2015)
	Reuse water	UV-C/H ₂ O ₂	100% of FRSM were removed via UV-C/H ₂ O ₂ treatment.	(SINGH <i>et al.</i> , 2015)
	Pure water	Electro-Fenton Anodic oxidation	The reaction rate constant of FRSM with hydroxyl radical was calculated to be $3.4 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$. During degradation aromatic by-products are formed and converted to carboxylic acids. Toxicity increases during treatment suggesting the formation of toxic intermediates. After 8h of treatment almost total degradation of FRSM was achieved with 95% mineralization via anodic oxidation and 85% via electro-Fenton.	(OLVERA-VARGAS <i>et al.</i> , 2015)
Losartan Potassium	Pure water	Electrochemical oxidation	Total removal of LP was achieved, leading to 56% mineralization in Cl ⁻ medium and 67% mineralization in the presence of SO ₄ ⁻ due to the formation of peroxydisulfate in the medium. 4 main transformation products were detected: 170, 238, 264, 208 m/z.	(SALAZAR <i>et al.</i> , 2016)

3.2 MATERIAL AND METHODS

3.2.1 Chemicals and reagents

Caffeine (CAF), Carbendazim (CBZ) Furosemide (FRSM) and Losartan Potassium (LP) were all purchased from Sigma-Aldrich. HPLC grade Methanol (MERCK) and Formic Acid (Sigma-Aldrich, $\geq 98\%$ purity) were used for analytical purposes.

3.2.2 UV-Vis Spectrophotometry

UV-Vis spectrophotometric analyses (Agilent Cary 1 and Cary 100) were performed for each of the compounds in water (10^{-4} M) and in different pH in order to determine maximum absorbance wavelength values for each compound. UV-Vis absorbance values were also used to calculate extinction coefficients ($\epsilon_{254\text{nm}}$) for each compound in the respective pH. $\epsilon_{254\text{nm}}$ were calculated as according to Equation 3.1.

$$\text{Absorbance}_{254\text{nm}} = \epsilon_{254\text{nm}} * l * C \quad (\text{Equation 3.1})$$

Where, “ l ” is the optical path length (1 cm), and “ C ” is the concentration (M) of the dissolved compound. pH was adjusted by adding HCl and/or NaOH (0.1 M and 0.01 M) to solutions.

3.2.3 Chemical Actinometry

Chemical actinometry tests were performed to quantify incident photonic flux (I_0) of the UV-C lamps used in UV-C reactors as according to Equation 3.2.

$$-d[C]/dt = (\Phi * I_0 / V) (1 - e^{-2.3 * \text{Abs}}) \quad (\text{Equation 3.2})$$

Where, “ t ” is the time in seconds (s), “[C]” is the concentration at time t (mol.L^{-1}), “ Φ ” is the quantum yield at 254 nm for the actinometer used in the system, “ I_0 ” is the incident photonic flux for that lamp (Einstein.s^{-1}), and V is the volume of solution (l). Hydrogen peroxide (H_2O_2)

and Atrazine (ATZ) ($\Phi_{\text{H}_2\text{O}_2} = 1$; $\Phi_{\text{ATZ}} = 0.046$) were both used as actinometers (C_0 : $\text{H}_2\text{O}_2 = 2\text{E}^{-3}\text{M}$, $\text{ATZ} = 5\mu\text{M}$) (NICOLE *et al.*, 1990; CANONICA *et al.*, 2008). Samples were taken during irradiation, in order to quantify the concentration of H_2O_2 and ATZ during UV-C irradiation by UV-Vis Spectrophotometry (254 nm). H_2O_2 was determined through TiCl_4 method (detailed bellow) (AMIN & OLSON, 1967), and ATZ was quantified through High Performance Liquid Chromatography (HPLC).

3.2.4 Quantum yield values (254 nm)

UV-C reactor used for the determination of quantum-yield values ($V = 3.5$ mL; $l = 1$ cm) was equipped with a UV-C lamp (LC8 LIGHTENNINGCURETM HAMAMATSU), and a filter (254 nm; Semrock MaxlampTM), which was placed at the light source (Figure 3.1). The incident photonic flux ($I_0 = 1,6 \times 10^{-8}$ Einstens. s^{-1}) was determined by actinometry experiments and Equation 4.2 was used to calculate the quantum-yield ($\Phi_{254 \text{ nm}}$) for each of the target compounds. In order to do so, solutions containing 2.2 μM , 3 μM , 5.2 μM , 5.5 μM for LP, FRSM, CAF and CBZ respectively ($1 \text{ mg}\cdot\text{L}^{-1}$ of each compound) were prepared and irradiated. Samples were taken during irradiation, so that the decay of each compound under UV-C irradiation (254 nm) could be quantified by HPLC analysis. Quantum yields were calculated using Equation 3.2 at acidic ($\text{pH} = 3$), without pH adjustment (≈ 6 and 7), and at basic pH (9) for all of the compounds. pH was adjusted by using HCl and NaOH solutions (0.1 M and 0.01 M).

FIGURE 3. 1 – UV-C lamp and filter (254 nm) used in the experiments for the calculation of quantum-yield values.



3.2.5 UV-C AOPs: experimental set-up

UV-C, UV-C/H₂O₂ and UV-C/Persulfate (UV-C/PS) reactions were performed in a 2 L cylindrical bench photo-reactor equipped with a low-pressure mercury vapor lamp emitting monochromatic radiation at 253.7 nm (Heraeus GPH212T5L/4, 10 W) in axial position (Figure 3.2). The incident photonic flux ($I_0 = 3,1 \times 10^{-6}$ Einstens.s⁻¹) was measured by chemical actinometry as described earlier (Chapter 2). Optical pathway was calculated as described elsewhere (BELTRAN *et al.*, 1995). The reactor was coupled to a cooling system and temperature was kept constant (20°C) during reactions.

FIGURE 3. 2 – UV-C reactor used for UV-C/H₂O₂ and UV-C/PS reactions.



Reactions were performed in pure water and SW. Initial concentrations of target compounds in water were 50 μM for CAF, LP and FRSM and 31 μM for CBZ due to its lower solubility.

These concentrations were chosen in order to enable TOC (theoretical initial concentrations: 4.8, 3.3, 13.2 and 7 mg TOC.L⁻¹ for CAF, CBZ, LP and FRSM, respectively). SW was collected from a lake (Lille, France) and filtered in a 0.45 cellulose membrane prior to reactions in order to simulate pre-treatment stages performed in water treatment plants such as coagulation/flocculation, followed by filtration. For reactions performed in SW, each compound was added at 10 µM (total concentration of 40 µM).

Reactor lamp was pre-heated for 20 minutes prior to the beginning of reactions. 2 L of solution were prepared and introduced to the reactor for each experiment. Then, H₂O₂ (commercial, 39%) or sodium persulfate (Na₂SO₈, Aldrich) were added (10⁻³ M; molar ratio H₂O₂ or PS/target molecule 20:1 for CAF, LP and FRSM, and 32:1 for CBZ). This concentration of reagent was chosen as according to the detection limits of the methods used for quantification of residual H₂O₂ and persulfate. In order to start the reaction, the pre-heated lamp was introduced to the reactor after temperature was stable (20°C) (t =0 min). Samples were withdrawn for the quantification of target compounds and TOC (TOC-VCSH Total Carbon Analyzer Shimadzu) during reactions. Consumption of H₂O₂ and PS were also monitored during reactions, as described in the following items.

3.2.6 Residual H₂O₂ analysis

H₂O₂ was quantified using Titanium Tetrachloride (TiCl₄) (BELTRAN *et al.*, 1995). Briefly, a solution of TiCl₄ was prepared in Sulfuric Acid (H₂SO₄, 2N) (0,01% vol:vol; 1 mL TiCl₄: 100 mL H₂SO₄ 2N). This solution must settle for 2 days until it becomes translucent. Then, the following items were added in sequence in a volumetric flask (20 mL): (i) 2 mL of TiCl₄ acidic solution; (ii) 2 mL of H₂SO₄ 36N; (iii) 2 mL of sample. Flask was shaken, and reaction occurred for 10 minutes. Then, samples were read using a UV/Vis Spectrophotometer at 410 nm.

3.2.7 Persulfate analysis

Persulfate ion ($S_2O_8^{2-}$) was quantified using potassium iodide (KI) (LIANG *et al.*, 2008) (adapted). Briefly, a solution of KI (20g) was prepared in water (1 L). Sodium carbonate ($NaHCO_3$) was added to this water, prior to KI, in order to avoid air-oxidation of iodide. Then, the following were added in this sequence in a volumetric flask (20 mL): (i) 4.5 mL of KI solution, (ii) 1 mL of sample. Flask was shaken, and reaction occurred for 15 minutes. Then, samples were read in the UV/Vis Spectrophotometer at 352 nm.

3.2.1 Quantification of target compounds in water and surface water

Prior to initial tests for the detection of target compounds through High Performance Liquid Chromatography (HPLC), a literature review was conducted and methods developed by various authors to quantify CAF, CBZ, FRSM and LP were carefully studied. HPLC equipped with a UV detector was used for the quantification of target compounds (Agilent 1260 Infinity II series, DAD detector equipped with a 60 mm high sensitivity cell) (Figure 2.1). This equipment is installed at the *Laboratoire de Spectrochimie Infrarouge et Raman (LASIR)* located at *Université de Lille 1 – Sciences and Technology* (Lille, France). Separation was performed using two C_{18} columns in sequence (one pre-column and one column): Poroshell HPH-C18 4.6 x 150 mm 2.7 μm , and 120 EC-C18 3 x 50 mm, 2.7 μm .

FIGURE 3. 3 - HPLC apparatus used in this work for the quantification of target compounds.



Ultra-pure water (A), MeOH (B) or both containing 0.1% Formic Acid (FAc) were used as mobile phases. Percentages of A and B, flow rate and monitored wavelength varied in each test (Table 2.1). Maximum pressure was limited to 400 bar. After a clear peak was detected, a calibration curve was performed in order to determine the Limit of Quantification (LOQ) for each of the compounds. LOQ listed on Table 2.1 apply to experiments conducted with the aim of analyzing the removal of target compounds in ultra-pure water and in surface water (Chapter 3) and which were already conducted in France.

TABLE 3. 2 - Conditions used on HPLC for the quantification of target compounds in water and surface water

Compound	Mobile phase			Flow mL min ⁻¹	Detector nm	Retention time min	LOQ µg L ⁻¹	Reference
	A	B	A:B					
CBZ	H ₂ O	MeOH	50:50	0.4	285	8.3	11	(EPA, 1993)
CAF	H ₂ O	MeOH	70:30	0.5	273	7.0	43	(EPA, 2007)
FRSM	H ₂ O 1/10 ³ FAc	MeOH 1/10 ³ FAc	40:60	0.5	240	4.9	16	(ANDERSON <i>et al.</i> , 2016)

3.2.2 Acute toxicity tests

Acute toxicity of samples were analyzed using the Microtox® device (Model 500 Analyser SDI, Azur Environment, Workingham, England), which assesses the sensibility of luminescent marine bacteria *Allivibrio fischeri* to samples (ISO 11348-3:2007) (ISO, 2007). Luminescence emitted by bacteria is measured after 5, 15 and 30 minutes of exposure to non-treated and treated samples in different dilutions, and data is analyzed using the MicrotoxOmni® Software (81.9% Basic Test). Results were converted to Acute Toxicity Unit (a.T.u.) as according to equation 2.3:

$$\text{a.T.U.} = 100/\text{EC}_{50} \quad (\text{Equation 2. 3})$$

Therefore, the higher the a.T.u. value, higher is the toxicity. The highest concentration assessed in the test is 81.9% which corresponds to 1.22 a.T.u. Thus, this is the detection limit for this test.

3.3 Results and discussion

3.3.1 Quantum yields and photolysis coefficient of target CEC

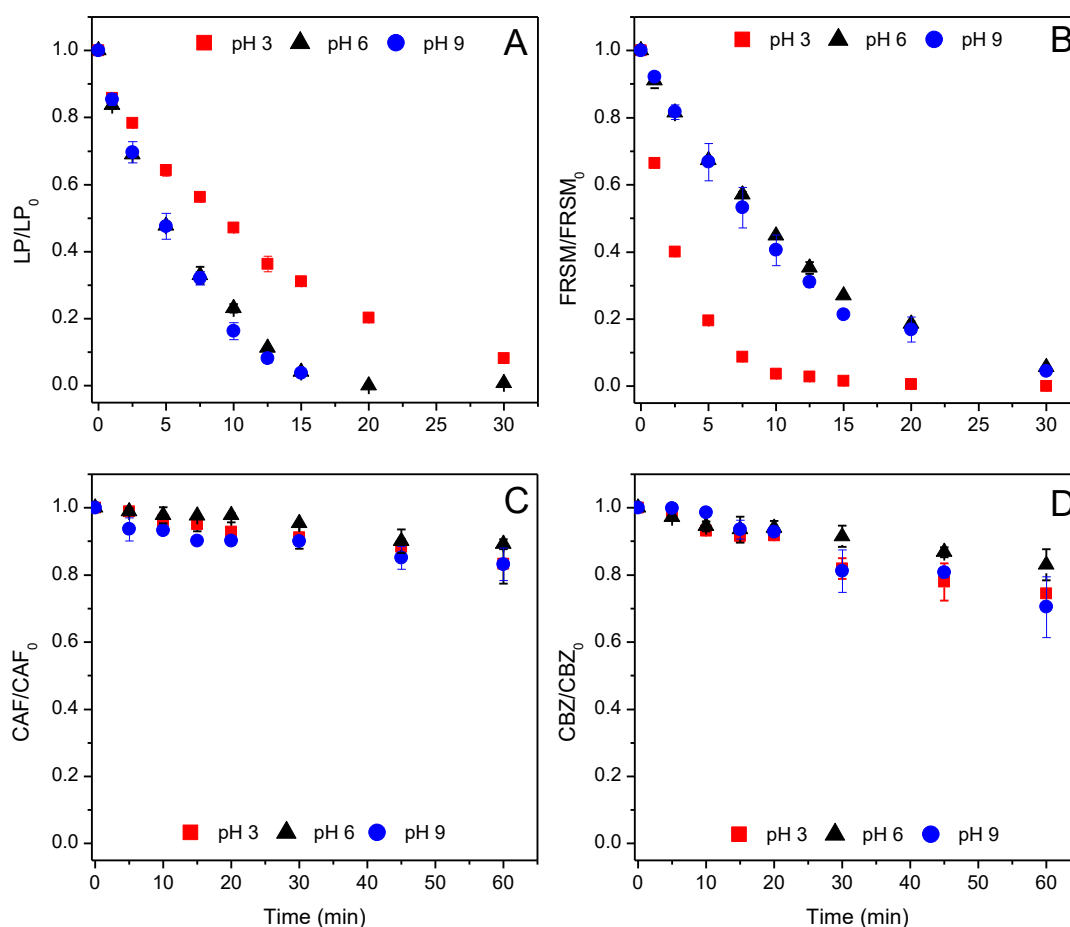
When submitted to UV-C irradiation, chemical compounds may absorb light on the UV-C range raising molecules to the excited state. However, the excitation of a molecule does not necessarily culminate on direct photolysis. The rate on which a compound undergoes direct photolysis during UV-C irradiation is dictated by its quantum yield ($\Phi_{254\text{nm}}$) and molar absorption coefficient ($\epsilon_{254\text{ nm}}$) (SHU *et al.*, 2013). Increased quantum-yield and molar absorption coefficients indicate that there is a higher chance that the compound will be transformed through direct photolysis. On the other hand, the lower the quantum-yield, greater is the compound photo-stability. Quantum yields and UV-C light absorption vary according to chemical structure and are usually higher when the compound contains aromatic rings and double bonds (C=C), as well as halogens and other elements such as sulfur and nitrogen in its structure (CHALLIS *et al.*, 2014; SERNA-GALVIS *et al.*, 2017). It is also important to consider that pH may affect the quantum yield and molar absorption coefficients of a compound once it may influence molecule structure. Therefore, for the purpose of mass balance studies and kinetic modeling related to the application of UV-C irradiated processes, it is valuable to be aware of the quantum yield and molar absorption coefficients of target compounds.

Considering that quantum yield and molar absorption coefficients are not available in the literature for all of the constituents of the water matrix, Hokanson *et al.*, (2016) proposed a photolysis coefficient (k_p or C_p) that may be applied to represent the effect of photolysis alone to a compound or microorganism. C_p is calculated as according to Equation 3.3.

$$C_p = (k_d \times U) / 2302 \quad (\text{Eq. 3.3})$$

Where k_d is the pseudo-first order rate constant ($\text{cm}^2 \cdot \text{J}^{-1}$), U is the energy per mol of photons at 254 nm ($\text{J} \cdot \text{E}^{-1}$), and 2302 is a factor used for unit conversion purposes. Figure 3.3 shows photolysis of each target compound in different pH and Table 3.2 presents quantum yields and C_p values on acid, natural (pH of solution without adjustment) and basic pH.

FIGURE 3. 4 – Photolysis (UV-C_{254 nm}) of each of the target compounds in ultrapure water and in acidic, near neutral and basic pH.



LP photolysis in medical formulation was reported previously (KOLLIPARA *et al.*, 2012). However, this is the first report on pure LP photolysis and quantum yield values which varied from 0.011 to 0.016 (Table 3.3) being lower at acidic pH when compared to basic and neutral pH (Figure 3.3A). Valsartan, another drug that belongs to the same class of LP is also confirmed to be photo-labile (BIANCHINI & KAUFMAN, 2013). C_p values obtained for LP

(Table 3.3) indicate that it is susceptible to photolysis. For an acidic pH, LP susceptibility to photolysis is comparable to that of atrazine and pentachlorophenol (HOKANSON *et al.*, 2016).

TABLE 3.3 – Chemical structures, quantum yields and photolysis coefficients (Cp) obtained for each of the compounds at different pH

	$\Phi_{254\text{ nm}}$			$C_p\ 254\text{ nm}$		
	3	n	9	3	n	9
LP	0.011±0.001	0.0159±0.0001	0.0162±0.0006	123.6	190.9	191.0
FRSM	0.0925±0.0001	0.024±0.006	0.025±0.0006	380.4	163.7	164.0
CAF	0.00077±0.00015	0.0007±0.0002	0.0009±0.0001	3.3	2.4	3.8
CBZ	0.0036±0.0001	0.0016±0.0001	0.0028±0.0001	7.6	4.7	9.5

n=natural pH of solution(6 for LP, 5.5 for FRSM, 5.8 for CAF and 7.1 for CBZ).

It is known that the pKa for FRSM is 3.9. Therefore, it is in its anionic form at neutral pH. Photo-instability of FRSM in its unionized form has been previously reported and the product of photolysis is known for its high toxicity (MOORE & BURT, 1981; ISIDORI *et al.*, 2006). When exposed to light, FRSM may initiate free radical reactions and excited-state energy transfer (MOORE & BURT, 1981). FRSM solution was colorless before photolysis and turned yellow during reaction, which was also observed elsewhere (KATSURA *et al.*, 2015). In addition, the quantum-yield determined at near neutral pH for this compound is in agreement with previously reported value (0.02) (WOLS *et al.*, 2014a). Acidic pH increases FRSM quantum-yield, thus leading to increased photolysis (Figure 3.3B). At pH 3, reported Cp is comparable to that of antibiotic sulphametazine, probably due the presence of similar chemical groups when compared to FRSM such as sulfonamide and chlorobenzene (HOKANSON *et al.*, 2016).

Quantum yield values calculated for LP and FRSM are superior to those calculated for CAF (0.0003 at pH 7) (SHU *et al.*, 2013) which is considered a photo-stable compound. In this study, quantum yield and Cp values calculated for CAF confirm its photo-stability in all of the tested pH (Figure 3.3 C and Table 3.3). Photo-stability of CAF contributes to its use as an

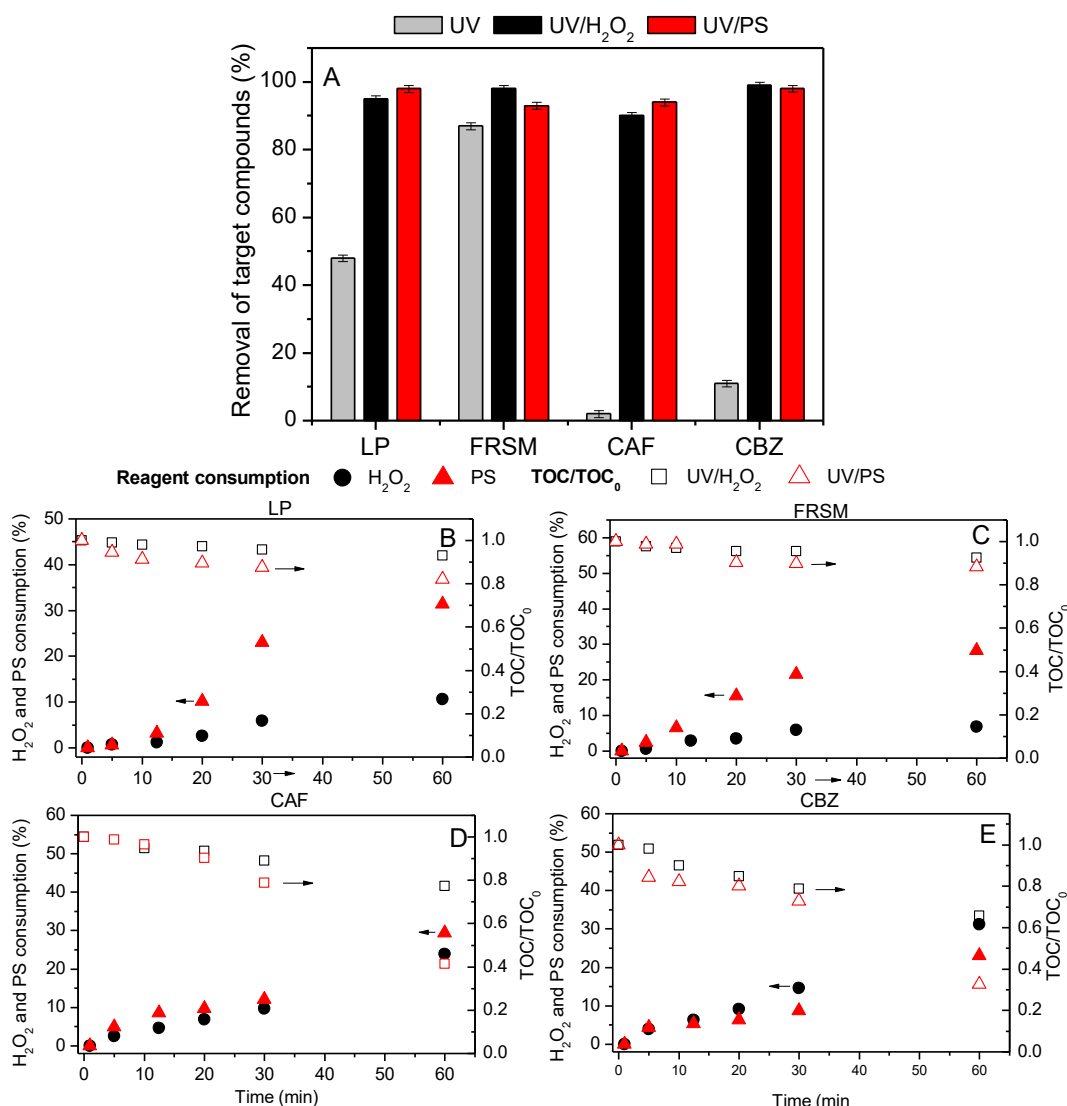
urban pollution tracer and indicator of illegal sewage disposal (SODRÉ *et al.*, 2010). Along with CAF, carbamazepine (reported $C_p = 7$) (HOKANSON *et al.*, 2016), has also been proposed as an indicator of human contamination and its resistance to photolysis was confirmed elsewhere (BUERGE *et al.*, 2003; DANESHVAR *et al.*, 2012). Reduced C_p values may also explain the persistence of CAF after UV-C treatment applied in WTP and WWTP facilities.

Finally, fungicide CBZ showed stable and reduced quantum-yield values in all of the tested pH which corroborates with previously reported results (PANADÉS *et al.*, 2000; MAZELLIER *et al.*, 2002) (Table 3.3). Regarding C_p , CBZ may also be considered a photo-stable compound (Figure 3.3D). When compared to other pesticides, such as atrazine and alachlor, CBZ is much more resistant to photolysis (HOKANSON *et al.*, 2016). Higher degradation of atrazine and alachlor may be related to the dechlorination of these compounds (CHOI *et al.*, 2013; SOUISSI *et al.*, 2013), which does not occur for CBZ since it has no chlorine in its structure.

3.3.2 Degradation of target compounds in pure water by UV-C/H₂O₂ and UV-C/PS

UV-C photolysis is already applied in various water and wastewater treatment plants for disinfection. However, photolysis rate varies greatly among the various chemical compounds present in surface water and wastewater. Therefore, converting UV-C reactors into systems used for UV-C AOPs could be an option to enhance the degradation rate when aiming at the removal of contaminants of emerging concern from these matrices, especially with regard to compounds that show reduced quantum-yield (SERNA-GALVIS *et al.*, 2017). Figure 3.5A shows the degradation (%) obtained for each of the target compounds under UV-C, UV-C/H₂O₂ and UV-C/PS processes. Control experiments consisted of H₂O₂ only and PS only and showed neither removal nor mineralization of target compounds (data not shown).

FIGURE 3. 5 Percent degradation of each of the target compounds by UV enhanced oxidation processes: UV-C/H₂O₂ and UV-C/PS, reagent consumption and mineralization rates.



(3.4 A) Degradation (%) of target compounds by UV-C, UV-C/H₂O₂ and UV-C/PS (C₀ = 50 μM of LP or FRSM or CAF or 31 μM of CBZ; H₂O₂ or PS = 10⁻³ M; Time: 60 min). Reagent consumption and mineralization of (3.4 B) LP, (3.4 C) FRSM, (3.4 D) CAF and (3.4 D) CBZ via UV/H₂O₂ and UV/PS.

As observed in Figure 3.5A, the addition of chemical reagents (20 to 32:1 molar ratio) to the UV-C irradiated system increased the removal of all target compounds leading to more than 90% degradation of each. This happens due to the formation of hydroxyl (HO[•]) and sulphate (SO₄^{•-}) radicals in these systems. These radicals show high redox potentials (E⁰ HO[•] = 1.8–2.7 V and E⁰ SO₄^{•-} = 2.55 – 3.1), thus increasing the degradation rate of target compounds in

their presence, mainly for CAF and CBZ (ANIPSITAKIS & DIONYSIOU, 2004; YANG *et al.*, 2016). For FRSM, photolysis led to 87% removal, which was nearly the rate achieved in the presence of oxidative radicals (98 and 93% for UV-C/H₂O₂ and UV-C/PS, respectively). This probably happens due to high photolysis coefficient presented by this compound. Similar degradation of FRSM in the absence and presence of HO[•] were also observed and modeled by Wols *et al.*, (2014b).

Final degradation obtained in this work via UV-C/H₂O₂ and UV-C/PS for each of the target compounds were similar (Figure 3.5 A). Lian *et al.*,(2017) compared the treatment of 15 emerging contaminants and, while UV/H₂O₂ was more efficient for some, UV-C/PS showed better results for others. In other studies, authors concluded that the effectiveness of each process varies as according to compound chemical structure as a consequence of different reaction mechanisms presented by both radicals (YANG *et al.*, 2016; SERNA-GALVIS *et al.*, 2017).

Reagent consumption and mineralization rates are important factors to compare evaluate the effectiveness of different oxidation processes. As shown in Figures 3.5B-E, H₂O₂ consumption was around 10% for LP and FRSM and 30% for CAF and CBZ. Lower consumption of H₂O₂ in the presence of LP and FRSM probably occurs because they are stronger light absorbents when compared to H₂O₂ due to their molar absorption and photolysis coefficient ($\epsilon_{254\text{nm, LP, pH7}} = 11,772 \text{ M}^{-1} \cdot \text{cm}^{-1}$, $C_{\text{pLP, pH 7}} = 190$, $\epsilon_{254\text{nm, FRSM, pH 6}} = 6700 \text{ M}^{-1} \cdot \text{cm}^{-1}$, $C_{\text{pFRSM, pH 6}} = 163$) (Table 2.5) which are higher than those presented by H₂O₂ ($\epsilon_{254\text{nm, H2O2}} = 19.6 \text{ M}^{-1} \cdot \text{cm}^{-1}$, $C_{\text{pH2O2}} = 21.8$) (BAXENDALE & WILSON, 1957; HOKANSON *et al.*, 2016). Therefore, in the first 10 minutes of reaction, LP and FRSM hindered light absorption by H₂O₂, thus limiting the formation of hydroxyl radicals. Therefore, in these systems, H₂O₂ consumption only accelerated after 10 minutes of irradiation (Figures 3.5B and C), when both

LP and FRSM concentrations were reduced to 40% of initial concentrations of LP and FRSM (data not shown). Pharmaceuticals diclofenac and mecoprop, strong light absorbents, also impaired the absorption of light by H₂O₂ during UV-C/H₂O₂ treatment (SHU *et al.*, 2013). A different pattern is observed for CAF and CBZ which do not absorb UV-C light as intensively as the two pharmaceutical drugs. Thus, UV-C light is promptly absorbed by reagents when in the presence of both CAF and CBZ, leading to higher consumption of H₂O₂ in these systems (Figure 3.5D and E).

Meanwhile, PS consumption was nearly 30% for all of the compounds and followed the same pattern in all systems. Larger consumption of PS when compared to that of H₂O₂ occurs due to higher molar extinction coefficient, quantum yield sensitivity and absorption of UV-C light by PS when compared to H₂O₂ (ANIPSITAKIS & DIONYSIOU, 2004; LUO *et al.*, 2015). PS efficiency to use photons was estimated to be five times higher than that of H₂O₂ (ANTONIOU & ANDERSEN, 2015). In addition, energy required to break S₂O₈ into two SO₄[•] radicals (140 kJ.mol⁻¹) is lower than the amount which is necessary for the cleavage of H₂O₂ (213 kJ.mol⁻¹) into hydroxyl radicals (REINTS *et al.*, 2000).

With regard to mineralization, UV-C/PS led to higher mineralization rates for LP, CAF and CBZ (Figures 3.5 B-E). Although LP and FRSM removal rates were greater than 90%, maximum TOC removals for LP and FRSM were limited to 10% and 6%, respectively after one hour of reaction (Figures 3.5 B and 2C). The same was observed for azathioprine degradation in water via UV-C/H₂O₂ and UV-C/PS systems for which total removal of the pollutant was achieved, despite a maximum of 23% mineralization (ZHANG *et al.*, 2016). These results indicate the accumulation of organic transformation products in the system. Identification of these transformation products will be discussed in the following section.

UV-C/H₂O₂ achieved 25% and 35% TOC removal for CAF and CBZ, respectively (Figures

3.5D and 2E). However, mineralization of CAF and CBZ via UV-C/PS were superior to those obtained in the presence of hydroxyl radicals, reaching 60% and 70%, respectively. Higher mineralization rates through UV/PS were also obtained during the degradation of 2,4-D, carbamazepine, azathioprine and iodoacids, probably due to greater redox potential, higher selectivity and lifespan of sulfate radicals when compared to hydroxyl radicals (ANIPSITAKIS & DIONYSIOU, 2004; DENG *et al.*, 2013; XIAO *et al.*, 2016; ZHANG *et al.*, 2016). In addition, hydroxyl radicals may be also be formed during UV-C/PS reactions, which may have happened in the CAF and CBZ systems once the pH showed slight increase during these experiments (7.8 to 9)(LIANG & SU, 2009). Specifically for LP and CAF, which contain β -lactam rings in their structure, higher mineralization through UV-C/PS may also be explained by the fact that this group is attacked prior to benzene ring by sulfate radicals (SERNA-GALVIS *et al.*, 2017).

Pseudo-first order kinetics model ($R^2 > 0.95$) was applied to the results obtained during the experiments and kinetic constants were calculated for each process for the different target compounds (Table 3.4). When compared to photolysis only, k values increased up to 100 times in the presence of hydroxyl and sulfate radicals. Kinetic constant values acquired for UV-C and UV-C/H₂O₂ degradation of CAF corroborate with those obtained by Shu *et al.*,(2013), who also observed higher increase in these constants for compounds that present reduced quantum yield (caffeine and carbamazepine).

TABLE 3. 4 – Pseudo-first order kinetic constants (min^{-1}) obtained for each of the processes for the different target compounds

Pseudo-first order constant ($k; \text{min}^{-1}$)	LP	FRSM	CAF	CBZ
k_{UV-C}	0.01	0.06	0.007	0.002
k_{UV-C/H_2O_2}	0.05	0.12	0.1	0.2
$k_{UV-C/PS}$	0.09	0.07	0.1	0.2

In order to properly compare the efficacy of UV-C/H₂O₂ and UV-C/PS to remove target compounds, the *Electrical Energy per Order* (EE/O, kWh.m^{-3}) was calculated for each of the

UV-C AOPs as reported elsewhere (ANIPSITAKIS & DIONYSIOU, 2004)(Table 3.5). EE/O values represent the amount of energy required to remove the compound by one order of magnitude. Thus, the smallest EE/O reveals the most effective process. EE/O calculated for UV-C/H₂O₂ and UV-C/PS with regard to LP and FRSM showed opposite results. While UV-C/H₂O₂ requires more energy to remove LP, it is more efficient on the removal of FRSM than UV-C/PS. EE/O values obtained for CAF degradation were the same, indicating equal performance of these processes to remove this pollutant from water. Both processes were also similarly effective on the degradation of carbamazepine, another photo-resistant compound (LIAN *et al.*, 2017). For CBZ, both processes showed near EE/O values.

TABLE 3.5 – Electrical Energy per Order (EE/O) in function of total flux entering the reactor obtained for UV-C/H₂O₂ and UV-C/PS for the different target compounds.

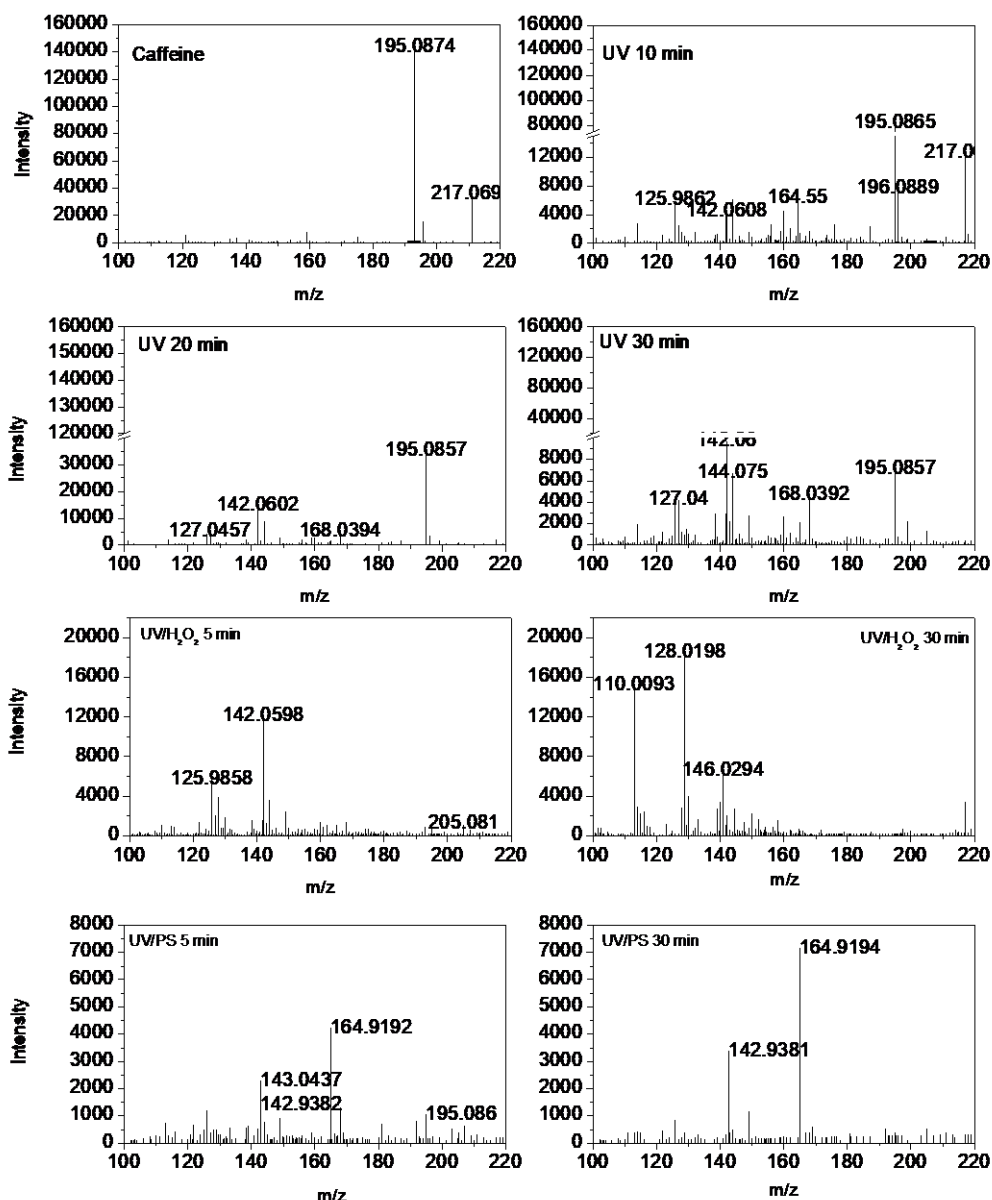
EE/O (kWh/m ³)	LP	FRSM	CAF	CBZ
UV-C/H ₂ O ₂	1.5 P	0.67 P	0.5 P	0.25 P
UV-C/PS	0.67 P	1.5 P	0.5 P	0.33 P

3.3.3 Identification of Transformation products

In order to identify the degradation products formed during reactions, ESI/MS analyses were performed with samples taken during reactions. These analyses were also helpful to understand and distinguish degradation routes that occurred during UV-C, UV-C/H₂O₂ and UV-C/PS for each compound.

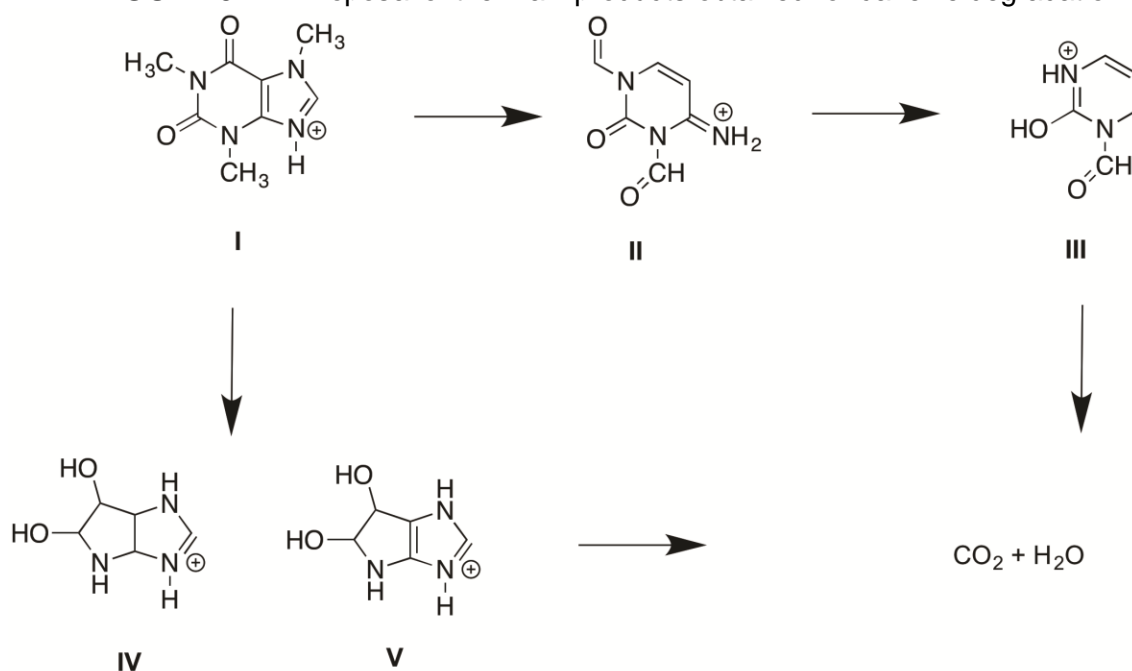
Mass spectra of caffeine under UV-C photolysis are shown in Figure 3.6. The high-resolution mass spectrometry results in a low error, only 9 ppm to protonated caffeine signal.

FIGURE 3. 6 – Mass spectra obtained during caffeine degradation under UV-C photolysis, UV-C/H₂O₂ and UV-C/PS



The electrospray study of caffeine before UV-C radiation (zero min) shows two peaks: protonated caffeine I [caffeine +H⁺], ($m/z = 195.08$) and another signal ($m/z = 217.07$) which refers to caffeine + sodium adduct. Figure 3.7 proposes the structure of degradation products formed during caffeine degradation.

FIGURE 3.7 – Proposal of the main products obtained for caffeine degradation.



After 10 min of UV-C radiation, the protonated caffeine signal reduces down to 50% of its initial value and others peaks appear. It is possible to observe the degradation products by two main pathways, one by oxidation and loss of part of the ion, generating the ion with $m/z = 168.04$ (II), successive oxidation and losses generate the ion with $m/z = 127.05$ (III). Another proposal accounts for a loss of a nitrogen atom in the six members ring, followed by a rearrangement, thus generating species IV and V. Species IV and V differ by a saturation in the ring, and present masses $m/z = 142.06$ and 144.07 , respectively. After 30 min of exposition to UV-C irradiation, the protonated caffeine shows only 5% of its initial value, and the successive oxidation consumes almost all of the caffeine present, leading to CO_2 and H_2O .

The loss of a nitrogen atom also happens in the UV-C/ H_2O_2 process, since the intermediate IV appears after 5 min of reaction. Intermediate IV was also detected by Dalmazio *et al.*, (2005) during the degradation of caffeine via UV-C/ H_2O_2 reaction. After 30 min, species showing $m/z = 128.02$ and 110.01 accumulate in the UV-C/ H_2O_2 system. Meanwhile, the transformation products that accumulated via UV-C/PS were different ($m/z = 164.92$ and

142.94), thus suggesting a different degradation pathway.

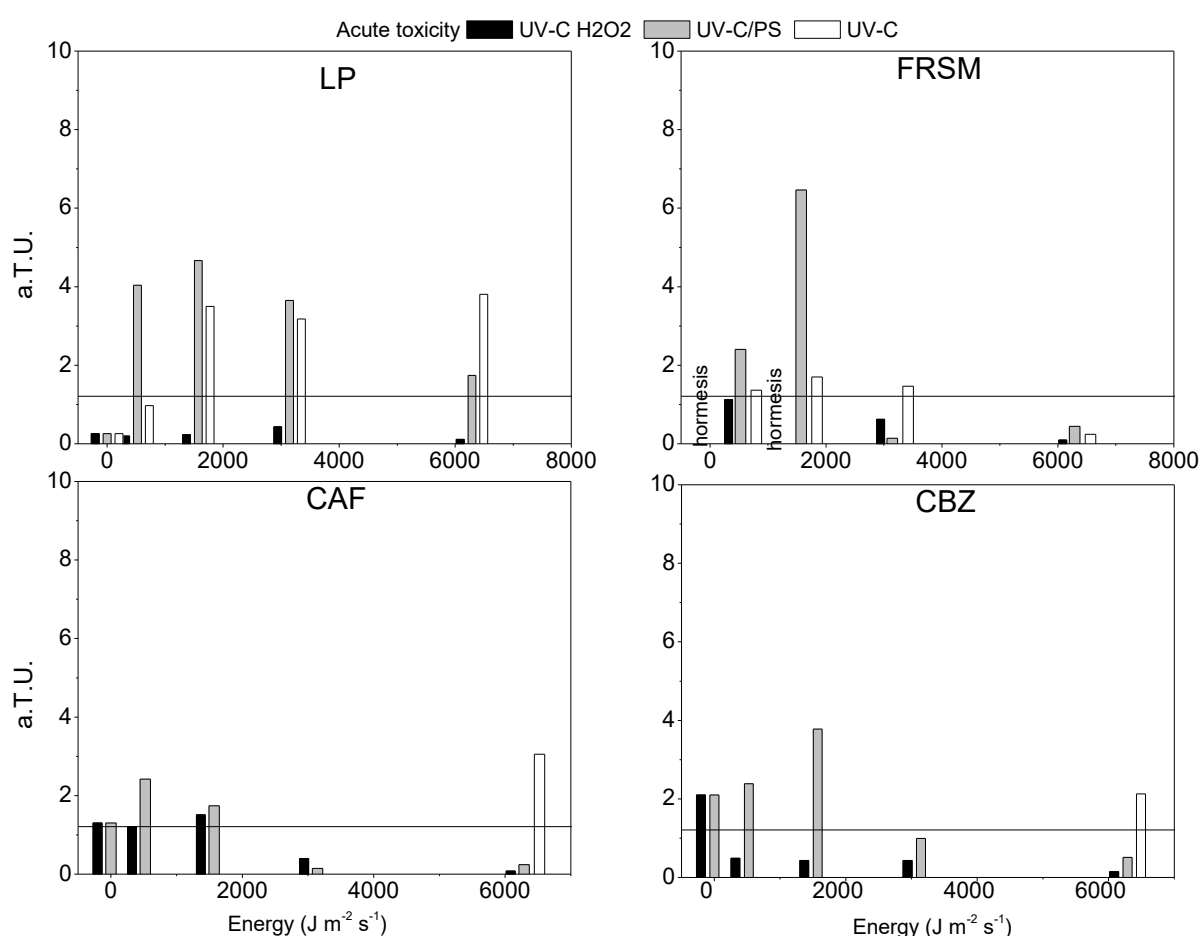
3.3.4 Evolution of acute toxicity

As shown in Figure 3.8, acute toxicity varied along treatments for all compounds indicating the formation of toxic intermediates during UV-C AOPS, as reported in the literature for various emerging contaminants (SHARMA *et al.*, 2018). LP solution was not toxic to *Allivibrio fischeri* ($aT.U = 0.26$), and no acute toxicity was observed during UV-C/H₂O₂ treatment. Despite high degradation of LP during UV-C alone and UV-C/PS (65% for UV-C and 98% for UV-C/PS), acute toxicity was developed and was not removed after treatment. According to Adachi *et al.*, (2008), cyanide ion is formed when LP is oxidized by sodium hypochloride. Therefore, this ion may also have been formed by oxidation during UV-C AOPs which may have contributed to an increase of acute toxicity. This difference between acute toxicity evolution by UV-C PS and UV-C H₂O₂ has been described in others works (YANG *et al.*, 2017). However, there is no report in the literature with regard to the formation of toxic transformation products during UV-C photolysis and UV-C/PS oxidation of LP or other sartans which show a similar structure. In contrast, EE/O values suggest that UV-C/PS is more efficient than UV-C/H₂O₂ on the removal of LP. This result elucidates that it is not adequate to consider EE/O value (Table 3.4) alone for selecting the best treatment alternative.

FRSM was reported as non-toxic to marine photobacterium *Vibrio fischeri* (ISIDORI *et al.*, 2006), yet its products of photolysis and electro-Fenton degradation are considered toxic (ISIDORI *et al.*, 2009; OLVERA-VARGAS *et al.*, 2015). In the present study, FRSM solution analyzed before treatment showed a beneficial stimulatory effect upon photobacteria known as *hormesis* (Figure 3.8). This effect occurs with luminescent bacteria as a consequence of exposure to small concentrations of toxic chemicals (KUDRYASHEVA & ROZHKO, 2015). As shown in Figure 3.7, FRSM acute toxicity was generated during

photolysis, and eliminated within $6000 \text{ J m}^{-2} \text{ s}^{-1}$ of incident energy, when this process achieved 80% of FRSM removal (Figure 3.4). Meanwhile, there was no generation of toxicity during UV-C/ H_2O_2 . In contrast, UV-C/PS followed a similar behavior to that of UV-C alone, since toxicity was generated at the beginning of the reaction, yet it was promptly eliminated within $3000 \text{ J m}^{-2} \text{ s}^{-1}$ of incident energy, faster than photolysis (Figure 3.8).

FIGURE 3. 8 - Acute toxicity of samples withdrawn during the degradation of target compounds via UV-C, UV-C/ H_2O_2 and UV-C/PS in function of incident energy ($\text{J m}^{-2} \text{ s}^{-1}$). The line represents the detection limit (1.21 a. T.U.) (bars crossing the line represent toxic samples).



CAF solution before treatment showed an inhibitory effect ($\text{Ec}_{50} = 76\%$; a. T. U = 1.3) to *Allivibrio fischeri*, as it has been reported in the literature for similar tests using marine photobacterium as a bioindicator (average $\text{Ec}_{50} = 62.8$) (JENNINGS *et al.*, 2001). Although a few authors have found no increase in CAF toxicity after AOP treatments (TROVÓ *et al.*,

2013; RODRIGUEZ *et al.*, 2017), no reports on the effect of UV-C/H₂O₂ and UV-C/PS upon CAF toxicity have been published. This is alarming since caffeine is detected in surface waters in various locations in concentrations up to $\mu\text{g L}^{-1}$ (STARLING *et al.*, 2018) and was considered an indicator of illegal sewage disposal (SODRÉ *et al.*, 2010). Both UV-C/H₂O₂ and UV-C/PS increased CAF toxicity in the beginning of treatment, although toxic effects were properly eliminated towards the end of reactions, when the concentration of this compound was below 10% of initial concentration (Figure 3.8). Thus, suggesting the formation and degradation of toxic transformation products during both processes. With regard to UV-C photolysis, for which only the final sample obtained during UV-C photolysis was analyzed due to the negligible effect of this process on the removal of this compound, an increase in toxicity was also observed.

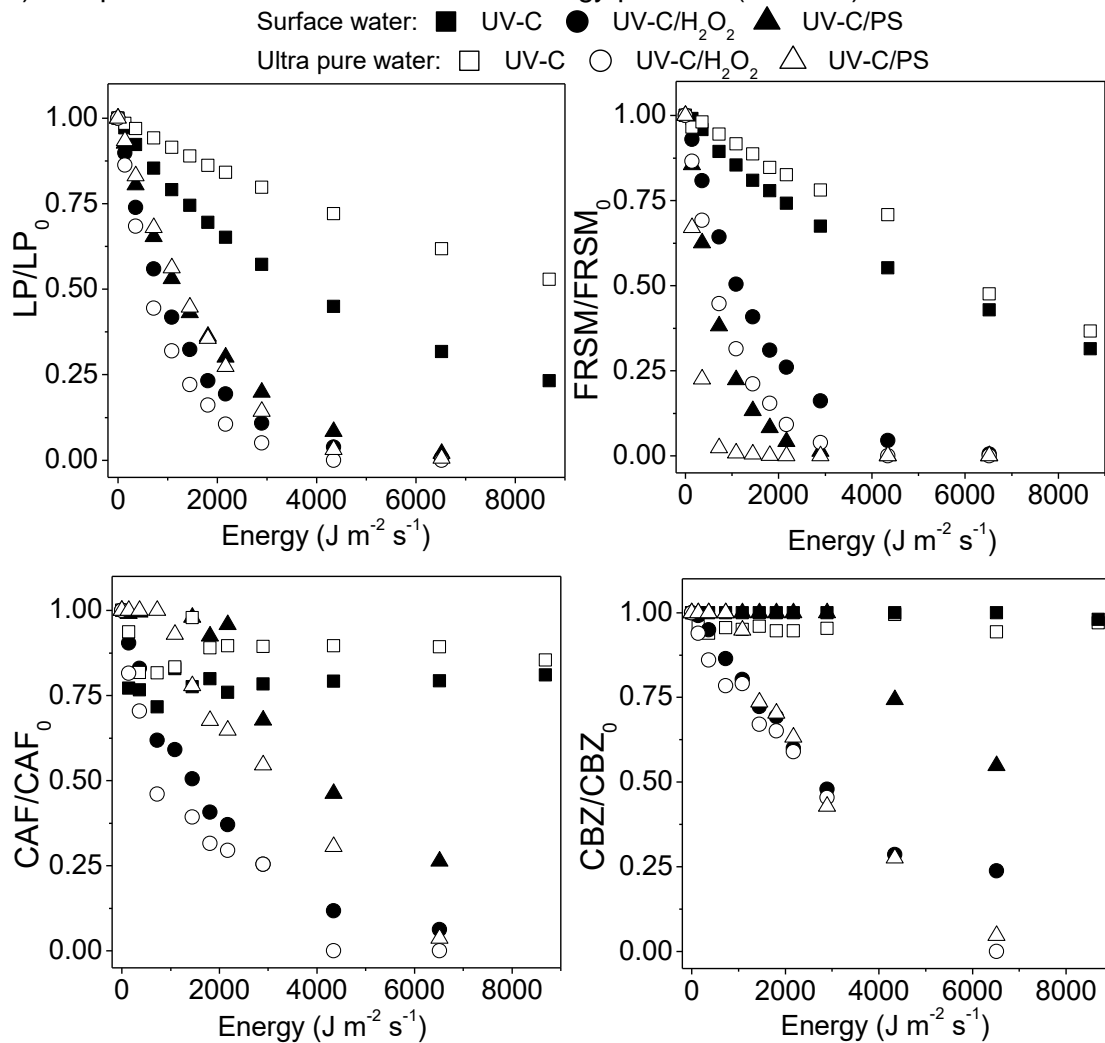
As it is confirmed in Figure 3.8, CBZ is known to be toxic to marine bacteria *Allivibrio fischeri* (DA COSTA *et al.*, 2018). As it occurred for CAF, UV-C photolysis alone was not able to remove CBZ due to low molar absorptivity and quantum-yield at 254nm associated to this compound. Consequently, UV-C photolysis had a negligible effect upon CBZ acute toxicity. Meanwhile, both UV-C/H₂O₂ and UV-C/PS eliminated the toxic effect of CBZ as it occurred for Fenton and photo-Fenton process under artificial and solar photo-Fenton (DA COSTA *et al.*, 2018). During UV-C/H₂O₂, CBZ degradation occurred along with acute toxicity removal (Figure 3.8). In contrast, acute toxicity increased during UV-C/PS at the first moment and decreased towards the end of the reaction, probably due to the formation of toxic transformation products. This result is in agreement with the EE/O (Table 3.5) as less energy is also required to remove CBZ acute toxicity via UV-C/H₂O₂ when compared to UV-C/PS.

3.3.5 Degradation of target compounds by UV-C/H₂O₂ and UV-C/PS in surface water

In order to assess the impact of the water matrix on the degradation of target compounds, UV-

C, UV-C/H₂O₂ and UV-C/PS reactions were performed in surface water and ultrapure water which were spiked with the mix of compounds (10µM of each). Although degradation was performed simultaneously, once all compounds were present in the same matrix, the degradation of each pollutant was quantified individually (Figure 3.9) and TOC removal and H₂O₂ and PS consumption were also monitored (Figure 3.10).

FIGURE 3. 9 - Degradation of LP, FRSM, CAF and CBZ (10µM of each) mixed in ultra-pure water and surface water by UV-C, UV-C/H₂O₂ and UV-C/PS processes (C₀;H₂O₂ or PS = 10-3 M) compounds as a function of incident energy per area (J m⁻² s⁻²).



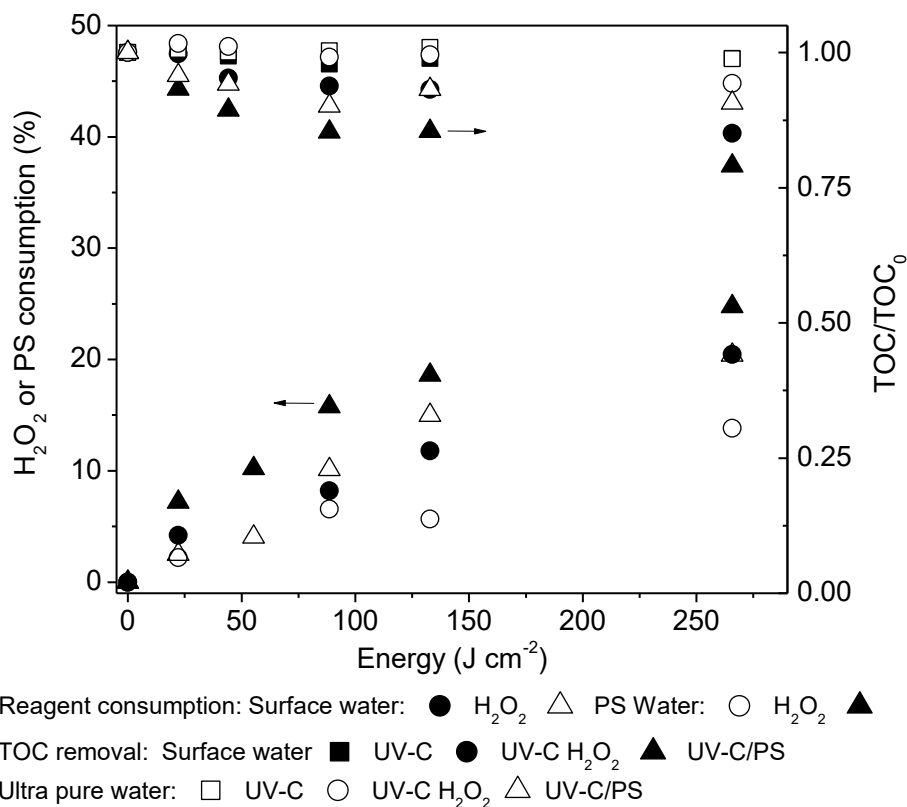
The presence of scavenger compounds that are naturally present in real surface water matrix - HCO₃⁻, natural organic matter (NOM), Cl⁻, among others - may lead to lower degradation of target compounds (ZHOU *et al.*, 2017). NOM is mainly composed of humic acids which

present various functional groups that compete with target compounds for hydroxyl and sulfate radicals (RICHARD *et al.*, 2007; TAN *et al.*, 2013). As it is shown in Figure 3.8, UV-C photolysis of CBZ in the real matrix and in the presence of the other target compounds was similar to that observed in pure water with insignificant decrease on the concentration of this compound for CBZ due to its reduced quantum yield and molar absorptivity at 254 nm (Table 3.2). On the other hand, the photolysis of LP, FRSM and CAF increased slightly in surface water when compared with pure water. This probably happened due the formation of oxidative radicals from the natural constituents of Lys River surface water, that presents a DOC of 1.2 mg L⁻¹; 8 mg L⁻¹ of O₂; 22 mg L⁻¹ of NO₃⁻; 0.1 mg L⁻¹ of PO₄³⁻ and 20 mgL⁻¹ of Cl⁻ and a high alkalinity with 330 mg L⁻¹ of HCO₃⁻. Higher photolysis of FRSM in natural waters when compared to pure water, was also observed elsewhere (WOLS *et al.*, 2014b). When NOM, dissolved oxygen and phosphate are submitted to UV-C_{254nm} irradiation, oxidative species such as NOM[•], singlet oxygen(¹O₂), and PO₄^{•2-} may be formed (PAUL *et al.*, 2006; KALSOOM *et al.*, 2012). Although these radicals present lower redox potentials when compared to HO[•] and SO₄^{•-} they may have contributed to enhancing the photolysis of LP, FRSM and CAF. Additionally, HO[•] may also be formed from the irradiation of NO₃⁻ present in surface waters (ZEPP *et al.*, 1987; GUAN *et al.*, 2018).

Lower degradation of LP and FRSM were found during UV-C AOPs in surface water when compared to pure water and the high level of carbonate ions may have contributed to the quenching of hydroxyl and sulfate radicals in reactions conducted in surface water. In contrast, for CAF and CBZ the effect of matrix constituents in oxidative radicals formed during UV-C AOPs could not be observed, probably because their reaction rate with radicals is extremely high as shown in Table 3.4. The relatively high content of chloride ion, which reacts strongly with sulfate radicals (FANG *et al.*, 2012), may have influenced the effectiveness UV-C/PS thus leading to the lower removal of target compounds in surface

water when compared to pure water.

FIGURE 3. 10 - Reagent consumption and TOC removal during UV-C AOPs in surface water (filled symbols) and pure water (empty symbols) as a function of incident energy per area ($\text{J m}^{-2} \text{s}^{-2}$).



Considering that H₂O₂ and PS were in excess, their consumption rates were below 25% in all of the tested conditions (Figure 3.10). H₂O₂ consumption in pure water was equivalent to 13% and increased to 20% in surface water, thus confirming higher consumption of this reagent in the presence of matrix components. On the other hand, PS consumption was very similar in the absence (20%) and in the presence of matrix components (24%). In addition, previous works have confirmed that UV-C/PS performance is not as disturbed by carbonate ions (HCO₃⁻) as UV-C/H₂O₂ performance, probably due to lower reaction constants of SO₄^{-•} radical with HCO₃⁻ ($k_{\text{SO}_4^{\bullet-}, \text{HCO}_3^-} = 2.8 \times 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$; $k_{\text{HO}^{\bullet}, \text{HCO}_3^-} = 8.5 \times 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$) (CHAWLA & FESSENDEN, 1975; BUXTON *et al.*, 1988; ANTONIOU & ANDERSEN, 2015; LUO *et al.*, 2015; ZHANG *et al.*, 2016). Furthermore, TOC removal obtained during UV-C/PS (9%

and 21% in pure water and surface water, respectively) were higher than those obtained for UV-C/H₂O₂ (5.7 and 14.9%) for both water matrices, thus corroborating with results obtained earlier in this study. Higher mineralization efficiency via sulfate radicals on the degradation of the natural organic matter was also observed elsewhere (KWON *et al.*, 2015).

3.4 CONCLUSION

UV-C _{254nm} alone was able to degrade Losartan Potassium and Furosemide, which did not occur for caffeine and carbendazim due to differences in chemical structure. Caffeine stability under photolysis was confirmed in this study and corroborates with its use as an urban pollution tracer. UV-C /H₂O₂ and UV-C /PS were extremely effective on the removal of all of the target compounds leading to more than 90% degradation in water. Although the compounds were almost completely removed in these conditions, mineralization was limited, which indicates the accumulation of organic transformation products. Indeed, mass signals detected for caffeine during its degradation differed in the presence of hydroxyl and sulfate radicals probably due to diverse reaction mechanisms performed by each reagent. Acute toxicity results indicate that UV-C/H₂O₂ is more reliable when it comes to toxicity removal, while UV-C/PS and UV-C alone generated toxicity during the treatment of all target compounds. Thus, suggesting that the UV-C/H₂O₂ is the most suitable treatment when compared to UV-C/PS and UV-C photolysis. Additionally, NOM and inorganic ions present in surface water competed with target compounds for oxidative radicals, thus reducing degradation rate.

4 CHAPTER IV: TREATMENT OF TARGET CEC IN MWWTP EFFLUENT VIA SOLAR PHOTO- FENTON AND SOLAR PHOTO- FENTON LIKE AT NEUTRAL PH

4.1 INTRODUCTION

Once pharmaceutical drugs, personal care products and illicit drugs are consumed and excreted in metropolitan regions, chemical compounds present in these products are directed to the sewage system (when existing). Considering that conventional treatment systems used in municipal wastewater treatment plants (MWWTP) are generally not designed to remove these pollutants, MWWTP effluent constitute one of the main sources of these emerging contaminants (or contaminants of emerging concern, CEC) to the environment (RIBEIRO *et al.*, 2015). Once in surface waters in reduced concentrations ($\text{ng-}\mu\text{g.L}^{-1}$), CEC may lead to acute and chronic toxicity and other negative impacts to aquatic organisms (DAMIÀ BARCELÓ, 2008). Hence, the implementation of advanced treatments for the removal of CEC from MWWTP secondary effluent has been strongly recommended (when not imposed) by environmental and health agencies in developed countries (GIANNAKIS *et al.*, 2016; TIEDEKEN *et al.*, 2017). The application of tertiary treatments ensures water quality maintenance and ecosystem integrity and prevents negative effects of CEC upon local biota and human health.

Different technologies may be selected as tertiary treatment. Yet, considering the great variety of CEC present in MWWTP secondary effluent, the most appropriate technology must enable the degradation of most compounds, regardless of individual chemical structure, size or biodegradability. Therefore, the lower the selectivity of the chosen technology, higher is the chance that it will enable the removal of most CEC.

Due to the non-selectivity of hydroxyl radicals (HO^\bullet), advanced oxidation processes (AOP) have been proved as adequate alternatives for the removal of CEC present in water and wastewater (COMNINELLIS *et al.*, 2008). In addition, the convenience of oxidative processes over other advanced technologies is supported on the potential mineralization of

existing pollutants and/or their transformation onto inactive compounds (RIBEIRO *et al.*, 2015).

Among AOP, UV-C /H₂O₂ is one of the most recognized technologies and it is applied in real scale for the treatment of industrial wastewater (KRUITHOF *et al.*, 2007). During this process, photolysis and oxidation occur contributing to the degradation and partial mineralization of organic compounds. Recent studies have evaluated the potential of using this process as tertiary treatment for the removal of CEC in wastewater with successful results (DE LA CRUZ *et al.*, 2013; SHU *et al.*, 2013; KWON *et al.*, 2015; XIAO *et al.*, 2016; GIANNAKIS *et al.*, 2017). Indeed, some of these works compare the efficiency achieved via UV-C /H₂O₂ with that obtained via UV-C /Persulfate (S₂O₈²⁻). In the latter, rather than HO[•], sulfate radical (SO₄^{•-}) is formed as a peroxide. SO₄^{•-} reacts with CEC leading to high degradation rates. However, one of the main drawbacks inherent to both UV-C/H₂O₂ and UV-C /Persulfate (S₂O₈²⁻) is the high energy uptake imposed by the use of artificial Hg lamps (LI, 2016).

Solar irradiation has been intensively investigated as an alternative to energy-intensive UV-C AOPs. Among solar AOP, solar photo-Fenton is of particular interest once it assembles the use of renewable energy with an environmentally safe and cheap catalyst (iron, Fe²⁺) (PAPIĆ *et al.*, 2009; LITTER *et al.*, 2017). During solar photo-Fenton, species formed in the system (at acidic pH) are able to absorb light in the visible range (< 580 nm) leading to an extra pathway for the formation of hydroxyl radicals. The use of this type of treatment is especially favorable, yet underexplored, in tropical countries where solar irradiation is intense throughout the whole year (MARCELINO *et al.*, 2015). Nearly 95% removal of 22 emerging contaminants present in real MWWTP effluent was obtained via solar photo-Fenton in acidic and neutral conditions (KLAMERTH *et al.*, 2013).

Furthermore, as mentioned for the UV-C based AOP, solar-photo Fenton may also be modified with the use of Persulfate ($S_2O_8^{2-}$) rather than H_2O_2 . In this photo-Fenton like process (solar/ $Fe^{2+}/ S_2O_8^{2-}$), $S_2O_8^{2-}$ reacts with iron generating sulfate radicals. Solar/ $Fe^{2+}/ S_2O_8^{2-}$ system may be more favorable in natural matrices which contain natural organic matter (NOM) and ions that act as radicals scavengers (Cl^- , HCO_3^- , PO_4^{2-} , NO_3^-) since reaction rates of sulfate radical with natural scavengers are lower when compared to rates reported for hydroxyl radicals (LIAN *et al.*, 2017). In addition, in the presence of Cl^- , which occurs naturally in wastewaters, hydroxyl radical may be formed simultaneously with $SO_4^{\bullet-}$ in these systems (NIE *et al.*, 2018). Simultaneous presence of both radicals may contribute to the removal of intermediates which are resistant to oxidation by hydroxyl radicals yet sensitive to sulfate radical attack (MONTEAGUDO *et al.*, 2016)

The degradation of Carbamazepine in wastewater was promptly achieved via modified solar photo-Fenton (solar/ $Fe^{2+}/ S_2O_8^{2-}$) in 30 minutes (50 μM of $S_2O_8^{2-}$ and $S_2O_8^{2-}:Fe^{2+}$ of 2:1), confirming the feasibility of using this technology. In addition, scavenging compounds showed little influence on the reactivity of $SO_4^{\bullet-}$ (AHMED *et al.*, 2014). Another study investigated the degradation of six CEC, including caffeine, via traditional solar photo-Fenton (solar/ Fe^{2+}/ H_2O_2) and solar photo-Fenton like (solar/ $Fe^{2+}/ S_2O_8^{2-}$) in a CPC reactor. Results indicated that both processes were equally effective on the degradation of target compounds (AHMED *et al.*, 2014; MIRALLES-CUEVAS *et al.*, 2017).

Nevertheless, when it comes to both solar/ Fe^{2+}/ H_2O_2 and solar/ $Fe^{2+}/ S_2O_8^{2-}$, acidic pH is required. This is one of the most significant limitations to the application of these processes at real scale. Therefore, researches have been building up strategies to eliminate the two extra stages necessary in this technology: (i) acidification to optimum pH (2.8) prior to reaction, followed by (ii) neutralization before discharge. Besides increasing treatment costs, these

stages increase operational requirements and hazardousness, once chemical reagents (acid and base) must be stocked and manipulated on site. In order to avoid iron precipitation at higher pH (5-8), some studies have suggested the use of chelating agents (humic acid, citrate, oxalate, EDDS and EDTA) that complex with iron avoiding its precipitation. However, these complexes increase the organic carbon content, elevate treatment costs, have unknown persistence and toxicity in the environment and may increase heavy metal solubility in natural waters (CLARIZIA *et al.*, 2017). Therefore, alternative solutions were proposed, mainly for the traditional solar photo-Fenton, in the past years (CARRA *et al.*, 2013).

Carra *et al.*, (2013) proposed a strategy that enabled the application of solar photo-Fenton at mild pH by using intermittent additions of iron (5, 10 or 20 mg.L⁻¹) to the reactor (every 5 min), so that it could be kept in solution. The approach led to total removal of pesticides from wastewater. In the sequence, the author published another study comparing continuous (1 or 5 mg L⁻¹ per min) and sequential (20 mg.L⁻¹ 3 or 4 times leading to a total of 60 mg.L⁻¹) iron addition strategies. Iron was only available in the system during the entire reaction for the continuous strategy. The authors also concluded that carbonate ions concentration must be reduced prior to reaction. Using three additions of Fe²⁺ (20 mg.L⁻¹) at zero, 5 and 15 minutes, Freitas *et al.*, (2017), achieved 99% removal of micropollutants and toxicity removal in MWWTP effluent in 90 min of reaction at neutral pH (after the consumption of bicarbonates). The intermittent iron addition strategy was also successful at near neutral pH for micropollutant, toxicity and estrogenic activity removals elsewhere (RIVAS IBÁÑEZ *et al.*, 2017).

In addition to the CEC degradation, solar-photo-fenton was also effective for MWWTP effluent disinfection in neutral pH (20 mg.L⁻¹ of iron and 50 mg.L⁻¹ of H₂O₂) when Fe²⁺ was added all at once after carbonate removal (ESTEBAN GARCÍA *et al.*, 2017). The authors

observed iron precipitation (dissolved $\text{Fe}^{2+} = 0.7 \text{ mg.L}^{-1}$) and increase in turbidity (7.4 to 22 NTU in the RPR) in this study. In addition, they believe that precipitated iron hydroxides may have contributed to the generation of hydroxyl radicals. Considering the effectiveness and economical and technical advantages of conducting solar-photo Fenton in near neutral pH, research in this direction must be stimulated. This should be done not only for the traditional photo-Fenton process yet also to the photo-Fenton like system (solar/ $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$). After all, even though research on $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$ and solar/ $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$ has increased in the past few years (WACLAWEK *et al.*, 2017), intermittent iron addition strategies in near neutral pH have not been investigated for these systems so far. This is a promising strategy considering that in the natural pH of real matrices, $\text{SO}_4^{\bullet-}$ may react with hydroxide (OH^-) forming hydroxyl radical in the system (FANG *et al.*, 2012). Therefore, both radicals act simultaneously, granting higher stability of the UV-VIS/ $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$ at a broader pH range when compared to the traditional photo-Fenton system (WANG *et al.*, 2015).

Apart from CEC removal, it is also important to consider toxicity depletion prior to treated wastewater discharge. As it is widely known, toxic effects may persist (or even increase) over the course of AOPs while CEC may still be present below the limits of quantification pertaining to analytical assays (BILA *et al.*, 2007; TROVÓ *et al.*, 2012). Acute and chronic toxicity assays performed after the treatment of secondary effluent from MWWTP at neutral pH via solar photo-Fenton confirmed the removal of all 54 CEC and reduced wastewater toxicity (RIVAS IBÁÑEZ *et al.*, 2017).

Therefore, the aim of this chapter was to investigate the removal of three model CEC (caffeine - CAF, Carbendazim - CBZ, and losartan potassium - LP) in real MWWTP effluent via traditional (solar/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and modified (solar/ $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$) solar photo-Fenton at near-neutral pH. Assays were performed in a solar simulator and best treatment condition was

conducted in a Raceway Pond Reactor (RPR). Table 4.1 lists a few studies that have already assessed the degradation of some of these compounds in wastewater or synthetic wastewater via solar photo-Fenton in acidic and near neutral pH. Apart from CEC removal, acute toxicity and disinfection were also assessed during the experiment conducted in RPR.

TABLE 4. 1 – Studies conducted with MWWTP effluent for the degradation of CEC compounds targeted in this project.

Compound	Matrix	Treatment	Result	Reference
Caffeine	MWWTP effluent	UV-C UV-C /H ₂ O ₂	UV alone was more effective (90%) for the removal of CAF in wastewater than UV/H ₂ O ₂ (67%) probably due to low concentration of this compound in wastewater. Degradation of CAF by UV alone was equivalent to 10%. CAF and its metabolite paraxanthine displayed resistance to oxidization. UV dose of 2369 mJ.cm ² was necessary to reduce CAF to one tenth of its initial concentration. CAF degradation was 26, 88, 81 and 87 % when exposed to 5, 15, 20 and 25 mg.L ⁻¹ of H ₂ O ₂ .	(CLARIZIA <i>et al.</i> , 2017)
	MWWTP effluent	UV-C UV-C / H ₂ O	When in Milli-Q water, solar photolysis of CAF is negligible. Meanwhile, in secondary effluent, hydroxyl radical formed from natural organic matter in the system contributed to indirect photolysis of CAF. The presence of nitrate in wastewater samples also contributed to the degradation of caffeine under simulated solar irradiation. Photosensitizers present in a lagoon system may contribute to the degradation of CAF under solar irradiation.	(AFONSO-OLIVARES <i>et al.</i> , 2016)
	MWWTP effluent	Solar photolysis	When H ₂ O ₂ only was applied to sample, CAF was decreased by 6%. Under UV-C only, 15% of CAF was degraded compared to 90% when the UV-C /H ₂ O ₂ or S ₂ O ₈ ⁻² systems were applied. UV-C /S ₂ O ₈ ⁻² was more efficient than UV/H ₂ O ₂ due to lower recombination rate of sulphate radicals. For solar processes, both were similarly effective and able to remove up to 90% of CAF. Although solar processes are energetically economical, UV-C process do not require pH adjustment. Although no pH adjustment was performed, samples were acidified before experiment for carbonate release. 30% removal of caffeine was achieved via dark Fenton performed in neutral pH in synthetic wastewater and the rate increased to 94% after the reactor was exposed to sunlight after 90 min of reaction. Iron concentration and pH decreased during reaction. Caffeine degradation in MWWTP effluent was also above 90%. In the beginning of photo-Fenton reaction, there is an increase in toxicity. Degradation is faster in real effluent than in synthetic effluent due to natural organic matter.	(WANG <i>et al.</i> , 2017)
	MWWTP effluent	UV-C / H ₂ O UV-C /S ₂ O ₈ ⁻² solar photo-Fenton modified solar photo-Fenton	More than 90% removal of CAF were achieved within 15 min of reaction at pH 3. After 6 hours of reaction at neutral pH, CAF remained in solution. In the presence of a scavenger of hydroxyl radical, CAF degradation was strongly reduced in acidic pH and moderately reduced in neutral pH. CAF degradation decreased in the presence of humic acids.	(MIRALLES-CUEVAS <i>et al.</i> , 2017)
	Synthetic wastewater Simulated effluent MWWTP effluent	Solar photo-Fenton at neutral pH	RPR was operated in continuous flow for the degradation of various micropollutants. During the first batch, 93% removal of CAF was achieved. CAF degradation increased with increased hydraulic retention time being 71, 81 and 88% for 20 40 and 80 min respectively.	(KLAMERTH <i>et al.</i> , 2010)
	Distilled water Tap water MWWTP effluent	Solar photo-Fenton (acidic and neutral pH)		(BERNABEU <i>et al.</i> , 2012)
	Simulated secondary effluent MWWTP effluent	Solar photo-Fenton		(ARZATE <i>et al.</i> , 2017)

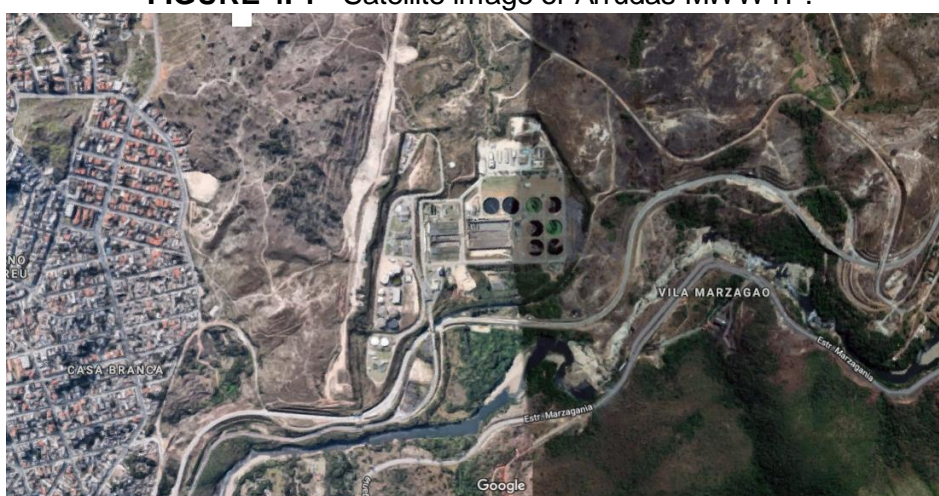
Compound	Matrix	Treatment	Result	Reference
	MWWTP effluent	Solar photo-Fenton Solar photocatalysis (TiO ₂) Ozonation	CAF was hardly degraded via solar/TiO ₂ process. More than 98% degradation of CAF took place after 3 min of solar photo-Fenton (0.56 kJ/L). Ozonation also led to fast degradation (20 min) over 98%.	(PRIETO-RODRÍGUEZ <i>et al.</i> , 2013)
	Pure water Surface water MWWTP effluent	photo-Fenton Solar photo-Fenton	Different concentrations of H ₂ O ₂ , CAF and Fe were tested for the degradation of CAF. Optimum conditions were obtained using: 52.0 mg L ⁻¹ CAF, 10.0 mg L ⁻¹ Fe ²⁺ and 42.0 mg L ⁻¹ H ₂ O ₂ . 20 min of reaction in the optimum condition were enough to decrease CAF levels below the detection limit in pure and surface water, while 40 minutes were necessary for the same purpose in secondary wastewater due to the presence of organic matter and carbonate in the real matrix. Solar photo-Fenton in a pilot plant reactor achieved higher mineralization in pure water when compared to lab scale reactor.	(TROVÓ <i>et al.</i> , 2013)
Caffeine	MWWTP effluent	Solar photo-Fenton (neutral pH)	100% removal of CAF were achieved during solar photo-Fenton performed at near neutral pH	(FREITAS <i>et al.</i> , 2017)
	MWWTP effluent	Solar photo-Fenton (pH 3) Solar photo-Fenton (neutral pH using complexants)	Final caffeine concentration was lower during solar photo-Fenton conducted at pH 3 (99%), followed by the experiment performed with humic acid (95%) and EDDS (93%) as complexants. Lower consumption of H ₂ O ₂ occurred in the presence of humic acid, pH decreased to 4.7 in the end of reaction and the degradation rate was much slower. Although H ₂ O ₂ consumption was also lower with EDDS, the pH remained at 6.3.	(KLAMERTH <i>et al.</i> , 2013)
	MWWTP effluent	Coagulation-Flocculation + Filtration + UV-C/Cl	Filtration-UV-C/Cl alone led to 20% removal of CAF in the summer and in the winter, only 10% was removed. Degradation percentage in wastewater via the complete treatment route 9%.	(MATAMOROS & SALVADÓ, 2013)
Losartan Potassium	MWWTP effluent	Solar/TiO ₂	LP was completely removed after 10 kJ of accumulated energy. LP and was degraded during the Zhan-Wellens test.	(SOUSA <i>et al.</i> , 2012)

4.2 MATERIAL AND METHODS

4.2.1 Sampling and spiking

MWWTP secondary effluent was sampled at the output of the activated sludge reactor located at *Arrudas* MWWTP. This treatment plant is located in Sabará and receives sewage from 1.5 million inhabitants of the metropolitan region of Belo Horizonte, treating $3,375 \text{ L}\cdot\text{s}^{-1}$ (Figure 4.1).

FIGURE 4. 1 - Satellite image of Arrudas MWWTP.



Source: Google maps

After sampling, wastewater was characterized for Chemical Oxygen Demand (APHA 5220 D, COD, $\text{mgO}\cdot\text{L}^{-1}$), pH, Total Organic Carbon (Shimadizu TOC-V CPN, TOC, $\text{mg}\cdot\text{L}^{-1}$), Turbidity (NTU), Total Suspended Solids (TSS, $\text{mg}\cdot\text{L}^{-1}$), Volatile Suspended Solids (VSS, $\text{mg}\cdot\text{L}^{-1}$), Total Dissolved Solids (TDS, $\text{mg}\cdot\text{L}^{-1}$), Alkalinity (APHA 2320 B, $\text{mgCaCO}_3\cdot\text{L}^{-1}$), Conductivity (APHA 2510 B $\mu\text{S}\cdot\text{cm}^{-1}$) (APHA, 2012). A characterization of samples withdrawn in different samplings during this study is shown in Table 4.2. For Sample 3, characterization was also performed with regard to total coliform and *E. coli*, and acute toxicity using marine photobacterium *Allivibrio fisheri*. Detailed procedures of these bioassays are described below in Section 4.2.4. Prior to each reaction, the wastewater was spiked with $100 \mu\text{g L}^{-1}$ of each of the target CEC (Total CEC concentration = $300 \mu\text{g L}^{-1}$).

TABLE 4. 2 – Characterization of the MWWTP effluent used in this study

<i>Parameter</i>	<i>Unit</i>	<i>Sample</i>		
		<i>1</i>	<i>2</i>	<i>3</i>
pH		6.6	7.1	7.5
Temperature	Celsius	27.2	23	23
TOC	mg L ⁻¹	14.8	10.9	-
IC	mg L ⁻¹	22.3	25.3	-
COD	mg O L ⁻¹	158	106	100
TSS	mg L ⁻¹	90	482	360
VSS	mg L ⁻¹	75.5	60	44
TDS	mg L ⁻¹	284.5	448	328
VDS	mg L ⁻¹	60.5	22	18
Conductivity	µS	427.8	769	638
Hardness	mg CaCO ₃ .L ⁻¹	22.8	18.82	20.3
Hardness	g Mg L ⁻¹	4.9	5,64	3.4
Alkalinity	mg CaCO ₃ L ⁻¹	81.2	222.4	241.4
Total Coliform	NMP/100 mL	8.8 x 10 ⁵	-	10 ⁴
E. coli	NMP/100 mL		ND	2E6
Acute toxicity*	a.T. U.	-	-	0.62

-: not performed for this sample; ND: not detected; *:after spiking.

4.2.2 Chemicals and reagents

Caffeine (CAF), Carbendazim (CBZ) and Losartan Potassium (LP) were all purchased from Sigma-Aldrich. HPLC grade Methanol (MERCK) and Formic Acid (Sigma-Aldrich, ≥98% purity) were used for analytical purposes.

4.2.3 Quantification of target CEC in MWWTP effluent

Identification and quantification of target compounds in MWWTP effluent was performed using a Ultra High Pressure Liquid Chromatographer (UHPLC; Shimadzu) system connected to a QTOF mass spectrometer (Bruker Daltonics, Impact II). The UHPLC was equipped with a C₁₈ column (Agilent Poroshell HPH-C18 4.6 x 150 mm, 2.7 µM) for separation. Mobile phases consisted of (A) Methanol (MeOH) acidified with 0.1% formic acid and water acidified with 0.1% formic acid at 0.25 mL min⁻¹. The detector was set at 240 nm. The method starts with 60% of A until up to 8 minutes. From 8 to 10 minutes, the concentration of A increases to 90% and the run proceeds in this condition until 20 minutes. Retention times

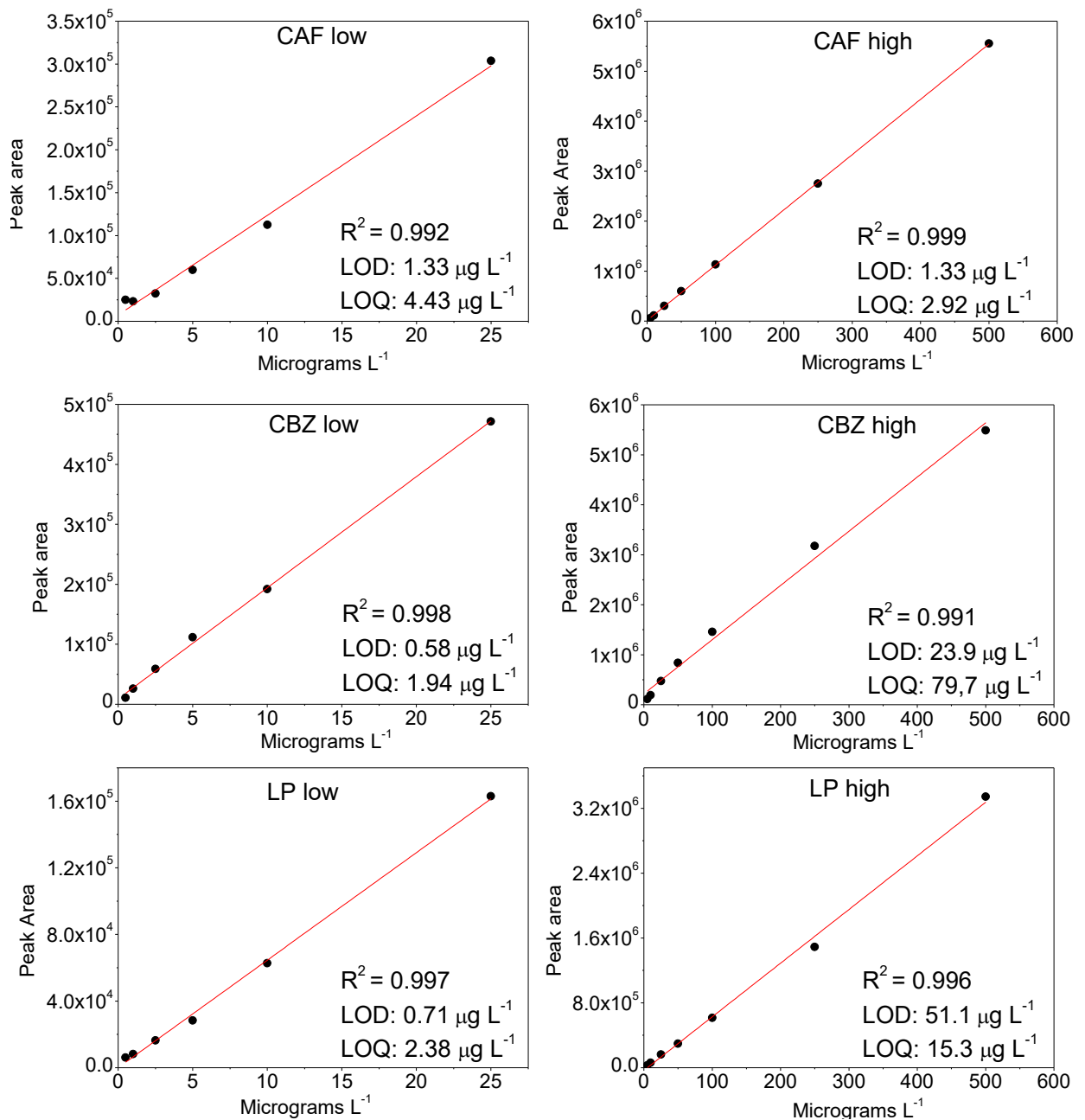
were 6.4 min for Carbendazim, 6.8 min for Caffeine and 15 min for Losartan Potassium. Positive ionization mode enabled the detection of all target compounds as shown in Figure 4.2. The QTOF mass spectrometer was operated under the following conditions during all runs: capillary 4500 V, nebulizer 0.4 bar, drying gas 5 L/min, gas temperature 180 °C.

FIGURE 4. 2 – Mass spectrum view of (top) CAF, (center) CBZ and (bottom) LP obtained in the matrix containing 500 µg L⁻¹ of each compound using HPLC connected to QTOF



Due to the complexity of the matrix used in these experiments and possible interference of matrix components in the absorbance of target compounds, samples were filtered in 0.22 µm PVDF filters prior to injection. Calibration curves were performed in the real matrix after filtration, concentrations varied from 0.01 µg L⁻¹ to 500 µg L⁻¹ of each target compound present simultaneously in the matrix. Two curves were constructed for each compound, one for the lower concentration and another for the higher concentrations. Mass spectra and calibration curves (low and high) obtained for each compound, as well as limits of detection (LOD) and quantification (LOQ) are shown in Figure 4.3.

FIGURE 4.3 – Calibration curves and limits of detection (LOD) and quantification (LOQ) obtained for the quantification of each of the target compounds using HPLC connected to QTOF



4.2.4 Experimental procedures

4.2.4.1 Traditional solar photo-Fenton (solar/iron/H₂O₂) at neutral pH

Traditional solar photo-Fenton experiments were performed in a bench scale solar simulator chamber (SUNTEST CPS⁺, ATLAS) which contains a Xenon lamp that emits light in the UV-Vis region simulating the solar spectrum (Figure 4.4). The irradiance range used during the

experiments was set at 268 W m^{-2} (330 to 800 nm), which is equivalent to 30 W m^{-2} (300 to 400 nm), the annual average irradiance in Belo Horizonte. Chamber temperature was set at 35°C , the lowest temperature possible for this chamber.

FIGURE 4. 4 - SUNTEST (left) and RPR reactor (right) used for solar photo-Fenton experiments.



Source: (COSTA, 2017)

Minimum and maximum concentrations proposed for iron and hydrogen peroxide are shown in Table 4.3 and were determined as according to values reported by other authors who investigated the treatment of emerging contaminants in municipal wastewater treatment plant effluent using solar photo-Fenton and solar photo-Fenton like at acidic pH with no iron addition strategies (AHMED *et al.*, 2014; AHMED & CHIRON, 2014; MIRALLES-CUEVAS *et al.*, 2017). All of the solar photo-Fenton experiments were conducted with Sample 2 (Table 4.2). As shown in Table 4.2, the initial concentration of inorganic carbon (TIC) in the sample was already below 50 mg L^{-1} , which is the maximum concentration suggested by other authors to enable photo-Fenton treatment at neutral pH (ESTEBAN-GARCIA *et al.*, 2018). Although TIC concentration was favorable, sample pH was adjusted from 7.6 to 7.0 before experiments in order to guarantee that initial pH was the same for all conditions. After pH adjustment, the spiked wastewater was poured into 400 mL glass flask. For the experiments performed at neutral pH, both single and fractioned iron additions were tested. For comparison purposes, assays #7 to 10 were performed using the same minimum

and maximum concentrations of iron and H₂O₂ at pH 3. Control experiments consisted of dark Fenton (iron/H₂O₂), coagulation (iron alone) and simulated solar irradiation alone (Table 4.3). All conditions were conducted under continuous stirring and in duplicates.

TABLE 4. 3 - Experimental conditions performed for the solar photo-Fenton treatment at neutral pH in a solar chamber and controls

Type	Name	Fe ²⁺		H ₂ O ₂		Fe addition	pH
		mg L ⁻¹	mM	mg L ⁻¹	mM		
Assay	# 1	5.5	0.1	10	0.3	single	7
	# 2	5.5	0.1	50	1.5	single	
	# 3	55.0	1	10	0.3	2x(20) + 3x (5.0)	
	# 4	55.0	1	50	1.5	2x(20) + 3x (5.0)	
	# 5	55.0	1	10	0.3	single	
	# 6	55.0	1	50	1.5	single	
	# 7	5.5	0.1	10	0.3	single	3
	# 8	5.5	0.1	50	1.5	single	
	# 9	55.0	1	10	0.3	single	
	# 10	55.0	1	50	1.5	single	
Control	Dark Fenton 1	5.5	0.1	10	0.3	single	7
	Dark Fenton 2	55.0	1	50	1.5	single	
	Dark Fenton 1f	5.5	0.1	10	0.3	2x(20) + 3x (5.0)	
	Dark Fenton 2f	55.0	1	50	1.5	2x(20) + 3x (5.0)	
	Coagulation 1	5.5	0.1	-	-	single	
	Coagulation 2	55.0	1	-	-	single	
	Solar only	-	-	-	-	-	

-: none

Samples were withdrawn during reactions so that (i) residual hydrogen peroxide (NOGUEIRA *et al.*, 2005), (ii) iron species (Fe²⁺, Total Fe) (ISO, 1998) and (iii) target compounds (15 and 60 min) could be quantified (UHPLC/TOF, Section 4.2.3). COD quantification was performed only before and after each of the proposed conditions. In order to stop reactions catalase enzyme (460 mg L⁻¹ in phosphate buffer) was added to each sample (enzyme solution: sample ratio of 0.1 mL:1.9 mL) prior to COD and TOC analyses (POOLE, 2004).

4.2.4.2 Solar photo-Fenton like (solar/iron/S₂O₈²⁻) at neutral pH

Solar photo-Fenton like experiments were also performed in the solar simulator illustrated in Figure 4.4 under similar conditions to those described for the traditional solar-photo-Fenton. These experiments were performed using sample 2 (Table 4.2). However, minimum and maximum iron concentrations applied for this process were lower and persulfate concentrations were equivalent to those applied for H₂O₂ in mol per liter (0.3 and 1.5 mM), which gives a higher concentration in mass of S₂O₈²⁻ when compared to H₂O₂, as shown in Table 4.4.

TABLE 4. 4 - Experimental conditions performed for the solar photo-Fenton like process at neutral pH in a solar chamber and controls

Type	Name	Fe ²⁺		S ₂ O ₈ ²⁻		Fe addition	pH
		mg L ⁻¹	mM	mg L ⁻¹	mM		
Assay	# 1	2.7	0.05	57.6	0.3	single	7
	# 2	2.7	0.05	288.2	1.5	single	
	# 3	27.5	0.5	57.6	0.3	2x(20) + 3x (5.2)	
	# 4	27.5	0.5	288.2	1.5	2x(20) + 3x (5.2)	
	# 5	27.5	0.5	57.6	0.3	single	
	# 6	27.5	0.5	288.2	1.5	single	
	# 7	2.7	0.05	57.6	0.3	single	3
	# 8	2.7	0.05	288.2	1.5	single	
	# 9	27.5	0.5	57.6	0.3	single	
	# 10	27.5	0.5	288.2	1.5	single	
Control	Dark Fenton 1	2.7	0.05	57.6	0.3	single	7
	Dark Fenton 2	27.5	0.5	288.2	1.5	single	
	Coagulation 1	2.7	0.05	-	-	single	
	Coagulation 1	27.5	0.5	-	-	single	
	Solar only	-	-	-	-	-	
	Solar/S ₂ O ₈ ²⁻	-	-	57.6	0.3	-	
	Solar/S ₂ O ₈ ²⁻	-	-	288.2	1.5	-	

-: none

In addition to Fe/S₂O₈²⁻, coagulation, and solar irradiation only, the control solar/S₂O₈²⁻ was also performed since S₂O₈²⁻ absorbs irradiation at 310 nm and may also be activated by heat (AHMED & CHIRON, 2014). At first, pH was adjusted to 7 or 3, iron was added by using a solution of FeSO₄ · 7H₂O (2 g L⁻¹ of Fe²⁺) and the sample was stirred in the dark for 5

minutes. Then, $S_2O_8^{2-}$ was added and the simulator was turned on. Samples were withdrawn during reaction for the assessment of (i) residual persulfate (LIANG et al., 2008) at 352 nm to eliminate interference due to iron absorption, (ii) iron species (Fe^{2+} and total) (ISO, 1998), and (iii) target compound quantification (UHPLC/TOF, Section 4.2.3). COD was monitored before treatment and after 60 minutes of reaction.

4.2.4.3 Traditional solar photo-Fenton and solar photo-Fenton like performed at semi-pilot scale

After analyzing the results obtained during traditional and solar photo-Fenton like in the solar chamber, reagent concentrations to be used in the semi pilot scale Raceway Pond Reactor (RPR) (Figure 4.4) were defined. The RPR is located at the rooftop of UFMG Engineering School, has a maximum volume of 28 L (water depth is at 12 cm), a length of 1.22 m and width of 0.2 m. The photo-reactor contains a paddlewheel which is connected to a motor, so the sample is mixed continuously during the experiment. A radiometer that measures UV irradiation (200-400 nm) (CUV 5Kipp&Zonen) is connected to the RPR. Irradiation measured every minute by this device is stored in a datalogger (METEON Kipp&Zonen) during the experiment. Once data is collected, accumulated UV irradiation (Q_{UV}) may be calculated per volume of sample (L) as according to (MALATO et al., 2009). As mentioned for at sections 4.2.4.1 and 4.2.4.2, sample 4 (Table 4.2) pH was adjusted to 7, and then reagents were added in the dark and reactions started when the RPR was uncovered.

In addition to the analyses mentioned for the experiments performed in bench scale, samples withdrawn during the optimum condition of each treatment performed in the RPR were also used to evaluate (i) total coliform and E coli removal during treatment, (ii) acute toxicity evolution, and (iii) kinetics of CEC removal during each treatment. Total coliform and acute toxicity analyses are described in section 4.4 below. In order to stop Fenton reaction after

each sampling, catalase enzyme (460 mg.L⁻¹ in phosphate buffer) was added to samples (enzyme solution: sample ratio of 0.1 mL:1.9 mL) withdrawn during traditional solar-photo Fenton prior to characterization (POOLE, 2004). Interruption of the reaction of Fe²⁺ with S₂O₈²⁻ was performed with the addition of ascorbic acid. Both of these quenching agents were selected since they have negligible effect on sample acute toxicity as reported in the literature and confirmed by blank tests (OLMEZ-HANCI *et al.*, 2014).

4.3 Bioassays

4.3.1 Acute toxicity tests

Acute toxicity of samples were analyzed using the Microtox® device (Model 500 Analyser SDI, Azur Environment, Workingham, England), which assesses the sensibility of luminescent marine bacteria *Allivibrio fischeri* to samples (ISO 11348-3:2007) (ISO, 2007). Luminescence emitted by bacteria is measured after 5, 15 and 30 minutes of exposure to non-treated and treated samples in different dilutions, and data is analyzed using the MicrotoxOmni® Software (81.9% Basic Test). Results are converted to Acute Toxicity Unit (a.T.u.) as according to equation 2.3:

$$\text{a.T.U.} = 100/\text{EC}_{50} \quad (\text{Equation 2.3})$$

Therefore, the higher the a.T.u. value, higher is the toxicity. The highest concentration assessed in the test is 81.9% which corresponds to 1.22 a.T.u. Thus, this is the detection limit for this test which means that only a.T.u. values above 1.22 are considered toxic.

4.3.2 Disinfection assays

Disinfection assays were performed to evaluate the decay of total coliform (TC) and *Escherichia coli* (Method 9223 A) as according to (APHA, 2012) after tertiary treatment. These methods explore the ability of these bacteria to cleave a chromogenic substance due to

the production of enzymes β -D-galactosidase and β -glucuronidase for TC and *E. coli*, respectively, thus producing chromogenic substances. In the presence of total coliform bacteria, there is a color change after 18 or 24 h which is a result of the cleavage of the chromogenic substrate (ortho-nitrophenyl- β -D-galactopyranoside, ONPG or red- β -D-galactopyranoside, CPRD) by β -D-galactosidase. Meanwhile, *E.coli* will be detected through absorbance changes at 365 nm which is the wavelength of absorbance of the product formed when β -glucuronidase cleaves 4-methyl-umbelliferyl- β -D-glucuronide (MUG). Table 4.5 shows the color of growth media when in the presence of these bacteria (positive growth). These methods were applied using *Colilert* kits from IDEXX and procedures were performed as according to manufacturer instructions which follow the *Standard Methods* (APHA, 2012).

TABLE 4.5 – Change of color on the substrate in the presence of Total coliform and *E coli*

Bacteria	Substrate	
	ONPG-MUG	CPRD - MUG
Total coliform	Yellow	Red or magenta
<i>E. coli</i>	Blue fluorescence	Blue fluorescence

4.4 RESULTS AND DISCUSSION

4.4.1 Traditional solar photo-Fenton (solar/Fe(II)/H₂O₂)

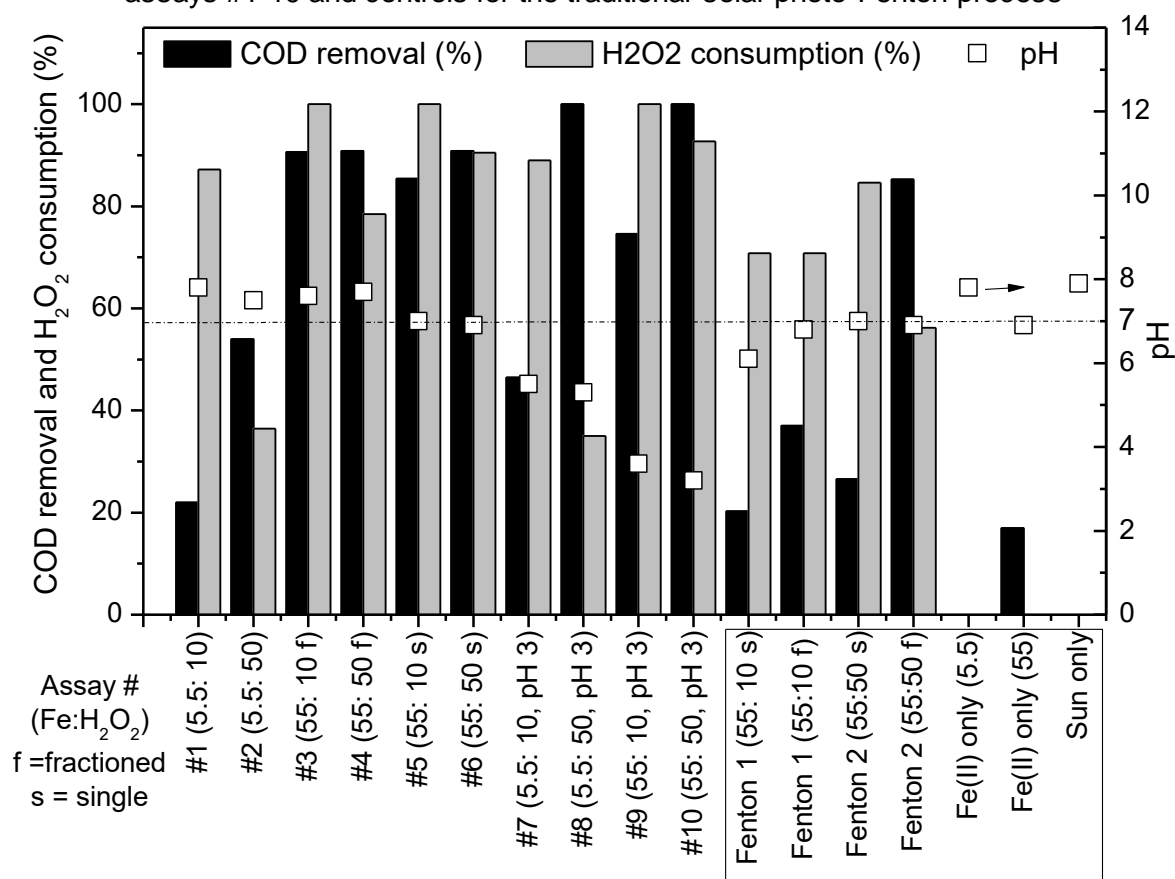
Figure 4.5 shows final COD removal and H₂O₂ consumption and pH obtained for all of the traditional solar-photo Fenton conditions tested in this study and controls. As expected, highest COD removal was obtained at pH 3, once this is the most favorable condition for the solar-photo-Fenton system. Therefore, before interpreting results obtained at neutral pH, it is important to evaluate H₂O₂ consumption and Fe²⁺ profiles obtained during assays performed at this pH.

4.4.1.1 Acidic pH

H₂O₂ consumption was equivalent to 100% and 92% in assays #9 (55 mg L⁻¹ of Fe²⁺ and 10 mg L⁻¹ of H₂O₂) and #10 (55 mg L⁻¹ of Fe²⁺ and 50 mg L⁻¹ of H₂O₂), respectively, in which

Fe(II) was available in its maximum concentration. As the reaction between Fe and H₂O₂ generates OH⁻, pH increased slightly to 3.6 and 3.2 in the end of both reactions (TARR, 2003). Meanwhile, for the reaction conducted with the lower concentration of iron, assays #7 and #8, pH was equivalent to 5.3 and 5.6 after one hour. In contrast to observations made by Carra *et al.*, (2013) and Freitas *et al.*, (2017), there was no drop in the pH for the conditions performed at pH 7, probably because a lower concentration of Fe(II) was used in this study when compared to these other authors. This is an advantage considering that no pH adjustment would be necessary after treatment.

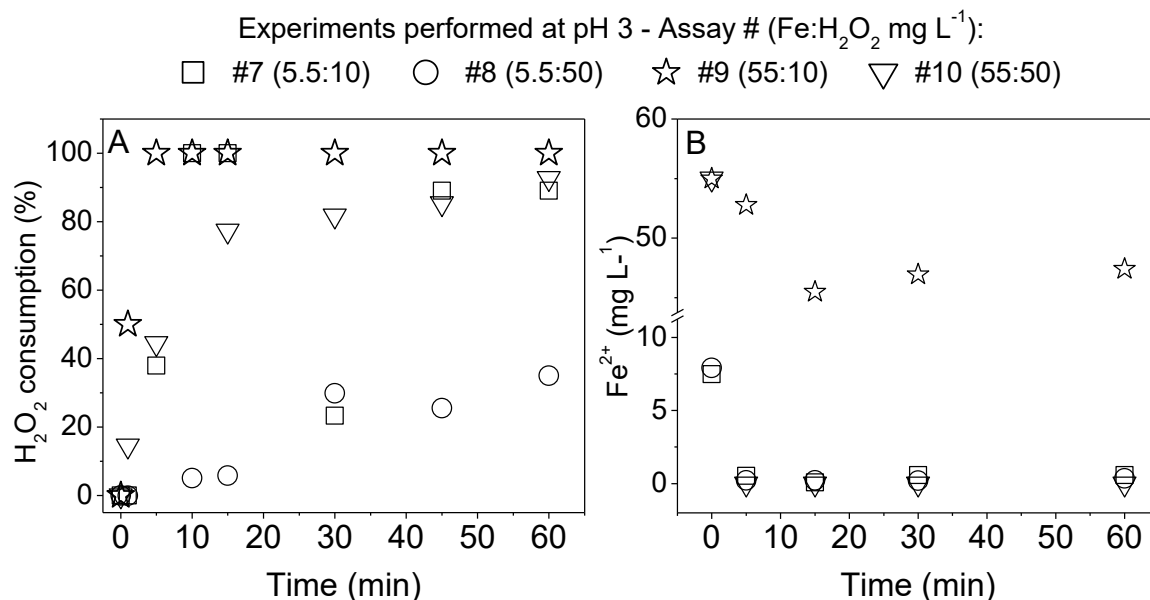
FIGURE 4.5 –COD removal (%) and H₂O₂ consumption (%) and final pH obtained after assays #1-10 and controls for the traditional solar photo-Fenton process



COD was below the detection limit (>99% removal) after 60 minutes of irradiation (1013 KJ/m²) in assays #8 (5.5 mg L⁻¹ of Fe²⁺ and 50 mg L⁻¹ of H₂O₂) and #10 (55 mg L⁻¹ of Fe²⁺ and 50 mg L⁻¹ of H₂O₂). As shown in Figure 4.6A, H₂O₂ was gradually consumed in

during assay #8, reaching 34% after 60 min (17 mg L^{-1} of remaining H_2O_2). In contrast, Fe(II) concentration dropped quickly to 0.2 mg L^{-1} within 5 minutes (Figure 4.6 B). Quick drop of Fe^{2+} probably occurred because H_2O_2 concentration was 10 times higher than that of iron. Therefore, all Fe(II) was promptly converted to Fe(III) through the Fenton reaction. Although Fe^{2+} regeneration is expected to occur under solar irradiation at acidic conditions this could not be observed during assay #8, probably because the regenerated iron was quickly consumed by excess H_2O_2 remaining in the system. In contrast, Fe^{2+} regeneration could be observed during assay #9 (55 mg L^{-1} of Fe^{2+} and 10 mg L^{-1} of H_2O_2) (Figure 4.6B) during which Fe^{2+} concentration was higher and H_2O_2 was promptly consumed within 5 minutes. In addition, considering that H_2O_2 was in excess during experiment #8, self-scavenger reactions probably occurred in the system, with the formation of H_2O_2 from hydroxyl radicals, thus limiting H_2O_2 consumption in (TARR, 2003).

FIGURE 4. 6 – (A) H_2O_2 consumption (%) and (B) Fe^{2+} concentration during the assays conducted in acidic pH



On the other hand, in assay #10 (55 mg L^{-1} of Fe^{2+} and 50 mg L^{-1} of H_2O_2), 45% of the H_2O_2 was consumed within 5 minutes, due to the Fenton reaction, as a consequence, Fe(II) quickly

dropped to nearly zero. Similarly to assay #8, in assay #10, it is likely that Fe(II) regeneration did take place, as H₂O₂ consumption continued to occur along reaction. However, this could not be observed during Fe(II) analysis due to rapid reaction between iron and remaining H₂O₂. For assay #7, in which the lowest concentration of both reagents were applied, COD removal was limited to 46% while H₂O₂ consumption was 89%, with only 2 mg L⁻¹ remaining in the system, thus COD removal was limited by lack of reagents in the system.

Therefore, considering all assays applied at pH 3 (#7, 8, 9 and 10), assay #8, which reached 100% COD removal using the lowest concentration of iron (5.5 mg L⁻¹; 0.1 mM), may be considered the best condition with regard to COD removal and reagent consumption. These results are in agreement with Miralles-Cuevas et al., (2017), who conducted solar photo-Fenton at acidic pH in a CPC pilot plant for the removal of CEC from MWWTP effluent. As H₂O₂ consumption was limited to 34% in this assay, initial H₂O₂ concentration could be optimized to an even lower concentration at this pH. However, lower concentrations are probably not applicable for reactions conducted at neutral pH which require higher concentrations of reagents, mainly iron, to achieve the same levels of removal obtained at acidic pH (CARRA et al., 2013).

4.4.1.2 Neutral pH

As it was seen for some of the solar photo-Fenton conditions conducted at acidic pH, COD removal was above 85% in four assays conducted at neutral pH: assays #3, #4, #5 and #6 (Figure 4.5). In all of these conditions, 55 mg L⁻¹ of Fe(II) were applied to the system, although in assays #3 and #4, this reagent was added intermittently during reaction which should contribute to higher concentrations of dissolved iron in the system throughout the treatment (CARRA *et al.*, 2014). Meanwhile, in assays #1 and 2, the lowest iron concentration (5.5 mg L⁻¹, 0.1 mM) was applied with 10 and 50 mg L⁻¹ of H₂O₂, respectively. COD removals in these assays were limited to 22 and 44% respectively. In contrast, these same

conditions led 46 and >99% removal of COD at acidic pH, thus confirming the need to use a higher concentration of reagents at near neutral pH when compared to pH 3.

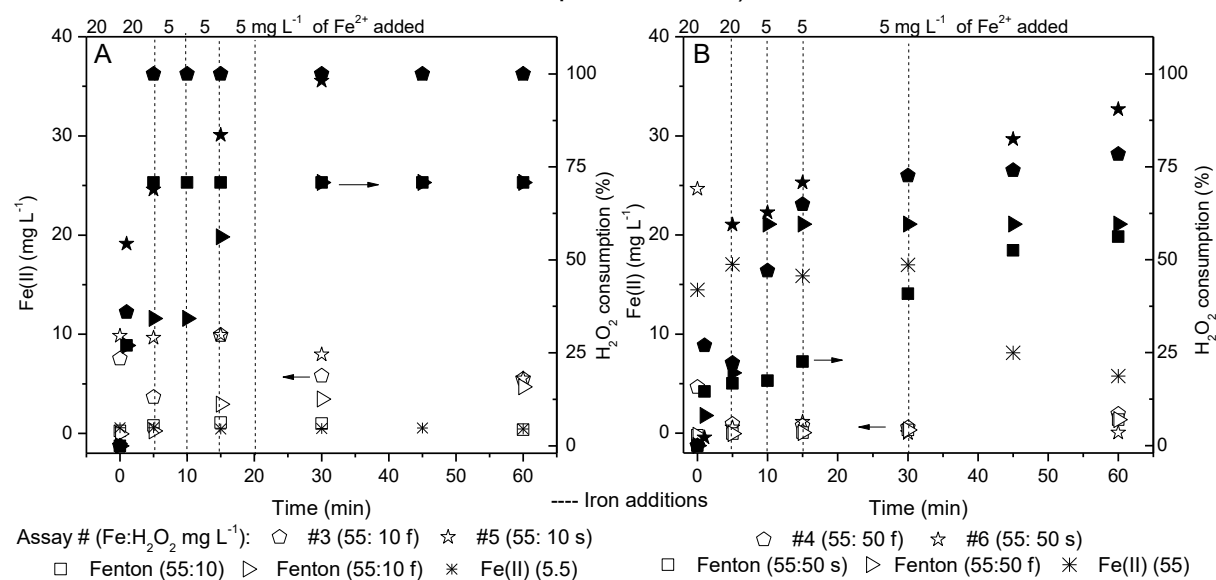
During assay #3, iron was added at times 0 (20 mg L⁻¹), 5 (20 mg L⁻¹), 10 (5 mg L⁻¹), 15 (5 mg L⁻¹) and 30 min (5 mg L⁻¹) (Total Fe²⁺ added: 55 mg L⁻¹) and all H₂O₂ (10 mg L⁻¹) was added at once in the beginning. This same condition was applied in assay #5, yet iron was added in a single addition of 55 mg L⁻¹. Both systems led to 100% H₂O₂ consumption, due to reduced concentration of this reagent in the system (Figure 4.5). COD removal in assay #3 (fractioned iron addition) reached 90% being slightly higher than that observed in assay #5 (85%) (Figure 4.5).

Figure 4.7A shows Fe²⁺ concentrations and H₂O₂ consumption during assays #3, #5 and the dark Fenton reactions performed as control using the same concentrations and iron additions. When 55 mg L⁻¹ of iron were added all at once (assay #5), 54% of the H₂O₂ were consumed in the first minute of reaction, while in assay #3, H₂O₂ consumption was equivalent to 36% in one minute since Fe(II) was lower in the beginning of reaction (20 mg L⁻¹). However, H₂O₂ consumption in assay #3 increased abruptly within 5 min and before the second iron addition reaching 100% in 5 minutes. Meanwhile, for assay #5, in which iron was added all at once, 58% of total H₂O₂ were consumed in 5 minutes and 100% H₂O₂ consumption were only reached after 30 minutes. Considering that both reactions were conducted at pH 7 and that iron precipitated generating turbidity, higher turbidity observed in assay #5 from the beginning of reaction probably hindered photo-Fenton reactions, which did not occur in assay #3 (FREITAS et al., 2017). Although limited by turbidity, iron regeneration did occur in assays #3 and #5 as Fe²⁺ concentrations were higher than observed during both dark Fenton reactions performed as controls (Figure 4.7A). As expected, H₂O₂ consumption during dark Fenton reactions performed with the same concentration of reagents applied in assays #3 and

#5 were limited to 70% which also resulted in lower COD removal (20 and 37% for the single and fractioned iron addition respectively) as shown in Figure 4.5.

Due to iron regeneration, Fe(II) concentration was stable at around 10 mg L^{-1} during assay #5 decreasing slightly only after 15 minutes. In the end of assays #3 and #5, Fe(II) concentration was similar in both, which was expected since total iron and H_2O_2 consumption were similar in both systems. Considering that H_2O_2 consumption was lower during the non-irradiated Fenton (55:10 f) reaction (Figure 4.7A), it is possible to observe an increase in Fe(II) concentration in this system in the end of reaction which is due to the iron addition strategy.

FIGURE 4.7 – (A) COD removal and H_2O_2 consumption obtained during assays #3 and #5 and Fenton performed as controls and (B) COD removal and H_2O_2 consumption obtained during assays #4 and #6 and Fenton performed as controls. (Fe(II) – \square empty; H_2O_2 consumption – \blacksquare filled)



In contrast to results obtained in assays #3 and #5, for which the lowest concentration of H_2O_2 was used, Fe(II) was below 0.5 mg L^{-1} in assays #4 and #6 (50 mg L^{-1} of H_2O_2) (Figure 4.7B) due to faster reaction between Fe(II) and H_2O_2 generating Fe(III) as H_2O_2 was more available in the system. The same occurred for both dark Fenton reactions performed as controls. In contrast, Fe(II) concentrations were higher in the absence of H_2O_2 , decaying towards the end

of reaction due to iron precipitation. Despite intermittent additions of Fe(II) in assay #4, it was not possible to observe an increase in Fe(II) concentration during reactions since H₂O₂ was in excess in the system and samples were taken only before iron addition. As it was observed by Carra *et al.*, (2013), Fe(II) decays quickly after intermittent additions.

In assay #6, H₂O₂ consumption occurred within the first minute of reaction, although assay #4 reached a similar consumption pattern only after the second addition of iron (Figure 4.7B). Final H₂O₂ consumption was 78% for assay #4 and 92 % for assay #6, yet both systems reached 90% COD removal, thus confirming excess of H₂O₂. In the dark Fenton reactions conducted using the same concentrations of reagents, H₂O₂ consumption occurred gradually, reaching a maximum of 56% consumption in the reaction with intermittent iron addition. Considering that Fe²⁺ regeneration occurs in a much slower rate in the dark and that H₂O₂ consumption occurred gradually, it is likely that heterogeneous Fenton also took place in this reaction (FREITAS *et al.*, 2017).

Hence, with regard to MWWTP effluent COD removal and H₂O₂ consumption via solar photo-Fenton at neutral pH (Figure 4.5), assay #3 may be selected as the best treatment condition, since it reached more than 90% removal using the lowest concentration of H₂O₂. This was only possible due to intermittent iron additions performed in the system.

4.4.1.3 CEC removal via traditional solar photo-Fenton

Solar photo-Fenton at acidic pH was proved effective as tertiary treatment for the removal of various CEC from MWWTP effluent (CARRA *et al.*, 2014; ARZATE *et al.*, 2017; GIANNAKIS *et al.*, 2017). However, research on the use of this treatment at neutral pH is novel and requires more attention, since operating at neutral pH may reduce treatment costs (MIRALLES-CUEVAS *et al.*, 2017). Therefore, the removal of three target CEC by solar photo-Fenton at neutral pH was evaluated in this study and compared to reference

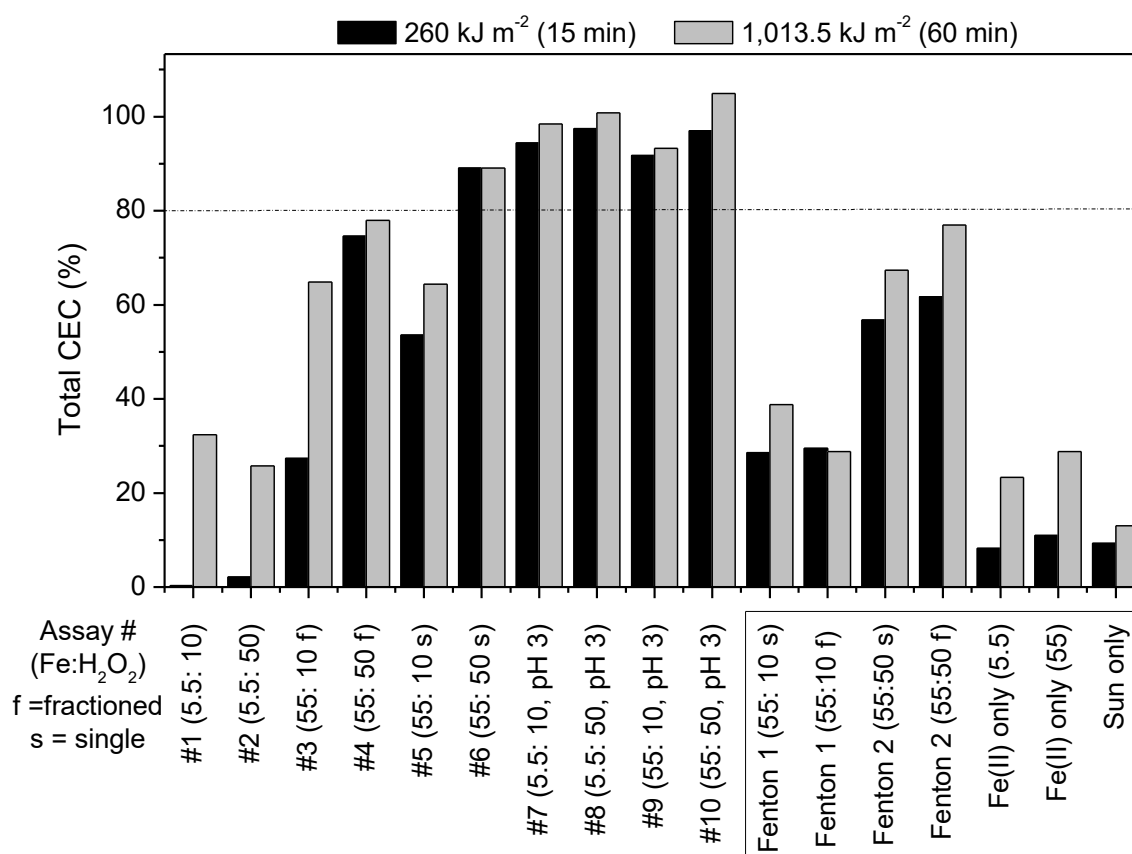
experiments conducted at acidic pH and controls performed in the absence of solar irradiation. Considering that Swiss legislation is, to this date, the only legislation related directly to the removal of emerging contaminants from municipal sewage prior to disposal in surface waters, and requires a total removal of 80%, this percentage was used as a reference to evaluate the performance of treatment conditions proposed in this study.

As it is shown in Figure 4.8, when Fe(II) (5.5 or 55 mg L⁻¹) or solar irradiation were applied alone to the spiked matrix, CEC removal rates were limited to 23, 28 and 19%, thus confirming the need of applying chemical reagents for the appropriate removal of CEC. CEC decay under solar irradiation alone may occur via direct and indirect solar photolysis. In the first one, compounds absorb photons, leading to degradation. In indirect photolysis, matrix components, such as dissolved organic matter and ions (nitrate, phosphate, among others), act as photosensitizers leading to the formation of oxidative radicals in the system (WANG *et al.*, 2017). Considering that target compounds investigated in this study do not absorb light in the UV-Vis range (>310 nm) (data not shown). It is likely that indirect photolysis contributed to 19% degradation observed during treatment in the solar box simulator without the addition of chemical reagents. Regarding the removal by coagulation alone, complexation with iron may be the cause of pollutant decay, as it was seen for amoxicillin in wastewater (NORTE *et al.*, 2018). However, this mechanism is strongly related to the chemical structure of each compound.

Although COD removal percentages indicated that assay #3 was effective as tertiary treatment, reagent concentrations used in this assay did not lead to 80% removal of target CEC (Figure 4.8). Therefore, in neutral pH, a higher concentration of hydrogen peroxide is needed to guarantee the oxidation of target compounds when compared to natural organic matter present in MWWTP effluent. As the organic content corresponding to CEC is negligible when

compared to that of natural organic matter present in MWWTP effluent (BERNABEU *et al.*, 2012), it is extremely important to evaluate the decay of target compounds to guarantee their removal, instead of evaluating COD alone.

FIGURE 4. 8 – Total CEC removal obtained after 260 and 1,013 kJ m⁻² of accumulated energy in each assay performed in neutral and acidic pH and controls



As observed in Figure 4.8, all conditions performed at pH 3 led to more than 90% CEC removal within 15 min of reaction, even assay #7, in which the lowest concentration of both reagents were applied. This occurred due to higher availability of Fe(II) in acidic pH and higher concentration of Fe(OH)²⁺ which absorb irradiation in the UV-Vis range, leading to an extra pathway for the formation of hydroxyl radicals.

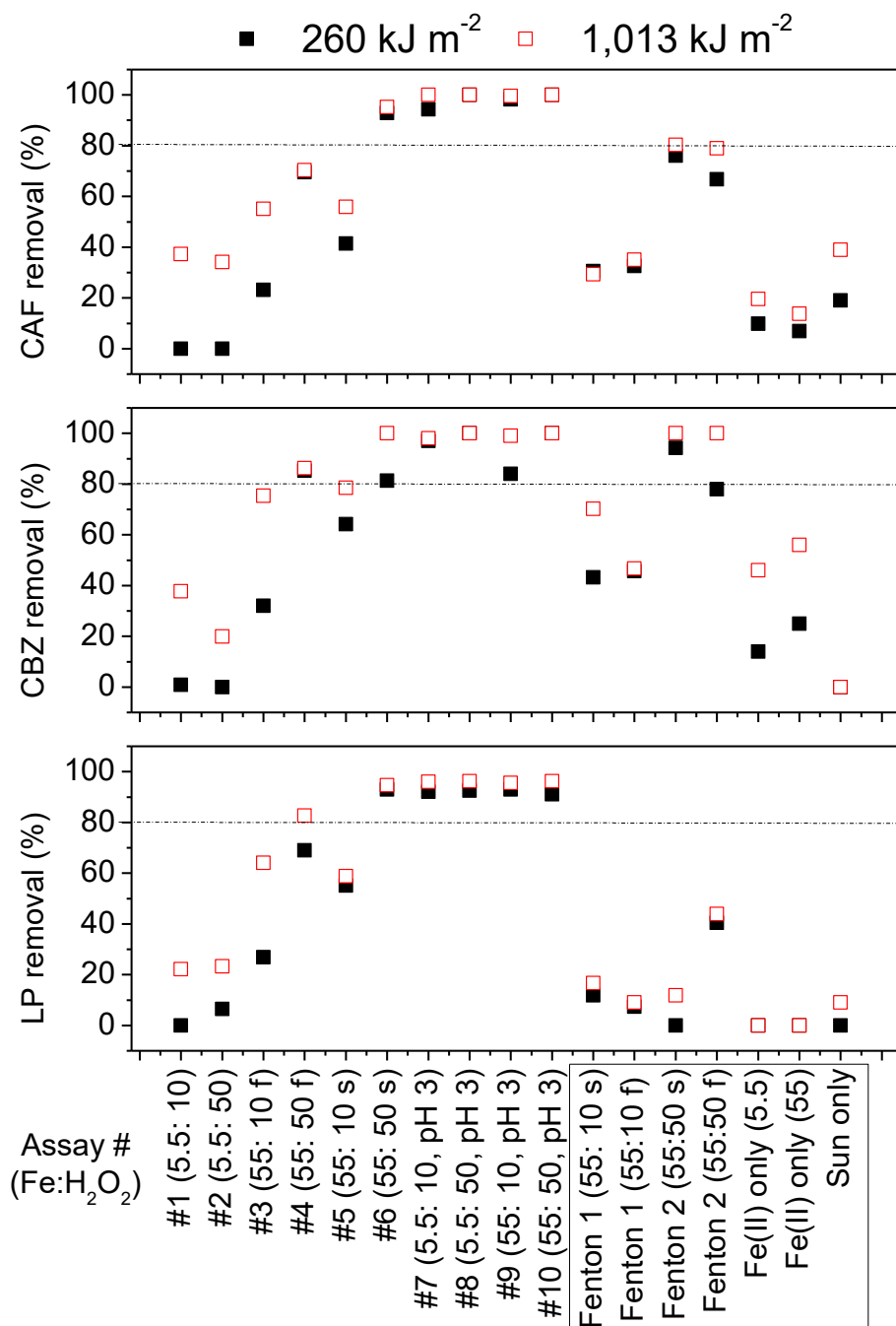
Nevertheless, in neutral pH, only assay #6 led to more than 80% CEC removal (Figure 4.8). Indeed, percent removal during this assay was the same after 260 and 1,013 kJ m⁻² of accumulated irradiation, indicating that CEC removal occurred quickly due to Fenton reaction, as shown for the control performed in the dark (Fenton 2 s) which achieved 56 and 67% of CEC removal. However, solar irradiation did contribute to an increase in the removal, as CEC removal was higher under solar irradiation. Interestingly, assay #4, in which intermittent iron additions were applied, a similar behavior was observed, as 74% removal were obtained in 15 min and 77% after 60 min. As 45 mg L⁻¹ of Fe(II) were present in assay #4 after 15 minutes of reaction, when compared to 55 mg L⁻¹ in assay #6, iron concentration was not sufficient to reach 80% removal in 15 minutes. Despite that, iron additions performed in the sequence did collaborate to a slight increase in the removal of CEC reaching 77% towards the end of reaction. Thus indicating that if 45 mg L⁻¹ of iron had been applied from the beginning, when H₂O₂ concentration was at maximum, with smaller iron additions later, a better removal rate could have been achieved (CARRA *et al.*, 2013).

Caffeine removal during each assay and controls is shown in Figure 4.9. CAF decay did occur (39% removal) in the absence of chemical reagents as a result of direct and indirect photolysis. This was also observed by Wang *et al.*, (2017) who confirmed that the degradation of CAF occurred due to the generation of radicals from dissolved organic matter and nitrate ions. Indeed, solar photolysis was more preminent than the complexation with iron for this compound which reached a maximum of 19%.

Regarding the photo-Fenton conditions tested at neutral and acidic pH, CAF removal is very similar to what was observed for the total removal, as only assays #6 (neutral pH) and #7 to 10 (acidic pH) reached more than 80% removal. Meanwhile, total removal of CAF (non-spiked matrix, CAF concentration in the ng L⁻¹ range) via solar photo-Fenton at near neutral

pH using intermittent iron additions ($3 \times 20 \text{ mg L}^{-1}$) was obtained elsewhere (FREITAS *et al.*, 2017). Interestingly, the dark Fenton performed at neutral pH using the highest concentrations of both reagents also led to 80% removal.

FIGURE 4.9 – Removal of CAF, CBZ and LP obtained after 260 and 1,013 kJ m^{-2} of accumulated energy in each assay performed in neutral and acidic pH and controls



In contrast to what was observed for CAF, CBZ removal did not occur under photolysis alone in the presence of matrix constituents and the complexation with iron reached up to 56% removal of CBZ when 55 mg L⁻¹ of Fe(II) were applied. Da Costa *et al.*, (2018) observed no photolysis of CBZ in pure water and 20% removal of CBZ in water via ferric coagulation in the presence of 1.5 mg L⁻¹ of Fe(III), which is below the concentration used here. In addition, dark Fenton was as effective on the removal of this compound as the solar photo-Fenton performed at neutral and acidic pH. Solar photo-Fenton conducted in acidic pH in a RPR reactor using 5 mg L⁻¹ of iron and 100 mg L⁻¹ of H₂O₂ reached total removal of CBZ in water, while here this same rate was obtained in MWWTP effluent in neutral pH using 55 mg L⁻¹ of iron and 50 mg L⁻¹ of H₂O₂. Higher concentration of reagents to achieve total removal were necessary in this study due to higher pH, which favors Fe(II) precipitation, and due the occurrence of secondary consumption of hydroxyl radicals by matrix components.

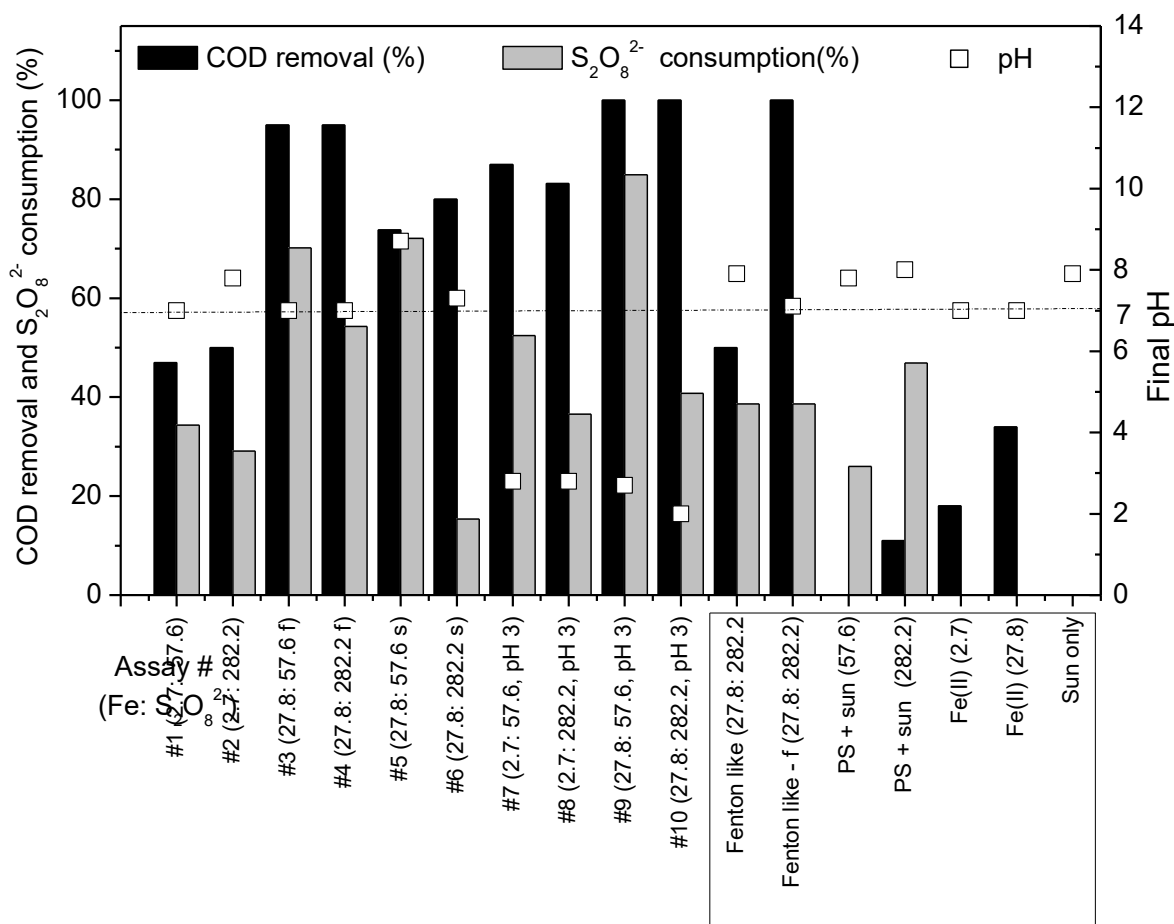
Curiously, 80% removal of LP was only reached in the photo-Fenton systems (assays #6 to 10) and both solar irradiation and coagulation played negligible roles on the removal of this compound. In addition, assay # 4, performed at neutral pH was also affective on the removal of LP. It is important to observe that more than 80% removal of LP was achieved within 15 minutes of reaction in all assays that were effective on the removal of this compound. This was also observed for CAF and CBZ and indicates that an optimization of treatment conditions and reagent concentrations could lead to satisfactory removal rates using a lower concentration of iron even at neutral pH.

4.4.2 Solar photo-Fenton like (solar/Fe(II)/S₂O₈²⁻)

In the solar photo-Fenton like treatment, H₂O₂ is replaced by S₂O₈²⁻. This reagent reacts with Fe(II) generating sulfate radicals in the system. Similarly to the traditional photo-Fenton process, the effectiveness of this process is also limited by the pH, as the reaction between

Fe(II) and $S_2O_8^{2-}$ is favored when dissolved Fe(II) is present in the system. This process has been proven effective for the removal of CEC from MWWTP effluent (AHMED & CHIRON, 2014; MIRALLES-CUEVAS *et al.*, 2017). Despite efforts from the scientific community to perform the traditional solar photo-Fenton at neutral pH, to this date, no studies have been published on the application of the solar photo-Fenton like process at neutral pH as it is proposed in this study. Figure 4.10 shows COD removal percentage, $S_2O_8^{2-}$ consumption and pH values obtained after 60 minutes of all of the assays performed for the solar photo-Fenton process at acidic and neutral pH and controls.

FIGURE 4. 10 – COD removal (%) and H_2O_2 consumption (%) and final pH obtained after assays #1-10 and controls performed for the solar photo-Fenton like process



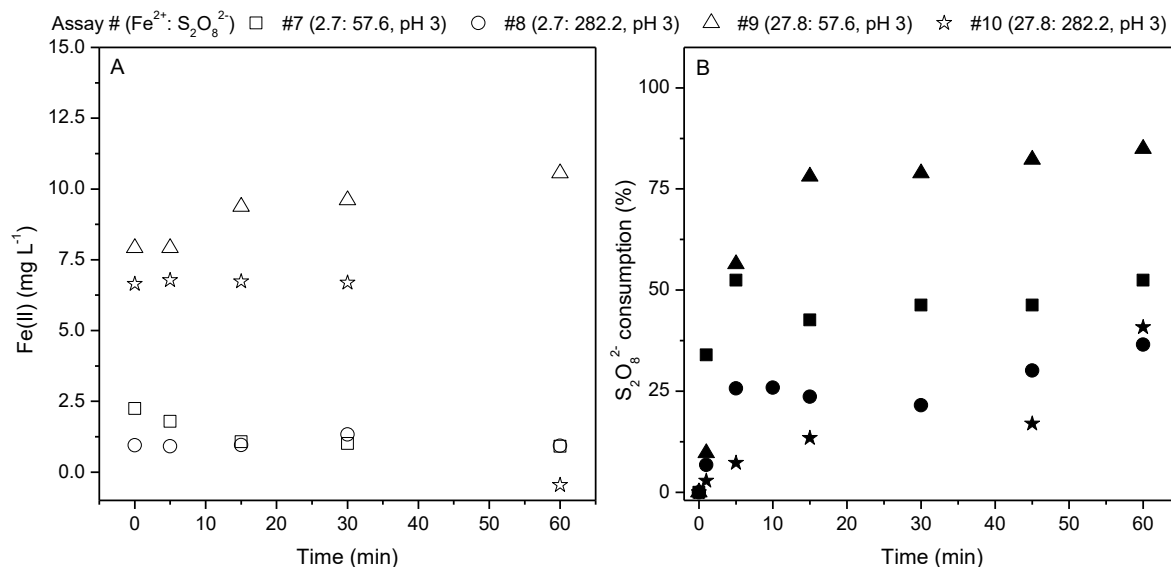
Considering that this reaction is favored at acidic pH, it is important to interpret results obtained during the conditions performed in this condition before interpreting the results obtained at neutral pH.

4.4.2.1 Acidic pH

As shown in Figure 4.10 for assays #7-10 performed in acidic pH, COD removal was maximum for assay #9 and #10, for which the highest concentration of Fe(II) was applied in the presence of minimum and maximum $S_2O_8^{2-}$ concentrations. $S_2O_8^{2-}$ consumption was nearly 85% in assay #9 and was limited to 40% in assay #10, which had nearly five times the initial concentration of $S_2O_8^{2-}$ present in assay #9. Therefore, 167 mg L^{-1} of $S_2O_8^{2-}$ remained in the system after assay #10. As this reagent was in excess self scavenger reactions probably occurred, leading to the regeneration of $S_2O_8^{2-}$ during this reaction (KWON *et al.*, 2015). For both reactions pH decay was observed.

As shown in Figure 4.11 A, in assays #7 and 8, for which the lowest concentration of Fe(II) was applied, the concentration of this reagent dropped within the first 10 minutes of reaction, when $S_2O_8^{2-}$ consumption reached its maximum level for both systems (Figure 4.11 B) and stabilized after that and no Fe(II) regeneration could be observed. Meanwhile, for assays #9 and 10, in which the highest concentration of Fe(II) was applied, Fe(II) regeneration could only be observed during assay #9 after $S_2O_8^{2-}$ consumption stabilized at a maximum of 84%. In contrast, in assay #10, no regeneration was observed as $S_2O_8^{2-}$ was slowly consumed in the beginning of reaction reaching higher consumption after 30 minutes, when Fe(II) concentration dropped abruptly. These results confirm that $S_2O_8^{2-}$ was in excess in assay #10, as suggested earlier.

FIGURE 4. 11 – (A) Fe(II) concentration and (B) S₂O₈²⁻ consumption (%) obtained during assay #7, 8 9 and 10 conducted at acidic pH using the solar photo-Fenton like process. Empty symbols (□) represent Fe(II) concentrations and filled symbols (■) represent PDS consumption.



Therefore, when considering COD removal and S₂O₈²⁻ consumption obtained for all of the solar photo-Fenton like conditions performed at acidic pH, reagent concentrations applied in assay #9 were the most favorable reaching 100% COD removal and 84% PDS removal. This is in agreement with Ahmed & Chiron, (2014) who found an optimum Fe(II): S₂O₈²⁻ ratio of 2:1, as obtained here.

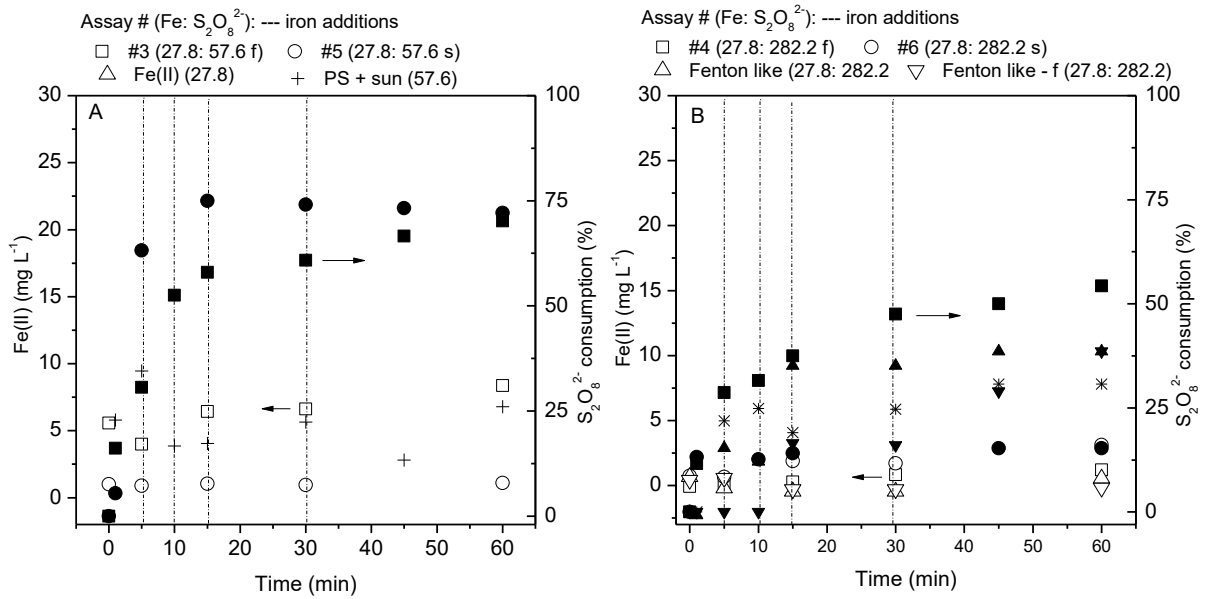
4.4.2.2 Neutral pH

When it comes to solar photo-Fenton like assays performed at neutral pH, assays #3, 4, 5 and 6, were the most favorable for the removal of COD (Figure 4.10). As expected, assays #3 and #4, during which intermittent iron additions were performed, showed higher COD removal (95%) when compared to assays #5 and #6, in which iron was added all at once using the same concentrations of S₂O₈²⁻ applied in assay #3 and #5, respectively. This indicates that the strategy proposed by Carra *et al.*, (2014) for the solar photo-Fenton, may also be effective for the solar photo-Fenton like process. Due to reduced Fe(II) concentrations in the system, assays #1 and #2 led to limited 50% COD removal and 34 and 29% S₂O₈²⁻ consumption,

respectively. In addition, as observed for traditional solar photo-Fenton reactions, no pH decay was observed after solar photo-Fenton like reactions performed at neutral pH. In fact, an increase in pH was observed for assays #1 to 6 and controls. This is an advantage considering that no pH adjustment must be performed after treatment and that hydroxyl radicals may be generated as sulfate radicals react with OH^- (WACLAWECK *et al.*, 2017).

Figure 4.12 shows Fe(II) concentration and $\text{S}_2\text{O}_8^{2-}$ consumption profiles obtained during solar photo-Fenton like assays #3 to #6 and controls performed in the same conditions. During assays #5, performed using the lowest concentration of $\text{S}_2\text{O}_8^{2-}$ (Figure 4.12 A), Fe(II) concentration was stable at reduced values since the beginning of reaction and $\text{S}_2\text{O}_8^{2-}$ was promptly consumed in the first five minutes of reaction. Meanwhile, in assay #3, during which Fe(II) was added intermittently during reactions, Fe(II) concentration was stable at nearly 5 mg L^{-1} , thus contributing to gradual $\text{S}_2\text{O}_8^{2-}$ consumption throughout the treatment. It is important to observe that solar irradiation alone led to 25% $\text{S}_2\text{O}_8^{2-}$ consumption in 60 min, which probably occurred because this reagent absorbs UV-Vis irradiation at 320 nm and also undergoes temperature decay (AHMED & CHIRON, 2014).

FIGURE 4. 12 – (A) Fe(II) concentration and (B) S₂O₈²⁻ consumption (%) obtained during assay #3 and 5 and controls and (B) Fe(II) concentration and S₂O₈²⁻ consumption (%) obtained during assay #4 and 6 and controls Empty symbols(□) represent Fe(II) concentrations and filled symbols (■) represent PDS consumption.

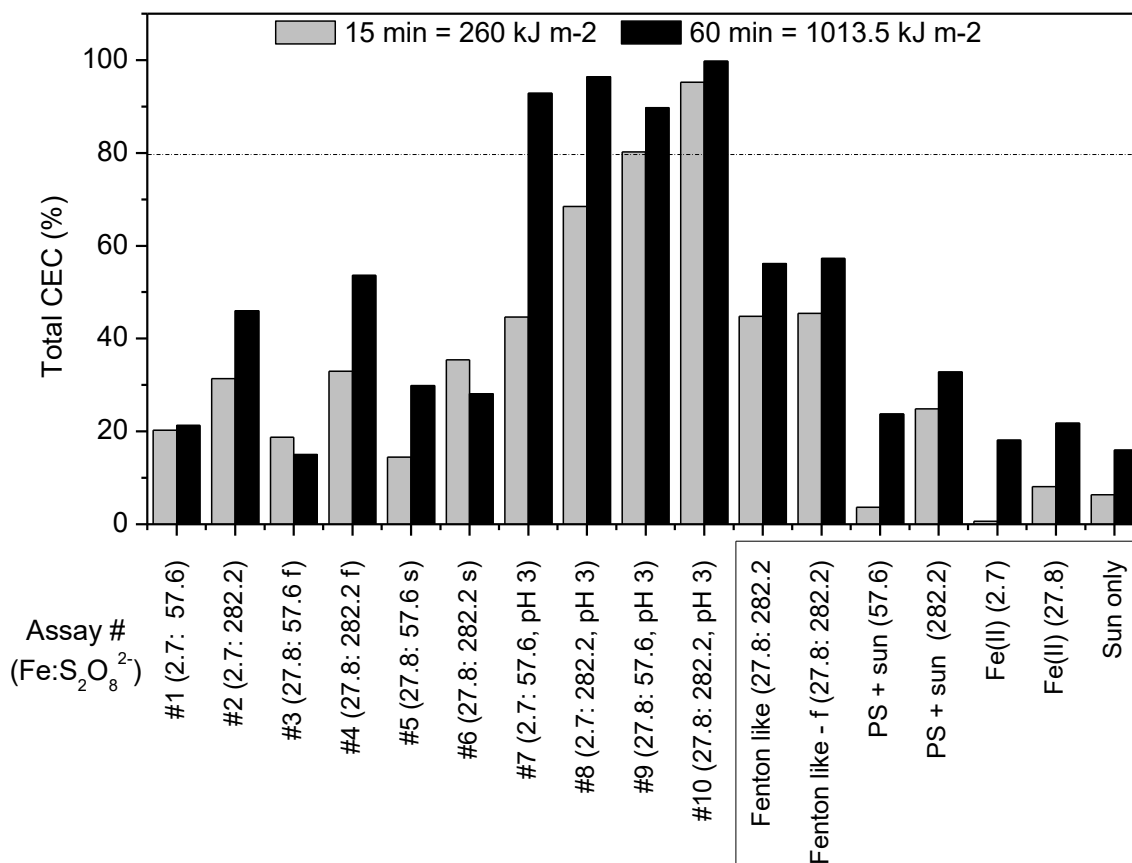


In contrast, during assays #4 and 6, in which highest concentration of S₂O₈²⁻ was applied, Fe(II) concentrations were reduced during the entire reaction and it was not possible to observe an increase in Fe(II) concentration after intermittent additions, since the Fe(II) was probably immediately converted to Fe(II) due to the Fenton like reaction. As intermittent Fe(II) additions were performed during assay #4, S₂O₈²⁻ was gradually consumed reaching 54% in the end of reaction. On the other hand, there was no S₂O₈²⁻ decay in assay #6, in which Fe(II) was added all at once. PDS decay was also confirmed to occur during Fenton reactions conducted using the same conditions applied in assay #4 and #6 and for solar irradiation only (25%). Negligible S₂O₈²⁻ decay in assay #6 probably occurred due to high turbidity observed from the beginning of reaction, thus limiting Fe(II) regeneration and PDS decomposition by light absorption (FREITAS *et al.*, 2017).

4.4.2.3 CEC removal via solar photo-Fenton like at neutral pH

Despite satisfactory COD removal via solar photo-Fenton like at neutral pH, none of the conditions applied for this process at neutral pH were able to remove more than 80% of total CEC, as shown in Figure 4.13.

FIGURE 4.13 – Total CEC removal obtained after 260 and 1,013 kJ m⁻² of accumulated energy in each assay performed in neutral and acidic pH and controls



In contrast, all of the four conditions performed at acidic pH were effective for CEC removal within 15 minutes of reaction (260 kJ m⁻² of accumulate energy). More than 90% removal of CEC, including CAF, were achieved by other authors using this solar photo-Fenton like treatment using 55 (0.1 mM) of Fe(II) and 50 mg L⁻¹ of S₂O₈²⁻ at pH 3 (MIRALLES-CUEVAS *et al.*, 2017). The same concentration of Fe(II) with 0.2 mM of persulfate were also successful on the removal of carbamazepine via solar photo-Fenton like at acidic pH (AHMED & CHIRON, 2014). Results obtained here at acidic pH are more satisfactory,

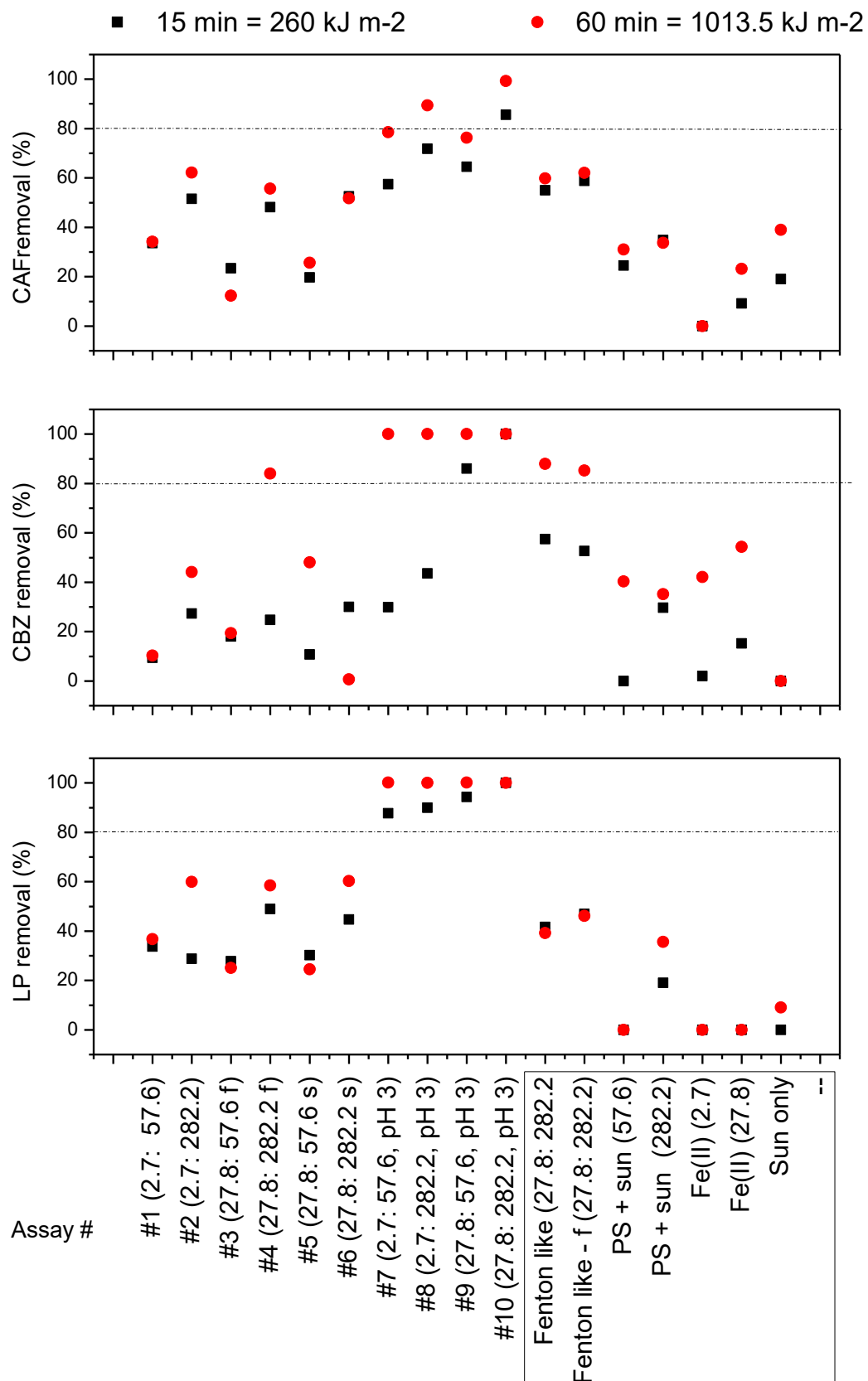
considering that assay #7 reached 92% total COD removal with 2.75 mg L⁻¹ of Fe(II) (0.05 mM) and 57.6 mg L⁻¹ of persulfate (0.3 mM). The best Fe:H₂O₂ here molar ratio was 1:6, which is similar to that obtained as the optimum ratio in Wang *et al.*, (2015), when treating sulfamethazine via solar/Fe(II)/S₂O₈²⁻ under UV-Vis LED irradiation.

Regarding reactions performed at neutral pH, CEC removal obtained in the irradiated assay #4 were similar to those obtained in the dark Fenton like reaction performed with the same concentrations of reagents, thus suggesting that CEC removal was not enhanced by solar irradiation. There are two possible reasons for this outcome: (i) Fe(II) concentration was too low considering that reactions were conducted in neutral pH (CARRA *et al.*, 2014) and (ii) due to turbidity generated by Fe(II) precipitation, Fe(II) regeneration was hindered thus leading to similar behavior in the irradiated and non irradiated systems as observed in Figure 4.12 for PDS in these systems (FREITAS *et al.*, 2017).

Interestingly, S₂O₈²⁻ alone (282, 8 mg L) under solar irradiation led to 32% removal of target CEC at neutral pH, which probably occurred due light absorption by S₂O₈²⁻ and thermal decomposition of this reagent, leading the formation of sulfate radicals. Ahmed & Chiron, (2014) achieved 8% of carbamazepine removal via solar/S₂O₈²⁻ at acidic pH. Higher CEC removal obtained here may be related to the pH, once hydroxyl radicals are likely to be formed when sulfate radical reacts with OH⁻ ions, thus contributing to higher removal of target compounds (WACLAWECK *et al.*, 2017).

Regarding CAF, only the reactions conducted at acidic (#7 to 10) pH reached 80% removal of this compound (Figure 4.14). These are the same assays that led to proper removal of total CEC. In the traditional solar photo-Fenton system, results obtained for CAF also matched with total CEC removal. Therefore, suggesting that CAF could be explored as an indicator of total CEC removal for oxidative processes (BUERGE *et al.*, 2003).

FIGURE 4. 14 - CAF, CBZ and LP removal obtained after 260 and 1,013 kJ m⁻² of accumulated energy during solar photo-Fenton like assay performed in neutral and acidic pH and controls



In neutral pH, maximum CAF removal (62%) was achieved during assay #2 (2.7: 282.2 mgL⁻¹ of Fe(II) and PDS, respectively). Meanwhile, the dark Fenton-like assay performed with the highest concentrations of both reagents using intermittent iron addition strategy reached 61% removal. Therefore, lower concentrations of reagents were necessary to achieve the same removal rate obtained under solar irradiation.

Apart from solar photo-Fenton like reactions performed at acidic pH, assay #4 (27.5: 282.2 mgL⁻¹ of Fe(II) and S₂O₈²⁻, respectively) and dark Fenton-like reactions conducted using the same concentrations of reagents at neutral pH were also effective on the removal of CBZ (Figure 4.14). As assay #4 was conducted using the intermittent iron addition strategy, it is likely that continuous availability of this reagent contributed to appropriate removal of CBZ. Despite Fe(II) concentrations used for the solar photo-Fenton like assay were lower than those applied for the traditional solar photo-Fenton, the complexation with iron also led to 50% CBZ removal here as it was seen earlier. This suggests that CBZ is likely to make complexes and precipitate with iron at neutral pH. This phenomenon may also have occurred during the dark Fenton like reactions, thus contributing to effective removal rates during this process.

When it comes to LP, solar photo-Fenton-like reaction conducted at acidic pH are much more effective than all of the other conditions tested. Interestingly, the solar/ S₂O₈²⁻ system at the highest concentration of this reagent did lead to 35% removal of this compound.

4.4.3 Traditional solar photo-Fenton and solar photo-Fenton like (solar/Fe(II)/S₂O₈²⁻) at neutral pH conducted at semi-pilot scale RPR

Results indicated that iron concentrations applied in the solar photo-Fenton like system were not adequate for considerable S₂O₈²⁻ consumption. As minimum and maximum iron concentrations applied for the solar/Fe/H₂O₂ system were two times higher than those applied in the solar/Fe/S₂O₈²⁻ system, iron did not limit H₂O₂ consumption in the traditional process.

In addition, only the experiment performed using maximum concentrations (50 mg L⁻¹ of H₂O₂ and 55 mg L⁻¹ of Fe²⁺) of both reagents for the traditional solar-photo-Fenton performed at neutral pH in the solar chamber led to satisfactory removal of CEC. Therefore, 55.5 mg L⁻¹ of iron, added intermittently to the reactor, was the concentration chosen to be applied in semi-pilot scale for both systems. Regarding oxidant concentrations, 50 mg L⁻¹ were maintained for the traditional solar photo-Fenton and the equivalent in mols of S₂O₈²⁻ was used for the alternative process (282.2 mg L⁻¹). Experiments were performed using Sample #3 which was collected and submitted to treatment within 24 hours to enable the analysis of total coliforms and *E. coli*. As only one RPR was available, it was not possible to perform both simultaneously. Therefore, even though both reactions were conducted in sequence, a slight variation in accumulated energy (Q_{UV}) was observed during the experiments, as shown in Figure 4.15.

FIGURE 4. 15 – (A) COD, total emerging contaminant (CEC) decay and reagent consumption, and (B) pH and temperature monitored during traditional solar photo-Fenton and solar-photo-Fenton like assays conducted at neutral pH in a semi-pilot scale RPR

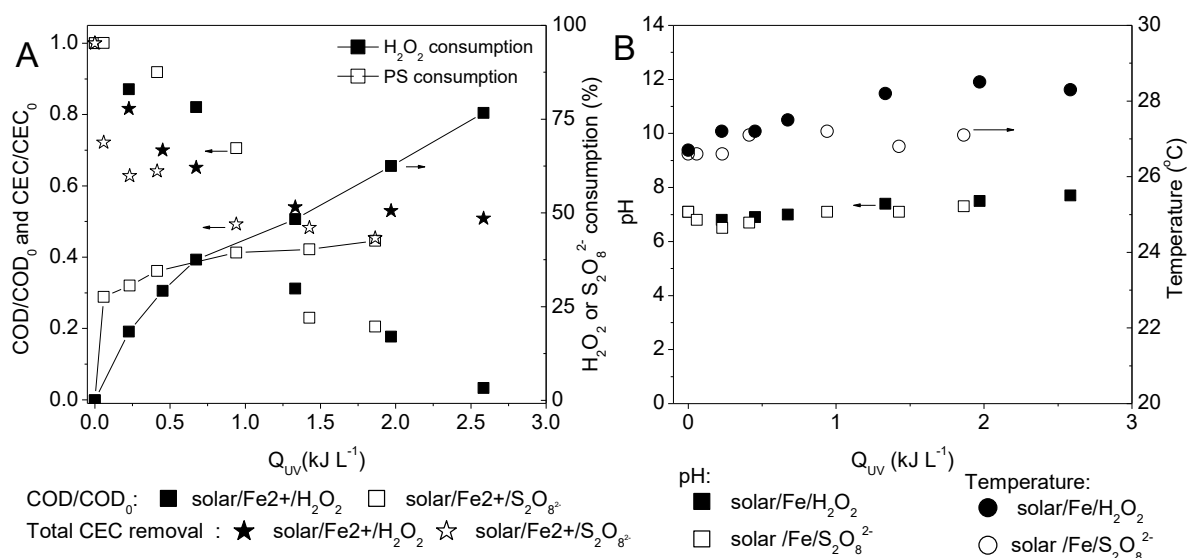


Figure 4.15A shows COD and CEC decay and reagent consumption with time. As observed by Miralles-Cuevas *et al.*, (2017), S₂O₈²⁻ consumption was faster in the beginning of reaction

when compared to H_2O_2 , showing a slower consumption after 0.5 kJ L^{-1} of accumulated irradiation. Meanwhile, H_2O_2 consumption did increase along the reaction reaching up to 75% consumption. In the solar/ $\text{Fe}/\text{S}_2\text{O}_8^{2-}$ system, total CEC decay pattern is parallel to that of reagent consumption, as it occurs very quickly in the beginning of reaction and stabilizes after $\text{S}_2\text{O}_8^{2-}$ reaches a slower consumption rate. In the traditional solar photo-Fenton system, even though H_2O_2 consumption continuous to increase along reaction, total CEC removal also shows a plateau. For both systems, COD decreases continuously along reaction indicating that these reagents are being consumed by matrix components which are present in a much higher concentration than that of target CEC. Higher temperatures observed during the traditional solar photo-Fenton system (Figure 4.15B) may also have contributed to H_2O_2 decomposition and continuous consumption of this reagent (ZAPATA *et al.*, 2010).

Total CEC removal obtained during traditional solar photo-Fenton reached 49%, while 55% removal was observed for the solar photo-Fenton like process. As the same molar concentration of both reagents was used in both systems, yet lower accumulated irradiation was obtained during the solar/ $\text{Fe}/\text{S}_2\text{O}_8^{2-}$ system, this process may be considered as more effective on the removal of CEC from wastewater at neutral pH. CEC removal rates are not as high as those obtained by Miralles-Cuevas *et al.*, (2017) and Ahmed & Chiron (2014), who reached more than 90% removal of a mixture of CEC and carbamazepine, respectively. However, these authors worked at acidic pH, which increases photo-Fenton reaction rates due to higher Fe^{2+} concentration in the system. Moreover, 1.9 kJ L^{-1} of accumulate irradiation accumulated during the solar photo-Fenton like system led to 80% and 55% COD and CEC removals, respectively, while the traditional system led to 83% and 50% removal of COD and CEC removal suggesting that the traditional system is slightly more reactive towards matrix components when compared to the solar photo-Fenton like at neutral pH (WANG *et al.*, 2015).

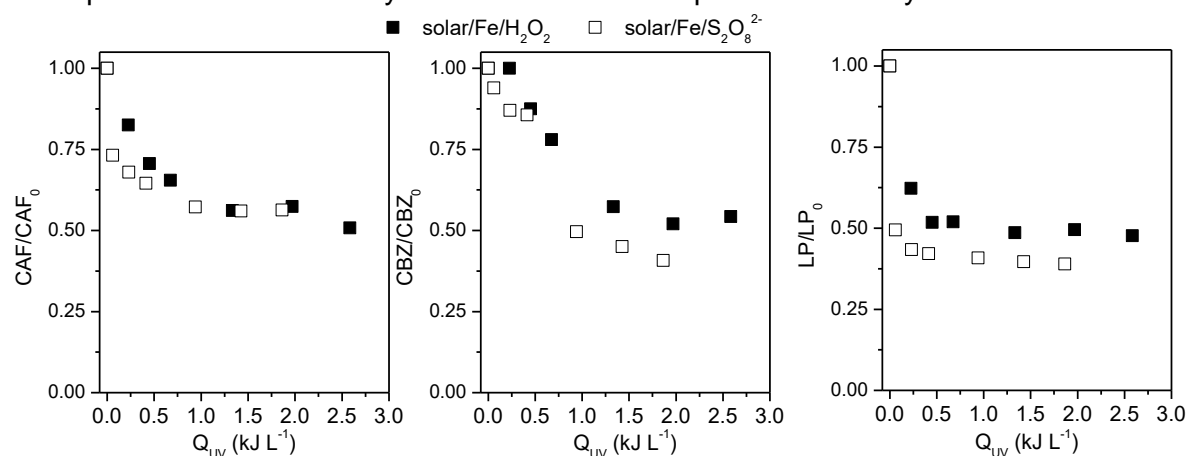
When applying traditional solar photo-Fenton at neutral pH using different iron addition strategies, Carra *et al.*, 2013 observed pH decay after every iron addition due to the hydrolysis of Fe(II). As shown in Figure 4.15B, and also noted in the bench scale tests performed in the former sections of this study, no pH decay was observed during reactions performed in this study. This is an advantage considering that no pH adjustment is needed before treatment nor prior to wastewater disposal.

Figure 4.16 shows the decay of each of the target compounds during the proposed treatments. Final removal rates obtained for CAF, CBZ and LP after traditional solar photo-Fenton at near neutral pH were 49%, 45% and 52%, respectively. When this same condition was conducted in the solar chamber for the traditional solar photo-Fenton system, final removals were 70%, 81% and 81% of CAF, CBZ and LP, respectively. Higher removal rates obtained in the solar chamber when compared to observations made at semi-pilot scale under natural irradiation may be a consequence of higher incident irradiation in the solar chamber when compared to the Raceway Pond reactor and better stirring conditions which promotes higher chemical reaction rates. In the RPR, precipitated iron is likely to sediment in the bottom of the reactor in regions that are away from the paddlewheel.

Regarding the removal of CEC via solar photo-Fenton like at neutral pH, removals were 43, 59 and 61% for CAF, CBZ and LP, respectively. While 0.9 kJ L^{-1} of accumulated energy were necessary to achieve 43% of CAF removal in the solar photo-Fenton like process, this rate was achieved after 1.3 kJ L^{-1} in traditional process (Figure 4.16). Final CAF removal was very similar for both processes and this was also observed elsewhere for CAF degradation in MWWTP effluent under UV-C/H₂O₂ and UV-C/PDS (RIVAS *et al.*, 2011). The final removal of CAF obtained in this study via traditional solar photo-Fenton (49%) was above the 20% reached by Klammerth *et al.*, (2010) under solar irradiation using 5 mg L^{-1} of Fe and 50 mg L^{-1}

of H_2O_2 at neutral pH. In addition, results obtained for the traditional system are in agreement with observation made by Bernabeu *et al.*, (2012), in which 60% of initial CAF concentration remained in solution after 6 hours of solar photo-Fenton reaction at neutral pH. On the other hand, Freitas *et al.*, (2017) reached 100% CAF removal from MWWTP effluent after solar photo-Fenton at neutral pH using intermittent iron addition strategy ($3 \times 20 \text{ mg L}^{-1}$) with 50 mg L^{-1} of H_2O_2 in a RPR after 90 min of treatment. Initial concentration of CAF in the referred study was $4.2 \mu\text{g L}^{-1}$, the concentration present naturally in the matrix.

FIGURE 4. 16 – CAF, CBZ and LP decay during traditional solar photo-Fenton and solar-photo-Fenton like assays conducted at neutral pH in a Raceway Pond Reactor



When it comes to CBZ, it is interesting to observe that both reactions follow the same pattern, with slower removal before 0.5 kJ L^{-1} of accumulated energy, and faster decay after that (Figure 4.16). While 2 kJ L^{-1} of accumulated energy are necessary to remove 50% of CBZ via traditional solar photo-Fenton, the same rate was achieved after 1 kJ L^{-1} of accumulated irradiation under solar photo-Fenton like both at neutral pH. Meanwhile, 96% CBZ removal in aqueous solution were achieved under solar photo-Fenton at acidic pH after 0.75 kJ L^{-1} of accumulated irradiation in the same RPR used in this study (da COSTA *et al.*, 2018). Thus, suggesting that matrix components and higher pH decrease CBZ degradation rate.

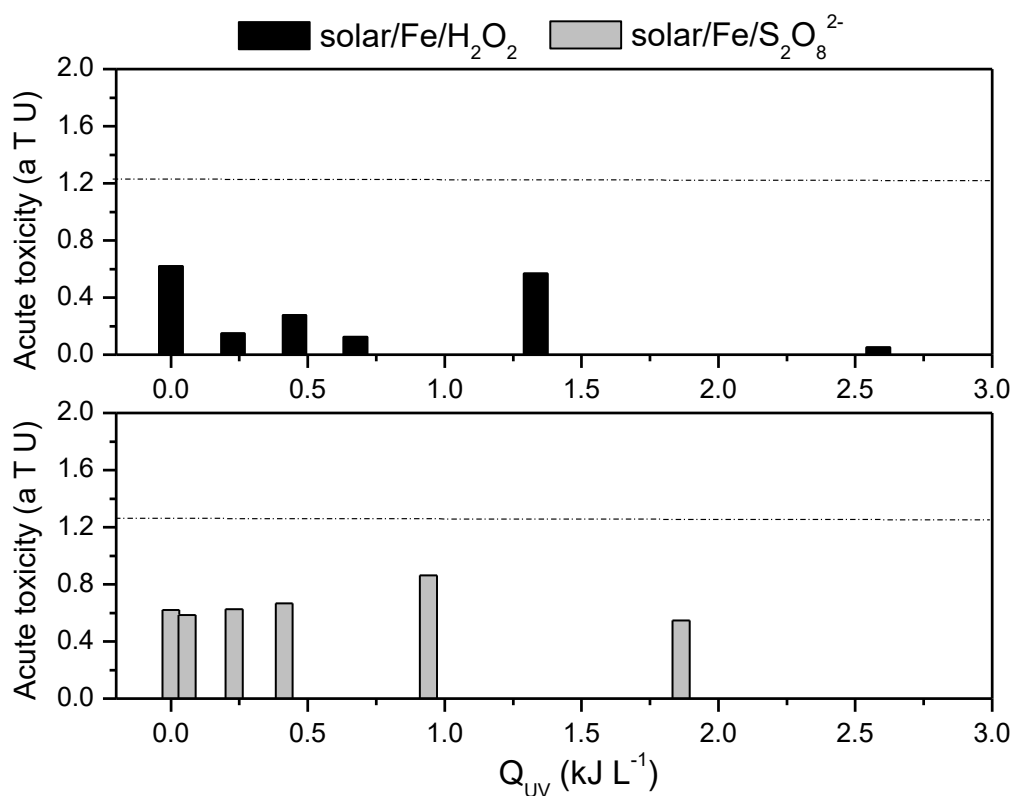
Among all of the target compounds, LP was the most sensible to proposed treatments showing 50% decay within 0.06 kJ L^{-1} of accumulated irradiation during solar photo-Fenton like process (Figure 4.16). LP removal during this treatment stabilized at nearly 60% removal after 0.9 kJ L^{-1} of accumulated energy, while maximum removal obtained via the traditional solar photo-Fenton was equivalent to 52% after 1.3 kJ L^{-1} of accumulated energy. Therefore, confirming the higher reactivity of LP to sulfate radical based AOPs when compared to hydroxyl radical based AOPs as observed in Chapter 3, since LP degradation in water was much faster via UV-C/PS when compared to UV-C/H₂O₂. However, as it was also shown in Chapter 3 of the present study, toxicity increased during the degradation of LP via UV-C/PS when compared to UV-C/H₂O₂. Therefore, apart from CEC removal it is also important to evaluate acute toxicity during treatment as AOP may generate transformation products which are more toxic than parent compounds.

4.4.4 Impact of treatments on acute toxicity and disinfection

Bernanbeu *et al.*, (2012) investigated the acute toxicity of a mixture of CEC present in MWWTP effluent, including CAF, in a concentration of 5 mg L^{-1} before and after treatment using luminescent bacteria *Allivibrio fischeri* as an indicator. Despite an increase in acute toxicity in the beginning, acute toxicity was properly removed after solar photo-Fenton treatment at neutral pH. The author also mentions that, considering the tiny concentration of CEC in the real matrix, this increase in toxicity should not be a concern. This was confirmed by Freitas *et al.*, (2017) who showed that this organism was not sensitive to MWWTP effluent containing CEC neither before nor after treatment by solar photo-Fenton conducted at near neutral pH. However, to this date, there are no studies reporting the evolution of acute toxicity during solar/Fe/S₂O₈²⁻ at neutral pH.

Acute toxicity assay was performed using samples withdrawn during traditional solar photo-Fenton and solar photo-Fenton like at neutral pH in the RPR reactor. Results are shown in Figure 4.17 and show that, similarly to what was observed by Freitas *et al.*, (2017) and Esteban Garcia *et al.*, (2017), MWWTP effluent was not toxic towards luminescent bacteria (a.T.U = 0.6), and that neither the traditional nor the alternative processes generated toxicity as all values are below 1.21 a. T. U (line). These results suggest that both processes performed at neutral pH would be appropriate to be applied prior to the disposal of this wastewater. However, it is important to emphasize that it is import to carry out at least one other type of bioassay to evaluate toxicity as different organisms show variable sensitivity to samples and the national legislation requires at least two test organisms from different phylum (BRASIL, 2011).

FIGURE 4. 17 –Acute toxicity values obtained for samples withdrawn during traditional solar photo-Fenton and solar-photo-Fenton like assays conducted at neutral pH in a Raceway Pond Reactor. Values above line(---) are toxic.



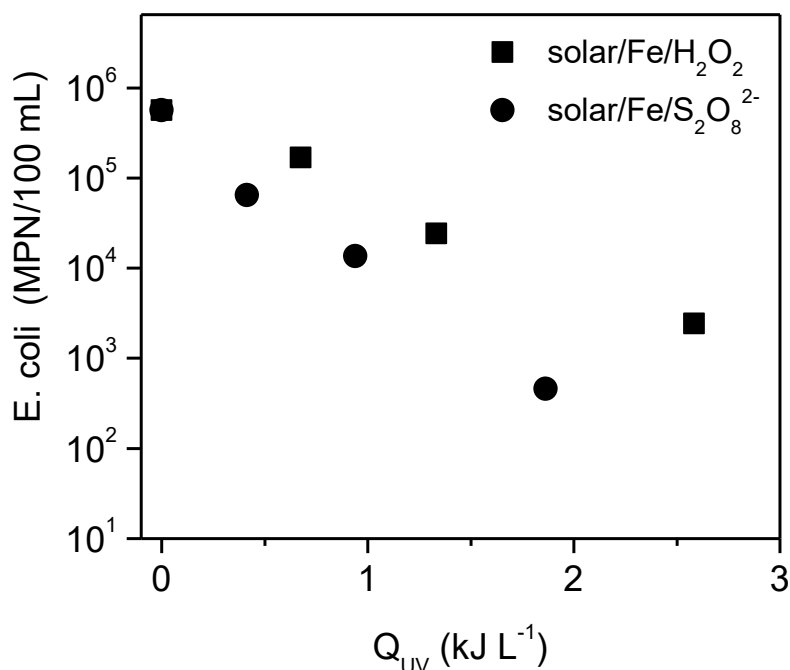
When it comes to disinfection, Freitas *et al.*, (2017) was the first study to report wastewater disinfection in a RPR. Solar photo-Fenton performed in the referenced study at neutral pH led to a drop of one log (10^4 to 10^3) in the total concentration of Total coliform and *E coli* after 90 minutes of reaction. Then, Esteban Garcia *et al.*, (2018) compared the efficiency of RPR with that of Compound Parabolic Reactor (CPC), on the disinfection of wastewater and found no differences between both reactors, both being effective on microorganism inactivation. Yet, none of these authors have assessed the impact of solar/ $\text{Fe}/\text{S}_2\text{O}_8^{2-}$ on disinfection and this is the first study to report such investigation.

Regarding Total coliform, MWWTP effluent initially showed a median concentration 5.6×10^5 MPN 100 mL⁻¹. Unfortunately, dilutions used for the samples withdrawn during traditional solar photo-Fenton treatments were not adequate to quantify TC per 100 mL. In contrast, the solar photo-Fenton like treatment did lead to a decay in TC after 60 min of treatment leading to a final concentration of 6.87×10^2 MNP 100 mL⁻¹. Since dilutions were the same for both treatments, the treatment using persulfate instead of hydrogen peroxide was more effective on the removal of TC, reaching the removal of three log units. Therefore, when considering TC removal obtained in the MWWTP (4 log units) and the additional treatment applied in this study, the resultant global removal is equivalent to seven log units. In this context, the solar photo-Fenton like treatment does complement the treatment applied in the MWWTP for the removal of TC.

Figure 4.18 shows *E. coli* removal with accumulated irradiation during both proposed treatments conducted at neutral pH in the RPR. As it may be observed in Figure 4.18, solar/ $\text{Fe}/\text{S}_2\text{O}_8^{2-}$ was much more effective on the removal of *E coli* leading to the removal of three log units while only two were removed via traditional solar photo-Fenton. Three log units of removal were also observed after 90 minutes of solar photo-Fenton at neutral pH

elsewhere (FREITAS *et al.*, 2017). Meanwhile, results obtained by Esteban Garcia *et al.*, (2017) with regard to *E. coli* removal for the traditional solar photo-Fenton system were similar to those observed here for the solar photo-Fenton like system after 60 minutes of treatment. However, in the referred study, as the reaction was conducted for 90 minutes continued, total *E. coli* removal was achieved during treatment. Thus, confirming the effectiveness of this system on disinfection of MWWTP effluent. Global *E. coli* removals (MWWTP + solar photo-Fenton) were equivalent to six log units for the traditional solar photo-Fenton system and seven log units for the solar photo-Fenton like system, both conducted at neutral pH.

FIGURE 4. 18 – *E. coli* decay during traditional solar photo-Fenton and solar-photo-Fenton like assays conducted at neutral pH in a Raceway Pond Reactor.



Moreover, as *E. coli* decay continues to take place even after 0.5 kJ L⁻¹ of accumulated irradiation, when persulfate consumption reaches a slower rate and most of the iron added to the system is precipitated at this point (Fe²⁺ concentration = 0.6 mg L⁻¹)(data not shown), it is likely that heterogeneous Fenton like reactions contributed to *E. coli* decay at this point, as

observed elsewhere (ESTEBAN GARCIA *et al.*, 2017). In fact, iron precipitation generates a sludge that must be treated/disposed or recycle after treatment which influences treatment costs. However, concerning legal requirements, treated wastewater is in agreement with disposal standards with regard to pH and dissolved iron concentration (maximum 15 mg L⁻¹) (BRASIL, 2011).

4.5 CONCLUSION

Traditional solar photo-Fenton conducted at neutral pH was able to remove CEC from MWWTP effluent at levels above 80% in a solar chamber. However, reagents concentrations needed to achieve this removal rate were 10 times higher than those required at acidic pH, as it had been reported by other authors (CARRA *et al.*, 2013). The pH did not decay during reactions which is an advantage considering that no pH adjustment would be required neither before nor after treatment. CAF and CBZ decay were similar for non-irradiated and irradiated Fenton using the same concentrations of reagents. Meanwhile, LP removal was only obtained in the irradiated processes. Results indicate that Fe(II) was in excess and that turbidity may have impaired photo-Fenton reactions.

Solar photo-Fenton like performed using half of the total iron concentration applied in the traditional system and conducted at neutral pH was not able to achieve 80% removal of total CEC. Although, up to 60% removal of total CEC were reached. Again, CAF and CBZ removals obtained in the dark were similar to those observed for the irradiated Fenton like system. In addition, there was no pH decrease during treatment, which was nearly 7 at the end of reaction.

Solar/Fe/H₂O₂ and solar/Fe/S₂O₈²⁻ conducted at neutral pH in a Raceway Pond Reactor using the same concentrations of Fe(II) and molar equivalent concentrations of oxidants at neutral

pH, led to a maximum of 49 and 54% of CEC removal respectively. This was the first time solar photo-Fenton like using persulfate is investigated at neutral pH for CEC removal, toxicity and disinfection. The alternative system was more effective on the removal of CEC reaching a higher removal rate under lower accumulated irradiation. In addition, this system was also more effective on the disinfection of MWWTP effluent, removing three log units of both Total Coliform and *E coli*. None of the treatments generated acute toxicity as indicated by *Allivibrio fischeri* and may safely be used as tertiary/quaternary treatment prior to disposal of MWWTP effluent.

5 CHAPTER VI: COST-BENEFIT ANALYSIS

5.1 INTRODUCTION

Treatment cost is one of the main factors to influence decision makers on the choice of treatment to be applied in Municipal Wastewater Treatment Plants (MWWTP). Once authorities begin to impose minimum levels for the removal of emerging contaminants in these facilities, the race for the most affordable technology to be applied as tertiary treatment will begin. Hence, it is essential to perform an economic assessment to support the feasibility of different technologies.

For many years, advanced oxidation processes (AOP) have been considered as expensive treatments, thus hindering their application in real scale (MIRALLES-CUEVAS *et al.*, 2017). High operation costs of AOP are usually related to reagent prices. During operation, costs with chemical reagents will be proportional to the dose of reagent that is applied. In addition, the use of alternative energy sources such as solar irradiation may lower operational costs (KLAMERTH *et al.*, 2013; LI, 2016).

In order to properly assess the cost-benefit ratio pertaining to a technology, it is important to consider (i) investment costs and (ii) operating costs. Regarding AOP, investment costs are associated to each reactor which depends on the process that will be applied. Therefore, it is important to perform research involving the development of low cost reactors to increase the chances of the application of AOP in MWWTP (MALATO *et al.*, 2009). Nearly 95% removal of 22 emerging contaminants present in real MWWTP effluent was obtained via solar photo-Fenton in acidic and neutral conditions (KLAMERTH *et al.*, 2013). This rate was achieved in a semi-pilot Compound Parabolic Collector (CPC), a solar reactor that was designed for the concentration of solar beams, thus enabling the employment of solar treatment technologies. Although results were promising, the CPC seemed too expensive for the purpose. Therefore,

in the past years, scientists focused their attention on the design of solar reactors for the removal of CEC.

One of the most recent developments directed to the application of solar reactors for the removal of CEC via photo-Fenton was the adaptation of the Raceway Pond Reactor (RPR), originally designed for the growth of algae. RPR consists of a water tank which contains a paddle wheel for wastewater circulation. Contrastingly with CPC, RPR does not allow for the concentration of incident irradiation. Recent studies comparing the efficiency of the CPC with that obtained with RPR for the removal of CEC from wastewater indicate that sunlight concentration is not as important for the removal of these compounds, which are present in reduced concentrations in MWWTP effluent (ARZATE *et al.*, 2017; DE LA OBRA, PONCE-ROBLES, *et al.*, 2017). This is economically advantageous once the RPR is nearly 40 times cheaper than the CPC (CARRA *et al.*, 2014). Similar results were obtained for disinfection, as both reactors showed similar patterns of total coliform and *E coli* inactivation, reaching the same removal rate (ESTEBAN GARCIA *et al.*, 2017).

When it comes to UV-C treatment, which is a highly disseminated technology, UV-C reactors have been sold in commercial scale for a few years (KRUITHOF *et al.*, 2007). Therefore, UV-C reactors are not as costly when compared to solar reactors. However, operational costs related to electrical energy uptake may be the most important factor regarding UV-C treatment costs. Artificial Hg and Xe lamps are energy intensive devices and, during operation, high percentage of the electrical energy required by the lamp is converted into heat instead of light. This contributes to higher electric energy requirements and shorter lifespan of these lamps. As an alternative, reactors exploring LED semiconductors for the application of AOP have been intensively studied in the past few years with successful results (CARRA *et al.*, 2015; DOMINGUEZ *et al.*, 2016; LI, 2016).

Meanwhile, operational costs vary mainly with the concentration of reagents applied during AOP. Total operational cost of solar photo-Fenton (solar/Fe²⁺/H₂O₂) was compared to that of solar photo-Fenton like (solar/Fe²⁺/S₂O₈²⁻), both conducted in a CPC, and to UV-C based AOP (UV-C/H₂O₂ and UV-C/ S₂O₈²⁻) for the degradation of CEC. Among these processes solar/Fe²⁺/H₂O₂ and UV-C/H₂O₂ showed lower operational costs (0.18 €·m⁻³), followed by UV-C/S₂O₈²⁻ (0.26-0.28 €·m⁻³) and solar/Fe²⁺/S₂O₈²⁻ (MIRALLES-CUEVAS *et al.*, 2017). The application of solar photo-Fenton and solar photocatalysis using TiO₂ was also compared in relation to costs for the removal of pesticides from industrial wastewater and the cost-benefit of solar photo-Fenton (5.2 € m⁻³) was considerably higher than that of solar/ TiO₂ (8.59 €·m⁻³) (GAR ALALM *et al.*, 2015). Costs of two different strategies of hydrogen peroxide addition were compared for the solar photo-Fenton process applied for water treatment in a CPC. Although the strategy did not influence financial costs, the authors recognized the importance of optimizing reagent concentrations to reduce operational costs (CARRA, IRENE *et al.*, 2013).

In this context, the aim of this chapter was to develop a cost-benefit analysis of solar photo-Fenton (solar/Fe²⁺/H₂O₂) and solar photo-Fenton like (solar/Fe²⁺/S₂O₈²⁻) on the treatment of model CEC present in real wastewater.

5.2 MATERIAL AND METHODS

Considering that laboratory conditions are fairly distinctive of field conditions, cost-benefit analysis were performed only for optimum conditions conducted in the semi-pilot reactor RPR discussed in Chapter 4. The methodology used for the cost analysis was adapted from MIRALLES-CUEVAS *et al.*, 2017. According to this methodology, total cost (TC) related to the application of a technology (TC, €/m³) refers to: (i) amortization cost (AC) of the reactor

and other equipment, (ii) operational costs (OC), and total volume to be treated per year (V_t ; m^3) (Equation 6.1):

$$TC (\text{€/m}^3) = (AC + OC) / V_t \quad (\text{Equation 6.1})$$

AC will be calculated considering 7,5% of interest rate (BRASIL, 2017) in the investment cost and 20 years as plant life-time period. Regarding solar technologies, main cost is related to total irradiated surface area which is related to accumulated UV energy (Q_{UVG} for solar systems). Q_{UVG} depends on the average solar UV irradiation in a location (UV_G) and on the number of hours of operation in a year ($H_s = 12h*365$). Therefore, the surface area for solar (S_s) irradiated reactors may be calculated as follows (Equation 6.2 and 6.3):

$$S_s = (Q_{UVG} * V_T / H_s * UV_G) \quad (\text{Equation 6.2})$$

Where S_s is the surface area required for the solar system, Q_{UVG} (kJ L^{-1}) is the amount of accumulated energy required to remove 50% of total CEC in each process, V_T (L) is the total volume of wastewater treated in a year, H_s is the total hours of operation in a year and UV_G is the average local global irradiation (30 W m^{-2} for Belo Horizonte). 50% removal was chosen considering the results obtained in Chapter 4.

After surface area is determined, investment costs may be defined as according to Equation 6.3:

$$IC_S = C_b * (S_s / S_b) \quad (\text{Equation 6.3})$$

Where C_b corresponds to the cost of the reactor with a surface area S_s . Considering that total cost per area of RPR reactor is 40 times lower than costs calculated for CPC (CARRA *et al.*, 2014), the cost of an RPR with a surface area of 1000 m^2 (S_{RPR}) is estimated to be $12,090 \text{ €}$ (S_b)(WATER, 2016; MIRALLES-CUEVAS *et al.*, 2017).

Reagent prices and electricity costs detailed in Table 5.1 were used to calculate operational costs (OC). Costs related to each reagent were calculated considering the dose of each reagent to be applied per m³ of MWWTP effluent. In addition, a total volume of 1,000 m³ day⁻¹ was considered for calculations.

TABLE 5. 1 - Reagent prices used to calculate operational costs

Reagent	Price (€ L ⁻¹ or € kg ⁻¹)
H ₂ O ₂ 33% (v/v)	0.45
Na ₂ SO ₈	11.8
FeSO ₄ ·7H ₂ O	0.71
H ₂ SO ₄	0.1
NaOH	0.12

5.3 RESULTS AND DISCUSSION

5.3.1 Amortization costs (AC)

As explained in the methodology, total cost (TC) (m³) is given by the sum of amortization costs and operational costs. Amortization cost is related to investment cost, interest rates and reactor lifespan. Considering solar processes, investment costs vary according to reactor surface area. Table 5.2 shows reactor surface area required for each of the proposed treatments. As the solar photo-Fenton like process required 0.9 kJ L⁻¹ of accumulated irradiation to reach 50% removal of CEC in neutral pH and the traditional solar photo-Fenton reached the same removal rate after 1.9 kJ L⁻¹ of accumulated irradiation, surface area required for the solar/Fe/S₂O₈²⁻ process was nearly two times lower than that required for the traditional solar photo-Fenton process.

TABLE 5. 2 – Surface area required for the application of traditional solar photo-Fenton and solar photo-Fenton like processes

Solar photo-reactor surface area (S _s)			
Variable	unit	solar/Fe/H ₂ O ₂	solar/Fe/S ₂ O ₈ ²⁻
QUV _G	kJ L ⁻¹	1.9	0.9
V _t	L	365,000	365,000
H _s	h	4,380	4,380
UV _G	W m ⁻²	30	30
Surface area	m ²	4,750	2,250

Miralles-Cuevas *et al.*, (2017), obtained surface area values equivalent to 3,300 m² for the traditional solar photo-Fenton process and 3,200 m² for the solar/Fe/S₂O₈²⁻ treatment in a CPC type reactor. These values obtained in the referred study were calculated for solar photo-Fenton treatment performed at acidic pH and in a reactor that concentrates direct and diffuse solar beams (CPC reactor). Therefore, one would expect the area required in the present study to be much higher than that obtained by Miralles-Cuevas (2017). Although, surface area calculated here for the solar/Fe/S₂O₈²⁻ treatment is lower than that obtained in the reference study. This is related to lower average local global incident irradiation in Almeria, Spain (UV_G = 18.6 W m⁻²) when compared to the average incident irradiation in Belo Horizonte (UV_G = 30 W m⁻²), thus confirming the high potential of using solar irradiation in tropical locations (MARCELINO *et al.*, 2015; ESTEBAN-GARCIA *et al.*, 2017).

Considering the surface area of solar reactor required for each process, it was possible to calculate investment costs and amortization costs, which are shown in Tables 5.3.

TABLE 5.3 – Investment costs and amortization costs calculated for traditional solar photo-Fenton and solar photo-Fenton like treatments in a RPR considering reactor lifespan of 20 years

Investment costs (IC)				
Variable	unit	solar/Fe/H₂O₂		solar/Fe/S₂O₈²⁻
Cb	€	12,090		12,090
Sb	m ²	4,750		2,250
Sb	m ²	1,000		1,000
Total IC	€	57,427.5		27,202.5
Amortization cost (AC)				
Variable	unit	solar/Fe/H₂O₂		solar/Fe/S₂O₈²⁻
IC	€	57,427.5		27,202.5
interest rate (%)	m ²	7.5		7.5
period	year	20		20
Total IC	€/year	430,706.25		204,018.75

As expected, investment cost related to the solar photo-Fenton like process was lower than that obtained for the traditional solar photo-Fenton process, since the required surface area was lower. Thus, amortization cost related to the solar photo-Fenton like process is also nearly half of costs related to the traditional system. Meanwhile, amortization costs obtained by Miralles Cuevas *et al.*, 2017 were not only similar values for both solar photo-Fenton treatments, yet also lower than the ones obtained here (0.24 and 0.23 € m⁻³ for traditional and solar photo-Fenton like, respectively). This is related to the interest rate in each country, if the 6% interest rate applicable to Spain was to be applied in this study, AC would drop to 0.9 and 0.4 € m⁻³ for the traditional and solar photo-Fenton like treatments, respectively. Thus costs would be closer to those obtained in the study performed in Spain.

5.3.2 Operating costs (OC)

Operational costs were calculated for both solar photo-Fenton treatments: traditional solar photo-Fenton (solar/Fe/H₂O₂) and solar photo-Fenton like (solar/Fe/S₂O₈²⁻), both using 55 mg L⁻¹ of Fe (1 mM) and 50 mg L⁻¹ of H₂O₂ or 282.2 mg L⁻¹ of S₂O₈²⁻ (1.47 mM of each reagent). Although no major pH adjustment was required, wastewater pH was set at 7 prior to all experiments. Therefore, the volume of acid used for this purpose was used in the calculation of operational costs for both treatments. Table 5.4 shows the costs related to each reagent per day of operation using the prices detailed in Table 5.1.

TABLE 5. 4 – Operational costs related to the application of traditional and solar photo-Fenton like at neutral pH

Operating costs (OC)			
Reagent	unit	solar/Fe/H₂O₂	solar/Fe/S₂O₈²⁻
H ₂ O ₂ 33% (v/v)		68.63	none
Na ₂ SO ₈	€ day ⁻¹	none	3,329.96
FeSO ₄ .7H ₂ O		39.05	39.05
H ₂ SO ₄		4.17	4.17
NaOH		none	none
Total OC	€ day⁻¹	111.84	3,373.18

In contrast to values obtained for investment and amortization costs for each of the proposed treatments, operational costs were much higher for the solar photo-Fenton like process when compared to the traditional solar photo-Fenton treatment (Table 5.4). Increased operational costs related to the solar/Fe/S₂O₈²⁻ are related to the price of sodium persulfate which is 26 times more expensive than hydrogen peroxide (Table 5.1). MWWTP effluent treatment conducted in a RPR via traditional solar photo-Fenton treatment also at neutral pH gave a total operational cost of 16,959 € related to reagents only (ESTEBAN-GARCIA, 2017), while the OC per year of the traditional treatment obtained in this study was equivalent to 42,343 €. Considering that the concentration of hydrogen peroxide was the same in both studies, this difference in costs is related to lower Fe(II) concentration applied by Esteban-Garcia, who used 20 mg L⁻¹ in their study when compared to 55 mg L⁻¹ used here. In the referred study, the authors kept the reaction running for longer when compared to our study. In addition, they only evaluated disinfection and did not investigate CEC decay, which would probably increase required reagent concentrations.

Operating costs related to the application of S₂O₈²⁻ in the solar photo-Fenton system when compared to H₂O₂ were 12 times higher in Miralles-Cuevas *et al.*, (2017). However, in the present study S₂O₈²⁻ cost were 48 times higher than costs calculated for H₂O₂. This occurred because, in the referred study, H₂O₂ and S₂O₈²⁻ were compared in mg L⁻¹ and not in mol L⁻¹ as it was done in this study. Considering that molar mass of S₂O₈²⁻ (192.12 g mol⁻¹) is 5.6 times higher than that of H₂O₂ (34 g mol⁻¹) a higher mass of sodium persulfate is required to achieve the same molar concentration, thus increasing costs.

A hypothetical simulation was performed to estimate the cost of each treatment in acidic pH instead of neutral pH, using 5.5 mg L⁻¹ of Fe (0.1 M), as this concentration was effective in bench scale for the traditional solar photo-Fenton process (Chapter 4). The cost related to each

oxidant in neutral pH was kept for calculations made in acidic pH considering that bench scale conditions under artificial solar irradiation may differ from conditions obtained in semi-pilot scale under natural solar irradiation as it was seen in Chapter 4. For this purpose, a higher amount of H₂SO₄ was considered to lower MWWTP effluent pH to 3 and costs related to the application of NaOH to neutralize the effluent after treatment were added to calculations as well. For both treatments, reducing costs related to Fe(II) and adding costs related to acidification and neutralization prior and after treatments led a slight reduction in costs from 0.11 and 3.37 € m⁻³ for traditional and solar photo-Fenton like, respectively, to 0.10 to 3.36 € m⁻³. This corresponds to 8 € of reduction in the daily operational costs for each treatment, or 3024 € year⁻¹. This difference may be worth it considering the risk related to the manipulation of concentrated acid and base in treatment sites (CARRA et al., 2013).

5.3.3 Total cost (TC)

After amortization and operating costs were calculated, it was possible to obtain the total cost of each of the proposed treatments. As shown in Table 5.5, although the operational costs related to the application of solar photo-Fenton like at neutral pH is increased due to high prices associated to sodium persulfate, the lower surface area required for this process pushed the total cost of the operation to a lower price than that observed for the traditional solar photo-Fenton system.

TABLE 5.5 – Total costs (TC) related to the application of traditional solar photo-Fenton and solar photo-Fenton like at neutral pH for the treatment of MWWTP effluent

		Total cost (TC)	
Variable	unit	solar/Fe/H ₂ O ₂	solar/Fe/S ₂ O ₈ ²⁻
AC	€ year ⁻¹	430,706.25	204,018.75
OC	€ day ⁻¹	111,84	3,373,18
Vt	m ³	365,000	365,000
TC	€ m ⁻³	1.18	0.57

Total cost calculated here is above those obtained elsewhere for the traditional solar photo-Fenton system at acidic and neutral pH (0.42 € m⁻³; 0.15 € m⁻³) (MIRALLES-CUEVAS *et al.*, 2107; ESTEBAN GARCIA *et al.*, 2017). However, when it comes to the solar photo-Fenton like treatment, TC for operation at near neutral pH in this study is lower than the cost estimated by Miralles Cuevas *et al.*, (2017) (0.72 € m⁻³) who conducted this treatment at acidic pH, yet in a more expensive reactor. The difference in price may be related to the fact that the cost analysis performed in the referred work also considered other costs of operation such as maintenance and personnel. As there is no other work related to the application of this process at neutral pH, it was not possible to compare treatment costs obtained here with other studies.

Finally, total costs obtained in this study for each of the proposed treatments are competitive when compared to other advanced technologies used for the treatment of CEC in MWWTP effluent. A total cost of 1.1-1.9 € m⁻³, for example, was estimated for the treatment of wastewater containing a mix of pesticides by combined photo-Fenton/membrane bioreactor. Other technologies such as adsorption and reverse osmosis alone may cost from 0.07 to 90 USD mg⁻¹ of pollutant and lead to the generation of a solid waste or concentrated solution, respectively, which must be disposed of or treated afterwards (ADELEYE *et al.*, 2016). In addition, UV-C based processes are usually associated to higher operational prices as electric energy is required with costs varying from 0.4-1.4 € m⁻³ depending on the volume of wastewater treated (ROCCARO *et al.*, 2013).

5.4 CONCLUSION

Total treatment costs were calculated for traditional solar photo-Fenton and solar photo-Fenton like processes at neutral pH using 55 mg L⁻¹ of iron and 50 mg L⁻¹ of H₂O₂ or 282.2 mg L⁻¹ of S₂O₈²⁻ as according to amortization costs and operational costs. Considering that the

solar/iron/ $S_2O_8^{2-}$ system showed a faster removal of total CEC spiked to MWWTP effluent, the surface area of reactor required for this process was nearly half of that required by the traditional process. As a consequence, even though prices associated to sodium persulfate are higher than commercial H_2O_2 prices, the total cost of the solar/iron/ $S_2O_8^{2-}$ process was pushed down to 0.57 € m^{-3} when compared to 1.18 € m^{-3} for the traditional process. These prices are competitive against other advanced technologies and combined treatment systems for the removal of CEC from MWWTP effluent.

6 CHAPTER VI: FUTURE RECOMMENDATIONS

6.1 INTRODUCTION

Considering that each chapter of this Thesis is very particular and distinctive, recommendations are exposed with regard to each chapter separately in the following sections.

6.1.1 Chapter II: State of the art on the occurrence control and fate of CECS in Brazil and on the application of AOPS on the treatment of CECS

The literature review performed in Chapter 2 brings about three main topics of concern: (i) investment in basic sanitation infrastructure must be performed prior to the imposition of limits related to the control of CEC in Brazil; (ii) studies related to the occurrence, control and fate of CEC in Brazil are still incipient and limited to the southeast region; and (iii) more studies on the control of these contaminants must be stimulated in the country, especially concerning the application of sustainable technologies. Therefore, a few recommendations related to these topics are delineated bellow:

- Governmental data related to the consumption of the different classes of CEC per region in Brazil should be collected and made available for research institutions, so that studies related to the occurrence of CEC are directed towards these contaminants, instead of randomly searching for chemicals which are highly consumed elsewhere;
- Based on the use list, research should focus on the selection of a limited list of CEC used as indicators of the presence of various CEC in different environmental compartments, as this will lead to cheaper monitoring strategies;
- The investigation of different and sustainable technologies for the control of CEC in MWWTP in Brazil as tertiary treatment should be stimulated from now, so that data

may be used in the process of decision making for the implementation of tertiary treatment in real scale in the future;

- Research on the impact of CEC on local aquatic biota and population health must be performed as well as on the impact of possible treatment technologies on these effects;
- Research on the impact of possible treatment technologies on the effects promoted by CEC on local aquatic biota and population health must be assessed;
- The design of municipal wastewater treatment plants to be installed as a consequence of basic sanitation infrastructure improvement, could consider the area required for the installation of tertiary treatment in the future.
- Research on the application of solar AOPs as tertiary treatment should be more stimulated in Brazil, considering the average incident irradiation in the country.

6.1.2 Chapter III: Treatment of target CEC in pure water and surface water via UV-C AOPS

As it was shown in Chapter III, UV-C based technologies are highly effective on the degradation of target CEC. However, a few extra analyses could be performed to elucidate some topics related to results obtained here after the application of UV-C/H₂O₂ and UV-C/S₂O₈²⁻, such as:

- As secondary reactions may take place under UV-C irradiation and hydroxyl radicals may be formed simultaneously with sulfate radicals during UV-C/S₂O₈²⁻, the use of radical scavengers during each treatment process would clarify which is/are the reactions contributing to the degradation of each compound during UV-C/H₂O₂ and UV-C/S₂O₈²⁻;

- The identification and separation of transformation products formed during the oxidation of LP, FRSM and CBZ must be better investigated in order to clarify acute toxicity results obtained mainly during UV-C/S₂O₈²⁻.

6.1.3 Chapter IV: Treatment of target CEC in MWWTP effluent via solar photo-Fenton and solar photo-Fenton like at neutral pH

Considering that this was the first study to apply solar photo-Fenton like treatment at near neutral pH and to assess its effects upon toxicity and total coliform and *E coli* inactivation, there are still many factors to be investigated to improve the treatment itself and to evaluate its performance when compared to the traditional solar photo-Fenton system:

- A factorial planning could be conducted using different concentrations of iron and sodium persulfate and iron dosage strategies using the concentrations applied here as a reference in order to optimize the treatment and to evaluate the possibility of achieving higher CEC removal with lower concentration of reagents at neutral pH;
- Radical scavenging agents could be applied to each reaction in order to elucidate mechanisms taking place in each system for the degradation of CEC and *E coli* inactivation;
- Toxicity analysis must be performed for other indicator organisms rather than *Allivibrio fischeri* alone;
- The elimination of antibiotic resistant bacteria and resistance genes could be assessed for each of the proposed solar photo-Fenton treatments;
- The application of both reagents simultaneously could be evaluated as according to CEC removal, acute and chronic toxicity and disinfection;

6.1.4 Chapter V: Cost-benefit analysis

Cost benefit analysis performed in Chapter 5 indicated that the technologies proposed in this work for the removal of CEC in MWWTP effluent are competitive against other advanced treatments. However, a few considerations for future studies should be taken into account:

- The calculation of operational costs should also include costs with maintenance and personnel;
- Solar photo-Fenton reactions could be promoted in simpler system such as facultative ponds which are commonly used in MWWTP in Brazil, thus reducing investment costs.

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