UNIVERSIDADE FEDERAL DE MINAS GERAIS
Escola de Engenharia
Programa de Pós-Graduação em Saneamento, Meio Ambiente e Recursos Hídricos

Elizângela Pinheiro da Costa

REMOVAL OF CONTAMINANTS OF EMERGING CONCERN AND DISINFECTION IN SECONDARY MUNICIPAL WASTEWATER BY CIRCUMNEUTRAL SOLAR PHOTO-FENTON IN OPEN REACTORS

Belo Horizonte
2021

Elizângela Pinheiro da Costa

REMOVAL OF CONTAMINANTS OF EMERGING CONCERN AND DISINFECTION IN SECONDARY MUNICIPAL WASTEWATER BY CIRCUMNEUTRAL SOLAR PHOTO-FENTON IN OPEN REACTORS

Thesis presented to the Post-Graduation Program on Sanitation, Environment and Water Resources of the Federal University of Minas Gerais, as a requirement to obtain the Ph.D. title on Sanitation, Environment, and Water Resources.

Research field: Environment

Research line: Characterization, prevention, and control of pollution

Supervisor: Prof. Dr. Camila Costa de Amorim Amaral

Co-supervisor: Prof. Dr. Sixto Malato Rodríguez

Belo Horizonte
2021

C837r

Costa, Elizângela Pinheiro da.
Removal of contaminants of emerging concern and disinfection in secondary municipal wastewater by circumneutral solar photo-Fenton in open reactors [recurso eletrônico] / Elizângela Pinheiro da Costa. - 2021.
1 recurso online (223f. : il., color.) : pdf.

Orientadora: Camila Costa de Amorim Amaral.
Coorientador: Sixto Malato Rodríguez.

Tese (doutorado) - Universidade Federal de Minas Gerais, Escola de Engenharia.

Apêndices: 201-223.

Bibliografia: f. 187-200.
Exigências do sistema: Adobe Acrobat Reader.

1. Engenharia sanitária - Teses. 2. Meio ambiente - Teses. 3. Desinfecção e desinfetantes - Teses. 4. Águas residuais - Purificação - Teses. I. Amaral, Camila Costa de Amorim. II. Malato Rodríguez, Sixto. III. Universidade Federal de Minas Gerais. Escola de Engenharia. IV. Título.
CDU: 628(043)

Ficha catalográfica elaborada pela bibliotecária Roseli Alves de Oliveira CRB/6 2121
Biblioteca Prof. Mário Werneck, Escola de Engenharia da UFMG

UNIVERSIDADE FEDERAL DE MINAS GERAIS
[ESCOLA DE ENGENHARIA]
COLEGIADO DO CURSO DE GRADUAÇÃO / PÓS-GRADUAÇÃO EM [SANEAMENTO, MEIO AMBIENTE E RECURSOS HÍDRICOS]

FOLHA DE APROVAÇÃO

REMOVAL OF CONTAMINANTS OF EMERGING CONCERN AND DISINFECTION IN SECONDARY MUNICIPAL WASTEWATER BY CIRCUMNEUTRAL SOLAR PHOTO-FENTON IN OPEN REACTORS

Elizângela Pinheiro da Costa

Tese de Doutorado defendida e aprovada, no dia 26 de maio de 2021, pela Banca Examinadora designada pelo Colegiado do Programa de Pós-Graduação em Saneamento Meio Ambiente e Recursos Hídricos da Universidade Federal de Minas Gerais constituída pelos seguintes professores:

Prof. Dr. Sergio Francisco de Aquino **- Membro Externo**

UNIVERSIDADE FEDERAL DE OURO PRETO - UFOP

Prof. Dr. Alam Gustavo Trovó **- Membro Externo**

UNIVERSIDADE FEDERAL DE UBERLÂNDIA - UFU

Profª. Drª. Carla Sirtori **- Membro Externo**

UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL - UFRGS

Prof. Dr. Thiago de Alencar Neves **- Membro Interno**

UFMG

Prof. Dr. Sixto Malato Rodriguez **- Coorientador**

PLATAFORMA SOLAR DE ALMERIA-CIEMAT

Profª. Drª. Camila Costa de Amorim Amaral **- Orientadora**

UFMG

APROVADA PELO COLEGIADO DO PPG SMARH

Sonaly Cristina Rezende Borges de Lima - Coordenadora

Belo Horizonte, 26 de maio de 2021.

Documento assinado eletronicamente por **Camila Costa de Amorim Amaral**, **Professora do Magistério Superior**, em 26/05/2021, às 12:26, conforme horário oficial de Brasília, com fundamento no art. 5º do Decreto nº 10.543, de 13 de novembro de 2020.

Documento assinado eletronicamente por **Thiago de Alencar Neves**, **Professor do Magistério Superior**, em 26/05/2021, às 12:27, conforme horário oficial de Brasília, com fundamento no art. 5º do Decreto nº 10.543, de 13 de novembro de 2020.

Documento assinado eletronicamente por **Alam Gustavo Trovó**, **Usuário Externo**, em 26/05/2021, às 13:23, conforme horário oficial de Brasília, com fundamento no art. 5º do Decreto nº 10.543, de 13 de novembro de 2020.

Documento assinado eletronicamente por **Carla Sirtori**, **Usuário Externo**, em 26/05/2021, às 15:05, conforme horário oficial de Brasília, com fundamento no art. 5º do Decreto nº 10.543, de 13 de novembro de 2020.

Documento assinado eletronicamente por **Sixto Malato Rodriguez**, **Usuário Externo**, em 27/05/2021, às 08:34, conforme horário oficial de Brasília, com fundamento no art. 5º do Decreto nº 10.543, de 13 de novembro de 2020.

Documento assinado eletronicamente por **Sérgio Francisco de Aquino**, **Usuário Externo**, em 27/05/2021, às 13:43, conforme horário oficial de Brasília, com fundamento no art. 5º do Decreto nº 10.543, de 13 de novembro de 2020.

Documento assinado eletronicamente por **Sonaly Cristina Rezende Borges de Lima**, **Coordenador(a) de curso de pós-graduação**, em 09/07/2021, às 17:33, conforme horário oficial de Brasília, com fundamento no art. 5º do Decreto nº 10.543, de 13 de novembro de 2020.

A autenticidade deste documento pode ser conferida no site https://sei.ufmg.br/sei/controlador_externo.php?acao=documento_conferir&id_orgao_acesso_externo=0, informando o código verificador **0744101** e o código CRC **76758A57**.

Referência: Processo nº 23072.226702/2021-14 SEI nº 0744101

AGRADECIMENTOS/AGRADECIMIENTOS

Agradeço imensamente aos meus pais, Rosângela e José Eli, por me apoiarem em todos os momentos da minha vida, mesmo com todas as dificuldades enfrentadas. Obrigada por toda a educação que vai além da sala de aula: de respeito aos demais, noções de responsabilidade e dedicação, além do cuidado com o meio ambiente. Todo esse ensinamento é a base de tudo que sou e tento realizar. Agradeço à minha família e amigos, sempre presentes e torcendo por mim.

Agradeço à professora Camila pela oportunidade de desenvolver trabalhos tão relevantes na área ambiental através do GruPOA, desde a época de aluna de graduação em projetos de iniciação científica. Agradeço pelas oportunidades de aprendizado, desenvolvimento profissional e de aprimoramento. Também aproveito para agradecer o constante incentivo de sempre fazer o melhor possível e almejar a excelência, independentemente das circunstâncias; esse ensinamento levo para a vida!

Estoy muy agradecida por toda la atención prestada por el Dr. Sixto Malato durante las etapas de mi estancia en la Plataforma Solar de Almería. Desde cuando sometí la propuesta en Brasil hasta el desarrollo de las actividades, con una supervisión cuidadosa y por los enseñamientos “telegráficos” de cada día. Muchísimas gracias en especial a los técnicos Elisa, Isabel Fernandes y Francisco (Panchy) por asistirme en los experimentos. Aprovecho para saludar a todos los compañeros en la PSA (Ilaria, Melina, Samira, Irene, Ana, Dennis, Gracía, Immaculada y Isabel Oller) por todo el cariño y apoyo durante la estancia. ¡Os echo de menos!

Agradeço muito aos colegas do PPGSMARH, em especial aos eternos membros do GruPOA (Sue, Cacá, Marília, Rafa, San, Luiz, Lídia, Adri, Pedro Camillo, Felipe, Gi, Shei, Pam e Val) e da estatística (Lívia, Ana e Carol), pela troca contínua de experiências, tanto acadêmicas quanto de vida, pelos momentos de discussão ou simplesmente de desabafo e descontração. De maneira resumida, por compartilharem e compreenderem bem todo o esforço e a dedicação necessários para a realização de uma pesquisa.

Gostaria de agradecer aos funcionários do DESA e ao corpo docente do PPGSMARH, em especial a todos aqueles que contribuíram diretamente para o projeto. Agradeço também à Elayne nessa reta final no apoio às análises de microbiologia e em especial a Sheilane por todo o companheirismo e força no laboratório nesse momento difícil de pandemia que enfrentamos.

Agradeço à banca examinadora, por aceitar avaliar e contribuir para o desenvolvimento deste trabalho.

Gostaria de agradecer ao CNPq pela bolsa de pesquisa concedida no Brasil, que foi essencial ao desenvolvimento e dedicação exclusiva a esta pesquisa, e à CAPES pela bolsa concedida para o doutorado sanduíche (PDSE CAPES/Edital nº.47/2018, processo 88881.187715/2018-01), que foi uma etapa essencial, elevou o nível do trabalho e enriqueceu muito minha jornada científica. Agradeço também ao CNPq, à CAPES e à FAPEMIG pelos recursos necessários ao desenvolvimento da pesquisa na forma de projetos diversos e manutenção da infraestrutura na universidade.

Por fim agradeço à Deus e as forças que regem inexplicavelmente esse universo, incrível e belo em sua complexidade, no qual temos a dádiva de viver

RESUMO

Os contaminantes de preocupação emergente (CECs) - agrotóxicos, hormônios, fármacos - são continuamente introduzidos no ambiente e, devido à insuficiente remoção destes por processos convencionais de tratamento de efluentes, são encontrados em baixas concentrações, podendo impactar o ambiente e a saúde humana. Tecnologias são necessárias para a remoção de CECs, especialmente nas Estações de Tratamento de Esgotos (ETEs), uma das principais fontes de entrada desses contaminantes no ambiente. Os Processos Oxidativos Avançados (POA) são indicados para o tratamento de matrizes contaminadas por compostos recalcitrantes a partir da geração de radical hidroxila e outras espécies reativas. Nesse contexto, considerando o elevado potencial de POA para o tratamento avançado de águas residuais usando o fotorreator de baixo custo RPR (*Raceway Pond Reactor*) e aproveitando a luz solar como fonte alternativa de energia e abundante no Brasil, este trabalho propõe a aplicação do foto-Fenton modificado a pH neutro com o agente complexante Fe^{3+}-EDDS (1:2) no RPR para a remoção de CECs e desinfecção. Este trabalho apresentou inicialmente uma revisão de literatura sobre a simultânea remoção de CECs e desinfecção utilizando uma metodologia de análise bibliométrica e sistêmica, que permitiu a identificação de pontos fortes, obstáculos e oportunidades de trabalho no assunto. Resultados demonstraram que a maioria dos artigos publicados segregam resultados de remoção de CECs e desinfecção, enquanto os efluentes secundários mais investigados provem de sistema LAC (lodos ativados convencional). No Brasil, por exemplo, diferentes processos biológicos são usados no tratamento secundário, incluindo lagoas facultativas, reatores anaeróbios e filtros biológicos. Em seguida, uma superfície de alumínio aplicada no fundo do reator foi investigada. Efluente secundário real de LAC e água natural foram fortificados com uma mistura de seis CECs (acetaminofeno, cafeína, carbamazepina, diclofenaco, sulfametozaxol e trimetoprima) em diferentes concentrações iniciais (20 e 100 µg L^{-1}), assim como um total de 60 contaminantes foi determinada no efluente secundário (25 ± 5 µg L^{-1}). A superfície de alumínio melhorou a eficiência da reação, atingindo eficiências semelhantes com menor dose (0,054 mM e 0,1 mM de Fe^{3+}) de catalisador a uma maior altura do líquido (15 cm), sendo a cafeína a mais resistente em todos os tratamentos avaliados. Contudo, a avaliação de diferentes matrizes mostrou a influência da matéria orgânica natural e turbidez como principais fatores na eficiência e no tempo de reação, mais do que os constituintes inorgânicos da matriz. Finalmente, um efluente de um sistema RAFA+FBP (Reator Anaeróbico de Fluxo Ascendente + Filtro Biológico Percolador) foi tratado em condições similares (0,1 mm-Fe, 1,47 mM H_2O_2, 10 cm) e apresentou uma elevada remoção de CECs (86 %) e de desinfecção (2,47±0,78 log de remoção de coliformes totais e 2,53 log de remoção de *E. coli*).

Palavras-chave: CECs, desinfecção, foto-Fenton, POA, reatores solares, RPR.

ABSTRACT

Contaminants of emerging concern (CECs) - pesticides, hormones, pharmaceuticals drugs – are introduced in the environment, and due to their low removal efficiency in conventional wastewater treatment technologies they are found at low concentrations and can impact the environment and human health. Advanced treatment is required to deal with CECs, in special for Municipal Wastewater Treatment Plants (MWWTP), a hotspot for the release of CECs in the environment. Advanced Oxidative Processes (AOPs) are indicated for the treatment of water contaminated with recalcitrant compounds by hydroxyl and other ROS (reactive oxygen species) generation. In this context, considering the high potential of AOP for advanced wastewater treatment using the low-cost RPR (Raceway Pond Reactor) and harnessing solar light as a sustainable source of energy widely available in Brazil, this work proposed the application of the solar modified neutral photo-Fenton with Fe^{3+}-EDDS complex (1:2) in RPR for removal of CECs and disinfection in different secondary effluents. This work initially presents a detailed literature review on this simultaneous treatment of CECs and disinfection with the use of a bibliometric and systemic review methodology, that allowed to identify the highlights, obstacles, and opportunities to work on this topic. Results showed that most published papers segregate disinfection and CECs results, while the most investigated secondary effluents originate from CAS (conventional activated sludge) treatment. In Brazil, for example, different biological secondary treatments are applied, including facultative ponds, anaerobic reactors, and biological filters. Following, an aluminum surface applied in the bottom of the reactor was investigated. Secondary effluent and natural water were spiked with a mixture of six CECs (acetaminophen, caffeine, carbamazepine, diclofenac, sulfamethoxazole, and trimethoprim) at different initial concentrations (20 and 100 $\mu g\ L^{-1}$), as well as a total of 60 contaminants was determined in the secondary effluent ($25 \pm 5\ \mu g\ L^{-1}$). The aluminum surface improved the overall efficiency of the reaction, enabling similar efficiencies with lower catalyst dose requirement (0.054 mM and 0.1 mM of Fe^{3+}) at higher liquid depth (15 cm), and caffeine was the most resistant in all treatment conditions. The evaluation of different matrixes showed the influence of natural organic matter and turbidity as main factors on reaction efficiency and treatment time, rather than the inorganic content. Finally, a secondary effluent from a UASB-TF (Upflow Anaerobic Sludge Blanket + Trickling filter) system was treated in similar conditions (0.1 mm-Fe, 1.47 mM H_2O_2, 10 cm) and achieved a high removal of CECs (86 %)

as well disinfection was achieved (2.47±0.78 log unit's removal for total coliforms and 2.53 log unit's removal for *E. coli*).

Keywords: CECs, disinfection, photo-Fenton, AOP, solar reactors, RPR.

INDEX OF FIGURES

Figure I.1.1 – Schematic of anthropogenic contamination sources to the environment (water bodies and soil) and the use of those contaminated natural resources afterward 31
Figure I.1.2 – Number of total search results of published materials obtained from basic keywords search on the ScienceDirect database: a) micropollutants" OR "contaminants of emerging concern" and "disinfection" and "wastewater", and b) "micropollutants" OR "contaminants of emerging concern" and "wastewater, without filters............34
Figure I.1.3 – Speciation diagram of 0.5 mM Fe(III) between pH 1 and 4 at 25°C and ionic strength of 0.1 (MACHULEK; QUINA; GOZZI, 2012).............36
Figure I.3.1 – Detailed ProKnow-C methodology applied for the literature review.....40
Figure I.4.1 – Number of manuscripts found in the search for keywords which are synonyms to "contaminants of emerging concern" in the Science Direct database from 2008-2019 44
Figure I.4.2 – Number of manuscripts found in the search for keywords "micropollutants", "contaminants of emerging concern", and "emerging contaminants" in the Science Direct database from 2008-2019............44
Figure I.4.3 – Map of keywords which were most present in the title, abstract and keywords sections of all manuscripts (407 manuscripts) retrieved in the search after adherence stage of the methodology 48
Figure I.4.4 – Map of keywords which were most present in the titles, abstract and keywords sections of manuscripts selected for the final portfolio (40 manuscripts)...48
Figure I.4.5 – Number of citations of keywords of molecules present in title, abstract and keywords sections of all manuscripts (407 manuscripts) retrieved in search after adherence stage of the methodology, and in the final portfolio (40 manuscripts)......49
Figure I.4.6 – Number of citations of keywords related to treatment technology present in the title, abstract and keywords sections of selected manuscripts in a) the final portfolio (40 manuscripts) and b) all manuscripts (407 manuscripts) retrieved in the non-refined search after the adherence stage of the methodology 51
Figure I.4.7 – Raceway pond reactor general scheme 75
Figure II.3.1 – Sampling loading............96
Figure II.3.2 – Cartridge drying step with nitrogen............96
Figure II.3.3 – Color change in the solid cartridge phase when dry............96
Figure II.3.4 – Sample elution with methanol 96
Figure II.3.5 – Evaporation under nitrogen flux............96
Figure II.3.6 – Reconstitution with H_2O MiliQ: Acetonitrile 90:10............96
Figure II.3.7 – Solid phase extraction recovery (%) for each micropollutant............97
Figure II.3.8 – UPLC-UV/DAD calibration curves for each investigated compound, concentration (µg L^{-1}) versus peak area, for a) 50 µL volume of in injection and a) 100 µL volume of injection............100
Figure II.3.9 – Mass spectrometer AB Sciex Instruments QTRAP 5500 101
Figure II.3.10 – Plataforma Solar de Almería location in the Tabernas desert, Andalucía, Spain 107
Figure II.3.11 – Effluent filtering unit: sand filter and cartridges microfilters (25 and 5 µm)............109
Figure II.3.12 – Secondary effluent from MWWTP El Ejido aspect before and after filtration............110

Figure II.3.13 – Lab-scale reaction vessels used for experiments, with and without a reflective surface 114
Figure II.3.14 – Solar simulator (Sun-Test XLS+, Atlas) equipment used in lab-scale experiments..115
Figure II.3.15 – Diagram of total solar light AM 1.5 (ISO) reflectance for the reflexive aluminum surface (Miro-Sun®) 115
Figure II.3.16 – Raceway pond reactors, with and without the aluminum surface on the bottom. 117
Figure II.3.17 – Raceway pond reactor mixing time determination with saline pulse test 118
Figure II.3.18 – Experiment's protocol with Fe^{3+}-EDDS complex 120
Figure II.3.19 – Flowchart of experiments executed with natural water...................122
Figure II.3.20 – Flowchart of experiments executed in real secondary effluent with target contaminants or identified MPs 123
Figure II.4.1 – a) Degradation of six MPs (100 µg L^{-1} each) by solar photo-Fenton with 0.054 mM of iron and 15 cm liquid depth; b) hydrogen peroxide consumption, Fe^{3+}-EDDS complex, and dissolved iron concentration evolution. 124
Figure II.4.2 – Control experiments with 100 µg L^{-1} of each micropollutant: photolysis a) at 7cm and b) at 15 cm liquid depth; MPs and H_2O_2 consumption in photolysis-H_2O_2 c) at 7 cm, d) at 10 cm, and e) at 15 cm liquid depth; f) MPs in dark Fenton, g) H_2O_2 consumption and Fe-dissolved in dark Fenton with 0.054 mm of iron and 10 cm liquid depth 126
Figure II.4.3 – Solar photo-Fenton with Fe:EDDS using 0.054 mm (empty symbols) and 0.1 mm (full symbols) of iron, for different liquid depths (green, blue and black colors for 7 cm, 10 cm and 15 cm, respectively) and MPs initial concentration of 100 µgL^{-1} each: a) ΣMP mass evolution, b) caffeine mass evolution and c) dissolved iron profile. 128
Figure II.4.4 – Solar photo-Fenton with 0.054 mM and 0.1 mM of iron, at 15 cm of liquid depth for MPs initial concentration of 20 µg L^{-1} each: a) profile of the degradation of MP mass and b) caffeine mass. 129
Figure II.4.5 – ΣMP mass degradation profile comparison with (half-full symbols) and without (empty symbols) aluminum surface for MPs initial concentration of 100 µg L^{-1} each, 10 cm of liquid depth and iron initial concentration of 0.018 mM, 0.036 mM and 0.054 mM 132
Figure II.4.6 – Schematic of light reflection inside the reactor when using an aluminum surface in the bottom of the reactor. 132
Figure II.4.7 – Solar photo-Fenton with 0.054 mM or 0.1 mM of iron, at 15 cm of liquid depth for MPs initial concentration of 20 µg L^{-1} each with and without aluminum surface in the reactor: a) profile of the degradation of MP mass and b) caffeine mass........133
Figure II.4.8 – Solar photo-Fenton in the RPR with 0.054 mM of iron and using the aluminum surface and with 0.1 mM of iron without using the aluminum surface: profile of the degradation of a) ΣMP mass; b) caffeine mass; c) hydrogen peroxide consumption; and d) dissolved iron concentration. MPs initial concentration of 20 µg L^{-1} and 100 µg L^{-1} each, at 15 cm of liquid depth. Average solar irradiation of 41 W m^{-2} and 46 W m^{-2} for experiments with 100 µg L^{-1} of each MP with and without aluminum surface, respectively, and 47 W m^{-2} and 50 W m^{-2} for experiments with 20 µg L^{-1} of each MP, with and without aluminum surface, respectively....................................134
Figure II.4.9 – Degradation of six MPs (100 µg L^{-1} each) in spiked real secondary effluent by solar photo-Fenton with 0.1 mM of iron and 15 cm liquid depth.............136

Figure II.4.10 – Solar modified photo-Fenton reactions with Fe(III):EDDS 1:2 at 15 cm of liquid depth in spiked real secondary effluent from MWWTP at lab-scale for MPs initial concentration of 20 μg L^{-1}: a) degradation of ΣMP mass, b) dissolved iron concentration and hydrogen peroxide consumption. 136

Figure II.4.11 – Solar modified photo-Fenton reactions with Fe(III):EDDS 1:2 at 15 cm of liquid depth in real secondary effluent from MWWTP in RPR at different iron concentrations: a) degradation of ΣMP mass, b) dissolved iron concentration and hydrogen peroxide consumption. 142

Figure II.4.12 – Solar modified photo-Fenton reactions with Fe(III):EDDS 1:2 at 15 cm of liquid depth in real secondary effluent from MWWTP in RPR: concentration of most identified compounds with: a) 0.054 mM-Fe without the aluminum surface, b) 0.054 mM-Fe with the aluminum surface, c) 0.1 mM-Fe without the aluminum surface, and d) 0.1 mM-Fe with the aluminum surface. 144

Figure II.4.13 – Solar modified photo-Fenton reactions in real secondary effluent in the RPR with Fe(III):EDDS 1:2 at 15 cm of liquid depth: evolution of the concentration of a) 4-FAA, b) imidacloprid, c) 4AAA, d) gabapentin, e) O-venlafaxine, f) tramadol, g) caffeine, h) antipyrine, and i) levofloxacin. 147

Figure III.1.1 – Most frequently used treatment processes in Brazil by number of MWWTP. Source: Adapted from (ANA, 2017)..157

Figure III.1.2 – UASB reactor (green to the left size) and biological filters (blue in the right)..161

Figure III.3.1 – Pre-treatment filtering process: stainless steel mesh filters (100 μm and 5 μm) and medium flow quantitative paper..173

Figure III.3.2 – Secondary effluent from the UASB + SBTF system aspect before and after filtration..173

Figure III.3.3 – SunTest CPS+ (ATLAS) and covered glass reactor (right side)......175

Figure III.3.4 – Glass covered reactor in the inside and as positioned in the SunTest CPS+ (ATLAS) 176

Figure III.4.1 – Degradation of six MPs (100 μg L^{-1} each) in spiked real secondary UASB+SBTF effluent by solar photo-Fenton modified with Fe^{3+}:EDDS 1:2, 0.1 mM of iron, 1.47 mM H_2O_2, and 10 cm liquid depth. 178

Figure III.4.2 – ΣMPs removal in spiked (100 μg L^{-1} each MP) real secondary UASB+SBTF effluent by solar modified photo-Fenton, photolysis and photo-H_2O_2. Fe^{3+}:EDDS 1:2..178

Figure III.4.3 – Hydrogen peroxide consumption during -▲- solar photo-H_2O_2 treatment and solar modified photo-Fenton in real secondary UASB+SBTF effluent -▲- spiked (S) at MPs 100 μg L^{-1} each or ■ not spiked (NS), at 10 cm liquid depth with Fe^{3+}:EDDS 1:2, 0.1 mM of iron, and 1.47 mM H_2O_2..180

Figure III.4.4 – Total (black symbols) and dissolved (red symbols) iron during modified solar photo-Fenton in real secondary UASB+SBTF effluent -●- -●- spiked (S) at MPs 100 μg L^{-1} each or -■- -■- not spiked (NS) at 10 cm liquid depth with Fe^{3+}:EDDS 1:2, 0.1 mM of iron, and 1.47 mM H_2O_2..180

Figure III.4.5 – a) Total coliforms and b) *E. coli* results during ▲ solar photo-H_2O_2, ● solar photolysis, and modified solar photo-Fenton in real secondary UASB+SBTF effluent ▲ spiked (S) at 100 μg L^{-1} each MP and ■ not spiked (NS), at 10 cm liquid depth with Fe^{3+}:EDDS 1:2, 0.1 mM of iron, and 1.47 mM H_2O_2..............................182

INDEX OF TABLES

Table I.3.1 – Systemic analysis summary: lens and goals used in the analysis........42
Table I.4.1 – Updated portfolio construction: search input keywords and number of manuscripts found as published material on the topic between 2008-2019 45
Table I.4.2 – Detailed Portfolio construction with each database results for each search input keywords and number of manuscripts found as published material on the topic between 2008-2019..46
Table I.4.3 – Filtered manuscripts from bibliometric analysis of the portfolio 53
Table I.4.4 – Bibliometric analysis summary: final selected articles and statistical data of the number of citations and other indices 54
Table I.4.5 – Systemic analysis of the manuscript: Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? (MARGOT *et al.*, 2013) 57
Table I.4.6 – Summary of the systemic analysis: main strengths and weaknesses detected in each paper and specific questions proposed for future research............62
Table I.4.7 – Recently investigations with raceway pond reactors: operational and reaction parameters, micropollutants and disinfection...77
Table II.3.1 – Gradient flux of solvents during HPLC analysis..................................98
Table II.3.2 – UPLC-UV/DAD wavelength of maximum absorbance, retention time, limits of detection and quantification, and calibration curve parameters for each investigated compound at 50 µL injection volume (n = 3) 99
Table II.3.3 – Gradient flux of solvents during HPLC-MS/MS analysis....................102
Table II.3.4 – Water matrixes used for each set of experiments during research....107
Table II.3.5 – Natural tap water average composition (n=4)....................................108
Table II.3.6 – Characterization of effluent from the secondary treatment of MWWTP El Ejido 109
Table II.3.7 – Main properties of model micropollutants 111
Table II.3.8 – Raceway pond reactor dimensions..116
Table II.3.9 – Raceway pond reactor saline pulse test determination of mixing time 118
Table II.4.1 – Initial degradation rate (r_0, µg min^{-1}) and treatment time for attaining 80% ($t_{80\%}$, min) degradation of MPs by solar photo-Fenton reactions with Fe:EDDS using 0.054 mm and 0.1 mm of iron, for each liquid depth (7 cm, 10 cm and 15 cm) and MPs initial concentration of 100 µg L^{-1} each. Treatment Capacity for 100^1 and 20^2 µg L^{-1} is also included. 130
Table II.4.2 – Initial concentrations and respective statistics of compounds identified on the real secondary effluent from MWWTP..140
Table II.4.3 – Initial degradation rate (r0, ng min^{-1}) and treatment time for attaining 80 % (t80%, min) degradation of MPs (4-FAA, imidacloprid, 4AAA, gabapentin, O-venlafaxine, tramadol, caffeine, antipyrine, and levofloxacin) by modified photo-Fenton reactions with Fe(III):EDDS 1:2 at 15 cm of liquid depth in real secondary effluent from MWWTP in RPR at different iron concentrations...146
Table II.4.4 – Main properties of micropollutants detected at the higher concentration on the EMWWTP (4-FAA, imidacloprid, 4AA, gabapentin, O-venlafaxine, 4AAA, tramadol, caffeine, antipyrine, and levofloxacin)..149
Table III.1.1 – Average quality of effluent in treatment processes of MWWTP in Brazil. Source: Adapted from (SPERLING, 2016). 158

Table III.1.2 – Comparison of secondary effluent quality in different biological treatment processes of two MWWTP from Brazil and Spain. 160
Table III.1.3 – Some recommended uses for MWWTP effluent reuse in Brazil 164
Table III.1.4 – Some recommended parameters values for treated municipal wastewater reuse in Brazil...165
Table III.3.1 – Gradient flux of solvents during HPLC analysis in Brazil 168
Table III.3.2 – UPLC-UV/DAD wavelength of maximum absorbance, retention time, and calibration curve parameters for each investigated compound at 50 μL injection volume in demineralized water matrix (n =5)..169
Table III.3.3 – UPLC-UV/DAD wavelength of maximum absorbance, retention time, and calibration curve parameters for each investigated compound at 50 μL injection volume in filtered secondary effluent matrix (n =5)..169
Table III.3.4 – Characterization of effluent from the secondary treatment of UASB+SBTF system (n = 4)...174
Table III.4.1 – Initial degradation rate (r_0, μg min^{-1}) and treatment time for attaining 80 % ($t_{80\%}$, min) degradation of MPs by modified photo-Fenton reaction with Fe^{3+}:EDDS 1:2 in spiked (100 μg L^{-1} each MP) real secondary UASB+SBTF effluent...............179
Table III.4.2 – Sulfates, total and filtrable orthophosphates, nitrates, and pH in the effluent before and after treatment after solar photo-H_2O_2, solar photolysis, and solar photo-Fenton treatments in real secondary UASB+SBTF effluent spiked (S) at 100 μg L^{-1} each MP and not spiked (NS). 181

LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS

4-AA – 4-aminoantipyrine

4-AAA – 4-acetylaminoantipyrine

4-FAA – 4-formylaminoantipyrine

ACE – Acetaminophen

ACS – American Chemical Society

ACTM – Acetamiprid

ANA – Agência Nacional das Águas

AOP – Advanced Oxidation Processes

ARB – Antibiotic Resistant Bacteria

ARG – Antibiotic Resistant Gene

AS – Activated Sludge

ASCE – American Society of Civil Engineers

BF – Biological Filter

BOD – Biochemical Oxygen Demand

CAF – Caffeine

CAR – Carbamazepine

CCL – Contaminant Candidate List

CECs – Contaminants of Emerging Concern

CFU – Colony Forming Unity

CIEMAT – Centro de Investigaciones Energéticas Medioambientales y Tecnológicas

CIESOL – Center for Solar Energy Research

CPC – Compound Parabolic Collector

DBPs – Disinfection Byproducts

DIC – Diclofenac

DOC – Dissolved Organic Carbon

E. Coli – Escherichia Coli

EC – European Community

EDDS – Ethylenediamine-N,N'-disuccinic acid

EDTA – Ethylenediaminetetraacetic acid

EMWWTP – Effluent of Municipal Wastewater Treatment Plant

ESI – Electrospray Injection

EU – European Union
GBP – Gabapentin
GO-TiO_2 – Composite of Graphene Oxide and Titanium Dioxide
HPLC – High-Performance Liquid Chromatography
HRT – Hydraulic Retention Time
IC – Inorganic Carbon
IO – Inverse Osmosis
MBR – Membrane Bioreactor
MF – Microfiltration
MPs – Micropollutants
MS/MS – Tandem Mass Spectrometry
MWWTP – Municipal Wastewater Treatment Plant
NF – Nanofiltration
NOM – Natural Organic Matter
O-DSMT – O-desmethyl-tramadol
O-DSMV – O-desmethylvenlafaxine
ORP – Oxidation-reduction Potential
PF – Photo-Fenton
PSA – Plataforma Solar de Almería
QTRAP – Quadrupole-Linear Ion Trap Mass Spectrometer Analyzer
Q_{UV} – Accumulated UV Energy per Volume Unity
RO – Reverse Osmosis
RPM – Rotations per minute
RPR – Raceway Pond Reactor
SBTF – Sponge Bed Trickling Filter
SJR – Scientific Journal Rankings
SPE – Solid Phase Extraction
SRM – Selective Reaction Monitoring
SRT – Solids Retention Time
SUL – Sulfamethoxazole
TBZ – Thiabendazole
TC – Treatment Capacity
TF – Trickling Filter

TIC – Total Inorganic Carbon

TOC – Total Organic Carbon

TOF – Time of Flight

TP – Transformation Products

TRI – Trimethoprim

TSS – Total Suspended Solids

UASB – Upflow Anaerobic Sludge Blanket

UF – Ultrafiltration

UPLC – Ultra-Performance Liquid Chromatography

USEPA – United States Environmental Protection Agency

UV – Ultraviolet light

$\overline{UV}$ – Average Ultraviolet Irradiance

UV/DAD – Ultraviolet Diode Array Detector

VRPA –Volumetric Rate of Photon Absorption

ΣMP – Mass Sum of Contaminants

TABLE OF CONTENTS

1. INTRODUCTION 22
2. JUSTIFICATION 26
3. THESIS HYPOTHESIS 28
4. OBJECTIVES 29
  4.1. GENERAL OBJECTIVE 29
  4.2. SPECIFIC OBJECTIVES 29
CHAPTER I – REMOVAL OF CONTAMINANTS OF EMERGING CONCERN AND DISINFECTION IN DOMESTIC WASTEWATER: A BIBLIOMETRIC AND SYSTEMIC ANALYSIS OF THE LITERATURE 30
I.1. INTRODUCTION 31
I.2. OBJECTIVES 37
  I.2.1. GENERAL OBJECTIVE 37
  I.2.2. SPECIFIC OBJECTIVES 38
I.3. METHODOLOGY 38
  I.3.1. BIBLIOMETRIC AND SYSTEMIC ANALYSIS OF THE LITERATURE 38
    I.3.1.1. Portfolio selection: definition of keywords 40
    I.3.1.2. Portfolio selection: definition of databases 40
    I.3.1.3. Portfolio selection: search for articles and adherence stage 41
    I.3.1.4. Final portfolio and visualization of keywords 41
    I.3.1.5. Bibliometric analysis 41
    I.3.1.6. Systemic analysis 42
  I.3.2. RACEWAY POND REACTORS: APPLICATIONS IN THE ENVIRONMENTAL FIELD, USE FOR ADVANCED SOLAR OXIDATION AND OPERATIONAL PARAMETERS 42
I.4. RESULTS AND DISCUSSION 43
  I.4.1. BIBLIOMETRIC AND SYSTEMIC ANALYSIS OF THE LITERATURE 43
    I.4.1.1. Development of the Portfolio 43
    I.4.1.2. Bibliometric analysis of the portfolio 52
    I.4.1.3. Systemic analysis of final selected manuscripts 56
  I.4.2. RACEWAY POND REACTORS: APPLICATIONS IN THE ENVIRONMENTAL FIELD, USE FOR ADVANCED SOLAR OXIDATION AND OPERATIONAL PARAMETERS 74
I.5. CONCLUSIONS 85
CHAPTER II – EVALUATION OF THE USE OF A REFLEXIVE SURFACE IN AN OPEN SOLAR REACTOR FOR THE REMOVAL OF CECS IN SECONDARY EFFLUENT FROM MWWTP 89
II.1. INTRODUCTION 90
II.2. OBJECTIVES 94
  II.2.1. GENERAL OBJECTIVE 94
  II.2.2. SPECIFIC OBJECTIVES 94
II.3. MATERIALS AND METHODS 94
  II.3.1. CHEMICALS 94
  II.3.2. ANALYTICAL METHODS 95

II.3.2.1. Sample preparation *95*
II.3.2.2. Micropollutants monitoring *97*
II.3.2.2.1. Target compounds 97
II.3.2.2.2. Compounds in real effluent 100
II.3.2.3. Iron-EDDS complex monitoring *103*
II.3.2.4. Ionic chromatography analyses *103*
II.3.2.5. Dissolved Organic Carbon analyses *104*
II.3.2.6. Total and dissolved iron analyses *105*
II.3.2.7. Hydrogen peroxide analyses *106*

II.3.3. EXPERIMENTAL SET-UP 106

II.3.3.1. Investigated matrixes *107*
II.3.3.2. Target micropollutants (MPs) *110*
II.3.3.3. Lab-scale experiments with artificial sunlight *113*
II.3.3.4. Semi-pilot scale experiments with natural sunlight *116*
II.3.3.5. Experiments routine *119*

II.4. RESULTS AND DISCUSSION 124

II.4.1.1. Lab-scale results with natural water *124*
II.4.1.2. Lab-scale results with natural water: effect of an aluminum reflexive surface *131*
II.4.1.3. Semi-pilot plant scale results with natural water: effect of an aluminum reflexive surface in RPR under solar irradiation *133*
II.4.1.4. Lab-scale results with spiked real secondary EMWWTP: effect of an aluminum reflexive surface 135
II.4.1.5. Semi-pilot scale results with real secondary EMWWTP: effect of an aluminum reflexive surface in RPR under solar irradiation *140*

II.5. CONCLUSIONS 151

CHAPTER III – MODIFIED CIRCUMNEUTRAL PHOTO-FENTON REACTIONS ON THE REMOVAL OF SELECTED CECS AND DISINFECTION IN REAL SECONDARY EFFLUENTS FROM UASB+ SBTF SYSTEM 155

III.1. INTRODUCTION 156

III.2. OBJECTIVES 167

III.2.1. GENERAL OBJECTIVE 167

III.2.2. SPECIFIC OBJECTIVES 167

III.3. MATERIALS AND METHODS 167

III.3.1. CHEMICALS 167

III.3.2. ANALYTICAL METHODS 168

III.3.2.1. Sample preparation *168*
III.3.2.2. Micropollutants monitoring *168*
III.3.2.3. Chemical Oxygen Demand analyses *170*
III.3.2.4. Total and dissolved iron analyses *170*
III.3.2.5. Hydrogen peroxide analyses *170*
III.3.2.6. Sulfate's analyses *171*
III.3.2.7. Nitrate and orthophosphate analyses *171*
III.3.2.8. Total coliforms and E. coli *172*

III.3.3. EXPERIMENTAL SET-UP 173

III.3.3.1. Investigated matrix *173*
III.3.3.2. Target micropollutants (MPs) *174*
III.3.3.3. Lab-scale experiments with artificial sunlight *175*

III.4. RESULTS AND DISCUSSION 177

III.4.1. REMOVAL OF MPS IN THE UASB+SBTF SECONDARY EFFLUENT BY MODIFIED CIRCUMNEUTRAL PHOTO-FENTON REACTION 177

III.4.2. DISINFECTION IN THE UASB+SBTF SECONDARY EFFLUENT BY MODIFIED CIRCUMNEUTRAL PHOTO-FENTON REACTION 182

III.5. CONCLUSIONS 186

5. CONCLUSIONS 188

6. RECOMMENDATIONS 191

REFERENCES 193

APPENDICES 207

APPENDIX I – FINAL PORTFOLIO OF PEER-REVIEWED MANUSCRIPTS WITH RESPECTIVE NUMBER OF CITATIONS 208

APPENDIX II – COMPLETE SYSTEMIC ANALYSIS: FINAL MANUSCRIPTS 211

APPENDIX III – INFORMATION FOR THE FINAL FIVE SELECTED MANUSCRIPTS OF THE SYSTEMIC ANALYSIS: TREATMENT TECHNOLOGY, EVALUATED MATRIX, TREATMENT SCALE, MICROPOLLUTANTS, AND DISINFECTION EFFICIENCY, TOXICITY AND OTHER EFFECTS, AND TREATMENT COSTS 221

APPENDIX IV – CHROMATOGRAM OF 100 µG L^{-1} STANDARD SOLUTION INJECTION 226

APPENDIX V – SELECTED MICROPOLLUTANTS SPECTRUM UNDER DIFFERENT PH VALUES 229

1. INTRODUCTION

Different anthropogenic activities have been responsible for the deterioration of natural water resources due to the contribution with emission and dispersion of several pollutants. Industrial and municipalities' wastewater are continuously introduced into the environment without treatment or with insufficient treatment. This continuous discharge causes contamination with pathogenic organisms, organic matter, nutrients, metals, microplastics, organic micropollutants (pesticides, hormones, pharmaceuticals, solvents, personal care products – PCPs), etc.

The concern over the presence of some substances in the environment has been raised over the last decades, and such substances have been usually denominated as emerging pollutants or contaminants of emerging concern (CECs). Different organic micropollutants (MPs) such as pharmaceuticals, pesticides, and personal care products have been included in the CECs category. The CECs are pollutants found at very low (ng L^{-1} to µg L^{-1}) concentrations in the environment, detected by advanced analytical techniques such as solid-phase extraction followed by chromatographic analysis coupled to tandem mass spectrometry. Also, these compounds may harm the environment and human health even at low concentrations, or do not present enough information over their effects, and are rarely present in water regulatory policies over the world (ZHAO; YE; ZHANG, 2018).

Some of these compounds have a maximum permitted concentration values, mainly in local monitoring legislations, such as natural water and drinking water in Brazil (drinking water legislation GM/MS n° 888 of May 4, 2021, of the Health Ministry, CONAMA resolutions 357 of March 17, 2005, and 430 of May 13, 2011), in the USA (National Primary and Secondary Drinking Water Regulation, Toxic Substances List and the Priority Substances List) and in European Union (Watch List of substances in Decisions 2015/495/EU of 20 March 2015 and 2018/840/EU of 5 June 2018, Drinking Water Directive 98/83/EC). But those represent only a few substances and classes that are released into the environment and considered CECs.

Municipal wastewater discharge can be considered as an important point-source of pollution for CECs, once conventional water and wastewater technologies are usually inefficient in the degradation of CECs. In some cases, these technologies may only achieve a substrate transference of pollutants, removing them from the liquid phase and generating residues (sludge or concentrate) that require post-treatment (LUO *et al.*, 2014; TRAN; REINHARD; GIN, 2018). Several MWWTP in Switzerland have adopted advanced technologies such as ozonation or adsorption in activated carbon followed by sand filtration to achieve the required disinfection and CECs treatment efficiency (BOURGIN *et al.*, 2018).

In Brazil, the most applied conventional wastewater treatment technologies in terms of number of MWWTP are facultative ponds (anaerobic followed by facultative or just facultative), primary treatment (septic tank followed by biological filter), and anaerobic reactors, that together are used in 1 287 MWWTP (46 % out of a total of 2 768) (ANA, 2017). Among these technologies, UASB (Upflow Anaerobic Sludge Blanket) reactors present lower BOD (biological oxygen demand) efficiency (< 60 %) against conventional activated sludge systems (CAS) (60 – 80 %) but are a technological choice in the favorable Brazilian climate due to lower operational costs in comparison to the CAS, that is the system used most frequently for MWWTP in larger cities (ANA, 2017). Small-sized MWWTP have been related to more operational and maintenance problems, causing lower efficiency even for the removal of conventional pollutants (NOYOLA *et al.*, 2012). Studies about the advanced treatment of secondary effluents from MWWTP to remove CECs usually focus on effluents from activated sludge (CAS or Membrane Bioreactor – MBR) because these systems are the most applied around the world in MWWTP (TRAN; REINHARD; GIN, 2018).

In this context, different advanced technologies have been investigated for the removal of CECs in wastewater systems. Among them, Advanced Oxidative Processes (AOP) can be indicated for the treatment of highly non-biodegradable substances and are based on the production *in situ* of hydroxyl radical (HO•) and other radicals (DEZOTTI, 2008). Over the last years, some technologies have achieved status as consolidated technologies, which are already in the implementation and expansion stage, including ozonation, which is an AOP (RIZZO *et al.*, 2019). In comparison to those, there are other processes, the “new” technologies, that still lack development and application on a larger scale, including the photo-Fenton (PF) process in this case. The main modifications of the classical Fenton’s reagent over the last decades have focused on applying this process at a larger scale, including using solar light as a sustainable irradiation source, the use of reduced concentration of reagents (Fe and H_2O_2), and different strategies to work at circumneutral pH (CLARIZIA *et al.*, 2017).

In this line of improvement of the photo-Fenton reaction at pilot-scale and costs reduction, an open reactor configuration has been studied over the last few years for tertiary treatment in MWWTP, the Raceway Pond Reactor (RPR). This reactor is a non-concentrating type and can be constructed as ponds or tanks on which the liquid is recirculated by paddlewheels, and have been used successfully for a long time for microalgal biomass production on a large scale, using low-cost materials such as plastics or durable concrete walls (CHISTI, 2016). This reactor has been pointed as effective on the removal of MPs as well for disinfection (DE LA OBRA JIMÉNEZ, I. *et al.*, 2019; RIVAS IBÁÑEZ *et al.*, 2017). RPR reactors have shown reduced implementation costs and energy consumption (10 € m^{-2}, 4 W m^{-3}), and the possibility to operate at different liquid depths (15 to 30 cm) to change reaction's path length considering factors such as solar radiation availability (RIVAS *et al.*, 2015).

Finally, in Brazil, different secondary biological treatments are usually applied, from CAS systems to anaerobic reactors, ponds, and biological filters in medium to small-size plants. Furthermore, in Brazil, there is a high and continuous availability of solar radiation in a vast part of the country. Even though there are still few studies that dedicate to the treatment of wastewater by renewable solar energy (MARCELINO *et al.*, 2014), the solar photo-Fenton is a promising new advanced technology that could promote advanced treatment in MWWTP effluents. In this manner, the use of circumneutral solar photo-Fenton reactions for wastewater post-treatment in Brazil as a low-cost advanced treatment is an important technical option to be studied.

In this way, this work proposes to evaluate the applicability of the circumneutral solar photo-Fenton reactions using RPR to treat aerobic and anaerobic MWWTP secondary effluent, aiming the disinfection and removal of CECs. Initially, a detailed literature review was performed **(Chapter I)** to evaluate information on the removal of pathogens (disinfection) and of CECs in municipal secondary effluents using different advanced technologies. From this review, it was possible to identify the gaps in the literature, allowing the novelty, as well as opportunities to research in this area.

In consequence, in **Chapter II,** this work proposed a modification in the RPR to improve the solar photo-Fenton treatment of CECs in municipal wastewater in this reactor and, at the same time, reduce operational costs (costs of reagents and energy). An aluminum surface was applied in the bottom of RPR, aiming for the improvement of the solar UV-Vis light pathway inside the reactor **(Chapter II)**. Initially, assays were evaluated in natural water and later in real secondary effluent from CAS MWWTP. Finally, the efficiency of the circumneutral photo-Fenton reactions applied previously were evaluated in a secondary effluent from a demonstration-scale

UASB + trickling filter system in Brazil to remove selected CECs and disinfection (**Chapter III**).

2. JUSTIFICATION

The current Brazilian MWWTP scenario can be considered quite challenging. There is a low coverage in both collection (61.4 % of the population) and collection plus domestic wastewater treatment (42.6 % of the population) in the country (ANA, 2017). Furthermore, several MWWTP in the country have been reported to operate in inadequate conditions due to financial, technical, and low maintenance limitations (NOYOLA *et al.*, 2012). At the same time, a “new” category of contaminants - the CECs - has been dealt with increasing effort around the world (BOURGIN *et al.*, 2018) and could be considered as a “future challenge” to the already challenging MWWTP general scenario in Brazil and non-developed countries.

One class of CECs in particular, the antibiotics, has been a priority health topic at a global level because of the increase of antibiotic resistant bacteria with the intensified release of these CECs in the environment (WHO. WORLD HEALTH ORGANIZATION, 2018). In this way, besides removing CECs, the occurrence and combating of antibiotic-resistant bacteria and antibiotic-resistant genes has been a priority globally (KARAOLIA *et al.*, 2018; MOREIRA *et al.*, 2018). Thus, it is highly relevant to investigate the removal of CECs, including pharmaceuticals as antibiotics, and disinfection, involving the removal of pathogens, from total coliforms to antibiotic-resistant bacteria.

Considering the conventional biological wastewater treatment technologies available, the removal efficiency of CECs is much variable for each substance, MWWTP technology, operating conditions, among other factors (TRAN; REINHARD; GIN, 2018). Besides, most of the observed efficiency in these cases might be due to sorption onto solids, not going through biodegradation, but only transferred to the solid phase. In this way, the use of advanced treatment technologies is indicated. Among these, AOP processes such as ozonation, photocatalysis, Fenton’s reagent, and photo-Fenton can promote the oxidation of both organic compounds and pathogens, leading to higher effluent quality.

Even though ozonation and activated carbon adsorption are the main solutions chosen in Switzerland to remove CECs (BOURGIN *et al.*, 2018), these might not always be the most appropriate technologies in every case. For example, in Brazil, these technologies could involve high costs, especially for small-size MWWTP. Other options for technologies should be investigated. Considering the Brazilian scenario with a high solar and land availability, it is highly relevant the investigation of circumneutral photo-Fenton reactions in open solar reactors such as the RPR, making it a low cost, sustainable, low energy, and low maintenance tertiary technology.

In terms of the application of solar circumneutral photo-Fenton reactions for domestic wastewater treatment, different factors need to be developed and optimized to allow a possible scaling-up of this process (RIZZO *et al.*, 2019). Some factors have been investigated, including strategies to work at near-neutral pH conditions and the use of open reactors with higher treatment capacity and lower cost. Still, there is room for further improvement of the reaction and solar photoreactors to achieve a future continuous operation with a higher effluent flow at a real scale.

In this way, considering i) a high potential of circumneutral photo-Fenton reaction to promote both disinfection and advanced effluent treatment, ii) the use of solar irradiation as an alternative and sustainable source of energy, iii) the current MWWTP scenario in Brazil that needs improvement in treatment efficiency, considering the variety of technologies applied and iv) a future scenario following the international trend on which the removal of CECs will be mandatory; this work proposes the application of the solar photo-Fenton reaction in open photoreactors to promote removal CECs and disinfection in secondary municipal effluents.

3. THESIS HYPOTHESIS

- Most studies published about the tertiary treatment of secondary effluents from the biological treatment in MWWTP do no present information on the simultaneous removal of pathogens (disinfection) and the removal of CECs;

- Most studies published about the tertiary treatment of secondary effluents from MWWTP focus on effluents from conventional activated sludge systems, and there is less information about other secondary biological treatments (in special for anaerobic technologies);

- Open solar photoreactors such as the RPR can be modified with the use of a reflexive surface in its bottom face to improve circumneutral photo-Fenton reactions with a low concentration of reagents for the removal of CECs in secondary effluents from biological treatment from MWWTP;

- Circumneutral photo-Fenton reactions are efficient for both disinfection and removal of CECs in effluents from the secondary biological treatment from an anaerobic reactor, followed by a biological filter (UASB+SBTF), a process frequently used in Brazilian MWWTP, as well as they are reported to be for the treatment of secondary aerobic effluent.

4. OBJECTIVES

4.1. General objective

The main objective of this work is to investigate the applicability of the circumneutral solar photo-Fenton reactions using an open photoreactor for the treatment of municipal secondary effluent from aerobic and anaerobic biological processes, considering the disinfection and removal of following CECs (acetaminophen, caffeine, trimethoprim, sulfamethoxazole, carbamazepine, and diclofenac).

4.2. Specific objectives

The specific objectives of this work are as follows:

- Perform a systemic review of the literature regarding treatments for the simultaneous removal of CECs and disinfection in municipal wastewaters and identify the highlights, obstacles, and opportunities to work with solar photo-Fenton treatment in open reactors;
- Evaluate the effect of applying an aluminum reflexive surface in the RPR for circumneutral solar photo-Fenton reactions aiming the removal of selected CECs in natural water and real secondary aerobic effluent from MWWTP, at bench-scale and semi-pilot scale;
- Evaluate the efficiency of circumneutral solar photo-Fenton reactions on the removal of selected target CECs and disinfection (*E. Coli* and Total Coliforms) in secondary anaerobic+aerobic effluent from MWWTP.

CHAPTER I[1] – REMOVAL OF CONTAMINANTS OF EMERGING CONCERN AND DISINFECTION IN DOMESTIC WASTEWATER: A BIBLIOMETRIC AND SYSTEMIC ANALYSIS OF THE LITERATURE

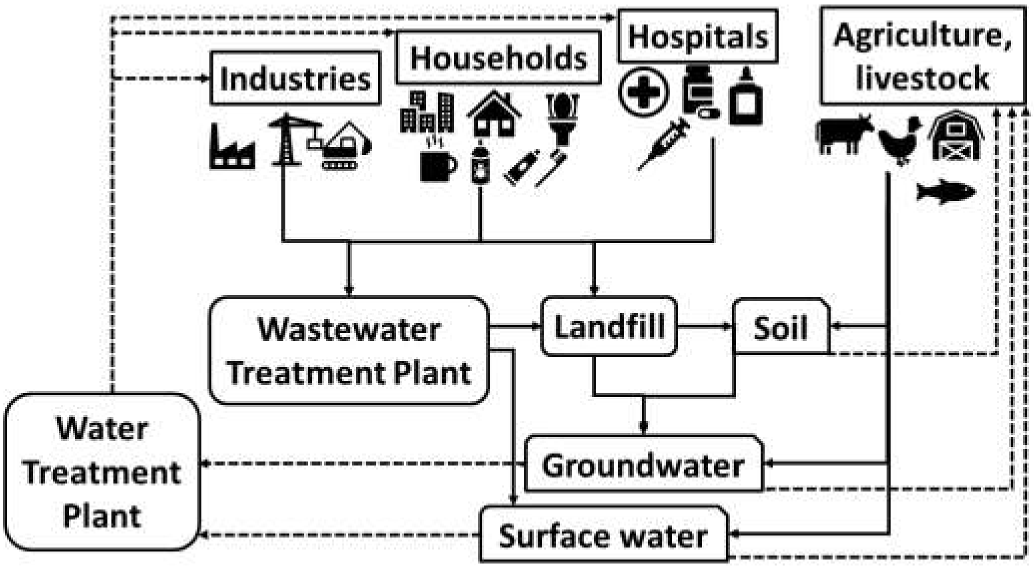
---

[1] A manuscript was published with results of this chapter: COSTA, Elizângela Pinheiro; STARLING, Maria Clara Vieira Martins; AMORIM, Camila C. *Simultaneous removal of emerging contaminants and disinfection for municipal wastewater treatment plant effluent quality improvement: a systemic analysis of the literature*. Environmental Science and Pollution Research, 14 jan. 2021. DOI: https://doi.org/10.1007/s11356-021-12363-5

I.1. INTRODUCTION

Among the different contaminants that are released by many anthropogenic sources (Figure I.1.1), CECs have been intensively investigated over the last decades, under this denomination or others such as micropollutants. Different substances have been gathered under this group, including pesticides, industrial contaminants, pharmaceuticals, and personal care products (PPCPs), hormones, drugs of abuse, and others (ZHAO; YE; ZHANG, 2018).

FIGURE I.1.1 – Schematic of anthropogenic contamination sources to the environment (water bodies and soil) and the use of those contaminated natural resources afterward



These contaminants have in common their presence at low concentrations (ng L^{-1} to µg L^{-1}) in different environmental matrixes, which requires advanced analytical sample preparation and detection method. In this way, organic micropollutants (MPs) such as pharmaceuticals, pesticides, and personal care products are considered CECs. Furthermore, some substances might have harmful effects on human health and the environment even at such levels of concentration, or even effects individually or in a synergetic association which is not yet fully comprehended (LUO *et al.*, 2014; SCHWARZENBACH, 2006).

Among all mentioned sources of anthropogenic contamination with CECs, MWWTP is an especially relevant point-source pollution site due to the huge stream of contaminants released to water bodies (Figure I.1.1). Different studies around the world have indicated the presence of these substances in MWWTP effluents streams (BARBOSA *et al.*, 2016; CHINNAIYAN *et al.*, 2018; GANI; KAZMI, 2017; GWENZI; CHAUKURA, 2018; LIU; ZHANG; CHANG,

2018; MADIKIZELA; TAVENGWA; CHIMUKA, 2017; STARLING; AMORIM; LEÃO, 2019). The removal of these substances is much variable and depends on different factors, including the influent concentration (specific to local consumption pattern, for example), the treatment process applied (its operation and maintenance), as well as to specific biological and physicochemical properties of substances (TRAN; REINHARD; GIN, 2018).

CECs are poorly regulated in water matrixes monitoring policies over the world. In Brazil, within the Health Ministry drinking water legislation GM/MS n.º 888 of May 04, 2021, maximum concentration levels are established for drinking treated water and just for a few compounds, most of them pesticides and their metabolites. At the same time, the National Council on the Environment – CONAMA resolution 357 of March 17, 2005 (modified later by CONAMA resolution 430 of May 13, 2011) set environmental standards and established limits for the disposing of effluents, but mostly focused on pesticides and industrial organic contaminants.

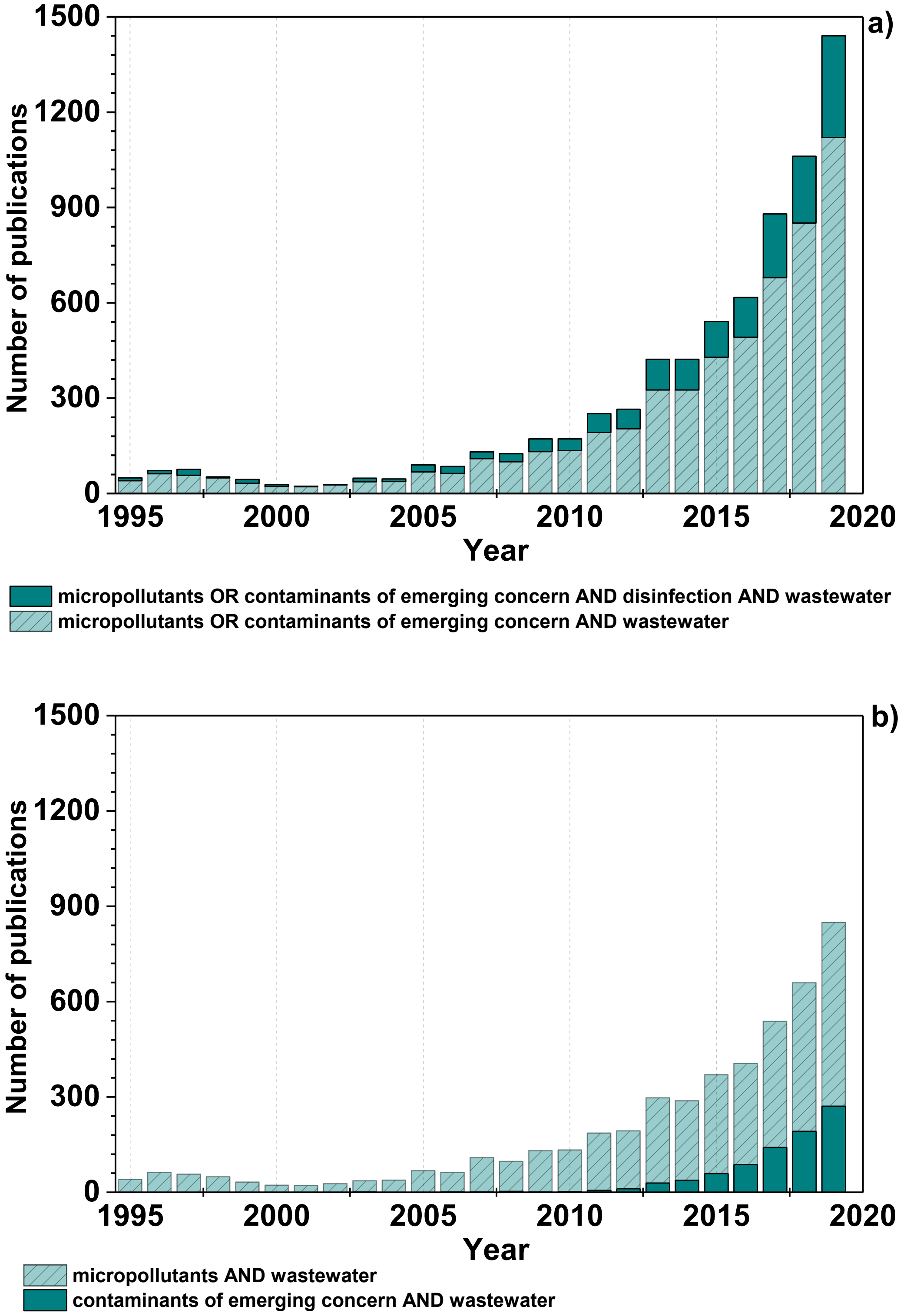
In the USA, the Environmental Protection Agency – USEPA is responsible for both water resources and drinking water quality standards. Through the Clean Water Act, it establishes standards for the disposal of pollutants in waters and quality of surface waters within two lists, the Toxic Substances List and the Priority Substances List. Both include several solvents, disinfection by-products, and pesticides, but no PCPs. While both the National Primary and Secondary Drinking Water Regulations establish limits in drinking water for several contaminants, some PCPs, plasticizers, and hormones are only included on the Contaminant Candidate List (CCL). The CCL is a list of contaminants that are not subject to any regulations but can occur in public water systems and may require future regulation. The CCL is already on its 4th edition from November 17, 2016, with 97 chemicals or chemical groups and 12 microbial contaminants.

Regarding the European Union, the newer European Union Directive 2013/39/EU recommended monitoring and treatment solutions for a group of 45 priority substances meeting the requirements of environmental protection. The first Watch List of substances for European Union-wide monitoring was reported in the Decision 2015/495/EU of 20 March 2015 and upgraded in Decision 2018/840/EU of 5 June 2018. As previously mentioned, only Switzerland has established a removal goal for some CECs for treated effluent of MWWTP (BOURGIN *et al.*, 2018). A removal efficiency of 80% is required for a selected group of 12 target contaminants (amisulpride, benzotriazole, candesartan, carbamazepine, citalopram, clarithromycin, diclofenac, hydrochlorothiazide, irbesartan, methylbenzotriazole, metoprolol and venlafaxine). To achieve such goal, processes such as ozonation or adsorption in activated carbon, followed by sand filtration are the most applied in the country.

In this way, the relevance of research on this topic of CECs, regarding either their fate, removal or health, and environmental effects is unarguably and reflects on an increased number of published material (among review and research papers, conference papers, technical notes, etc.) over the years (Figure I.1.2 a and b). The term MPs has been used for a longer time, and many materials can also be found with this term.

Considering that tertiary treatment applied to improve MWWTP effluent quality aims at the removal of MPs and disinfection, both of these responses should be investigated simultaneously when analyzing the efficiency of advanced treatment technology. However, most papers evaluate both of these parameters separately, and only a limited number of papers present CECs removal along with disinfection (Figure I.1.2 a). This emphasizes the relevance of conducting a systematic literature investigation regarding the topic in order to enable the identification of highlights, obstacles, and gaps/opportunities related to urban wastewater advanced treatment in order to guide future research conducted on the field.

FIGURE I.1.2 – Number of total search results of published materials obtained from basic keywords search on the ScienceDirect database: a) micropollutants" OR "contaminants of emerging concern" and "disinfection" and "wastewater", and b) "micropollutants" OR "contaminants of emerging concern" and "wastewater, without filters



In general, conventional biological processes in MWWTP are not efficient on the degradation of CECs and different advanced treatments have been proposed and applied with the goal to remove these contaminants (LIU; ZHANG; CHANG, 2018; RIZZO *et al.*, 2019). Some of these advanced technologies are extensively discussed in a recent review that focused on aspects such as efficiency, advantages, and drawbacks, technically, and economically feasibility (RIZZO *et al.*, 2019). Consolidated technologies were considered those who are already in implementation and expansion stage, such as ozonation, activated carbon adsorption, and membrane filtration. While the "new" technologies were those that still lack development and application on a larger scale, mainly Advanced Oxidation Processes AOP - UV/H_2O_2, photo-Fenton, UV/TiO_2. Even though solar-based AOPs appeared to be competitive on geographical areas with high yearly average solar irradiation, due to these technologies' lower level of "technical readiness" an adequate comparison to those consolidated technologies was difficult. Besides, the fact that new processes or a new combination of processes have been mainly investigated on a small scale and under laboratory far from realistic conditions was pointed out as an obstacle for comparison of new and conventional technologies. Also, to make a conclusive decision on which kind of treatment could be the best and cost-effective choice for CECs removal in MWWTP accordingly to each location's reality, more studies on those new technologies are needed regarding not only CECs abatement but also bacteria inactivation, among other factors (RIZZO *et al.*, 2019).

Regarding the AOP, they can be indicated for the treatment of water contaminated with non-biodegradable substances, which present low degradation or final removal efficiency by conventional physical-chemical and biological technologies (DEZOTTI, 2008). These processes are based on the production in situ of hydroxyl radical (HO•) and other oxidant radicals, which promote removal by the degradation of the compounds and can also achieve mineralization in determined conditions. The most interesting aspect of this radical is its non-selective oxidation capacity, which allows the reaction with many organic pollutants regardless of their characteristics.

There are many different AOP, and some of the most known are Fenton's reagent and its irradiated version, the photo-Fenton process, which is more efficient than the first one and can make use of a lower concentration of reagents. In Fenton's reagent reaction, the formation of hydroxyl radicals from hydrogen peroxide addition occurs in acidic conditions (with pH around 2.8), and it is catalyzed by ferrous iron species oxidation to ferric iron (ANDREOZZI, 1999).

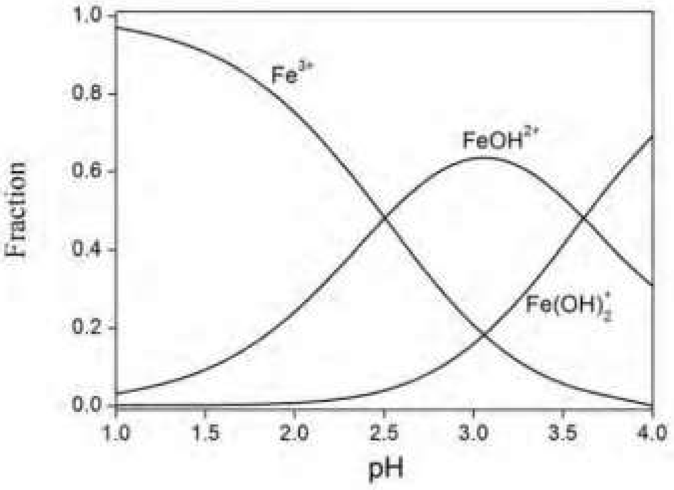
During the photo-Fenton process with continuous irradiation (UV-visible) of the reaction medium, the ferric iron aqueous complexes (predominantly $Fe(OH)^{2+}$ ion for pH around 3.0 as shown in Figure I.1.3) are reduced back to the ferrous state and generate more radical species (Equations I.1 to I.3). This photocatalytic cycle of the photo-Fenton increases the overall reaction efficiency and lowers the required amount of iron, further decreasing the formation of chemical sludge in this process.

$$HO_{2(aq)}^{\cdot} + H_2O_{2\,(aq)} \rightarrow HO^{\cdot}_{(aq)} + H_2O_{(l)} + O_{2(g)} \qquad \text{(Eq. I.1)}$$

$$Fe^{2+}{}_{(aq)} + H_2O_{2\,(aq)} \rightarrow Fe^{3+}{}_{(aq)} + OH^{-}{}_{(aq)} + HO^{\cdot}_{(aq)} \qquad \text{(Eq. I.2)}$$

$$Fe(OH)^{2+}{}_{(aq)} \overset{hv}{\rightarrow} Fe^{2+}{}_{(aq)} + HO^{\cdot}_{(aq)} \qquad \text{(Eq. I.3)}$$

FIGURE I.1.3 – Speciation diagram of 0.5 mM Fe(III) between pH 1 and 4 at 25°C and ionic strength of 0.1 (MACHULEK; QUINA; GOZZI, 2012).



Many studies have shown the possibility of modification of the photo-Fenton reaction to keep iron soluble in a neutral pH range, which allows it for application in water and wastewater treatment without the need for pH acidification and neutralization steps, which can increase the treatment costs (CLARIZIA *et al.*, 2017).

Solar photoreactors have been applied as a renewable source of irradiation to promote the catalytic iron renovation cycle in the photo-Fenton reaction. These reactors are usually categorized into concentrating and non-concentrating collectors, considering their capacity to make use of only direct radiation or also diffuse radiation (SPASIANO *et al.*, 2015).

Many studies have proven and optimized the highly efficient Compound Parabolic Collector (CPC) photoreactor for photocatalytic water treatment, including removal of pathogens as a possible alternative for conventional disinfection as chlorination (MALATO *et al.*, 2009), and wastewater treatment of highly concentrated streams (MANENTI *et al.*, 2015; PINTOR; VILAR; BOAVENTURA, 2011; STARLING; DOS SANTOS; *et al.*, 2017).

Despite the high efficiency of this concentrating type of reactor for different purposes, an open non-concentrating configuration with lower energy demand and simpler structure has been investigated as a lower cost possibility for specifically treating MWWTP effluents. In this way, raceway pond reactors (RPR) have been tested for these applications (CARRA *et al.*, 2014, 2015; FREITAS *et al.*, 2017; RIVAS *et al.*, 2015; SORIANO-MOLINA; PLAZA-BOLAÑOS; *et al.*, 2019) and are a promising technology for tertiary treatment. Recent studies have demonstrated elevated micropollutants removal efficiency at short reaction time and, therefore, high treatment capacity at neutral pH (ARZATE *et al.*, 2017; DE LA OBRA *et al.*, 2017).

Since there is an extensive and good solar irradiation availability in Brazil (MARCELINO *et al.*, 2014), the use of RPR in Brazil as a low-cost advanced treatment for both disinfection and CECs removal is an interesting possibility. Furthermore, this “new” technology requires further studies to promote its application on a real scale in the future.

In this way, a literature review was performed considering recent publications regarding the RPR application for MWWTP secondary effluent treatment to fully understand all parameters involved in the process and all aspects that are necessary to be further investigated. But, at first, a literature review regarding the simultaneous CECs removal and disinfection, in general, was necessary since it was observed in a first search that few works reported in detail these two parameters removal at the same time. For this, a methodology based in a bibliometric analysis and a systemic review of the literature was chosen to evaluate possible gaps and highlight the essential aspects to be studied for this topic.

I.2. OBJECTIVES

I.2.1. General objective

The main objective of this chapter is to perform a systemic review of the literature regarding treatments for the simultaneous removal of CECs and disinfection in domestic wastewaters and identify the highlights, obstacles, and opportunities to work with solar photo-Fenton treatment on open reactors.

I.2.2. Specific objectives

The specific objectives of this chapter are as follows:

- Organize a bibliographic portfolio of articles regarding treatments for the simultaneous removal of CECs and disinfection in domestic wastewaters published over the last ten years;
- Perform a bibliometric analysis of the organized portfolio considering academic relevance of the selected articles, their authors, and of the published journals;
- Perform a systematic analysis of a relevant selected sample of articles obtained in the bibliometric analysis, considering a set of research interest questions regarding the subject "treatments for the simultaneous removal of CECs and disinfection in domestic wastewaters";
- Review specific published articles regarding the solar photo-Fenton treatment for the removal of CECs or disinfection in domestic wastewaters and determine the usual values for each essential parameter involved in the process.

I.3. METHODOLOGY

I.3.1. Bibliometric and systemic analysis of the literature

Among different types of research (experimental, documental, case studies, etc.) a bibliographic research is based on the detailed analysis of published material, and for this task, there are distinct methodologies that can be applied in order to reduce possible bias during the selection of material for the research, including systematic review, integrative reviews, qualitative reviews, and others.

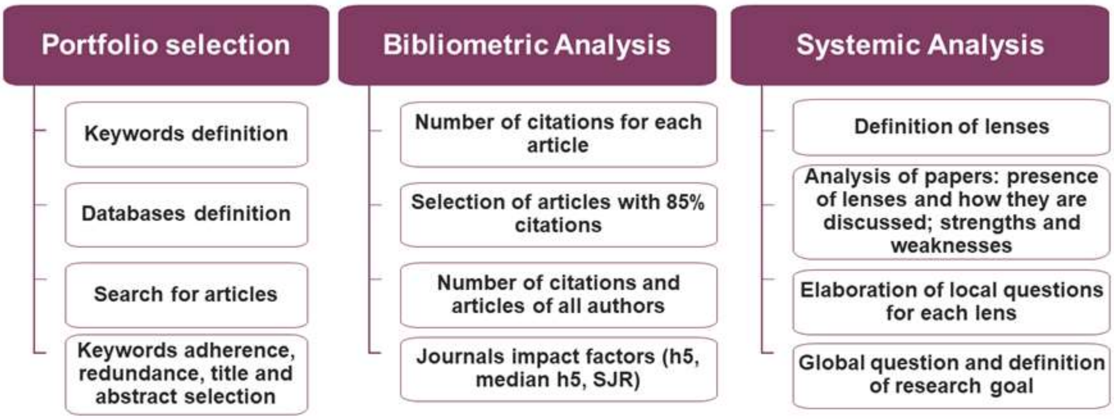
There are mapping studies, which focus on the linkages of information of the published materials and not exactly on their content, bringing up knowledge, for example, over what are the most researched topics of some area and where in the world they have been investigated (COOPER, 2016).

Another methodology widely applied is a systemic or systematic review of the literature, constituting an in-depth evaluation of the material through three stages. These methodologies generally involve an initial gathering of relevant primary material (published research), followed by an evaluation of this material by standardized method and later by a systematic synthesis that can be qualitative or quantitative ("meta-analysis") (NATIONAL HEALTH AND MEDICAL RESEARCH COUNCIL, 2000). This methodology has the advantages of reducing bias and providing reproducibility. In this way, the selection of a relevant material collection is essential in this methodology. One possibility is the combination of a portfolio construction with a bibliometric analysis, thus providing a filtering system to reduce the extensive set of materials to a reduced final list which is representative of the whole search (ENSSLIN; ENSSLIN, 2012; STAEDELE; ENSSLIN; FORCELLINI, 2019). After this final list of relevant papers is reached, the synthesis evaluation is applied only to this highly selected material.

A combined study of bibliometric analysis and systemic analysis of the literature was used in this search to determine what was developed regarding the simultaneous removal of CECs and pathogens in wastewaters in the last ten years (2008-2019). The methodology applied was a Knowledge Development Process – Constructivist type denominated ProKnow-C (ENSSLIN; ENSSLIN, 2012; STAEDELE; ENSSLIN; FORCELLINI, 2019), developed by a research group in the Brazilian Federal University of Santa Catarina (UFSC) *("Laboratório de Metodologia Multicritério em Apoio a Decisão – LabMCDA/UFSC")*. The main advantages of this methodology are: (i) it generates initial knowledge about a subject of interest, and (ii) gives the researcher a critical reflection on published materials providing for an alignment of ideas which enables the formulation of scientific research questions to guide future work (TASCA *et al.*, 2010). In this way, the ProKnow-C methodology can be a useful tool to structure a scientifically pertinent portfolio and help identify relevant research questions. As such, this methodology can go beyond its initial area of application of process management and performance evaluation.

This methodology consists basically of three main stages (Figure I.3.1):): (i) a selection of a bibliographic portfolio of manuscripts; (ii) a bibliometric analysis of the portfolio highlighting the relevance of the collection gathered by statistical data; and, finally, (iii) a systemic analysis of a relevant set of manuscripts selected within the portfolio is performed through some guiding questions designated as "lenses". These lenses assist the comprehension of the studied field and also the identification of highlights, obstacles, and opportunities towards development on the field (ENSSLIN; ENSSLIN, 2012; STAEDELE; ENSSLIN; FORCELLINI, 2019).

FIGURE I.3.1 – Detailed ProKnow-C methodology applied for the literature review



I.3.1.1. Portfolio selection: definition of keywords

During the search for manuscripts in this study, different synonyms to the term "contaminants of emerging concern" were initially investigated, including: "emerging contaminants", "micropollutants", "microcontaminants", and "micro-contaminants". All these keywords were used on a preliminary search for manuscripts published in scientific journals (review + research) in the last ten years using Science Direct database. The most relevant terms obtained on the preliminary search were then applied with different combinations with other search input keywords (''disinfection'' or "microorganisms", and ''domestic wastewater'' or some variant of it), aiming to find studies focused on the simultaneous removal of MPs and pathogens in domestic wastewater by various processes.

I.3.1.2. Portfolio selection: definition of databases

The databases used in this study were selected from those available in the "*Portal de Periódicos da CAPES"* a web page with access for scientific journal databases maintained by the Brazilian government for educational and scientific investigation purposes.

All databases selected had available complete texts, which were related to the environmental field (codified as "*Engenharias I"*) that is the research field of this thesis: ACS Journals Search, American Society of Civil Engineers – ASCE, ScienceDirect (Elsevier), Springer Link and Wiley Online Library.

I.3.1.3. Portfolio selection: search for articles and adherence stage

The search included the years of 2008-2019. The adherence stage of the ProKnow-C methodology follows strict rules. All input keyword combinations were searched within all previously selected databases until two criteria were achieved: a) a feasible number of manuscripts for the evaluation of title and abstracts (nearly 100 – 500); b) a minimum of two manuscripts which presented all keywords used in the search amongst their list of keywords. If the number of results was not adequate to reach the first goal, the search was repeated with a different combination of keywords. Also, in case no papers presented all the keywords which were initially used in the search, another set of keywords was chosen for a subsequent search.

After the identification and elimination of duplicates and evaluation of all titles and abstracts, manuscripts that were unrelated to the topic of interest (removal of MPs and disinfection in wastewater) were withdrawn, and a selected group of manuscripts was defined as the final Portfolio.

I.3.1.4. Final portfolio and visualization of keywords

An examination of the presence of selected keywords in the title, abstract, and keywords section of the manuscripts in the final Portfolio, as well as their relationships among each other, was performed. The VOSViewer software (VAN ECK; WALTMAN, 2010) was used in both non-refined searches after the adherence stage and the final Portfolio to provide for a visualization of the distribution map of keywords.

I.3.1.5. Bibliometric analysis

For the bibliometric analysis of the portfolio, manuscripts were arranged on a Microsoft Excel® sheet and classified according to their number of citations as according to Google Scholar (https://scholar.google.com.br/) and Scopus Preview Author search tool (https://www.scopus.com/freelookup/form/author.uri?zone=TopNavBar&origin=NO%20ORIGIN%20DEFINED) in June, 2020. Those manuscripts showing a number of citations higher than 85% of the total sum of citations were selected.

Then, another title and abstract analysis was performed to determine the final list of five selected manuscripts to be performed the systemic analysis.

Also, the number of citations for the most cited authors of the selected manuscripts was verified, as well as the journal's publication indexes such as *h5* and SJR (Scientific Journal Rankings).

I.3.1.6. Systemic analysis

In the final stage of the literature review the systemic analysis was applied. For this analysis, six lenses were chosen for proper evaluation of the selected papers regarding specifically relevant aspects as according to the purpose of this review (Table I.3.1). All lens were individually verified in each paper as according to their discussion, as well as all strengths and weaknesses. An in depth reading and discussion of the material was performed.

At the end of the analysis, six specific questions were elaborated as possible questions to guide future research on the subject, regarding possible gaps and possibilities for investigation on the subject.

TABLE I.3.1 – Systemic analysis summary: lens and goals used in the analysis

Nº	Lenses	Goal
1	Analytical parameters	What are analytical parameters monitored in the wastewater (physicochemical and microbiological)?
2	Studied matrices	What is the matrix in each study and its characteristics (real or synthetic wastewater, secondary effluent with or without pre-treatment, spiked with MP or not, secondary effluent from aerobic, anaerobic, or other processes)?
3	Treatment Conditions	Which parameters were studied or controlled for each treatment process (temperature, pH, reagent's doses, radiation source, reactor volume, flow, reaction time, batch, or continuous mode)?
4	Toxicity and other possible effects	Were the effects caused by non-treated and treated samples properly investigated (toxicity, estrogenicity, antibiotic-resistant bacteria, and antibiotic resistant genes, among other biological assays)?
5	Efficiency of proposed treatment	How efficient was the treatment and under which conditions?
6	Costs analysis	Do authors present a cost analysis for the proposed treatment performed in the study?

I.3.2. Raceway Pond Reactors: applications in the environmental field, use for advanced solar oxidation and operational parameters

A traditional literature search was performed for specific published articles regarding the solar Fenton-based treatments for the removal of CECs or disinfection in domestic wastewaters. This search was brief and without any specific methodology due to the reduced number of papers regarding this application of RPR, which is very recently, since around 2014-2015. This search included papers published until the beginning of 2019 searched in the ScienceDirect (Elsevier) database.

I.4. RESULTS AND DISCUSSION

I.4.1. Bibliometric and systemic analysis of the literature

I.4.1.1. Development of the Portfolio

The preliminary search using input keywords, which are synonyms to "contaminants of emerging concern", resulted in expressive relevance of the terms "micropollutants" and "emerging contaminants". These terms were intensively used in manuscripts (review + research) published in scientific journals in the last ten years as shown in the search using Science Direct database (Figure I.4.1). The term emerging contaminants (5 351) was the most used followed by MPs (5 334) (Figure I.4.2). Therefore, these two keywords were initially used within different combinations of search input keywords aiming to find studies focused on the simultaneous removal of MPs and pathogens from wastewater.

Most manuscripts found in initial searches using the keyword "emerging contaminants" (data not shown) are very recent papers (more than 60 articles within last 2 years - 2018-2019), which is not interesting because it might limit the portfolio to recent contributions only, leaving aside relevant articles published throughout the decade (2008-2019). In this way, only sets of combinations containing the keyword "micropollutants" were used (Table I.4.1).

Both initially defined adherence criteria (adequate number of manuscripts and finding at least two manuscripts that matched all search input keywords) were not obtained for the first seven attempts (Table I.4.1, nº 1 to 7). Therefore, other sets of search input keywords (nº 2 to 8) were selected and searched for until both criteria were fulfilled using the keywords combination n.º 8 (Table I.4.1).

FIGURE I.4.1 – Number of manuscripts found in the search for keywords which are synonyms to “contaminants of emerging concern” in the Science Direct database from 2008-2019

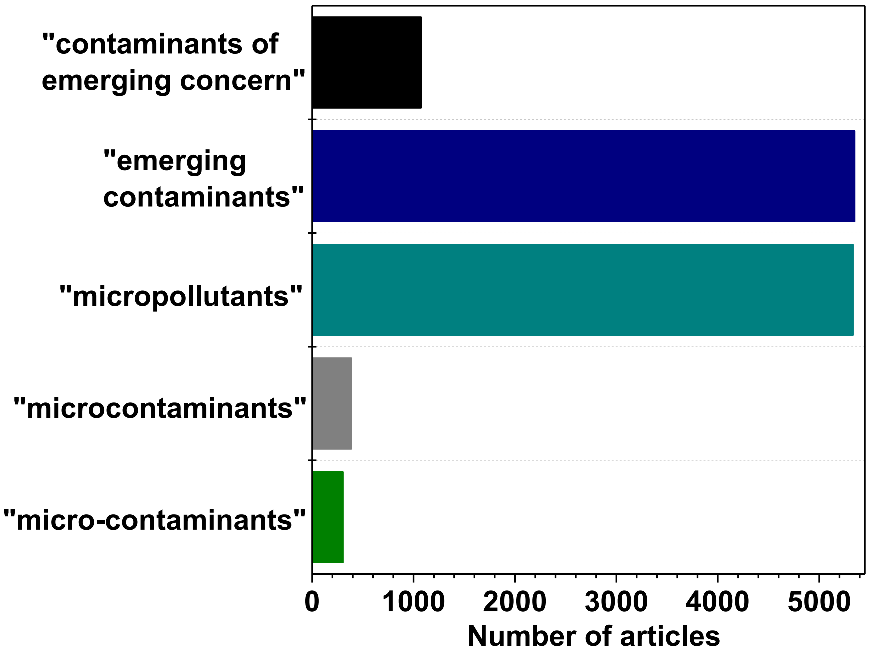


FIGURE I.4.2 – Number of manuscripts found in the search for keywords "micropollutants", "contaminants of emerging concern", and "emerging contaminants" in the Science Direct database from 2008-2019

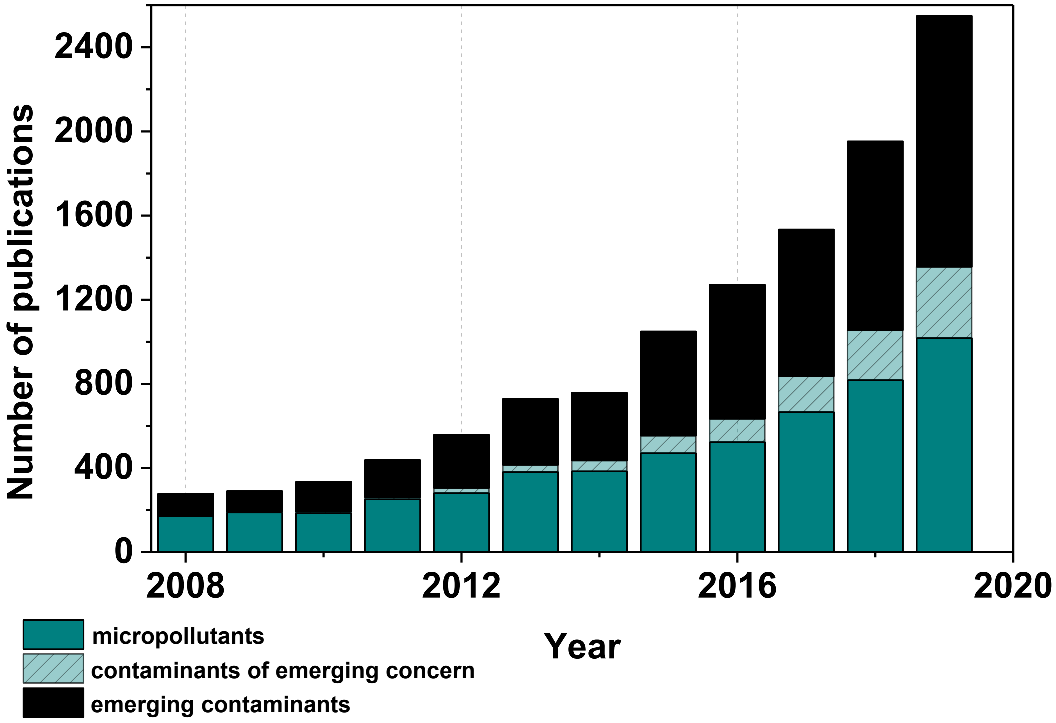


TABLE I.4.1 – Updated portfolio construction: search input keywords and number of manuscripts found as published material on the topic between 2008-2019

Nº	Keywords	Articles
1	"domestic wastewater" AND "disinfection" AND "micropollutants"	520
2	"real wastewater" AND "disinfection" AND "micropollutants"	372
3	"wastewater" AND "disinfection" AND "micropollutants"	1 548
4	"real wastewater" AND "microorganisms" AND "micropollutants"	556
5	"municipal wastewater" AND "microorganisms" AND "micropollutants"	921
6	"municipal wastewater" AND "disinfection" AND "micropollutants"	697
7	"wastewater" AND "treatment" AND "disinfection" AND "micropollutants"	1 541
8	**"wastewater" AND "treatment" AND "disinfection" AND "micropollutants" And "treatment" (search filter for words present on the title)**	407

Since various databases were used during the literature review and different search filters are available in each of them, all keywords were initially inserted in the filter search "anywhere within the paper" in order to apply a similar search method in all databases. Initial search results (nº 2 to 7) showed that, although some papers were related to wastewater, the keywords were mentioned just a few times within the papers which did not focus on treatment for simultaneous removal of MPs and disinfection. For example, a review about microalgal species cultivation in wastewater aiming at a sustainable production of biomass and lipids (WU *et al.*, 2014) which the word "micropollutants" once and the keyword "disinfection" six times appeared as a result of the search even though it is not related to the topic of interest within this review. After several failed attempts to fulfill the established criteria, a second search filter for the presence of the word "treatment" specifically in the title was applied (nº 8) in order to avoid papers which did not focus on domestic wastewater treatment.

A total of 407 manuscripts was obtained from all of the searched databases by using the combination of search input keywords nº 8 (Table I.4.2). The paper entitled *"Intensification of UV-C tertiary treatment: Disinfection and removal of micropollutants by sulfate radical based Advanced Oxidation Processes"* (RODRÍGUEZ-CHUECA *et al.*, 2018) included all keywords and the word "treatment" on the title. A second paper, which did not have a "keywords" section, included all keywords on the title: *"Treatment of Municipal Wastewater Treatment Plant Effluents with Modified Photo-Fenton As a Tertiary Treatment for the Degradation of Micro Pollutants and Disinfection"* (KLAMERTH *et al.*, 2012). As both criteria were fulfilled, the search was concluded.

TABLE I.4.2 – Detailed Portfolio construction with each database results for each search input keywords and number of manuscripts found as published material on the topic between 2008-2019

		Databases					
	Keyword combinations	**ACS Journals Search**	**American Society of Civil Engineers - ASCE**	**ScienceDirect (Elsevier)**	**SpringerLink**	**Wiley Online Library**	**Total**
1	'domestic wastewater" AND "disinfection" AND "micropollutants"	10	4	306	81	119	520
2	"real wastewater" AND "disinfection" AND "micropollutants"	13	4	126	100	129	372
3	"wastewater" AND "disinfection" AND "micropollutants"	159	11	957	212	209	1 548
4	"real wastewater" AND "microorganisms" AND "micropollutants"	13	8	164	162	209	556
5	"municipal wastewater" AND "microorganisms" AND "micropollutants"	39	13	486	204	179	921
6	"municipal wastewater" AND "disinfection" AND "micropollutants"	56	9	366	112	154	697
7	"wastewater" AND "treatment" AND "disinfection" AND "micropollutants"	158	11	955	209	208	1 541
8	**"wastewater" AND "treatment" AND "disinfection" AND "micropollutants" AND "treatment" on specific search filter for title**	**34**	**3**	**255**	**60**	**55**	**407**

Finally, 40 manuscripts were selected for the Portfolio (Appendix I) after duplicate results were identified, and all titles which did not apply to the topic of interest (simultaneous removal of MPs and disinfection in wastewater) were excluded. Most of the excluded papers were related to drinking water or sludge treatment, occurrence of MPs in surface water or in MWWTP effluents. These results highlight the importance of using appropriate tools to obtain an accurate search, including effective filters for the selection of different parameters on the database search webpage. The Portfolio was composed of almost 50 % / 50 % research (21) and review (19) manuscripts.

It is possible to observe that the most cited keywords and those which co-occurred in the network of manuscripts retrieved in the search after the adherence stage (Figure I.4.3) are related to different environmental matrices (*water, wastewater, water treatment plant, wwtp, greywater, sewage, influent, biosolid, matrice, and matrix*). After reading abstracts and excluding manuscripts out of the search scope, the network of keywords was refined on the final Portfolio (Figure I.4.4), and a change in the focus from raw to treated matrices was observed (*effluent, wastewater, water, biological wastewater, treated wastewater, wastewater effluent, and water and wastewater*).

The most cited words in the non-refined search were wastewater (2 769), removal (2 525), water (2 212), effluent (1 259), micropollutant (1 139), pharmaceutical (918), chemical (840), oxidation (774), disinfection (729), and WWTP (694) considering the title, abstract and keywords sections of the manuscripts. Meanwhile, these words were wastewater (197), disinfection (119), effluent (105), removal (87), water (72), micropollutant (68), oxidation (63), chemical (51), WWTP (50), and antibiotic (44) in the final Portfolio. These results emphasize that a different perspective can be obtained from the analysis of the map of keywords beyond the number of citations. Besides, these maps provide a better visualization of how keywords are connected in groups. Keywords present in these groups correspond to the most cited terms.

FIGURE I.4.3 – Map of keywords which were most present in the title, abstract and keywords sections of all manuscripts (407 manuscripts) retrieved in the search after adherence stage of the methodology

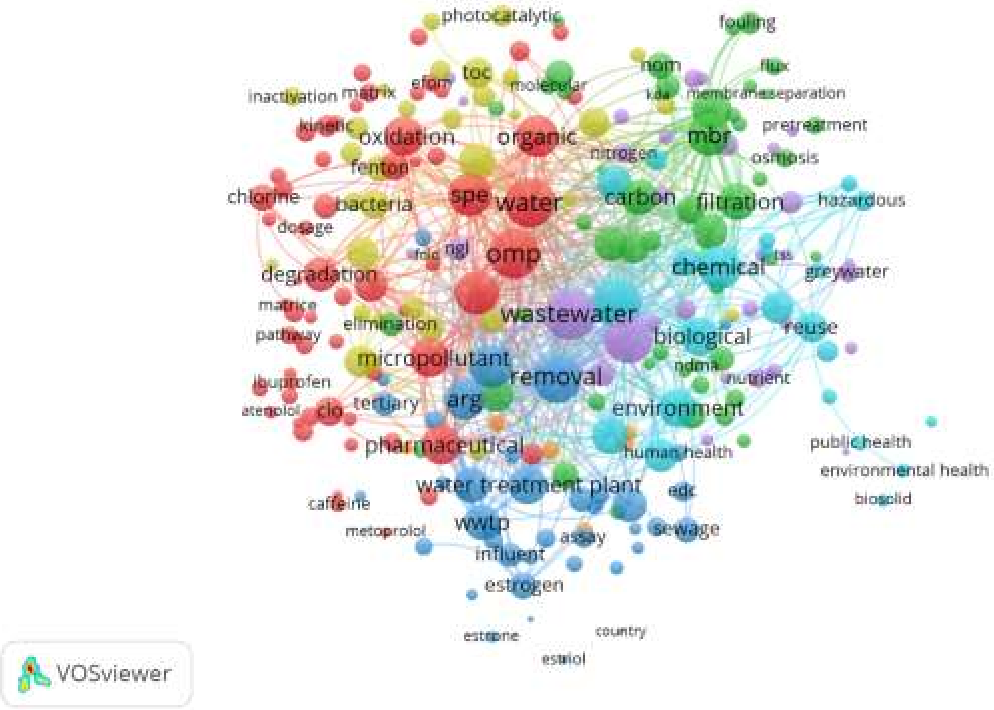
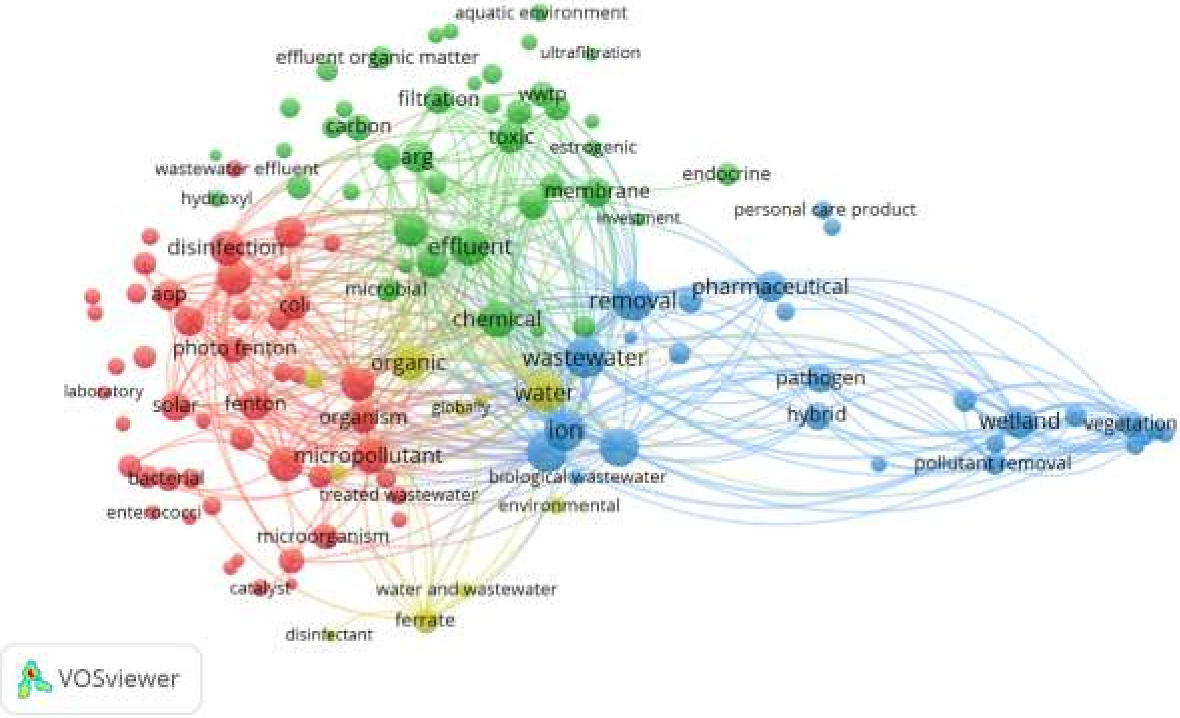


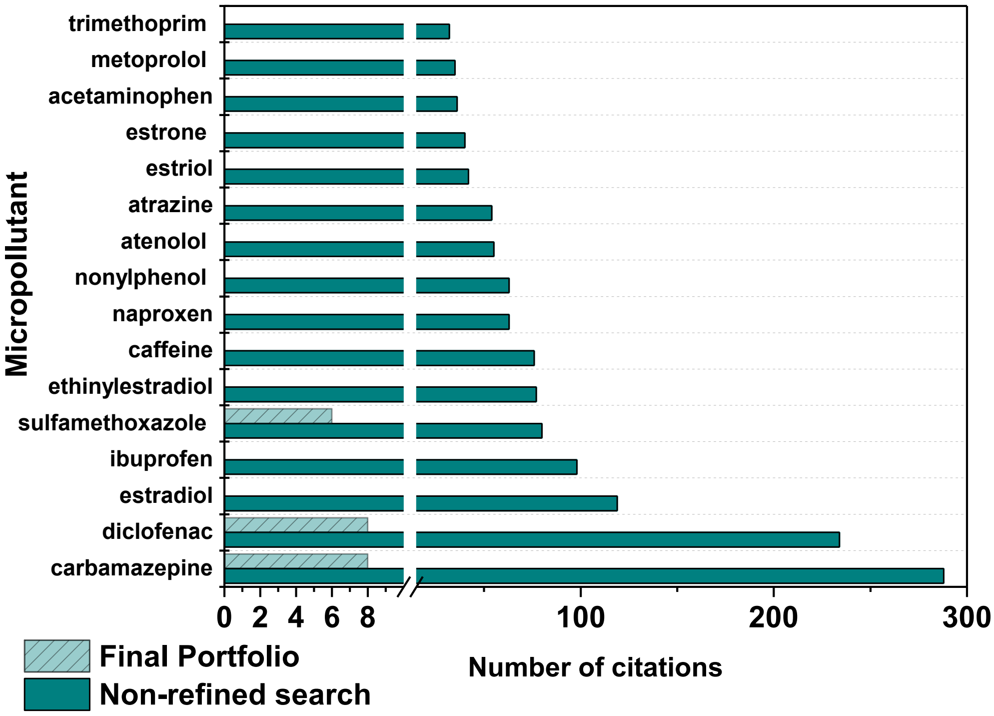
FIGURE I.4.4 – Map of keywords which were most present in the titles, abstract and keywords sections of manuscripts selected for the final portfolio (40 manuscripts)



In addition, it can be observed that in the non-refined search (Figure I.4.3) specific pharmaceutical drugs appear as highly cited (ibuprofen, atenolol, caffeine, metoprolol, estrone, and estriol). In contrast, in the refined Portfolio (Figure I.4.4), they are not as much co-cited among the network of selected manuscripts, giving place to the broader group to which they belong (pharmaceutical, micropollutant, etc.). Although a wide range of compounds can be observed throughout these manuscripts, the most important groups are pharmaceutical drugs, personal care products and endocrine disruptors/edc.

In the final Portfolio only carbamazepine, diclofenac, and sulfamethoxazole appear as separate terms with over 3 citations. These molecules are also the main emerging contaminants cited in the non-refined search (Figure I.4.5). These results are in accordance with the findings of Taoufik *et al.* (2020), even though in the referred work the search was focused only on pharmaceuticals and some molecules were identified in less than four publications (acetaminophen, estradiol). Also, a pesticide (atrazine) was frequently observed in the non-refined search.

FIGURE I.4.5 – Number of citations of keywords of molecules present in title, abstract and keywords sections of all manuscripts (407 manuscripts) retrieved in search after adherence stage of the methodology, and in the final portfolio (40 manuscripts)

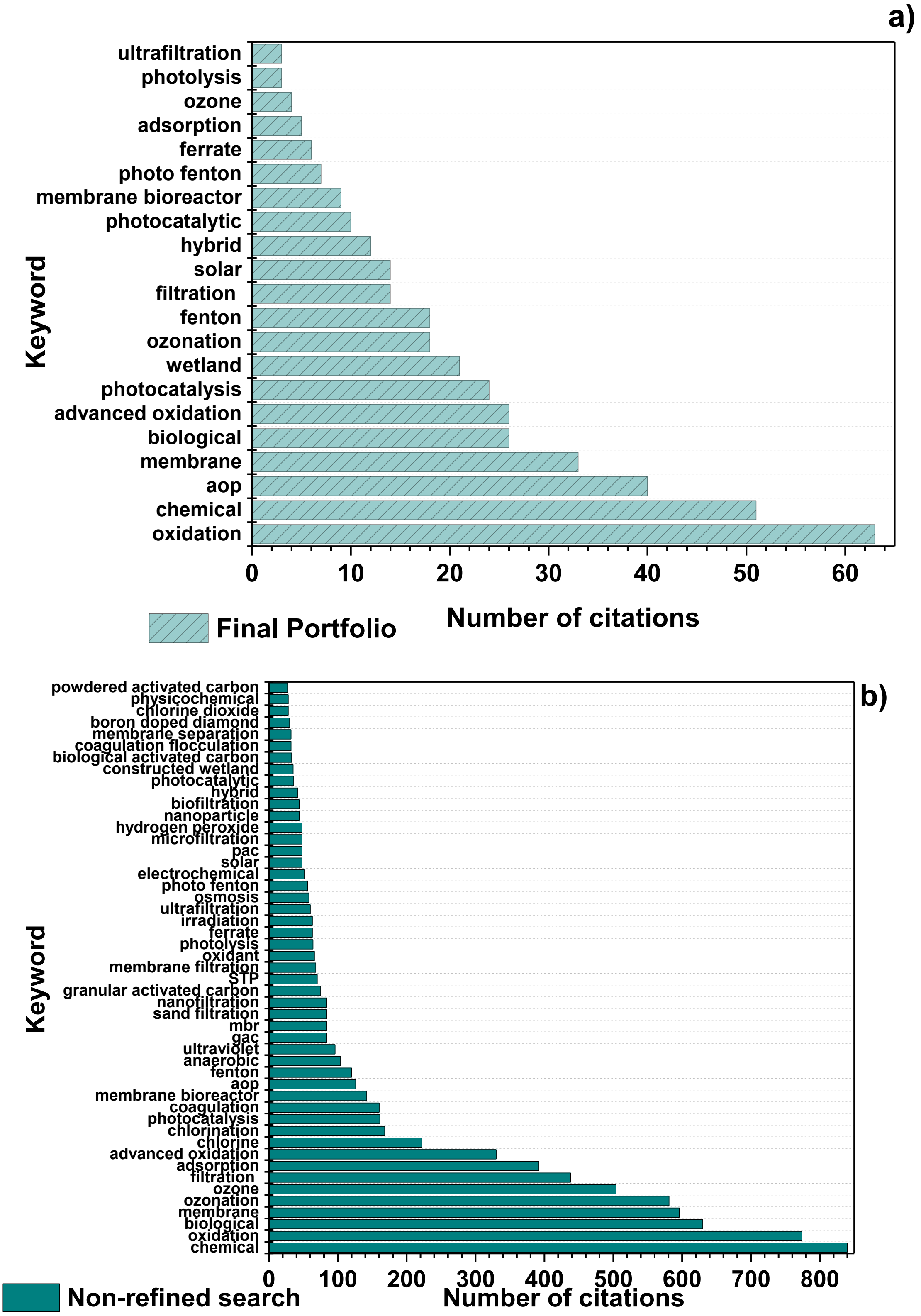


Three main clusters were formed regarding the treatment technology and considering co-citations in the Final Portfolio (Figure I.4.4). Among these technologies, advanced oxidation (keywords: aop, fenton, foto fenton, and catalyst), filtration, separation and adsorption (keywords: membrane, carbon, filtration, and ultrafiltration), and biological treatment (keywords: hybrid, wetland, and vegetation) are emphasized. A predominance of the words oxidation, chemical, AOP, and membrane is observed in the Final Portfolio, with over 30 citations each (Figure I.4.6a) in the title, abstract and keywords sections of the manuscripts. These were also predominantly the most cited words for all manuscripts in the non-refined search (Figure I.4.6b).

This predominance of chemical treatment technologies was also observed by Taoufik *et al.* (2020). However, in that study, a higher number of manuscripts dealing with adsorption was obtained (28 %). Most of the manuscripts dealing with adsorption were in water (ultrapure, deionized) matrices, thus explaining the difference in results obtained in this study, as the focus of that work was the removal of emerging molecules or pharmaceuticals in various aqueous matrices. All research papers selected in the Final Portfolio in this study dealt with real effluents (spiked or non-spiked with MP), while all review papers included results obtained for real effluents and also different aqueous matrices (synthetic, spiked water and real effluents) (Appendix I).

Regarding the scale of treatment investigated in manuscripts present in the Final Portfolio, all review papers reported different scales (laboratory scale, pilot scale, full-scale, mesocosm, and microcosm). Research papers dealt predominantly with lab-scale and pilot scale, and only two of them reported results obtained in full-scale treatment plants.

FIGURE I.4.6 – Number of citations of keywords related to treatment technology present in the title, abstract and keywords sections of selected manuscripts in a) the final portfolio (40 manuscripts) and b) all manuscripts (407 manuscripts) retrieved in the non-refined search after the adherence stage of the methodology



I.4.1.2. Bibliometric analysis of the portfolio

Starting from the 40 manuscripts that composed the portfolio, 12 manuscripts were selected in the bibliometric analysis stage. All these manuscripts contained at least 85% of the total sum of citations of the Portfolio (total sum of citations: 7 995; 85%: 6 796; total sum of selected manuscripts: 7 132). Another group of six manuscripts which showed really relevant titles and abstracts were added to the Portfolio as exceptions since they were published very recently and, therefore, had only a few citations (within the last three years, 2017-2019) (TASCA *et al.*, 2010). Thus, giving a total of 18 manuscripts (Table I.4.3).

The effectiveness of the applied methodology to perform a solid bibliometric search was confirmed in this study since a list of very relevant manuscripts published by highly cited authors was obtained at the end of the analysis (Table I.4.4). The final number of citations for each author was obtained via Scopus tool due to the absence of specific profiles for some co-authors on Google Scholar. Besides, considering authors with profiles available on both search tools, Google Scholar returned a higher number of manuscripts and citations in comparison to the Scopus tool, thus demonstrating its search efficiency.

Out of the 18 previously selected manuscripts, five manuscripts were chosen due to three main reasons: (i) focus on the simultaneous study of MP removal and disinfection, (ii) treatment of real effluent, and (iii) application of different treatment technologies. In alignment with most cited keywords (Figure I.4.6a), the selected manuscripts deal with AOPs (solar photo-Fenton, photocatalysis, ozonation), activated carbon adsorption, biological and membrane separation systems (conventional activated sludge – CAS, membrane bioreactor – MBR, among many combined systems) and photolysis.

TABLE I.4.3 – Filtered manuscripts from bibliometric analysis of the portfolio

Manuscript title	Reference	Number of citations
Recent developments in photocatalytic water treatment technology: A review	(CHONG *et al.*, 2010)	3 626
Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: A review	(MICHAEL *et al.*, 2013)	1 050
Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon?	(MARGOT *et al.*, 2013)	478
Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: A critical review	(AHMED *et al.*, 2017)	321
Advanced Oxidation Processes (AOPs) in Wastewater Treatment	(DENG; ZHAO, 2015)	308
Performance of UV and UV/H2O2 processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan	(KIM, I.; YAMASHITA; TANAKA, 2009)	288
Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: Micropollutant oxidation, by-product formation and disinfection	(ZIMMERMANN *et al.*, 2011)	218
Dissolved effluent organic matter: Characteristics and potential implications in wastewater treatment and reuse applications	(MICHAEL-KORDATOU *et al.*, 2015)	207
From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: A review	(GRANDCLÉMENT *et al.*, 2017)	196
Ferrates: Greener Oxidants with Multimodal Action in Water Treatment Technologies	(SHARMA, V. K.; ZBORIL; VARMA, 2015)	165
What have we learned from worldwide experiences on the management and treatment of hospital effluent? — An overview and a discussion on perspectives	(VERLICCHI; AL AUKIDY; ZAMBELLO, 2015)	147
Treatment of Municipal Wastewater Treatment Plant Effluents with Modified Photo-Fenton As a Tertiary Treatment for the Degradation of Micro Pollutants and Disinfection	(KLAMERTH *et al.*, 2012)	128

Manuscript title	**Reference**	**Number of citations**
Solar treatment (H2O2 , TiO2 -P25 and GO-TiO2 photocatalysis, photo-Fenton) of organic micropollutants, human pathogen indicators, antibiotic resistant bacteria and related genes in urban wastewater	(MOREIRA *et al.*, 2018)	48
A green solar photo-Fenton process for the elimination of bacteria and micropollutants in municipal wastewater treatment using mineral iron and natural organic acids	(VILLEGAS-GUZMAN *et al.*, 2017)	30
Integrated Evaluation Concept to Assess the Efficacy of Advanced Wastewater Treatment Processes for the Elimination of Micropollutants and Pathogens	(TERNES *et al.*, 2017)	27
Heterogeneous photocatalysis using UVA-LEDs for the removal of antibiotics and antibiotic resistant bacteria from urban wastewater treatment plant effluents	(BIANCULLO *et al.*, 2019)	16
Intensification of UV-C tertiary treatment: Disinfection and removal of micropollutants by sulfate radical based Advanced Oxidation Processes	(RODRÍGUEZ-CHUECA *et al.*, 2018)	15
Chemical, microbial and toxicological assessment of wastewater treatment plant effluents during disinfection by ozonation	(NASUHOGLU *et al.*, 2018)	10

TABLE I.4.4 – Bibliometric analysis summary: final selected articles and statistical data of the number of citations and other indices

Article	**Year**	**Citations**	**Most cited author**	**Citations of the author**	**Journal**	**Index h5**	**Median h5**	***Qualis*[1] *CAPES***	**Index SJR (2019)**
A green solar photo-Fenton process for the elimination of bacteria and micropollutants in municipal wastewater treatment using mineral iron and natural organic acids	2017	30	Pulgarin, C.	13 778	Applied Catalysis B: Environmental	153	189	Eng. I - A1	4.22
Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon?	2013	478	Barry, D.A.	8 784	Science of The Total Environment	131	176	Eng. I - A1	1.66

Article	Year	Citations	Most cited author	Citations of the author	Journal	Index h5	Median h5	*Qualis*[1] *CAPES*	Index SJR (2019)
Solar treatment (H_2O_2, TiO_2-P25 and GO-TiO_2 photocatalysis, photo-Fenton) of organic micropollutants, human pathogen indicators, antibiotic resistant bacteria and related	2018	48	Faria, Joaquim L.	8 221	Water Research	119	159	Eng. I - A1	2.93
What have we learned from worldwide experiences on the management and treatment of hospital effluent? — An overview and a discussion on perspectives	2015	147	Verlicchi, P.	2 732	Science of The Total Environment	131	176	Eng. I - A1	1.66
Intensification of UV-C tertiary treatment: Disinfection and removal of micropollutants by sulfate radical based Advanced Oxidation Processes	2018	15	Marugán, J.	2 445	Journal of Hazardous Materials	110	141	Eng. I - A1	2.01

(MARGOT *et al.*, 2013; MOREIRA *et al.*, 2018; RODRÍGUEZ-CHUECA *et al.*, 2018; VERLICCHI; AL AUKIDY; ZAMBELLO, 2015; VILLEGAS- GUZMAN *et al.*, 2017)[1]*Qualis CAPES* classification 2013-2016. *Qualis* is an evaluation of scientific production in Brazil, and periodic publication is classified in different areas (environmental journals are usually classified in "*Engenharias* I" field - "Eng. I"), and grades vary from A1(excellent); A2; B1; B2; B3; B4; B5; C – null weight.

A recent review used bibliometric analysis to evaluate publications with AOPs for wastewater treatment around the world and in Ibero-American countries between 1980 – 2018 (MACÍAS-QUIROGA *et al.*, 2020). Results point out that Journal of Hazardous Material, Water Research and Applied Catalysis B: Environmental comprise the 5 most cited journals and are amongst the 10 journals with most publications on AOPs. Most of the selected papers (3 out of 5) in the present study belong to these journals, with the exception of the journal Science of the Total Environment. Thus, confirming the relevance of these journals for publications in the treatment of wastewater by AOPs. Nonetheless, the journal Science of the Total Environment and all other journals are highly cited considering their *h*-index and SRJ index (Table I.4.4). Regarding the most cited authors from these selected papers, Pulgarin, C is also one of the top 10 authors with publications in AOPs, with an *h*-index of 65 (MACÍAS-QUIROGA *et al.*, 2020).

I.4.1.3. Systemic analysis of final selected manuscripts

Finally, the detailed systemic analysis was performed by verifying the presence of each lens and their discussion in each of the selected papers, along with the strengths and weaknesses of the paper regarding an individual lens, exemplified here with one of the selected manuscripts (Table I.4.5). The systemic analysis performed for the other papers is presented in the Appendix II. A comparison for each manuscript is shown in the Appendix III considering relevant topics of each lens (treatment technology, evaluated matrix, treatment scale, micropollutants, and disinfection efficiency, toxicity and other effects, and treatment costs).

TABLE I.4.5 – Systemic analysis of the manuscript: Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? (MARGOT *et al.*, 2013)

Lens	The research lens (concept) is dealt with in the paper?	If yes, highlight how this lens (concept) is dealt with in the paper	MAIN STRENGTHS Concept	MAIN WEAKNESSES Concept
Analytical parameters	Yes	Physical-chemical: Standard wastewater quality parameters (TSS, DOC, COD, BOD_5, NH_4, NO_3, NO_2, P_{total}, and $P_{soluble}$), pH, temperature, conductivity (online). and 58 MP (and two seasonal up to 120). Microbiological: indicator bacteria (Escherichia coli, intestinal enterococci, and total viable bacteria) and coliphages (F-specific (RNA) and somatic phages. Bioassays: YES, Combined Algal Assay, fish early life stage with rainbow trout	More than one bioassay, and microbiological indicator, as well as many different MP with different characteristics were analyzed. Composite samples from different campaigns	No weaknesses
Studied matrices	Yes	Complete description of the real wastewater and also of treatment facilities.	Pilot-scale of real municipal wastewater over 1 year	No weaknesses
Treatment conditions	Yes	Brings a description of the parameters	Continuous pilot-scale reactors, investigation with different ozone doses, nitrification on biological process, organic matter concentration for the coagulation stage	Mostly results for MP removal only and related to different operational parameters. But for disinfection only results for the main operational

Lens	The research lens (concept) is dealt with in the paper?	If yes, highlight how this lens (concept) is dealt with in the paper	MAIN STRENGTHS Concept	MAIN WEAKNESSES Concept
				conditions and presented briefly at the end of the article
Toxicity and other possible effects	Yes	Brings the description of the assays, with a good variety of assays	Estrogenicity study with YES, toxicity in different trophic levels (with combined algal and also early life stage rainbow trout). Also, bromate and toxic bromide byproducts investigated	No weaknesses
Efficiency of proposed treatment	Yes	Described in graphs, tables. Very complete. Arithmetic Average for MP %	Comparison of MP efficiencies with specific characteristics	Few results and combined in graphs with SD for the disinfection, not able to compare it in different situations
Costs analysis	Yes	Described in a table, including operating (staff, reagents, electricity), investment, interest rate, and amortization	Includes operational and investment, amortization rates different for different types of equipment (mechanical, or structural for ex.)	No details of the calculation method! Few results in a table, for just some of the operational conditions (80% average removal MP).

Based on the manuscripts selected throughout this bibliometric analysis it is possible to conclude that ozonation has been extensively studied over the last 7 years within practically all aspects of the defined lenses for wastewater treatment. Some of these aspects include: information regarding ecotoxicological tests; byproducts formation; real scale operation for long periods, and also concerning a substantial number of CECs. An extensive amount of information is also available with regard to adsorption by activated carbon. Although both processes showed high removal efficiency for MP (> 80% removal efficiency for 70 compounds detected in the real effluent), ozonation is apparently superior for a limited number of compounds (electron-rich moieties) while adsorption is effective for a wider range of substances (hydrophobic or positively charged compounds) (MARGOT *et al.*, 2013). The use of post-filtration with either sand filter or membrane separation after each system improved the final removal of persistent MP, toxicity, and macro-parameters (DOC, SST, color, phosphorus, etc.). Sand-filtration was essential to improve the removal of phosphorus, DOC, and BOD_5 after ozonation, which alone was not effective for these parameters (Appendix III). It is important to highlight that neither adsorption by activated carbon nor membrane filtration degrade MP into simpler molecules, yet these processes lead to pollutants transfer to a solid phase or concentration of contaminants in a reduced volume, respectively. From this perspective, ozonation or any other oxidative process would be advantageous over any of these processes.

Regarding membrane processes, nanofiltration (NF) and reverse osmosis (RO, also referred to as inverse osmosis - IO) have shown higher removal efficiency when compared to ultra or microfiltration membranes (UF or MF) (VERLICCHI; AL AUKIDY; ZAMBELLO, 2015). This has been demonstrated in a work with real secondary effluents from different biological and secondary treatments (including also anoxic–oxic process and sand filtration) (KRZEMINSKI *et al.*, 2017). The application of NF and RO increased removal of more persistent compounds (insect repellent DEET and organophosphorus flame retardants TCPP and TCEP) from < 20% to between 54 -99 %. Also, removal efficiency of macropollutants in comparison to UF was enhanced, from 30–50 % for COD, 80–95 % of Total Phosphorus (TP), up to 30 % of Total Nitrogen (TN) and NH_4, and a min of 2 log reduction of *E. coli*, to values for NF and RO, respectively, of 40-70% and 50-90 % of COD, 90-99 % and 80-97 % of TP, up to 30 % and 70-80 % of TN, 20-60% and 40-70% of NH_4, and 1.5-3 log for *E. coli* and total coliforms (evaluated just for NF). Nonetheless, the use of higher pore-size membranes associated to other technologies may improve overall treatment efficiency, for instance, on the sequence of the powered activated carbon (PAC) (MARGOT *et al.*, 2013). These processes can be applied to upgrade the biological treatment unit, for example with a membrane bioreactor (MBR). A higher solid retention time (SRT) in MBR in comparison to AS might increase the sorption of MPs, a major removal route for these contaminants in biological processes. Besides, MBR presented higher efficiency for macro-parameters, including a higher rejection of bacteria (VERLICCHI; AL AUKIDY; ZAMBELLO, 2015).

Apart from technologies cited above, there are also the "new" AOPs which are still under improvement, including photocatalysis with different materials and designs, photo-Fenton (especially solar irradiated), and UVC-combined with different oxidants (RIZZO *et al.*, 2019). These processes present many opportunities for research, particularly considering their application in large scale (pilot and real), the improvement of operational conditions and ecotoxicological evaluation of transformation products formed during oxidation.

UVC technologies are also interesting options for tertiary treatment in MWWTP which already apply this technology aiming at disinfection. MP removal may be increased under UVC irradiated advanced oxidation processes (AOPs) by adding oxidant species like hydrogen peroxide or persulfate (peroxymonosulfate, PMS; peroxydisulfate, PDS) to the system. Photolysis of these oxidants occur under UVC, thus forming oxidative radicals which lead to faster reactions within a reduced contact time for a higher disinfection rate than under the application of UVC alone. UVC AOPs also attained MP removal in real matrixes such as surface water and MWWTP effluent (RODRÍGUEZ-CHUECA *et al.*, 2018; STARLING *et al.*, 2019). Small doses of oxidants were sufficient (0.1 mM) for disinfection purposes only, while comparatively higher oxidant doses were necessary (up to 0.5 mM) for the removal of MP. The use of metal activation (Fe: oxidant proportion of 1:1) also increased removal efficiencies even with reduced contact time (RODRÍGUEZ-CHUECA *et al.*, 2018). Even so, a higher concentration of oxidant was necessary (up to 5 mM) to achieve 50 % mineralization. Similar improvement for the combination of UVC and oxidant was achieved in another work, when 29 out of 41 investigated compounds could not be removed for UVC only, even at a higher UV dose of 2 768 mJ cm^{-2}, and removal efficiency was enhanced up to 90 % for most compounds (39) with H_2O_2 and lower UV dose of 923 mJ cm^{-2} (KIM, I.; YAMASHITA; TANAKA, 2009).

Regarding solar irradiated oxidation processes, a recent study compared the performance of photolysis, solar- H_2O_2, heterogenous photocatalysis with different materials and photo-Fenton at circumneutral pH at semi-pilot scale (MOREIRA *et al.*, 2018). Experiments with real spiked wastewater were performed along with a wide investigation on wastewater disinfection with regard to different bacteria indicators including antimicrobial resistant bacteria (ARB), DNA, antimicrobial resistant genes (ARG), and total community diversity. The combination of heterogeneous photocatalysis with H_2O_2 showed the best removal of MP, while all processes containing H_2O_2 were efficient to remove pathogen indicators (fecal coliforms, enterococci, and ARB equivalents) and prevented their increase after three days (72h) of sample storage.

Solar-H_2O_2 and heterogeneous photocatalysis (P25) with H_2O_2 were also efficient on the reduction total DNA, although treatments did not prevent reactivation nor population increase after three days (MOREIRA *et al.*, 2018). Interestingly, the photo-Fenton reaction was the least efficient on the removal of target MP and was only evaluated for bacteria indicators, which did not include ARGs and bacterial community analysis, even though it was efficient for the removal of cultivable bacteria indicators and prevented their regrowth after 3-days. Higher precipitation of iron occurred at circumneutral pH when no strategies were applied to keep iron in the soluble form, which may have reduced reaction efficiency.

In the case of photo-Fenton reaction, new chelating substances are currently under investigation to increase iron availability throughout reaction in order to improve process efficiency at neutral pH (CLARIZIA *et al.*, 2017). Some natural substances such as citric fruits, which are rich in organic acids (citric, caffeic, ascorbic, tartaric, among others), have been tested for heterogeneous photo-Fenton exploring a natural iron source (mineral from an iron mine) (VILLEGAS- GUZMAN *et al.*, 2017). This process was proved efficient for bacteria inactivation (total removal and no regrowth afterward) and MP removal (30 – 40 % elimination of compounds present in real effluent). Regardless of the preparation of the complex agent (juice or natural extract), the presence of natural additives enhanced MP and bacteria elimination, consisting of an efficient alternative and viable approach for improving the Fenton-based process at a suitable cost. Nonetheless, more studies are needed to evaluate sample toxicity during these processes and their application in larger scale.

The complete systematic analysis for each lens is summarized in Table I.4.6. In detail, follows in sequence the discussion of each lens.

TABLE I.4.6 – Summary of the systemic analysis: main strengths and weaknesses detected in each paper and specific questions proposed for future research

Nº	Main strengths and weaknesses	Specific question
1	A great variety of MP studied, mostly drugs. Analysis of compounds with different physicochemical properties to evaluate the efficiency towards groups with certain characteristics, in special selective technologies (for ex. ozonation). It is very important to analyze conventional macropollutants and physicochemical parameters to evaluate their influence on process efficiency (COD, carbon series - DOC, DIC, TOC, conductivity, alkalinity, pH, main cations and anions, etc.). Even so, works monitoring both MP and disinfection are more recent, and some lack a discussion about conventional parameters that may interfere in the process. In the case of disinfection studies, mostly only *E. coli* and total cultivable heterotrophic bacteria are analyzed, and total bacteria removal is more difficult than the removal of *E. coli* alone.	What are the indicator analytical parameters (physicochemical, microbiological, and micropollutants) required to assess the efficiency of advanced and alternative treatments of domestic wastewater?
2	Many papers conducted with real domestic wastewater and real concentrations of MP present in the effluent. When simulated domestic wastewater is used for disinfection studies, the added strain is usually *E. coli* K-12. Sometimes MP are also added to the effluent at µg L^{-1} (even in real samples). Many studies developed with activated sludge or coagulation/flocculation secondary effluents for domestic wastewater. Regarding hospital effluents only, technologies such as Upflow Anaerobic Sludge Blanket, stabilization ponds, and septic tank + anaerobic filters were evaluated. There is no consensus on the concept of pre-treatment of secondary effluent before the advanced treatment (and in most cases pre-treatment was applied).	What is the difference in the efficiency of advanced treatment of domestic wastewater treated by secondary effluents after different technologies (activated sludge, anaerobic processes, physical-chemical processes)?
3	Importance of evaluating process efficiency within varied operational conditions which may lead to distinct toxicity and byproducts. In case of disinfection, it is important to investigate longer periods after treatment to test for regrowth in ambient conditions (24, 48, or 72 h). For ozonation and activated carbon processes, there is more information about different operational conditions, as well as toxicity and other important assessments at a larger scale.	What are the best operational conditions of advanced treatment of secondary domestic wastewater (temperature, pH, reagent's doses, radiation source, flow, reaction time, batch, or continuous mode)?

Nº	Main strengths and weaknesses	Specific question
4	Not all studies dealt with toxicity, estrogenicity, antibiotic resistant bacteria, and genes, nor with the formation of byproduct, except for the ozonation study which is very complete.	What are the possible ecotoxicological and biological effects caused by the advanced treatment of domestic wastewater?
5	Different approaches to describe efficiencies. Many studies dealt separately with results for MP removal and disinfection, and some discussed MP just for real wastewater, while preliminary studies were accomplished in synthetic wastewater fortified with one *E. coli* strain (or vice-versa). Usually, longer reaction time is required for MP removal in comparison to disinfection. Differences in overall removal efficiency and in individual results for each compound (simple average or weighted average were used).	What is the simultaneous efficiency of MP removal and disinfection during advanced treatment of domestic wastewater?
6	Only two papers presented results regarding cost analysis of the advanced treatment processes. Little or no description of the cost estimation methodology used for calculations.	What are the estimated costs, including investment, operational, and maintenance costs for the advanced treatment of domestic wastewater?

Regarding the lens “Analytical Parameters” it was possible to verify a lack of discussion on the influence of removal of conventional pollutants and traditional physicochemical parameters on treatment performance related to the removal of CECs and disinfection. It is known that matrix composition may vary among different locations and according to applied MWW treatment technology and operation (TRAN; REINHARD; GIN, 2018), especially with regard to the presence and concentration of inorganic ions such as carbonate/bicarbonate, sulfate, chloride, phosphate, nitrate, MPs concentration, microbial diversity and abundance etc. As the performance of different advanced processes may be influenced by these components due to scavenging phenomenon, precipitation with the iron catalyst, formation of other oxidative species, among other possibilities, it is critical to evaluate matrix composition prior to treatments (LADO RIBEIRO *et al.*, 2019).

A review evaluation focused on the removal of natural organic matter (NOM) and some of its main components such as particulate effluent organic matter (pEfOM) and dissolved effluent organic matter (dEfOM) has been performed, and results for MWWTP in different countries with reuse purpose have been shown (MICHAEL-KORDATOU *et al.*, 2015). In the USA, California, groundwater replenishment was made with the treated effluents from MF, RO and UV/H_2O_2 process. In this case, MF showed substantial removal of pEfOM, while RO reduced dEfOM down to 0.5 mg L^{-1} (in terms of TOC). The combination of UV/ H_2O_2 + membranes provided elimination of PPCPs and NDMA (removal > 99 %) (MICHAEL-KORDATOU *et al.*, 2015).

An evaluation of macropollutants in the work of Margot *et al.* (2013) shows that with membrane separation a higher quality of effluent was produced by PAC-UF with DOC (54 ± 10 %), phosphorus (>90 %), NH_4 (85 ± 20 %) and BOD_5 (72 ± 18 %), and complete removal of TSS. When sand filtration was used, PAC-SF promoted similar removal efficiencies for COD, TOC, DOC, and NH_4, but lower removal efficiencies for TSS and Phosphorus. The ozonation process alone had no phosphorus removal, absence of DOC removal and a significant increase in BOD_5 (49 ± 54 %). In this case, the sand filter was the reason for most of the macropollutant removals after ozonation, with 80 ± 13 % of TSS, 79 ± 10 % of P_{total}, 59 ± 21 % of BOD_5, 44 ±34 % NH_4 and 20 ± 8 % of DOC (MARGOT *et al.*, 2013). A secondary effluent after CAS achieved higher disinfection (2-log difference) than the coagulation-flocculation (C/F) secondary effluent, and in this case, it was associated the higher concentration of solids (TSS) and organic matter content (TOC and DOC) in the C/F effluent for this lower disinfection efficiency under solar photo-Fenton reaction (RODRÍGUEZ-CHUECA *et al.*, 2018).

Results observed for the second lens ("Studied matrices") are also very relevant, as they indicate that the majority of the selected manuscripts presented results for secondary effluents which are fairly similar. Results presented in all of these manuscripts were obtained from the treatment of effluents sampled in MWWTP which apply activated sludge system or coagulation/flocculation as secondary/tertiary treatment stages, with the exception the review paper regarding hospital effluents, which presented a few different treatment technologies including Upflow Anaerobic Sludge Blanket (UASB), stabilization ponds, and septic tank + anaerobic filters.

These results are expected, since most studies on the removal of MP in MWWTP, in special those comprising detailed removal mechanisms, treat effluent generated from aerobic processes, mainly activated sludge (ALVARINO *et al.*, 2014, 2018). Several parameters, such as the temperature, hydraulic retention time (HRT), sludge retention time (SRT), pH, redox conditions, and microbial community influence the performance of biological treatment, not only concerning organic matter removal, yet also MP removal. The removal of MPs is also influenced by their toxicity and physicochemical properties (ALVARINO *et al.*, 2014; TRAN; REINHARD; GIN, 2018). Thus, indicating that it is important to promote research investigating the effectiveness of advanced technologies towards the treatment of effluents originated from a broader range of secondary treatment processes as activated sludge is mostly applied for the treatment of wastewater in urban areas rather than isolated areas (SPERLING, 2016).

Anaerobic reactors and stabilization ponds are amongst the alternative technologies used for the treatment of domestic wastewater. These technologies are applied in countries with area availability and favorable climate for their application (COGGINS; CROSBIE; GHADOUANI, 2019; NOYOLA *et al.*, 2012). In Brazil, for example, the most applied domestic wastewater treatment technologies (number of MWWTP using this technology) are: facultative ponds (anaerobic followed by facultative or just facultative), primary treatment (septic tank followed by biological filter - BF) and anaerobic reactors. These systems are used in 1,287 out of a total of 2,768 MWWTP present in the country (ANA, 2017; SPERLING, 2016). Anaerobic reactors and facultative ponds are a technological choice in Brazil as the climate is favorable for the application of these technologies, and due to lower operational costs in comparison to CAS. In terms of served population, CAS corresponds to around 16.5 million people (71.7 million in total are served in Brazil with wastewater treatment) and it is the most frequently used system for larger cities, corresponding to 110 MWWTPs in the country (ANA, 2017; SPERLING, 2016). As for Australia, stabilization ponds are also largely applied even to larger populations of 2.5 million people (COGGINS; CROSBIE; GHADOUANI, 2019). As neither activated sludge nor alternative biological treatments applied for the treatment of domestic wastewater are designed for the removal of organic contaminants, it is critical that studies aiming at the removal of MP and disinfection of MWWTP effluent prior to discharge do not only focus on the treatment of effluent generated by activated sludge treatment, yet also on effluents generated from a broader range of technologies.

Also, regarding biological treatment efficiencies, the quality of secondary effluents might vary from each technology and each treatment plant. MBR treatments could generally further reduce micropollutant concentrations by 20-50 % for those MP that showed an intermediate removal in CAS treatments (between 15 and 80 %) (GRANDCLÉMENT *et al.*, 2017). However, in the case of compounds which were already highly degraded by CAS processes or in the case of recalcitrant compounds, the results using MBR did not show any significant improvement. When comparing CAS system and a MBR operating at comparable SRT, there was no significant difference in the treatment efficiency. In this way, authors pointed out that there is still no clear definition for a general difference, but that several parameters can influence the removal for MP, including F/M, SRT, HRT, DO, temperature, pH, among others. In a reported work, these two systems were efficient to remove both hydrophobic compounds and hydrophilic ones that possess only EDG (electron-donating functional group). In contrast, the removal of hydrophilic compounds with EWG (electron-withdrawing functional group) was much lower (below 20%). These authors also point that membrane fouling, recalcitrance of some hydrophilic compounds, and adsorption on activated sludge flocs are important factors limiting the biodegradation of MP using conventional biological processes (GRANDCLÉMENT *et al.*, 2017).

In another review study authors come to similar conclusion, that first, conventional sewage treatment facilities were never designed to deal with MP such as pharmaceuticals, considering their highly variable physicochemical properties (chemical structure, solubility, octanol/water partition coefficient) an also the operational conditions of the biological treatment which produce highly variable removal efficiency for each type of compound (MICHAEL *et al.*, 2013). MBR systems were reported to be equal to or slightly more effective in removing some antibiotics compared to CAS treatment systems. Also, even though MBR was considered more expensive, yet it provides a higher quality effluent due to the inherent filtration. Another option if the application of advanced treatment downstream of conventional biological process, which can significantly improve antibiotics removal before effluent disposal or reuse. It its highlighted that although the costs (capital and operational) of an advanced treatment increase the overall costs of conventional process, a further improvement of the effluent regarding MP and other antibiotics removal, in line with possible more strict regulations might be hard to comply without advanced treatment (MICHAEL *et al.*, 2013).

A work performed a detailed comparison of different secondary biological technologies for the removal of MP, including CAS, MBR, MBBR (Moving Bed Biofilm Reactors) and a natural lower cost treatment CW (Constructed Wetlands) (KRZEMINSKI *et al.*, 2019). Considering a selected list of 33 MP in different processes, values found for removal of different groups were as follow: Pharmaceuticals (CAS <0-90 %; MBR<0-99 %; MBBR 0-100 %; CW 0-99 %); Antibiotics (CAS <0-90 %; MBR<0-99 %; MBBR <0-96 %; CW 0-100 %); Personal Care Products-PCPs (CAS 20-35 %); Estrogens (CAS 18-96 %; MBR 20-100 %; MBBR 65-100 %; CW 0-100 %); Neonicotinoids (CAS 11-18 %); Pesticides (Not Applicable for all); and Industrial chemicals (CAS <0-100 %; MBR <0-94 %; MBBR 43-76 %; CW 8-100 %). It is important to highlight that even though removal efficiencies of 100 % are shown in some works, such representations are incorrect and would be more adequately represented to a removal of analytes bellow the detection or quantification limit of the analytical method applied.

Considering the CAS, for pharmaceuticals the carbamazepine (CBZ) was poorly removed (−90)–(−3) %, while highest removal efficiencies were for ciprofloxacin (63–90 %) and sulfamethoxazole (35–84 %); as for hormones, there were higher removal efficiencies for 17β-estradiol than for estrone (91 % and 58 ± 31 %, in an MWWTP without nitrification), while removal can be increased ≥ 90 % for estrogenic compounds if there is nitrification during the process. There was a low to moderate removal of EHMC (a PCPs), few information on removal of pesticides and neonicotinoids (some below the detection limit in the influent), and a variable behavior for industrial chemicals with almost complete removal for BHT, TBBP-A, and BTA, and, on the other side, a wide range of removal for others such as NDMA. The MBR showed a slightly better removal efficiency than CAS, or similar at good operation conditions (SRT, HRT, temperature, etc.). Removal efficiencies for some compounds were: sulfamethoxazole (0–90 %), ciprofloxacin (15–94 %), diclofenac (<0–87 %,), carbamazepine (<0–96 %), BTA

(15–74 %), E1 (58–100 %), E2 (39-100 %), EE2 (20-100 %). There was no information available for pesticides and neonicotinoids and PCPs.

CW systems, just a few of the studied compounds showed removal up to 100 %, with benzotriazole and trimethoprim more effectively removed in vertical subsurface flow CW that in a surface flow CW. A minimum of three compounds had limited removal in CWs, due to their recalcitrance. In general, diclofenac, carbamazepine and sulfamethoxazole had poor removal in most studies, with only 1 or 2 studies showing higher removal. The study did no show information for removal of pesticides and neonicotinoids for CW, and for Industrial chemicals only BTA (8-100 %) (KRZEMINSKI *et al.*, 2019). Ahmed *et al.* (2017) also considered constructed wetland-based hybrid system less effective in the removal of many MP. On the other side, Tsihrintzis *et al.* (2017) has pointed out how effective these systems are for disinfection purposes. Various indicator microorganisms had removal varying from 94.0 to 99.99 % or from 0.2 to 4.8 log cycle (25 studies) and the author highlights that the choice of the design can improve MP removal, being vertical flow CWs more efficient compared to horizontal surface flow CW (good aeration of the substrate).

Another relevant information could be obtained from the lens “Efficiency of proposed treatment”, which revealed that most of the selected manuscripts are focused either on MP removal or disinfection. The simultaneous evaluation or at least the report of both results simultaneously are present mainly in the most recently published papers (2019-2020). In fact, many manuscripts focused on the removal of MP considering previously established “reaction or operating conditions” that were known to achieve efficient disinfection or elimination of pathogens in accordance with effluent disposal standards. For this reason, these manuscripts did not actively investigate nor presented actual results regarding the removal of pathogens, yet they considered that applied operating conditions were adequate for efficient disinfection. Even so, efficiencies and respective best-operating conditions (Lens 3 “Treatment conditions”) are presented in sequence.

In the work of Villegas- Guzman *et al.* (2017) ~35 – 40 % MP removal was achieved after 6 hours of treatment in the real effluent after CAS, using lime juice extract as a source of organic acids (citric, tartaric, and ascorbic) for circumneutral photo-Fenton reaction and applying 5 ppm of [M-Fe] and 25 ppm H_2O_2. Mineralization (40 %) and EfOM removal efficiencies (COD 50%) were achieved after 24 h. While total bacteria inactivation was reached within a lower treatment time (270 min, 4.5 h). For the work using low UV-C contact time (9 s, 3 L min^{-1}) and sulfate-based oxidants (0.5 mM), 19 J L^{-1} led to complete microbial inactivation and MP removal, with exception to sucralose (SCL) which was at high initial concentration in the effluent (ranging 20–24 μg L^{-1}) and for which 50 % of removal could only be achieved under strongest conditions (5 mM PS/Fe(II)/UV-C at 1 L min^{-1}; 57 J L^{-1}; 28 s). Lower dosages (0.01 mM) were enough for total inactivation of microbial populations, yet insufficient to degrade MPs. Iron activation in PMS/Fe(II)/UV-C and PS/Fe(II)/UV-C reached >50 % mineralization of MPs (RODRÍGUEZ-CHUECA *et al.*, 2018). In the work of Moreira *et al.* (2018) MP concentration was lower than the quantification limit within 4 h (0.2 g L^{-1} catalysts and 20 mg L^{-1} H_2O_2; 40 kJ L^{-1} for TiO_2 and TiO_2/H_2O_2). Fecal coliforms, *Enterococci sp.*, and ARB (tetracycline and ciprofloxacin) were below the detection limit (0.01 CFU mL^{-1}) for all treatments employing H_2O_2, and there was no regrowth after treated wastewater was stored for 3-days.

Efficient removal of pathogen indicators (Thermotolerant coliforms) and other bacteria was achieved by MBR + post-chlorination, ozonation, UV, AOPs ($UV/TiO_2/O_3$ the best, UV/TiO_2, UV/O_3, O_3/TiO_2, TiO_2) (VERLICCHI; AL AUKIDY; ZAMBELLO, 2015). For UV irradiated treatment, higher fluence was mentioned as necessary for virus and oocysts removal. Meanwhile, secondary treatments CAS and UASB were not efficient for virus removal (rotavirus A, human adenovirus, norovirus genogroups I and II, and hepatitis A viruses). The removal of viruses from MWWTP effluent by advanced technologies is hardly assessed, thus constituting one of the gaps identified in this review.

As for the work with ozonation and PAC, 80 % removal of MPs (over 70 compounds detected) was achieved with either average ozone dose (5.7 mg O_3 L^{-1}) or PAC (10-20 mg L^{-1}). Regarding disinfection performance, PAC-UF achieved complete removal of intestinal bacteria and coliphage (<5 UFP mL^{-1}, indicator of human viruses). PAC-SF only achieved 11 % and 79 % of *E. coli* and *Enterococci* removal, respectively. Meanwhile, ozonation reduced coliphage virus to levels below the detection limit (5 UFP mL^{-1}) (over 95 % removal) and removed over 97 % of fecal bacteria (MARGOT *et al.*, 2013). In the review of Verlicchi; Al Aukidy and Zambello (2015) pharmaceuticals were detected and evaluated in 60 % of the studies, with the most investigated technologies being MBR, PAC, ozonation and UV and respective best removal results by MBR (secondary stage) and PAC (tertiary stage) (for MP> 80 %).

It is worth to emphasize that several factors might affect comparison of compound concentrations from different effluent from several works, since distinct collection procedures (grab sample, 24 hour composite sample, etc.) might be employed, as well sample storage, extraction and preparation (ORT *et al.*, 2010; VANDERFORD *et al.*, 2011). This is also valid for ARB and ARG results, with many extraction kits available.

Lenses number 3, 4 and 6, which correspond respectively to “Treatment Conditions”, “Toxicity and other possible effects”, and “Costs analysis” reflected the level of readiness and implementation among the distinct processes evaluated in each paper as proposed by Rizzo *et al.* (2019). For the most consolidated technologies, in special ozonation, there was more information available regarding optimal operational conditions in large scale reactors, toxicity evaluation during treatment as well as other biological effects. Cost analysis were present only in two papers, and they lacked details on the applied methodology used for cost estimation.

Regarding the lens “Toxicity and other possible effects”, only the work by Villegas- Guzman *et al.* (2017) lacked investigation on the topic. As for results obtained by Moreira *et al.* (2018), TiO_2/H_2O_2 and solar-H_2O_2 had the most reduction in abundance (gene copy number per volume of wastewater) for 16s rRNA and ARGs. This reduction was transient for 16s and other genes, and there was regrowth of bacteria after 3-days storage. Another work that showed results for ARG was the review by Verlicchi; Al Aukidy and Zambello (2015), that very briefly mentioned that advanced biological and chemical processes show between 1–5 log units of efficiency for ARB and ARG removals. Regarding toxicity, studies with a perspective on risk assessment and sample toxicity before and after treatment via Microtox, and *D. magna* toxicity tests concluded that hospital effluent is 5–15 more toxic than urban wastewater due to the presence of detergents, disinfectants, free chlorine, AOX, ethanol, propanol, and metals including Zn, Cu, As and Pb.

For biological process, a review showed some results for ARB and ARG removals (KRZEMINSKI *et al.*, 2019). Considering cultivable ARB, CAS was able to reduce ampicillin and chloramphenicol-resistant coliforms and *Escherichia coli* (2-log), while it did not reduce the percentage of ARB among total bacteria (prevalence). The addition of a disinfection stage with peracetic acid reduced ampicillin-resistant *E. coli* further. On the other hand, bacteria harboring ARGs showed better survival than total bacteria even after chlorination. Similarly, remaining ARGs (tetA, tetB, tetE, tetG, tetH, tetS, tetT, tetX, sul1, sul2, qnrB and ermC) were still in high levels after chlorination. As for CW, 90–99 % removal of ARB was achieved, and planted sub-surface flow CWs were most efficient. CWs could also remove significant amounts of ARGs (45–99 %) belonging to tetracycline, fluoroquinolone, and sulfonamides antibiotic classes in both domestic/urban and livestock wastewaters (KRZEMINSKI *et al.*, 2019).

Considering other assays in the "Toxicity and other possible effects" lens, Rodríguez-Chueca *et al.* (2018) evaluated the total fungi population in samples besides bacterial population. The photolytic activation of PMS led to the total inactivation of bacteria (≈ 5.70 log) with the highest UV-C dose (57 J L^{-1}). A low dosage of reagents, which was enough for bacteria inactivation, was not suitable for fungi inactivation. H_2O_2/UV-C reached levels below detection limit for fungi population at 1 - 3 L min^{-1} (9 – 28 s), and values were higher than 3-log of removal with photolysis of PMS and PS, when 1 L min^{-1} was used, and higher than 2-log removal at 3 L min^{-1}. As it was discussed for the analysis of virus removal from MWWTP effluent via advanced technologies, studies rarely assess the effect of these treatments upon fungi.

The most complete work considering the lens "Toxicity and other possible effects" of Margot *et al.* (2013) applied several bioassays including: YES, Combined Algal Assay, and fish early life stage (Rainbow Trout). There was removal of toxicity by using 5.7 mgO_3 L^{-1} or 0.86 gO_3 $gDOC^{-1}$. PAC-UF was slightly more effective than ozone in reducing toxicity to algae (PAC: 84 % [79–88 %], OZ:75 % [67–81 %]), photosynthesis inhibition (PAC: 87 % [77–99 %], OZ:82 % [77–92 %]) and fish development impact (PAC: similar to control, OZ: delay in the development). On the other hand, ozone was slightly better in reducing estrogenic activity (PAC: 77 % [58–90 %], OZ: 89 % [85–92 %]). No genotoxicity or mutagenicity were detected in ozonation effluents despite the formation of bromate. In this way, in general PAC-UF performed slightly better and accordingly to the destination of treated effluent (e.g., discharge in receiving waters for drinking or recreational purpose). PAC-UF treatment was considered to be the most suitable option despite its possibly higher cost, enabling good removal of most MP (>80 %) and macropollutants, highest decrease in toxicity, and a total disinfection of the effluent. Such a complete evaluation of the effects of resulting effluent is rarely performed by research groups and should be stimulated in order to guarantee the prevention of undesirable environmental and health effects due to effluent discharge.

A review showed some full-scale reclamation plants in Australia which operated with ozonation followed by BAC (Biological Activated Carbon) filtration and several disinfection processes (including ozone, UV, and MF/UV) (MICHAEL-KORDATOU *et al.*, 2015). These systems achieved over 50 % and 90 % removal of DOC and microcontaminants generating high-quality effluent with low toxicity and estrogenic activity (removal of non-specific toxicity and estrogenicity higher than 70 % and 95 %, respectively).

Considering photo-Fenton systems, a work with circumneutral solar photo-Fenton with three iron additions (3 of 20 mg L^{-1} and 50 mg L^{-1} of hydrogen peroxide) has shown efficient removal of toxicity according to different ecotoxicity assessments in real secondary CAS effluent (FREITAS *et al.*, 2017). After 90 minutes of reaction, bacterial population was completely inactive and acute and chronic toxicity had been totally removed. The removal of MP was ~99 % at the same treatment conditions.

Finally, considering lens number 6 "Costs analysis", Verlicchi; Al Aukidy and Zambello (2015) was the manuscript which contained a deeper discussion on the topic. Costs for different processes were shown, with a few details regarding Operational and Maintenance (O&M) and Total Costs. The paper gave information on costs relate to the application of various processes such as: Photo-Fenton (O&M 0.38 € m^{-3}), MBR (O&M 0.45-0.163 € m^{-3}), MBR+ O_3 + UV (Investment 3.6 € m^{-3}), MBR + GAC (total 4.1 € m^{-3}), MBR+ O_3 + GAC (O&M 1.45 € m^{-3}, total 4.7 € m^{-3}), MBR+ MBR + PAC (O&M 1.65 € m^{-3}, total 5 € m^{-3}), MBR+ O_3 (O&M 1.85 € m^{-3}, total 5.5 € m^{-3}), O_3 (O& M 0.22-0.4 € m^{-3}), O_3 + H_2O_2 (O&M 0.34-1.08 € m^{-3}), PAC (O&M 1.08 € m^{-3}), ClO_2 (O&M 0.3 € m^{-3}), MBR+ O_3 (O&M 1 € m^{-3}). According to the authors, even though some technologies such as PAC and GAG seem efficient and competitive towards some AOPs, if the EfOM increases, there might be an increase in operational costs related to replacement of filter media and waste disposal. Also, it is important to highlight that although the treatment of hospital wastewater was more costly than treatment of domestic wastewater (€ m^{-3}), the treated volume is lower.

In the work of Margot *et al.* (2013), an ozone dose of 0.6 g O_3 $gDOC^{-1}$ (effluent DOC ~ 5 g m^{-3}) and 0.035 kWh m^{-3} wastewater were required, which was considered 12% of the total energy consumption of a typical nutrient removal plant (0.3 kWh m^{-3}wastewater). This occurs as additional energy (0.01-0.015 kWh m^{-3}) is required to produce pure oxygen.

In the case of MBR, investment costs can be 10-15 % higher than CAS, and O&M can vary 0.11-0.15 USD m^{-3} (0.093-0.3 € m^{-3} considering 1 USD = 0.85 €) for MBR and 0.07 USD m^{-3}

(0.059 € m^{-3}) for CAS, with energy costs corresponding to 30 % of this value. Energy consumption of 0.4-0.6 kWh m^{-3} was mentioned for MBR (BOLZONELLA *et al.*, 2010). Considering progressive reduction costs of membrane units, O&M were reduced from 400 USD m^{-2} in 2005 to 50 USD m^{-2}.

As for CW, investment costs in plants from European countries (Belgium, Spain, and Greece) might vary from 295 to 566 € PE^{-1} (20 to 3640 PE - population). In Greece, values range from 315 to 566 € PE^{-1} (467 ± 87), for a PE range of 540 to 3640 (1360 ± 1143), with operation costs ranging from 6.5 to 13.9 € $PE^{-1}year^{-1}$ (10.0 ± 2.4) or 0.12 - 0.25 € m^{-3} of treated effluent (0.18 ± 0.04) (TSIHRINTZIS, 2017). Krzeminski *et al.* (2019) mentioned that CWs have reduced investment costs compared to CAS. CAS, as a conventional treatment, would present lower costs than MBRs (membrane cost ca. 40–60 % of total capital costs) and MBBRs (which is lower compared to MBRs). Management costs are lower in CAS, with an energy consumption 0.2–1.4 kWh m^{-3}. MBR would have higher energy consumption (0.4–4.2 kWh m^{-3}) and require membrane replacement (ca.10–14 % of total operation costs), as well as chemicals for membrane cleaning. Energy requirement for MBBR is related to the need for a slightly higher aeration when compared to CAS, thus increasing costs of MBBR compared to CAS and CWs.

For the AOP photo-Fenton, based in a pilot scale study, the total cost of a full-scale unit for the treatment of 150 m^3 day^{-1} of secondary wastewater effluent was estimated to be 0.85 € m^{-3} (MICHAEL *et al.*, 2013). In a study of the performance and treatment cost of solar photo-Fenton reaction in three cities which receive elevate solar irradiation (Taberna, Spain; Arica, Chile; and Doha, Qatar) (CABRERA REINA *et al.*, 2020) respective treatment costs varied for each city (2.67-3.11 € m^{-3}, 2.45-2.55 € m^{-3}, 2.23-2.29 € m^{-3}). Such values considered amortization costs, which is related to price associated to land purchase for plant installation. These costs have affected total cost more than operational costs. It was mentioned that a combination of a biological process, such as MBR with the photo-Fenton process, could reduce costs to nearly 1.19 € m^{-3}. Even though a direct comparison of values among different works must be cautious due to variation in prices, in the applied method for calculation of costs, and in the matrix composition, costs associated to the application of photo-Fenton + MBR would be comparable to total costs related to the application of MBR + ozone and PAC/GAC shown for hospital wastewater treatment by Verlicchi; Al Aukidy and Zambello (2015).

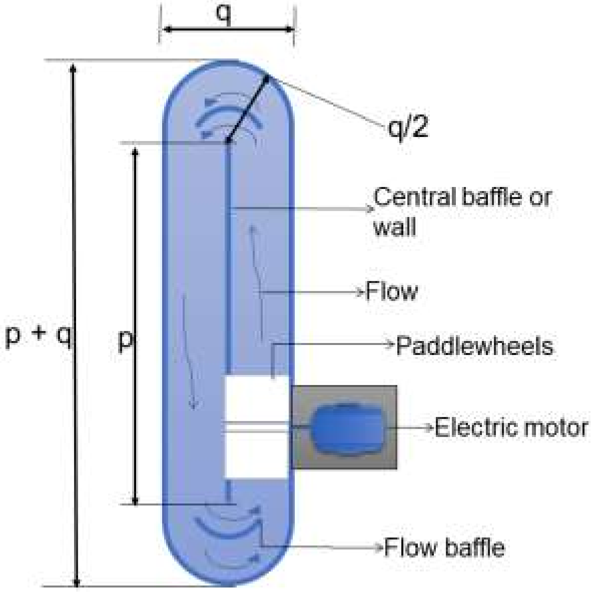
It is important to highlight that regardless of each process individual cost and efficiency, a throughout analysis considering the destination of the final treated effluent and waste generated by each technology should be made. Costs related to disinfection and removal of atrazine via UVC varied according to different reuse requirements, from less to more restrictive conditions: disinfection only (0.0680 kWh m^{-3} and total costs 0.0111 € m^{-3}), ATZ removal and 1st reuse category (0.5950 kWh m^{-3} and total 0.0828 € m^{-3}), 2nd reuse category (1.0 kWh m^{-3} and total 0.1386 € m^{-3}), 3rd reuse category (1.67 kWh m^{-3} and total 0.2226 € m^{-3}), and complete oxidant consumption (2.04 kWh m^{-3} and total 0.2646 € m^{-3}) (SOUZA *et al.*, 2013).

After all, all specific questions posed during the systemic analysis indicated important research aspects that should be investigated in this field of study. A global question for guidance of research on this subject was elaborated after this systemic analysis: "What are the optimum operational conditions for advanced treatment of wastewater when aiming at simultaneous removal of micropollutants and disinfection, considering process efficiency for different matrices and the influence of organic and inorganic macropollutants, as well as process costs and possible ecotoxicological effects?".

I.4.2. Raceway Pond Reactors: applications in the environmental field, use for advanced solar oxidation and operational parameters

Raceway ponds were initially developed for microalgae and cyanobacteria cultivation during 1950-1960 as open and shallow low-cost solar reactors (CHISTI, 2016; KUMAR *et al.*, 2015). These reactors might present a typical liquid depth of 0.25-0.30 m, length/width relation equal or greater than 10. For ponds with semicircular ends, flow deflector or baffles may be used for flow homogenization and dead zones minimization (Figure I.4.7).

FIGURE I.4.7 – Raceway pond reactor general scheme



p = central baffle or wall length. q= width

The configuration of open reactors is preferred for microalgae cultivation due to their small investment cost, use of freely available solar light and low requirement of energy for mixing in comparison to closed photobioreactors. 95 % of large worldwide scale production facilities are of this design against 5 % of closed ones (KUMAR *et al.*, 2015). Even though this is a low-cost facility with low energy demand, some factors can limit its application for algal production such as high land requirement and weather dependence (fluctuation in light and temperature, evaporation of water, and contamination).

High rate algal ponds have also been used for wastewater treatment with a simultaneous focus on the recovery of energy (biodiesel, for example) and other products. In the case of direct biological wastewater treatment, this type of reactor has been used for the activated sludge process, provided with aeration and sludge recirculation unit, known as oxidation ditch/pond.

In recent years another application for this reactor design was proposed, but for physical-chemical reactions rather than a biological process. Due to a combination of different factors, the application of raceway pond reactor (RPR) for the solar photo-Fenton reaction as an advanced treatment of MWWTP secondary effluent has been investigated.

At first, this type of effluent presents lower organic load and toxicity in comparison to industrial effluents, which allows working with open reactors and for evaporation not configuring such a problem. Secondly, it is ideal in domestic treatment to apply technology at circumneutral pH with low iron concentration, in order to produce an effluent with adequate parameters for later discharged into the environment or even reuse, for example, in agriculture. In this case, the modification of the photo-Fenton reaction with complexing agents (polycarboxylic acids, i.e., EDTA, EDDS, citric acid, etc.) it is an interesting approach to work at both near-neutral pH and using lower iron concentration. When working with polycarboxylic substances as complexing agents, lower doses and iron-ligand proportions are also necessary in order to not increase DOC concentration on the final treated effluent.

Also, the reaction should be effective at faster rates, to reduce treatment time and allow a higher treatment capacity per day. In this way, for effective reactions at lower iron concentration, the light path needs to be longer, what in the case of closed reactors such as CPC significantly increases the overall costs (pumping, tube diameter, reflectors, etc.). Considering all those factors, the raceway configuration allows working in a technically simple and feasible design already available at commercial scale due to other solar applications, with longer optical pathways and lower costs for mixing and implementation (CARRA *et al.*, 2014).

From some of the most recently published papers regarding RPR operation (Table I.4.7) it is possible to observe that the solar photo-Fenton reaction is very efficient in the removal of a wide range of CECs compounds under both conventional acidic pH operation or with circumneutral pH strategies (iron sequential addition or addition of complexing agents such as EDDS). Experiments developed with RPR in all the mentioned papers were performed with pre-filtration of the secondary effluent prior to the advanced treatment tests, which is necessary to reduce suspended solids and turbidity, allowing proper light absorption in order for the photoreaction to take place.

TABLE I.4.7 – Recently investigations with raceway pond reactors: operational and reaction parameters, micropollutants and disinfection

Goal	Matrixes	Micropollutants	Bacterial organisms	Reagents	pH	Temp. (ºC)	Volume	HRT	Liquid depth	Radiation[1]
[2]Degradation of two pesticides (acetamiprid – ACTM – and thiabendazole – TBZ) in batch mode, different liquid depths	Tap water, simulated secondary effluent	100 μg L^{-1} of ACTM and TBZ	-	$[Fe^{2+}]$ 1, 5.5 and 10 mg L^{-1} $[H_2O_2]$ 50 mg L^{-1}	2.8±0.05	28±2	120 – 360 L	-	5, 10 and 15 cm	Solar average 15±3W m^{-2}
[3]Modelling of treatment capacity in function of photo-absorption in batch mode.	Simulated secondary effluent	100 μg L^{-1} of ACTM and TBZ	-	$[Fe^{2+}]$ 1, 5.5 and 10 mg L^{-1} $[H_2O_2]$ 50 mg L^{-1}	2.8±0.05	28±2	120 and 360 L	-	5 and 15 cm	Solar variable between 10-30 W m^{-2}
[4]Degradation of commercial pesticides in bench scale (lab) for reagent optimization and further semi-pilot scale (RPR) in batch mode; transformation products (TP) investigation	Real secondary effluent	100 μg L^{-1} of ACTM and TBZ	-	$[Fe^{2+}]$ 10, 15 and 25 mg L^{-1} $[H_2O_2]$ 50, 75 and 100 mg L^{-1}	2.8±0.05	25±2	1 L (lab) 120 L (RPR)	-	5 cm	14±2 W m^{-2} (lab); 15±1 W m^{-2} (average - RPR)
[5]Operation of RPR in continous mode, effect of hydraulic retention time (HRT) and liquid depth	Simulated and real secondary effluents	200 μg L^{-1} of ACTM (simulated); 7 μg L^{-1} of the sum of 58 MPs (real)	-	$[Fe^{2+}]$ 5.5 mg L^{-1} $[H_2O_2]$ 30 mg L^{-1}	2.8	26 - 32	120 L- simulated, 18 and 80 L (real)	20, 40, 80 and 120 min	5 and 15 cm	Solar variable between 10-30 W m^{-2}

Goal	Matrixes	Micropollutants	Bacterial organisms	Reagents	pH	Temp. (ºC)	Volume	HRT	Liquid depth	Radiation[1]
[6]Photo-Fenton modelling in RPR: effect of temperature and irradiance	Simulated secondary effluent	100 µg L^{-1} of ACTM	-	[Fe^{2+}] 5.5 mg L^{-1} (lab); 1.01, 5.31 and 10.05 mg L^{-1} (RPR) [H_2O_2] 50 mg L^{-1}	2.8	10, 20, 30 and 40 (lab) 21-27 (RPR)	1.25 L (lab) and 360 L (RPR)	-	5 and 15 cm	5-40 W m^{-2} (lab); average of 27-29 W m^{-2}
[7]Modified photo-Fenton treatment at neutral pH with sequential iron addition in RPR; ecotoxicity study	Real secondary effluent	80 µg L^{-1}, the sum of 39 MPs	Total coliforms: 7.3×10^4 CFU mL^{-1} *E. coli*: 1.8×10^3 CFU mL^{-1}	[Fe^{2+}] 3 additions 20 mg L^{-1} (0, 5 and 15 min)	6.5±0.05	20±0.3	18 L	-	5 cm	Solar average 26±3 W m^{-2}
[8]Modified photo-Fenton treatment at neutral pH with sequential iron addition and Fe:EDDS complexing agent in RPR	Simulated and real secondary effluents	100 µg L^{-1} of carbamazepine, flumequine, ibuprofen, ofloxacin and sulfamethoxazole	-	[Fe^{2+}] 1, 2 or 3 additions 5.5 mg L^{-1} (every 10 min) [Fe^{3+}] 3 or 5.5 mg L^{-1} (Fe:EDDS) 1:2 [H_2O_2] 50 mg L^{-1}	7.3 – 8.5	-	120 L	-	15 and 20 cm	Solar average 34-37 W m^{-2}
[9]Ecotoxicity study in real MWWTP effluent modified photo-Fenton treatment at neutral pH with sequential iron addition and Fe:EDDS complexing agent	Real secondary effluent	96 µg L^{-1}, the sum of 54 MPs	-	[Fe^{2+}] 4 additions 5.5 mg L^{-1} (every 5 min) [Fe^{3+}] 5.5 mg L^{-1} [EDDS] 71.6 mg L^{-1} (Fe:EDDS)1:2 [H_2O_2] 30 mg L^{-1}	6.5±0.05	26.5±0.5	120 L		20 cm	Solar average 33±1 W m^{-2}

Goal	Matrixes	Micropollutants	Bacterial organisms	Reagents	pH	Temp. (ºC)	Volume	HRT	Liquid depth	Radiation[1]
[10]Disinfection in real MWWTP effluent: RPR and CPC comparison	Real secondary effluent	-	Total coliforms: $3.54\times10^6\pm 1.7\times10^5$ CFU mL^{-1} *E. coli*: $2.76\times10^4\pm 3.1\times10^2$ CFU mL^{-1} *Enterococcus sp:* $7.1\times10^3\pm 1.5\times10^1$ CFU mL^{-1}	[Fe^{2+}] 20 mg L^{-1} [H_2O_2] 50 mg L^{-1}	7.0±0.2	34±2.1 (CPC) 27±3 (RPR)	7 L (CPC) 18 L (RPR)	-	5 cm	Solar average 35±1.3 W m^{-2} (CPC) 30± W m^{-2} (RPR)
[11]Disinfection with operation of RPR in continous mode, effect of hydraulic retention time (HRT), iron concentration, and H_2O_2 on regrowth	Real secondary effluent	-	Total coliforms: $6.43\times10^5\pm 2.0\times10^1$ CFU mL^{-1} *E. coli*: $1.43\times10^4\pm 1.22\times10^1$ CFU mL^{-1} *Enterococcus sp:*	[Fe^{2+}] 20 mg L^{-1} and 10, 5 and 2.5 mg L^{-1} (in continous mode) [H_2O_2] 50 mg L^{-1} and 30 mg L^{-1} (in continuous mode)	7.1±0.2	25 (lab) 22 on winter 27 on summer	1 L (lab) 18 L (RPR)	15, 30 and 60 min	5 cm	30 W m^{-2} (lab); average around 14±5 W m^{-2} in winter and 34±2.5 W m^{-2} in summer

Goal	Matrixes	Micropollutants	Bacterial organisms	Reagents	pH	Temp. (ºC)	Volume	HRT	Liquid depth	Radiation[1]
			$3.65\times10^3\pm$ 0.5×10^1 CFU mL^{-1}							
[12]Removal of MPs in real MWWTP secondary effluents with different characteristics by modified photo-Fenton with EDDS	Real secondary effluents	6.2 – 52 μg L^{-1}, the sum of MPs identified among a list of 115 MPs	-	[Fe^{2+}] 5.6 mg L^{-1} (Fe:EDDS)1:1 [H_2O_2] 30 mg L^{-1}	7 - 8	22 - 28	19 L	-	5 cm	Solar average 28-35 W m^{-2}
[13]Moddeling of modified photo-Fenton with EDDS for removal of three higly present MPs in real MWWTP in RPR continuous mode	Real secondary effluents	O-DSMT (319–1976 ng L^{-1}), O-DSMV (684–1325 ng L^{-1}) GBP (943–7863 ng L^{-1})	-	[Fe^{2+}] 5.6 mg L^{-1} (Fe:EDDS)1:1 [H_2O_2] 30 mg L^{-1}	7 - 8	22 - 26	19 L and 78 L	10, 15, 20 and 30 min	5 and 15 cm	Solar average 28-35 W m^{-2}

[1] Irradiation: UVA (327 – 384 nm).[2](CARRA *et al.*, 2014). [3](RIVAS *et al.*, 2015). [4](CARRA *et al.*, 2015).[5](ARZATE *et al.*, 2017). [6](SÁNCHEZ PÉREZ *et al.*, 2017). [7](FREITAS *et al.*, 2017). [8](DE LA OBRA *et al.*, 2017). [9](RIVAS IBÁÑEZ *et al.*, 2017). [10](ESTEBAN GARCÍA *et al.*, 2018). [11](DE LA OBRA JIMÉNEZ, I. *et al.*, 2019). [12](SORIANO-MOLINA; PLAZA-BOLAÑOS; *et al.*, 2019). [13](SORIANO-MOLINA; GARCÍA SÁNCHEZ; *et al.*, 2019).

Regarding variation on solar irradiation over the year, even at lower irradiance levels (around 10 W m^{-2} of UV), the photo-Fenton process could be performed, presenting just limitation for its treatment capacity, which was half the capacity at higher irradiation (RIVAS *et al.*, 2015). In this way, the possibility of operating at different liquid depths and reagents concentration in RPR reactors can help the application of this technology even at moments and in locations with lower radiation availability. Considering that first investigations with RPR obtained good MPs removal at relatively short reaction times (few hours), (ARZATE *et al.*, 2017) evaluated a continuous mode operation for this reactor at a semi-pilot scale. In the location of Almería, Spain where some experiments were developed, a rate of 5 L m^{-2} day^{-1} of evaporation had been observed for microalgal raceway ponds installations. The water loss for a continuous operation described on a summer day would be just 2 % of the total volume of the reactor (ARZATE *et al.*, 2017).

Carra *et al.* (2014) obtained the first results in RPR for photo-Fenton at conventional acid pH. A fast degradation in tap water (5 min) for the pesticide TBZ (thiabendazole) was achieved, in contrast to acetamiprid (ACTM), which was chosen as a target contaminant for further investigation. The removal time for ACTM (20-40 min) was faster at higher iron concentrations. The higher the iron concentration, the higher was the influence of the liquid depth in association with the optical thickness of the solution. In simulated secondary effluent, the presence of inorganic and organic substances slowed down the reaction (40 – 60 min) but nonetheless remained efficient. The use of higher liquid depth and lower iron concentration significantly increased the treatment capacity for RPR (48 mg h^{-1} m^{-2}) in comparison to CPC (29 mg h^{-1} m^{-2}) for same 5.5 mg L^{-1} of iron, but 15 cm in RPR versus 5 cm in CPC.

Further studies investigated a model from the VRPA (volumetric rate of photo absorption) (RIVAS *et al.*, 2015). Under low irradiance (10 W m^{-2}) conditions lower iron concentrations and lower liquid depth were indicated to be used, on the maximum liquid depth of 10 cm and 5. mg L^{-1} Fe concentration for a goal of 100 L m^{-2} treatment capacity. At higher irradiance levels (30 W m^{-2}) higher treatment capacity (200 L m^{-2}) could be achieved with higher liquid depth (15 – 20 cm) and higher iron concentration (10 mg L^{-1}).

When evaluating real MWWTP secondary effluents, the best operational conditions obtained were: 25 mg L^{-1} Fe and 100 mg L^{-1} H_2O_2. 91 % ACTM degradation was obtained in 240 min, TBZ>99 % in just a few minutes and 85 mg L^{-1} H_2O_2 consumption. Dark Fenton reaction was performed for control and achieved 78 % ACTM degradation in 240 min, TBZ>99 % in few minutes and 40 mg L^{-1} H_2O_2 consumption, indicating a possible application of this reaction during the night alternating with the solar photo-Fenton. Chloride and sulfate species were responsible for high conductivity values of the effluent and were considered detrimental for the AOP reactions in real wastewater (CARRA *et al.*, 2015). Transformation products (TPs) of TBZ formed during the process were further eliminated at the end of the reaction, but some ACTM TPs persisted, which indicates the importance of toxicity tests, to evaluate whether treatment should be extended to remove such substances or not.

Arzate *et al.* (2017) evaluated a continuous operation mode for RPR semi-pilot reactors, first, a batch mode was performed for 1 hour, followed by the continuous addition of reagents and contaminated effluent in the studied HRT. During the night, the procedure was interrupted and continued the following day for more hours. A quasi-steady state was quickly achieved in both moments, keeping the efficiency of initial model contaminant ACTM removal at 90 %. During the night removal reached 100% with Fenton. Both liquid depths (5 and 15 cm) achieved similar micropollutants results on real concentration in the real effluent. While different HRT led to similar micropollutants removal, the residual hydrogen peroxide was higher with lower HRT, indicating optimization of hydrogen peroxide recommended as important to avoid expending this reagent unnecessarily. Treatment capacity varied from 450 L m^{-2} day^{-1} (5 cm, 6 h in winter, 40 min of HRT) to 2250 L m^{-2} day^{-1} (15 cm, 10 h in summer).

A mixture of pharmaceuticals (carbamazepine, flumequine, ibuprofen, ofloxacin, and sulfamethoxazole) was removed over 90 % with 1 kJ L^{-1} of accumulated irradiation using photo-Fenton different strategies to work at circumneutral pH. Two iron additions of 0.1 mM achieved this efficiency in 20 – 25 min (15 – 20 cm), while applying the complexing agent Fe:EDDS this time could be reduced to 9 – 20 min (0.05 mM iron) or 6 – 10 min (0.1 mM). Higher treatment capacity in RPR (1.07 – 1.08 mg kJ^{-1}) by comparison to previous results in CPC reactors (0.26 mg kJ^{-1}) was obtained for similar reaction conditions. Another condition tested was the initial neutralization of inorganic carbon (TIC) of the effluent with sulfuric acid. Final TIC of 5 mg L^{-1} showed better results for the photo-Fenton reaction at 20 cm (DE LA OBRA *et al.*, 2017).

An investigation of a photo-Fenton kinetic model for micropollutants removal in the function of irradiance, temperature, iron concentration, and light path length was performed (SÁNCHEZ

PÉREZ et al., 2017). It was observed that the temperature could accelerate the initial Fenton reaction and also increase the light absorption coefficient for iron, thus contributing to the photo-Fenton reaction in both stages. This model was performed for conventional photo-Fenton at acidic pH, and other models for photo-Fenton at neutral pH have been also made (SORIANO-MOLINA; GARCÍA SÁNCHEZ; MALATO; *et al.*, 2018).

Further on, different ecotoxicity assays have been performed and showed that the photo-Fenton reaction was not only able to remove CECs but also reduce the remaining toxicity of the secondary effluent treated by conventional activated sludge units (FREITAS *et al.*, 2017; RIVAS IBÁÑEZ *et al.*, 2017). Also, disinfection indicated by *E.coli* and Total coliforms was also achieved for solar photo-Fenton reaction (DE LA OBRA JIMÉNEZ, I. *et al.*, 2019; ESTEBAN GARCÍA *et al.*, 2018).

39 micropollutants (mainly pharmaceuticals) with a total concentration of 80 µg L^{-1} were identified on a real MWWTP secondary effluent and were efficiently removed by modified photo-Fenton at neutral pH (99 %) after 90 minutes of treatment. Toxicity bioassays indicated a sensitivity order of *Tetrahymena thermophila* > *Daphnia magna* > *Lactuca sativa* > *Spirodela polyrhiza* ≈ *Vibrio fischeri*. Initial *D. magna* inhibitory effect dropped from 20 % to 5 %, and *T. thermophilia* was completely removed (40 % to no effect). Removal efficiencies achieved were 56 % for DOC (9.1 mg L^{-1} after treatment), 99.4 % and 99.9 % for *E. coli* and Total coliforms (1 CFU mL^{-1} of each in the end, with no regrowth after 24 h in the dark, respectively after 90 minutes of treatment). No increase in ecotoxicity was observed for any of the tested organisms after the photo-Fenton treatment. Complete consumption of hydrogen peroxide was achieved. The final neutralization of the effluent was made due to a final pH decrease around 3.0 after iron addition (FREITAS *et al.*, 2017).

In an in-depth investigation of the ecotoxicity of secondary MWWTP effluents treated by photo-Fenton at circumneutral pH, four bioassays were performed: phytotoxicity, cytotoxicity, androgenic/glucocorticoid activity, and estrogenicity. Also, 54 out of 76 analyzed micropollutants were identified on the investigated real wastewater, which sum (around 96 µg L^{-1}) had 99 % of removal by both iron-dosage or EDDS-complexing methods of neutral solar photo-Fenton (50-60 minutes of reaction). Even though EDDS-complexing strategy can increase final DOC levels it does not require pH adjustment at the end of the reaction. All bioassays indicated efficient ecotoxicity removal in both strategies (over 80 % and 93 % for estrogenic and androgenic/glucocorticoid potency, respectively) (RIVAS IBÁÑEZ et al., 2017).

Regarding the disinfection process, in a comparison between CPC and RPR designs, both reactors reached inactivation below detection limit of 1 CFU mL^{-1} for *E. coli*, total coliforms and *Enterococcus sp* under 80 minutes of reaction (ESTEBAN GARCÍA *et al.*, 2018). In this case, the photo-Fenton treatment was operated at neutral pH without any complexing reagent or sequential addition, with concentrations of 20 mg L^{-1} Fe and 50 mg L^{-1} H_2O_2. In addition, chronic toxicity was reduced after treatment (*Tetrahymena thermophila* growth inhibition test), while acute toxicity did not present an increase after treatment (*Vibrio fischeri* bioluminescence inhibition and *Daphnia Magna* immobilization tests). In fact, even a slight stimulation of *T. thermophila* and *V. fischeri* could be detected and were possible explained by the availability of more biodegradable organic molecules after the advanced oxidation treatment, which would be more easily assimilated by those organisms.

As for disinfection in continuous mode, photo-Fenton at neutral pH has been also investigated in real MWWTP secondary effluent, with operation initially for 2 hours in batch mode with 20 mg L^{-1} Fe and 50 mg L^{-1} H_2O_2, followed by 300 minutes on continuous mode using specific conditions in three consecutive days (DE LA OBRA JIMÉNEZ, I. *et al.*, 2019). Control experiments of UVA/H_2O_2 and mechanical stress could remove 1 log of *E. coli* and total coliforms, but not *Enterococcus sp,* using the highest HRT of 60 minutes. An HRT of 15 minutes was insufficient for bacteria (*E. coli*, total coliforms, and *Enterococcus sp*) removal under the detection limit of 1 CFU mL^{-1}, and at least 30 minutes with an accumulated UVA radiation of 1 kJ L^{-1} were necessary for effective disinfection in lab scale. Also, at least a concentration of 30 mg L^{-1} H_2O_2 was necessary to remain in the system overnight to avoid further regrowth. Experiments outdoors in different seasons showed that during winter bacteria removal was not effective in batch mode stage for both HRT and on the first day for continuous mode with an HRT of 30 minutes (less than 1 kJ L^{-1} of accumulated UVA energy). During the following days, and for all experiments in summer (batch mode after 80 minutes), all conditions removed all bacteria to the detection limit. Afterward, lower concentration of iron was tested (2.5, 5 and 10 mg L^{-1}), but at least 5 mg L^{-1} were necessary for efficient disinfection (DE LA OBRA JIMÉNEZ, I. *et al.*, 2019).

The presence and concentration of inorganic ions such as carbonate/bicarbonate, sulfate, chloride, phosphate, nitrate, etc., are important parameters to be evaluated for photo-Fenton treatment of effluents from MWWTP, once they can vary among different locations and MWWTP technology and operation, as it happens to MPs composition (TRAN; REINHARD; GIN, 2018). Also, these substances play an important role in photo-Fenton processes considering scavenging phenomenon, precipitation with the iron catalyst, formation of other oxidative species, among other possibilities. In an recently study (SORIANO-MOLINA; PLAZA-BOLAÑOS; *et al.*, 2019) have shown the efficiency of the modified photo-Fenton reaction at circumneutral pH with Fe:EDDS 1:1 in RPR, that reached 83 % removal of MPs total load in less than 15 minutes regardless of the type of effluent, with 5.6 mg L^{-1} of Fe (0.1 mM) and 30 mg L^{-1} of H_2O_2 (0.88 mM). No correlation between the organic matter load and the removal of MPs could be detected. Also, it was pointed out that the nature of the organic matter rather than its concentration influenced the process.

The modified photo-Fenton with EDDS was modeled using the data from the previous work with effluents from different MWWTP, and validation was performed for one effluent with operation in continuous mode for different liquid depths and HRT (SORIANO-MOLINA; GARCÍA SÁNCHEZ; *et al.*, 2019). Three most abundant CECs detected on the effluents were selected as target compounds (O-desmethyl-tramadol (O-DSMT), O-desmethylvenlafaxine (O- DSMV) and gabapentin (GBP)). The model showed good adjustment to different parameters (H_2O_2 consumption, Fe-EDDS concentration, and the concentration of contaminants), with a better adjust for 5 cm liquid depth. With the model prediction for operation in different irradiation conditions of the year, a treatment capacity of 450 L m^{-2} d^{-1} could be reached at 5cm depth and HRT of 30 minutes, while in summer with higher irradiation and hours of light (10 hours of operation against 4.5 hours in winter), 4000 L m^{-2} d^{-1} would be reached for 80 % MPs removal. During summer, HRT can be reduced until 15 minutes, if a lower liquid depth (5 cm) is used. However, that can also reduce TC, while with an HRT of 30 minutes and 20 cm a TC of 9000 L m^{-2} d^{-1} could be achieved.

I.5. CONCLUSIONS

A bibliometric analysis and systemic review of the literature were performed regarding advanced treatments for simultaneous removal of CECs and pathogens (disinfection) from domestic wastewaters. A relevant selection of manuscripts was obtained, and their main strengths and weaknesses were evaluated through the analysis of six relevant aspects (monitored parameters, studied matrices, process parameters, toxicity, and other effects, process efficiency, and costs).

Most of the manuscripts gathered during the review focused either on the removal of micropollutants or disinfection, with only a few presenting simultaneous evaluations of both. There was an increase in the number of manuscripts regarding emerging contaminants in recent years (2018 and 2019), yet many of them focus on their occurrence rather than removal. This reflects the use of the term emerging contaminants as new and under continuous development, while the term micropollutants are more generic and less specific. These characteristics should be taken into consideration when performing any search once they might impact differently obtained results.

Regarding the studied matrices, only a few papers presented work with effluents produced from alternative biological treatments applied for domestic wastewater treatment (UASB, facultative ponds, etc.) as most of them performed advanced treatments with effluent sampled in the sequence of conventional activated sludge (aerobic process).

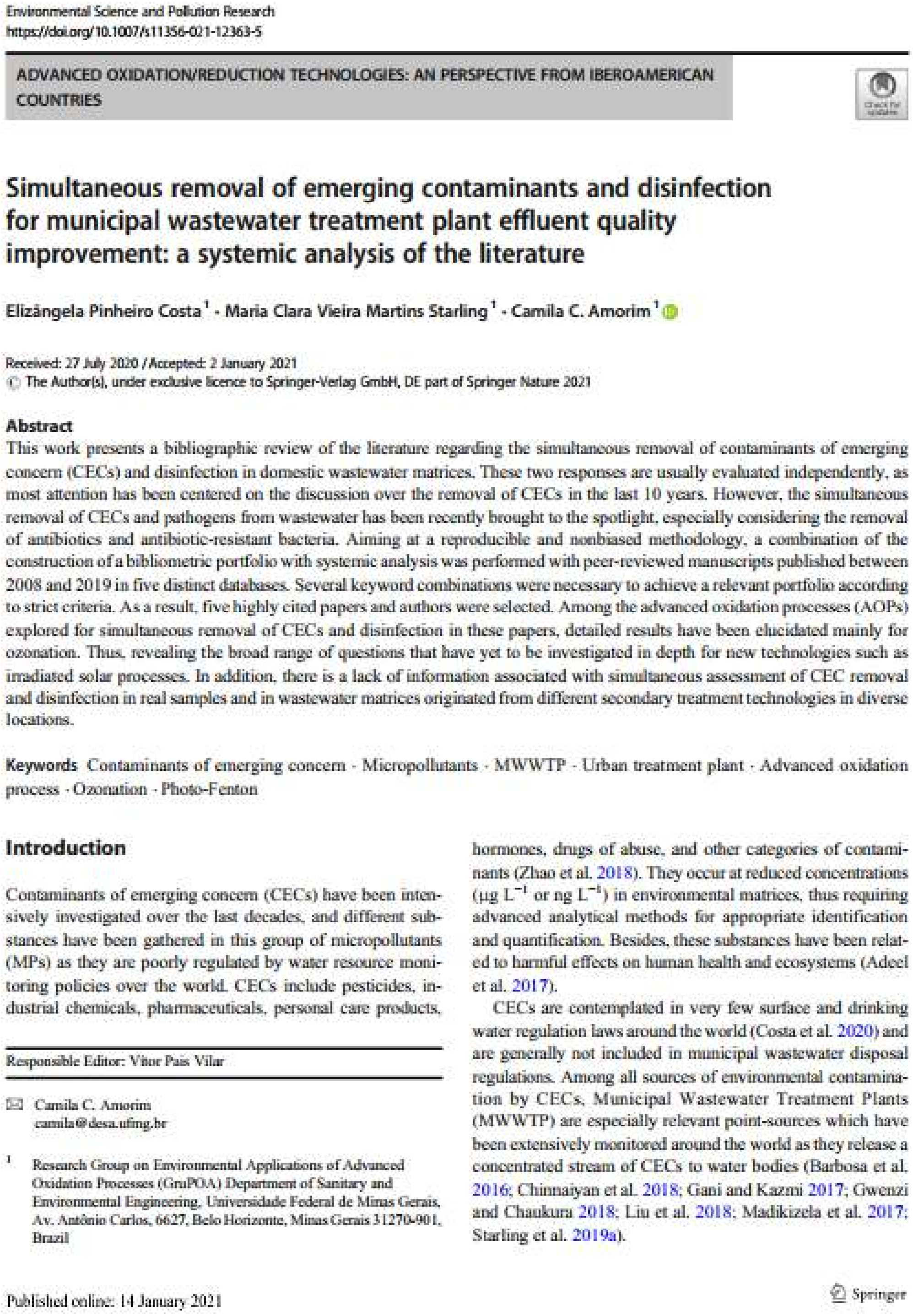
This systemic review of the literature allowed to identify the highlights, obstacles, and opportunities of innovative research in the field. Although pathogen indicators are usually evaluated after treatment, the removal of viruses and fungi, ARB and ARG, and a throughout the investigation of effluent toxic effects and formation of byproducts, are rarely performed. When it comes to cost analysis, studies hardly reveal the methodology applied to calculate costs and do not consider costs related to the treatment/disposal of waste generated during the proposed process.

Overall, to achieve a compromise between the desired effluent quality and feasible costs, different options might be evaluated with the association of different technologies. Furthermore, if a higher effluent quality is necessary (removing MP and disinfection), associated costs might be inarguably higher.

After that, it is very relevant to study the simultaneous removal of both CECs and pathogens from MWWTP effluents resulting from the application of CAS as well as alternative technologies applied for domestic wastewater treatment, and especially for “new” processes that still require implementation on a larger scale (irradiated processes as photocatalysis and Fenton-based reactions).

Furthermore, the literature review with studies specifically of solar photo-Fenton treatment of CECs and disinfection on RPR has shown most studies do not focus on secondary MWWTP effluents from anaerobic (exclusively, or in combination with aerobic) biological treatment processes. Also, most papers published with photo-Fenton reactions over the years initially considered only either CECs removal or disinfection. This seems to be changing in the last two years, with an increase of manuscripts between the middle of 2019 -2020.

In this way, it is very relevant to the study of the simultaneous removal of both parameters (CECs and pathogens) with solar processes since there are few papers with solar Fenton-based treatments on open reactors, in particular the treatment of effluents from biological processes other than CAS.



Environmental Science and Pollution Research
https://doi.org/10.1007/s11356-021-12363-5

ADVANCED OXIDATION/REDUCTION TECHNOLOGIES: AN PERSPECTIVE FROM IBEROAMERICAN COUNTRIES

Simultaneous removal of emerging contaminants and disinfection for municipal wastewater treatment plant effluent quality improvement: a systemic analysis of the literature

Elizângela Pinheiro Costa[1] · Maria Clara Vieira Martins Starling[1] · Camila C. Amorim[1]

Received: 27 July 2020 / Accepted: 2 January 2021

Abstract

This work presents a bibliographic review of the literature regarding the simultaneous removal of contaminants of emerging concern (CECs) and disinfection in domestic wastewater matrices. These two responses are usually evaluated independently, as most attention has been centered on the discussion over the removal of CECs in the last 10 years. However, the simultaneous removal of CECs and pathogens from wastewater has been recently brought to the spotlight, especially considering the removal of antibiotics and antibiotic-resistant bacteria. Aiming at a reproducible and nonbiased methodology, a combination of the construction of a bibliometric portfolio with systemic analysis was performed with peer-reviewed manuscripts published between 2008 and 2019 in five distinct databases. Several keyword combinations were necessary to achieve a relevant portfolio according to strict criteria. As a result, five highly cited papers and authors were selected. Among the advanced oxidation processes (AOPs) explored for simultaneous removal of CECs and disinfection in these papers, detailed results have been elucidated mainly for ozonation. Thus, revealing the broad range of questions that have yet to be investigated in depth for new technologies such as irradiated solar processes. In addition, there is a lack of information associated with simultaneous assessment of CEC removal and disinfection in real samples and in wastewater matrices originated from different secondary treatment technologies in diverse locations.

Keywords Contaminants of emerging concern · Micropollutants · MWWTP · Urban treatment plant · Advanced oxidation process · Ozonation · Photo-Fenton

Introduction

Contaminants of emerging concern (CECs) have been intensively investigated over the last decades, and different substances have been gathered in this group of micropollutants (MPs) as they are poorly regulated by water resource monitoring policies over the world. CECs include pesticides, industrial chemicals, pharmaceuticals, personal care products, hormones, drugs of abuse, and other categories of contaminants (Zhao et al. 2018). They occur at reduced concentrations ($\mu g\ L^{-1}$ or $ng\ L^{-1}$) in environmental matrices, thus requiring advanced analytical methods for appropriate identification and quantification. Besides, these substances have been related to harmful effects on human health and ecosystems (Adeel et al. 2017).

CECs are contemplated in very few surface and drinking water regulation laws around the world (Costa et al. 2020) and are generally not included in municipal wastewater disposal regulations. Among all sources of environmental contamination by CECs, Municipal Wastewater Treatment Plants (MWWTP) are especially relevant point-sources which have been extensively monitored around the world as they release a concentrated stream of CECs to water bodies (Barbosa et al. 2016; Chinnaiyan et al. 2018; Gani and Kazmi 2017; Gwenzi and Chaukura 2018; Liu et al. 2018; Madikizela et al. 2017; Starling et al. 2019a).

Responsible Editor: Vitor Pais Vilar

✉ Camila C. Amorim
camila@desa.ufmg.br

[1] Research Group on Environmental Applications of Advanced Oxidation Processes (GruPOA) Department of Sanitary and Environmental Engineering, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, Belo Horizonte, Minas Gerais 31270-901, Brazil

Springer

CHAPTER II[2] – EVALUATION OF THE USE OF A REFLEXIVE SURFACE IN AN OPEN SOLAR REACTOR FOR THE REMOVAL OF CECS IN SECONDARY EFFLUENT FROM MWWTP

---

[2] Two manuscripts were published with results of this chapter:

COSTA, Elizângela P. et al. *New trend on open solar photoreactors to treat micropollutants by photo-Fenton at circumneutral pH: Increasing optical pathway*. Chemical Engineering Journal, v. 385, n. December 2019, p. 123982, abr. 2020. DOI: https://doi.org/10.1016/j.scitotenv.2020.142624.

COSTA, Elizangela P. et al. *Aluminized surface to improve solar light absorption in open reactors: Application for micropollutants removal in effluents from municipal wastewater treatment plants*. Science of the Total Environment, v. 755, p. 142624, 2021. DOI: https://doi.org/10.1016/j.cej.2019.123982

II.1.INTRODUCTION

Different advanced technologies have been investigated to remove CECs from water and effluent of MWWTPs. Some of them are extensively discussed in a recent review, that focuses on aspects such as efficiency, advantages, drawbacks, technically, and economically feasibility. Advanced processes are divided into two groups for comparison, and the first one includes consolidated technologies as ozonation, activated carbon adsorption, and membrane filtration. The second group is called "new" technologies, which still lack development and application on a larger scale, mainly Advanced Oxidation Processes (AOP) as UV/H_2O_2, photo-Fenton, and UV/TiO_2 (RIZZO *et al.*, 2019).

The homogeneous photo-Fenton reaction is presented as a "new" technology with a short-term perspective, due to its high efficiency in removing CECs on complex matrixes (PRIETO-RODRÍGUEZ *et al.*, 2013) associated to its development in recent years. Modifications were made in the process to solve some of its limitations, such as the use of solar light as a renewable irradiation source, the use of reduced concentrations of reagents (Fe and H_2O_2), and different strategies to work at circumneutral pH, including alternatives to keep iron in solution at circumneutral pH. The criteria for achieving such goals have been recently defined, including the selection, mechanisms, and application of chelating agents (CLARIZIA *et al.*, 2017).

Among some of these mechanisms to perform photo-Fenton reactions at circumneutral pH there is the use of chelating or complexation agents. They undergo photoinduced reactions (Equation II.1 and Equation II.2), leading to photo-Fenton reactions (Equation I.4 and I.5) by ligand-to-metal charge transfer (LMCT) mechanism (CLARIZIA *et al.*, 2017).

$$[Fe^{3+}\,L]_{(aq)} \overset{hv}{\rightarrow} [Fe^{3+}\,L]^{*}{}_{(aq)} \qquad \text{(Eq. II.1)}$$

$$[Fe^{3+}\,L]^{*}{}_{(aq)} \rightarrow\; Fe^{2+}{}_{(aq)} +\; L^{\cdot}{}_{(aq)} \qquad \text{(Eq. II.2)}$$

These substances have the capacity to form water soluble complexes with iron species and avoid the formation of ferric hydroxides that would precipitate in circumneutral pH. In this way it is possible to apply a circumneutral Fenton reaction in wastewater treatment and avoid the acidification and neutralization processes. Besides, these complexes are able to absorb light more efficiently in near-UV and visible light. At acidic pH in conventional photo-Fenton

(Equation I.4 and I.5) the quantum yield for Fe^{2+} formation is 0.14 – 0.19 at wavelength of 313 nm and is lower for wavelength closer to visible range, with a value of 0.017 at 360 nm (FAUST; HOIGNÉ, 1990). With the use of oxalate, for example, Fe^{3+}-oxalate complexes can absorb UV-visible light up to 500 nm and achieve high quantum yield values of up to 1.0 -1.2 (CLARIZIA *et al.*, 2017; MALATO *et al.*, 2009).

Several substances have been proposed for this use as chelating, from natural agents (NOM, humic acids) and even organic matter degradation products (short carboxylic acids) to well-known ligands such as polycarboxylates (oxalate, citrate, ascorbic acid) and aminopolycarboxylates (NTA, EDTA, EDDS) (CLARIZIA *et al.*, 2017). The ethylenediamine-N,N′- disuccinic acid (EDDS) is an aminopolycarboxylate just as ethylenediaminetetraacetic acid (EDTA), one of the most known and applied chelating agents. Since EDDS is a structural isomer of EDTA and it is a strong chelating agent, with the additional advantages of biodegradability and non-toxicity, it has been proposed to replace EDTA. The isomer [S,S]- EDDS is the most used and has been proposed for wastewater treatment using photo-Fenton reactions at circumneutral pH successfully (KLAMERTH *et al.*, 2012, 2013).

Although Fe^3+-EDDS complexes can present lower quantum yield for its photolysis in comparison to Fe^{3+}-oxalate and Fe^{3+}-citrate complexes (CLARIZIA *et al.*, 2017), EDDS can efficiently complex Fe^{3+} in solution with lower Fe^{3+}:ligand ratio of 1:1 in comparison to those ligands (even up 1:10 for Fe^{3+}:oxalate) (CLARIZIA *et al.*, 2017; SORIANO-MOLINA; GARCÍA SÁNCHEZ; ALFANO; *et al.*, 2018; SORIANO-MOLINA; PLAZA-BOLAÑOS; *et al.*, 2019). A lower Fe^{3+}:ligand ratio is important once the addition of these chelating agents also represent an increase in the initial carbon concentration to be treated, and this addition of extra carbon source should be minimized as possible. Regarding costs, even though EDDS is still a high-cost reagent (3.5 € L^{-1}) that can represent 64 % of costs during MWWTP effluent solar modified photo-Fenton treatment (SÁNCHEZ PÉREZ *et al.*, 2020), the treatment at neutral pH is competitive in terms of disinfection and CEC removal with the reaction at acidic pH, and values are comparable to other advanced water technologies (0.56 W m^{-3}), as desalination (SÁNCHEZ PÉREZ *et al.*, 2020; SORIANO-MOLINA; MIRALLES-CUEVAS; *et al.*, 2019).

While the optimization of reagents parameters has been widely investigated, the use of solar reactors has allowed the use of a renewable source of irradiation to promote the catalytic iron renovation cycle in the photo-Fenton reaction. In this line, an open reactor non-concentrating configuration has been studied in recent years aiming the scale-up improvement and costs reduction of the reactor for photo-Fenton reactions, since the unfeasibility of treating huge volumes of wastewater by using the photoreactors traditionally employed in solar photocatalysis applications. Raceway Pond Reactors (RPR) have been studied and demonstrated to be very efficient in the removal of CECs and in disinfection (DE LA OBRA JIMÉNEZ, I. *et al.*, 2019; RIVAS IBÁÑEZ *et al.*, 2017). The RPR achieved higher treatment capacity (TC) in a few minutes of reaction in comparison to well-known solar photoreactors such as the CPC (Compound Parabolic Collector), a concentrating type of reactor. The CPC is a design more suitable for the treatment of bio-recalcitrant industrial wastewaters with high organic load, which requires long treatment time (MALATO *et al.*, 2009). Furthermore, the use of chelating agent EDDS has enabled effective removal of CECs at neutral pH in the RPR, with TC competitive on reaction at optimum acidic pH (SORIANO-MOLINA; GARCÍA SÁNCHEZ; MALATO; *et al.*, 2018).

The most important parameters that play an important role when optimizing the RPR are the liquid depth and iron concentration, which can be varied accordingly to the solar radiation availability (DA COSTA *et al.*, 2018; RIVAS *et al.*, 2015). These factors can be modified during different seasons (summer, winter), weather conditions (sunny or cloudy) and even geographic position (countries with more or fewer hours of solar radiation). In this way, the number of photons in the reactor can be adjusted to improve reaction kinetics and treatment capacity. A study on MPs removal by solar photo-Fenton modified with EDDS at neutral pH worked with the concept of volumetric rate of photon absorption (VRPA) and obtained that the VRPA is not directly related to treatment's capacity, but in fact to the reaction kinetics (degradation rate and treatment time). It was also pointed out by these authors that when working in the same photoabsorption (VRPA) condition, by increasing reactor's liquid depth from 5 cm to 15 cm, the treatment capacity was considerably improved, but keeping the same treatment time (SORIANO-MOLINA; GARCÍA SÁNCHEZ; MALATO; *et al.*, 2018).

Most applied concentrations of iron when working for the removal of MPs with solar photo-Fenton in circumneutral pH with complexing agents has been less than 5.5 mg L^{-1} (0.10 mM), proven as effective for the generation of effluent with good removal of MPs and obtaining low residual iron concentration, that allow the reuse for irrigation (CARRA *et al.*, 2014; DE LA OBRA *et al.*, 2017; KLAMERTH *et al.*, 2013; RIVAS *et al.*, 2015; SÁNCHEZ PÉREZ *et al.*, 2017). The use of very low iron concentration is less frequent and has been tested using artificial UVC irradiation sources (DE LA CRUZ *et al.*, 2012, 2013). High MPs removal has been achieved in circumneutral pH at very low iron concentration occurring in secondary effluents (1.5 mg L^{-1}, 0.03 mM). Regarding the liquid depth in RPR, up to 20 cm has been pointed out as a maximum value in general, taking into account a maximum Fe concentration of 5.5 mg L^{-1} (0.1 mM) under maximum solar irradiation (summer) (RIVAS *et al.*, 2015). However, in some cases, by increasing liquid depth not necessarily a higher treatment capacity would be obtained if there is not enough solar irradiation (DE LA OBRA *et al.*, 2017).

In this way, there are some possibilities to improve treatment in RPR. Treatment capacity can be amplified by increasing liquid depth at the cost of also increasing treatment time (SORIANO-MOLINA; GARCÍA SÁNCHEZ; MALATO; *et al.*, 2018). Another option would be to increase iron concentration, but this would increase reagent's costs. A higher iron concentration in the case of using Fe:EDDS complex would also cause an increase in dissolved organic content (DOC) of the effluent (PAPOUTSAKIS *et al.*, 2015). A new interesting option could be to work with modification in the reactor optical pathway without in fact changing the reactor liquid depth.

With this purpose, this work proposes to modify the reactor optical pathway using a reflexive surface on the bottom of the RPR. Thus, an aluminum surface was tested in order to reflect back the photons that were not absorbed under photo-saturation conditions. Aluminum has been previously demonstrated to be the best option to reflect solar UV-Vis light, the main source of photons for photo-Fenton processes (CASSANO *et al.*, 2002). For this, experiments of modified solar photo-Fenton with EDDS were performed using a mixture of six MPs (acetaminophen, caffeine, carbamazepine, diclofenac, sulfamethoxazole, and trimethoprim) spiked in natural water at both lab-scale and semi-pilot scale, with distinct lower iron concentrations and different liquid depths. Further on, experiments were performed in real secondary effluent from an MWWTP with conventional activated sludge process at lab-scale spiked with the mixture of those six MPs. Finally, experiments were performed at a semi-pilot scale with identification of compounds occurrence on the real effluent.

II.2. OBJECTIVES

II.2.1. General objective

The main objective of this chapter is to evaluate the effect of applying a reflexive surface in the reactor for circumneutral solar photo-Fenton reactions on the removal of selected CECs in natural water and real secondary effluent from MWWTP at bench-scale and semi-pilot scale.

II.2.2. Specific objectives

The specific objectives of this work are as follows:

- Select the best conditions for modified photo-Fenton reaction conditions with complexing agent EDDS at circumneutral pH in bench-scale with artificial solar irradiation for selected CECs removal in natural water;
- Evaluate the use of a reflexive surface in the reactor for modified photo-Fenton with complexing agent EDDS at circumneutral pH in both bench-scale solar artificial irradiation and natural solar semi-pilot scale Raceway Pond Reactor for selected CECs removal in natural water;
- Evaluate the use of a reflexive surface in the reactor for modified photo-Fenton with complexing agent EDDS at circumneutral pH in bench-scale solar artificial irradiation for selected CECs removal in real secondary effluent from MWWTP;
- Evaluate the use of a reflexive surface in the reactor for modified photo-Fenton with complexing agent EDDS at circumneutral pH in natural solar semi-pilot scale Raceway Pond Reactor for removal of CECs identified in real secondary effluent from MWWTP.

II.3. MATERIALS AND METHODS

II.3.1. Chemicals

All reagents used for liquid chromatography analysis were HPLC-grade and acquired from Sigma-Aldrich, including methanol, acetonitrile, formic acid, tetrabutylammonium bisulfate, and sodium formate. Six micropollutants as high purity solid powder standards were selected as model target compounds for this study: acetaminophen (Sigma-Aldrich), caffeine (Fluka), carbamazepine (Sigma-Aldrich), diclofenac (Sigma-Aldrich), sulfamethoxazole (Sigma-Aldrich), and trimethoprim (Sigma-Aldrich). This selection is further detailed in the section

II.3.2.2 Micropollutants monitoring. All reagents used during experiments and analysis were of analytical grade, including sulphuric acid (98 %; J.T. Baker), hydrogen peroxide (35 %; Sigma-Aldrich), ferric sulfate (75 %; J T. Baker), ethylenediamine disuccinic acid (EDDS, 35 %; Sigma-Aldrich), Ortho-phenanthroline (Merck), ammonium acetate (Sigma-Aldrich), acetic acid (J.T. Baker), ascorbic acid (Sigma-Aldrich) and titanium (IV) oxysulfate (Sigma-Aldrich).

II.3.2. Analytical methods

II.3.2.1.Sample preparation

All samples for chromatographic analysis were mixed with acetonitrile in a 90:10 sample:acetonitrile proportion to stop oxidative reactions and filtered through 0.22 µm PTFE Millipore® filter. Samples for identification of compounds in real wastewater were stored in pre-rinsed with H_2O MilliQ® 5 mL amber glass vials in the dark at 4 ºC until analysis execution, while samples with target model compounds were analyzed immediately after collection. For all other analyses, samples were filtered with 0.45 µm PVDF Millipore® filter.

For experiments with matrixes fortified at an initial concentration of MPs of 20 µg L^{-1} a solid phase extraction (SPE) was applied to pre-concentrate samples before UPLC-UV/DAD analysis (Figure II.3.1 to Figure II.3.6). A sample volume of 100 mL was extracted with an OASIS® HLB 6 cc, 200 mg cartridge (Part Number WAT106202) using a vacuum manifold (Supelco VISIPREPTM) and a pump (EZ-Stream^{TM} Pump, Millipore).

For cartridges conditioning step, 6 mL of methanol were applied, followed by 5 mL of ultrapure water MilliQ® at pH 7.5 - 8.0 adjusted with NaOH 0.1 M. Immediately in sequence samples were loaded at a flow of approximately 1 mL min^{-1}, and then cartridges were washed up with 4 mL of ultrapure water MilliQ® at pH 7.5 - 8.0 and dried under N_2 flux (30 minutes). Dry cartridges were eluted with 4 x 2 mL methanol. Eluted samples were evaporated until near dryness under N_2 flux at 35 °C (60 minutes) and finally reconstituted with H_2O MilliQ®: Acetonitrile 90:10 to a final volume of 5 mL or 10 mL (concentrating factor of 20 or 10) using a vortex for homogenization.

FIGURE II.3.1 – Sampling loading

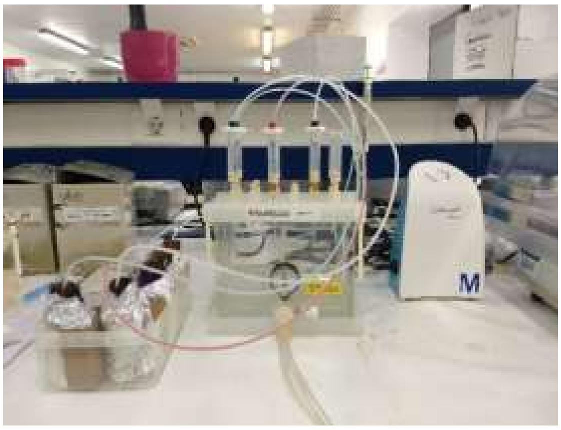


FIGURE II.3.2 – Cartridge drying step with nitrogen

FIGURE II.3.3 – Color change in the solid cartridge phase when dry

FIGURE II.3.4 – Sample elution with methanol

FIGURE II.3.5 – Evaporation under nitrogen flux

FIGURE II.3.6 – Reconstitution with H_2O MiliQ: Acetonitrile 90:10

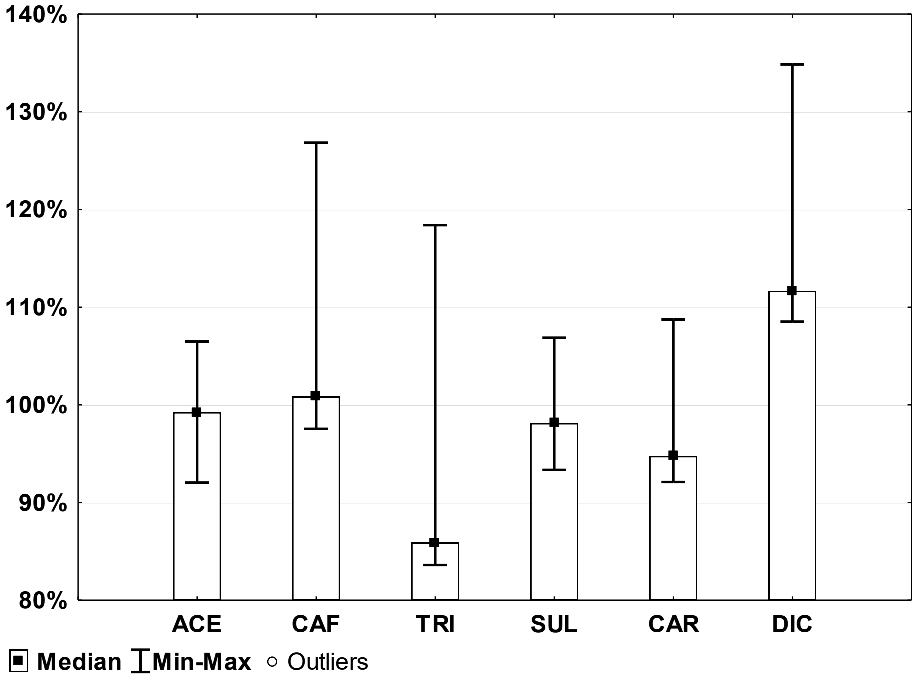
The recovery (R %) of target MPs in natural water matrix was evaluated by applying the SPE method to sample previously spiked with 20 μg L^{-1} of each micropollutant and comparing the recovered concentration (C_{SPE}) with the direct determination of the spiked sample concentration

(C_D) using the Equation II.3 Also, recoveries for lower concentration values (1, 3 and 10 µg L^{-1}) were tested.

$$R\ (\%) = {}^{C_{SPE}}/_{C_D} \times 100 \qquad \text{(Eq. II.3)}$$

Recovery for trimethoprim were the lowest (median of 86%) and highest for diclofenac (median of 112%) (Figure II.3.7).

FIGURE II.3.7 – Solid phase extraction recovery (%) for each micropollutant



II.3.2.2.Micropollutants monitoring

II.3.2.2.1.Target compounds

Quantification of target MPs was performed by ultra-performance liquid chromatography with an ultraviolet diode array detector (UPLC-UV/DAD) (Agilent Technologies, Infinity Series 1200).

In HPLC (high-performance liquid chromatography), the separation is based on the different intermolecular interactions between analytes, the stationary phase, and the liquid mobile phase. In reverse phase partition chromatography, the stationary phase is usually a silica packing with a liquid chemically bound to it, which results in a non-polar phase. Some usual alkyl groups (R) on the chain of reverse phase column packages are *n*-octyl (C_8) or *n*-octadecyl (C_{18}).

The mobile phase is predominantly polar, essentially water solutions with different organic solvents (methanol, acetonitrile, etc.) in a pH range from acidic to slightly basic (around 8.0) to avoid deterioration of the silica (SKOOG; HOLLER; CROUCH, 2009). The chromatography separation occurs with a variation on the polarity of the mobile phase, thus increasing or decreasing the affinity of the analytes with the stationary and the mobile phases. By changing the proportion and composition of the mobile phase (for example, using a gradient program) the retention time (t_r) of the analytes can be modified and the separation process optimized. The UPLC is an HPLC system with modifications on columns (smaller particle size and dimensions) and that endures higher pressure, which allows a higher sensitivity on the chromatographic separation, reduces both analysis time and reagents consumption, besides other advantages. A usual detector for UPLC is the UV/DAD detector, which consists of a PDA (photodiode array) that allows the simultaneous detection of a full ultraviolet-visible (UV-Vis) spectrum of the sample on the flow-cell of the equipment. This design of the detector allows a fast and reliable detection on multiple wavelengths.

All UPLC analyses were executed using a reverse-phase column Agilent Poroshell 120 EC-C18, 2.7 µm, 3.0 x 50 mm (Part Number 699975-302), with a flow of 1.0 mL min^{-1} and volume of injection of 50 µL. Solvent A was acetonitrile, and solvent B consisted of Milli-Q® water with 25 mM formic acid. A gradient flux was applied by varying solvents A and B accordingly to Table II.3.1. Total analysis time was 13 minutes, followed by 3 minutes of post-time for re-equilibrium of the column to initial conditions. The maximum and average pressure applied was 400 and 229 bar, respectively, while the maximum temperature was 30 °C.

TABLE II.3.1 – Gradient flux of solvents during HPLC analysis

Time (minutes)	Solvent A (%)	Solvent B (%)
0	0	100
10	50	50
12	100	0
13	100	0

Standards solutions of 10, 25, 50, 100 and 200 µg L^{-1} of the mix of the 6 MPs (acetaminophen, caffeine, trimethoprim, sulfamethoxazole, carbamazepine, and diclofenac) were prepared in 90 % Milli-Q® water with 10 % acetonitrile and filtered with 0.22 µm PTFE syringe filters.

Standard solutions for the calibration curve were prepared in Milli-Q® water from a standard intermediary solution of 1 mg L^{-1} also in Milli-Q® water. The intermediary solution was prepared from a stock solution of 2.5 g L^{-1} in methanol. All solutions were prepared in glassware previously rinsed with both Milli-Q® water and acetonitrile, including volumetric glass flasks and glass pipettes.

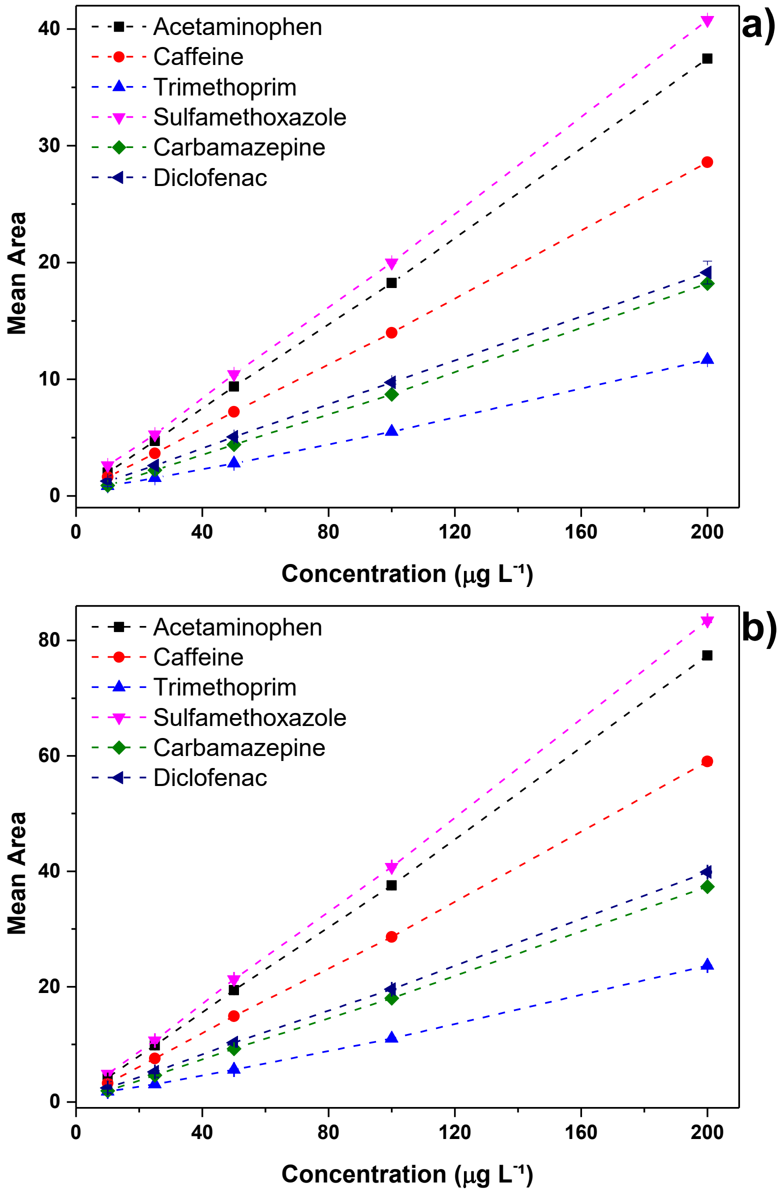
Each compound's retention time, maximum quantification wavelength, and calibration curve parameters (10 – 200 µg L^{-1}) are presented in Table II.3.2. Calibration curves for each compound were obtained using a linear equation, and the curve parameters (a, b and R^2) were determined. In APPENDIX IV is shown a chromatogram from an injection of a standard solution of 100 µg L^{-1} in Milli-Q® water (90 %) and acetonitrile (10 %).

TABLE II.3.2 – UPLC-UV/DAD wavelength of maximum absorbance, retention time, limits of detection and quantification, and calibration curve parameters for each investigated compound at 50 µL injection volume (n = 3)

Micropollutant	**λ_{max} (nm)**	**R_t (min)**	**a**	**b**	**R^2**
Acetaminophen	245	2.478	0.1864	-0.0032	0.9997
Caffeine	270	3.566	0.1419	0.0795	0.9997
Trimethoprim	270	3.938	0.0572	0.0614	0.9978
Sulfamethoxazole	267	5.013	0.2011	0.3341	0.9996
Carbamazepine	267	7.161	0.0910	-0.1251	0.9994
Diclofenac	285	10.619	0.0942	0.3093	1.0000

All calibration curves were also tested with an injection volume of 100 µL (Figure II.3.8).

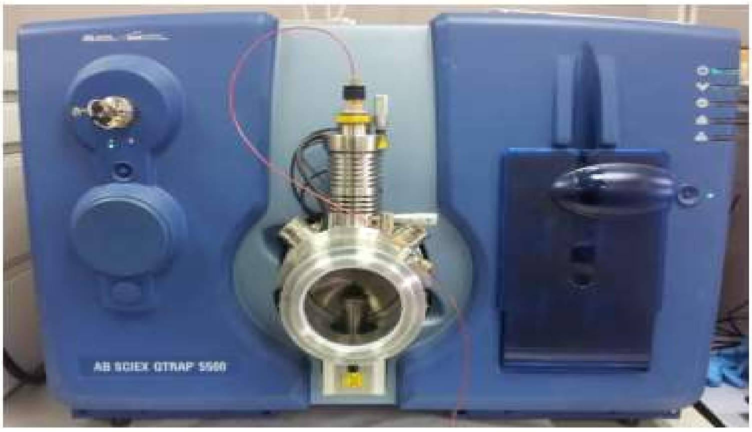
FIGURE II.3.8 – UPLC-UV/DAD calibration curves for each investigated compound, concentration (μg L^{-1}) versus peak area, for a) 50 μL volume of in injection and a) 100 μL volume of injection



II.3.2.2.2.Compounds in real effluent

Quantification of MPs on the real effluent after secondary wastewater treatment of the MWWTP of El Ejido was performed by liquid chromatography coupled to a quadrupole -linear ion trap mass spectrometer analyzer LC-QTRAP-MS/MS (Agilent Technologies, Infinity Series 1200/AB Sciex Instruments QTRAP 5500 - Figure II.3.9). All analyses were performed at the University of Almería, which is part of the Center for Solar Energy Research (CIESOL), a Joint Centre between the University of Almería - PSA/CIEMAT.

FIGURE II.3.9 – Mass spectrometer AB Sciex Instruments QTRAP 5500



The determination of compounds followed a methodology developed by Campos-Mañas *et al.* (2017), which consists of the direct injection of samples on a highly sensitive mass spectrometer, and is able to quantify MPs at ng L^{-1} levels of concentration. This method eliminates sample preparation steps, such as concentration on SPE, reducing analysis time and costs. All data were analyzed with the software Analyst 1.5.1 and MultiQuant 3.0.1 (Applied Biosystems, Concord, Ontario, Canada).

In general, a mass spectrometer have an inlet unit for the sample, an ion source to convert analytes into ions (these two units are usually combined into one), a mass analyzer that determines the ions accordingly to their mass/charge ratio (*m/z*) using electromagnetic fields and a detector that converts ions in electric signal that eventually is processed in a computer. A commonly used ion source is an ESI (electrospray injection), while other ionization methods can be chemical ionization, plasma, laser, thermospray, among others. Some mass analyzes configurations are the magnetic sector, quadrupole, TOF (time of flight), ion trap, and others. Two or more analyzers can be used in sequence, and this configuration is known as tandem mass spectrometry (MS/MS). In the QTRAP-MS/MS analyzer there are three quadrupoles in sequence where the first and the last (Q1 and Q3) are equal, but the second one (q) is in fact used as a collision cell which allows the generation of fragments known as products ions from the original (precursor) ions selected on the first quadrupole (Q1). Also, by using an associated SRM (selective reaction monitoring) method, different ions transitions can be selected and increase the sensitivity and selectivity of the mass spectrometer method.

This method evaluated a total of 150 compounds, considering two transitions for each one of them. Both positive and negative ionization modes were used, with an ion spray voltage of

±4500 V, source temperature 550 ºC; CAD gas, medium. High purity N_2 (purity >93 %) was used as a nebulizer gas, curtain gas, and collision gas (CAMPOS-MAÑAS *et al.*, 2017).

All analyses were executed with a reverse-phase column C18 Phenomenex Kinetex ® column, 2.6 µm, 4.6 x 150 mm (Part Number 00F-4462-E0), with a flow of 0.5 mL min^{-1} and volume of injection of 10 µL. Solvent A consisted of Milli-Q® water with 0.1% formic acid, and solvent B was methanol. A gradient flux was applied by varying solvents A and B accordingly to Table II.3.3. Total analysis time was around 22 minutes, including the post-time for re-equilibrium of the column to initial conditions. The maximum pressure applied was of 200 bar and a maximum temperature of 30 °C.

TABLE II.3.3 – Gradient flux of solvents during HPLC-MS/MS analysis

Time (minutes)	Solvent A (%)	Solvent B (%)
0	80	20
0.5	80	20
3	50	50
7	10	90
9.5	0	100
14	0	100
14.1	80	20
21	80	20

Standard solutions of 10, 50, 100, 500, 1000 and 2000 ng L^{-1} of the mix of all 150 MPs were prepared daily in 80 % diluted treated effluent with 10 % acetonitrile from a standard intermediary solution of 1 mg L^{-1} also in acetonitrile. The intermediary solution was prepared from another intermediary solution in acetonitrile of 10 mg L^{-1} that was prepared from a stock solution of 1000 mg L^{-1} in acetonitrile. A blank with non-spiked treated effluent and another with Milli-Q® water, both with 10% acetonitrile were also injected daily. Caffeine - C^{13} (1 µg L^{-1}) was added to each standard solutions, samples, and blanks previously to analysis as a surrogate for each injection.

All solutions were prepared in glassware previously rinsed with both Milli-Q® water and acetonitrile, including volumetric glass flasks and glass pipettes. All samples, standards, and blanks were filtered with 0.22 µm PTFE syringe filters.

II.3.2.3.Iron-EDDS complex monitoring

Fe^{3+}-EDDS complex was monitored by liquid chromatography (HPLC-UV/DAD, Agilent Technologies, Infinity Series 1100, column C18 5 µm, 3.0 x 150 mm). An isocratic gradient flow was applied during 8 min (retention time of 5.5 min) with 5% mobile phase A (methanol) and 95% of mobile phase B (15 mM of sodium formiate and 2 mM of tetrabutylamonium hydrogen sulfate in MilliQ® ultrapure water at pH 4 (SORIANO-MOLINA; GARCÍA SÁNCHEZ; ALFANO; *et al.*, 2018). Six distinct concentrations (0.05, 0.01, 0.02, 0.03, 0.04 and 0.1 mM) of Fe^{3+}:EDDS 1:1 were prepared in MilliQ® ultrapure (85 %) and acetonitrile (5 %). Standards were injected in triplicate, and a calibration curve was obtained (Equation II.4).

$$[Fe^{3+}: EDDS, mM] = 13.88 + (20712 \times Peak\ area) \quad R^2 = 0.9999 \qquad \text{(Eq.II.4)}$$

II.3.2.4.Ionic chromatography analyses

Cations and anions analyses were performed on HPLC/IC systems. For cations, a Metrohm 850 Professional IC with an isocratic flow was used, while a Metrohm 872 Extension Module 1 and 2 Professional IC with a gradient flow was applied for anions analyses. Both systems were equipped with a conductivity detector (Metrohm 850 Professional IC detector).

In ionic chromatography, the stationary phase of the column is a synthetic ion exchange resin on spherical particles, which have active basic (amines, quaternary or primary) or acidic (sulphonic or carboxylic acids) groups. The mobile phase consists of aqueous solutions with organic solvent and buffers (carbonate/hydrogen carbonate, tetraborate/boric acid) that contains ions that also compete with the analytes on the stationary phase. In this way, the chromatographic analysis must have a method for reducing the interference of the mobile phase ions on the analyte's detection. One of these methods consists of a conductivity detector provided with a membrane suppressor, which is based on ion exchange membranes that remove unwanted anions or cations with H_3O^+ or HO^- ions (SKOOG; HOLLER; CROUCH, 2009).

MWWTP samples were 1:10 diluted previously to injection with MilliQ® ultrapure water or whenever conductivity exceeds 1 mS cm^{-1}. All analyses were developed under a constant temperature of 45ºC, with an isocratic flow of 0.9 ml min^{-1} and total analysis time of around 47 minutes. Cations targeted in the research were sodium, ammonium, potassium, magnesium, and calcium, while anions were fluoride, chloride, nitrate, nitrite, bromide, phosphate and sulfate.

For cations analyses was used a Metrosep C4-250/4.0 column, 5 µm, 4.0 x 250 mm, and the mobile phase was a solution consisted of acetone (90 mL), nitric acid 2 N (850 µL) and 7.5 mL L^{-1} pyridine-2,6-dicarboxylic acid. As for anions analyses a Metrosep A Trap1-100/4.0 column, 570 µm, 4.0 x 100 mm was used, with the mobile phase consisted of a $NaCO_3$ 5 mM solution (0.53 g L^{-1}).

For quantification of the ions, signals were compared to calibration curves with concentrations between 0.1 – 20 mg L^{-1} for cations and between 0.1 – 5 mg L^{-1} for anions.

II.3.2.5.Dissolved Organic Carbon analyses

For Dissolved Organic Carbon (DOC) and Total Inorganic Carbon (TIC) measurement, a Shimadzu TOC-VCN analyzer was used.

The principle for quantification of total organic carbon (TOC) in aqueous samples is usually based on the difference of total carbon (TC) and TIC. The TC includes all carbon-based species present on the sample (organic and inorganic, including elemental carbon), while the TIC is the sum of elemental carbon, carbon oxides (CO_2, CO, HCO_3^-, CO_3^{2-}), cyanides, cyanates, and thiocyanates. The DOC is the TOC measure of a filtered sample, where all colloidal and suspend carbon have been removed.

The measurement of TC usually starts with a complete catalytic oxidation at high temperature (670 ºC), using purified air on a combustion tube (furnace) filled with catalyst (for example, platinum), where all the carbon on the sample is converted into CO_2, which is later quantified with a non-dispersive infra-red (NDIR) detector. As for TIC measurement, the sample is first acidified (with phosphoric acid, for example) and all IC is converted to CO_2, which is removed by a sparging process and measured with the NDIR detector. The difference between TC – TIC results in the TOC of the sample.

In some cases, where the TIC level is too high and close to TC values, this method might not be appropriate, thus leading to incorrect and sometimes negative values. In this case, other measurement methods should be used, such as the direct NPOC (non-purgeable organic carbon) method. It consists of firstly removing all carbonates (HCO_3^-, CO_3^{2-}) from the sample by acidification (with HCl) and gas sparging, with subsequently catalytic oxidation and NDIR detection as in the TC analysis. In this case, samples should not contain any volatile carbon species, and the NPOC is considered the TOC of the sample. In the unavailability of this method, whenever TIC values were too high, samples were previously acidified with two drops of concentrated sulfuric acid and left under agitation for 2 hours for CO_2 removal previously to TOC measurement.

A set of three calibration curves were prepared with potassium phthalate and sodium carbonate and hydrogen carbonate standards. For TC in three ranges: 1-10, 10-50, and 50-250 mg L^{-1}. For IC in the three following ranges: 5-20, 20-80, 80-200 mg L^{-1}.

II.3.2.6.Total and dissolved iron analyses

Total and dissolved iron concentration was measured spectrophotometrically at 510 nm accordingly to ISO 6332 (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 1988) with the 1,10-phenanthroline method. This method consists of measuring the absorbance of the orange-red complex formed between ferrous iron (Fe^{2+}) and 1,10-phenanthroline (molar absorbance of 11 x 10^3 L mol^{-1} cm^{-1}, $\lambda_{maximum}$ = 510 nm). The formation of this complex is fast and stable in pH values around 3.5 – 5.5, obtained with the addition of acetate buffer solution previously to the addition of the 1,10-phenanthroline solution.

For total iron measurement, ferric species (Fe^{3+}) are reduced to Fe^{2+} with the addition of ascorbic acid on the sample. This also reduces hydrogen peroxide interference. And, for dissolved total iron measurement, samples were pre-filtered with 0.45 µm PVDF membrane filters.

Some other interferences on this method are from heavy metals that might form complexes or precipitate with the phenanthroline. But it only happens at higher concentrations (10 times the iron concentration for cyanides, zinc, nitrite, phosphates, chromium, or above 2 mg L^{-1} for nickel and 5 mg L^{-1} for cobalt and copper), more typical on industrial effluents than on urban wastewaters.

The buffer solution was prepared with 62.5 g ammonium acetate, and 175 mL glacial acetic acid completed to 250 mL with deionized water, while the 1,10-phenanthroline solution was prepared by dissolving 100 mg 1,10-phenanthroline monohydrate ($C_{12}H_8N_2.H_2O$) in 100 mL water.

Always 4 mL of samples (diluted if necessary) were mixed with 1 mL of the 1,10-phenanthroline solution, 1 mL of the buffer solution and one tip of a micro spatula of ascorbic acid. After homogenization and 5 minutes stabilization, samples were measured in the spectrophotometer, and the concentration calculated from absorbance results against the calibration curve. A calibration curve from 0.2 up to 8 mg L^{-1} was prepared, which was linear on this interval (Equation II.5).

$$[Fe^{2+}, mg\ L^{-1}] = 0.0124 + (0.1304 \times Absorbance) \quad R^2 = 0.9997 \qquad \text{(Eq.II.5)}$$

II.3.2.7.Hydrogen peroxide analyses

Residual concentration of hydrogen peroxide during experiments was quantified using the titanium (IV) oxysulfate method accordingly to DIN 38402H15 (KLAMERTH *et al.*, 2012). This method consists of a fast and stable formation of a yellow complex between H_2O_2 and $TiOSO_4$ (Equation II.6 and Equation II.7).

$$TiOSO_4 + 5H_2O_{(l)} \rightarrow [Ti(OH)_3(H_2O)_3]^+_{(aq)} + HSO_4^-{}_{(aq)} \qquad \text{(Eq. II.6)}$$

$$[Ti(OH)_3(H_2O)_3]^+_{(aq)} + H_2O_2 \rightarrow [Ti(O_2)(OH)(H_2O)_3]^+_{(aq)} + 2H_2O_{\ (l)} \qquad \text{(Eq. II.7)}$$

Samples (5 mL) are mixed with the commercial reactive titanium (IV) oxysulfate solution (0.5 mL) and absorbance are measured on the wavelength of maximum absorption of 410 nm. The concentration is obtained against a calibration curve (Equation II.8, 0.1 – 60 mg L^{-1}).

$$[H_2O_2, mg\ L^{-1}] = 0.0081 + (0.0224 \times Absorbance) \quad R^2 = 0.9998 \qquad \text{(Eq. II.8)}$$

II.3.3. Experimental set-up

Experimentation was carried out at *Plataforma Solar de Almería* (Figure II.3.10) of the *Centro de Investigaciones Energéticas Medioambientales y Tecnológicas* (CIEMAT) from the Spanish Government. It is in Tabernas, Andalucía, Spain (37° N and 2.4° W). This exchange experience was part of a Ph.D. sandwich program (*Programa de Doutorado Sanduíche no Exterior da Capes* – PDSE/CAPES, n. 47/2017).

FIGURE II.3.10 – Plataforma Solar de Almería location in the Tabernas desert, Andalucía, Spain

II.3.3.1.Investigated matrixes

Experiments were performed with demineralized water, natural tap water, and real secondary effluent from MWWTP (EMWWTP). Table II.3.4 shows for all sets of experiments each water matrix was used.

TABLE II.3.4 – Water matrixes used for each set of experiments during research

Demineralized water	Natural water	Real secondary EMWWTP
Photolysis	Photo-Fenton at lab-scale spiked with different MPs initial concentration (20 and 100 µg L^{-1} each), different liquid depths (7, 10, 15 cm), iron concentration (1, 2, 3 and 5.5 mg L^{-1}), with and without an aluminum reflective surface	Photo-Fenton at lab-scale spiked with different MPs initial concentration (20 and 100 µg L^{-1} each), iron concentration (3 and 5.5 mg L^{-1}), with and without an aluminum reflective surface
Photolysis-H_2O_2	Photo-Fenton on RPR semi-pilot scale spiked with different MPs initial concentration (20 and 100 µg L^{-1} each), iron concentration (3 and 5.5 mg L^{-1}), with and without an aluminum reflective surface	Photo-Fenton on RPR semi-pilot scale with identification of MPs concentration by LC-MS in real effluent, iron concentration (3 and 5.5 mg L^{-1}), with and without an aluminum reflective surface

The natural water composition is presented in Table II.3.5, and to reduce total inorganic carbon (TIC) concentration a previously calculated amount of H_2SO_4 (2 N or concentrated, depending on the necessary volume) was added and left under agitation for 24 hours without covering for CO_2 dissipation. TIC was adjusted to around 15 mg L^{-1} previously in all experiments.

TABLE II.3.5 – Natural tap water average composition (n=4)

Parameter	Unity	Result
Conductivity[1]	mS cm^{-1}	2.6±0.1
pH[2]	-	7.4±0.1
Dissolved Organic Carbon[3]	mg C L^{-1}	2.5±1.4
Inorganic Carbon	mg C L^{-1}	212±30
Ca^{2+}	mg L^{-1}	86±10
Mg^{2+}	mg L^{-1}	62±6
K^{+}	mg L^{-1}	6±3
Na^{+}	mg L^{-1}	446±42
NO_2^{-}	mg L^{-1}	<LOQ[4]
SO_4^{2-}	mg L^{-1}	220±15
Cl^{-}	mg L^{-1}	324±8
Br^{-}	mg L^{-1}	<LOQ
F^{-}	mg L^{-1}	<LOQ
NO_3^{-}	mg L^{-1}	14±2
PO_4^{3-}	mg L^{-1}	<LOQ

[1]Conductive meter Crison GLP31. [2]pH/ORP D-72 meter $Lacqa_{act}$ (Horiba). [3]Analyses performed after sample acidification to reduce high inorganic carbon interference in the measure. [4]< LOQ = lower than the limit of quantification.

Real effluent (1 000 liters) after secondary wastewater treatment of the MWWTP of El Ejido, Spain was collected on March 26th 2019, around midday and a sample was characterized soon after (Table II.3.6). The El Ejido MWWTP has a conventional activated sludge system (pre-treatment for solids removal, primary treatment, activated sludge and final clarification with settling tank and sludge return for secondary treatment). This plant treats effluents from an equivalent population of 100 000 people and receives inputs from local greenhouses, plastic industry, and hospitals.

The effluent was pre-treated to remove suspended solids with a sand filter, followed by cartridges filters of 25 μm and 5 μm (Figure II.3.11), in this respective order. A sample of the effluent after this process was also characterized (Figure II.3.12 and Table II.3.6). Afterward, carbonates of the effluent were reduced to a TIC around 15 mg L^{-1} with the addition of sulfuric acid under agitation, as mentioned previously.

TABLE II.3.6 – Characterization of effluent from the secondary treatment of MWWTP El Ejido

Parameter	Secondary effluent	Filtered secondary effluent
pH	7.08	7.46
Temperature (ºC)	22.2	21.0
Condu. (mS cm^{-1}) at 25 ºC	2.18	2.27
TC (mg L^{-1})	97.6	109.0
IC (mg L^{-1})	84.7	97.0
TOC (mg L^{-1})	17.3	16.2
Turbidity (N.T.U.)[1]	342	11.9
Na^+ (mg L^{-1})	247	279
NH_4^+ (mg L^{-1})	16	16
K^+ (mg L^{-1})	22	28
Ca^{2+} (mg L^{-1})	103	98
Mg^{2+} (mg L^{-1})	64	66
Cl^- (mg L^{-1})	432	427
Br^- (mg L^{-1})	6	3
NO_2^- (mg L^{-1})	3	5
NO_3^- (mg L^{-1})	17	16
SO_4^{2-} (mg L^{-1})	130	140

[1] Turbidimeter Hach 2100N.

FIGURE II.3.11 – Effluent filtering unit: sand filter and cartridges microfilters (25 and 5 µm)

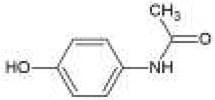
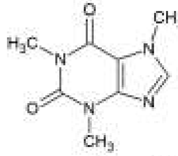
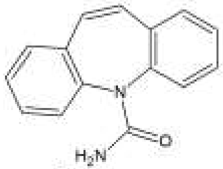
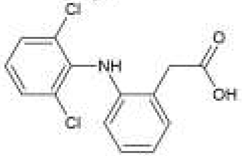
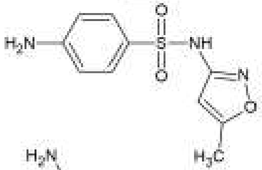
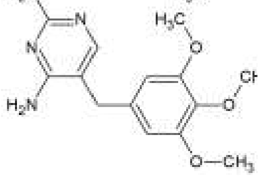
FIGURE II.3.12 – Secondary effluent from MWWTP El Ejido aspect before and after filtration

II.3.3.2.Target micropollutants (MPs)

Six pharmaceuticals were selected as target compounds for this work: acetaminophen (ACE), caffeine (CAF), carbamazepine (CAR), diclofenac (DIC), sulfamethoxazole (SUL), and trimethoprim (TRI) (Table II.3.7). These MPs are usually found in real wastewaters effluents from MWWTP around the world (BALAKRISHNA *et al.*, 2017; MADIKIZELA; TAVENGWA; CHIMUKA, 2017; MEADOR *et al.*, 2016; TRAN; REINHARD; GIN, 2018). These substances have also been detected in surface water in different States in Brazil (STARLING; AMORIM; LEÃO, 2019), and possess environmental and human health risk or unknown effects.

These compounds are not usually regulated in monitoring policies around the world, but there are some exceptions. The Watch List of Priority Substances (PSs) for European Union monitoring of surface water was launched in the Decision 2015/495, and originally included diclofenac, but it was removed with the upgraded Decision 2018/840/EU. Regarding municipal wastewaters, only Switzerland has established a removal efficiency of 80 % for 12 selected indicator substances on MWWTP, including carbamazepine and diclofenac, besides amisulpride, benzotriazole, candesartan, citalopram, clarithromycin, hydrochlorothiazide, irbesartan, methylbenzotriazole, metoprolol and venlafaxine (BOURGIN *et al.*, 2018). In the State of São Paulo, Brazil, caffeine is being monitored in around 7 stations (less than 70 % of total monitored stations) for surface water quality, even though there is no recommendation nor legislation at the national level for this kind of action.

TABLE II.3.7 – Main properties of model micropollutants

Micropollutant	Category	CAS Number #	Molecular formula	Molecular weight, g mol^{-1}	Water solubility[1] (mg L^{-1})	Log P	pKa	Structure
Acetaminophen (ACE)	analgesic	103-90-2	$C_8H_9NO_2$	151.17	14,000	0.46	9.38	
Caffeine (CAF)	central-nervous-system stimulant, analgesic adjuvant	58-08-2	$C_8H_{10}N_4O_2$	194.19	21,600	-0.07	14.0	
Carbamazepine (CAR)	anticonvulsant	298-46-4	$C_{15}H_{12}N_2O$	236.27	18	2.45	13.9	
Diclofenac (DIC)	anti-inflammatory	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.15	2.37	4.51	4.15	
Sulfamethoxazole (SUL)	antibiotic	723-46-6	$C_{10}H_{11}N_3O_3S$	253.28	610	0.89	1.6; 5.7	
Trimethoprim (TRI)	antibiotic	738-70-5	$C_{14}H_{18}N_4O_3$	290.32	400	0.91	7.12	

Source: National Center for Biotechnology Information. PubChem Database. https://pubchem.ncbi.nlm.nih.gov [1] at 25 °C (with exception sulfamethoxazole, at 37 °C).

These substances have been reported in a recent ecotoxicological risk assessment at territorial scale with 10 MWWTP in France (GOSSET *et al.*, 2021). While diclofenac showed low risk analyzed individually, its contribution for the risk considering the mixture of effluent from MWWTP was high. Nonetheless, all investigated contaminants contributed to the total risk, including carbamazepine and the antibiotics sulfamethoxazole and trimethoprim. It is important to highlight the difference in results in different campaigns at a same site, once the dilution factor can influence these assessments as shown for sulfamethoxazole, which showed risk quotient (RQ) of 31.17, 0.94 and 8.35 over three campaigns (GOSSET *et al.*, 2021).

Another environmental risk assessment study showed the potential risk of diclofenac and trimethoprim, both with values of RQ above 1 among other pharmaceuticals (PAPAGEORGIOU; KOSMA; LAMBROPOULOU, 2016). A study with predicted environmental concentrations of acetaminophen, carbamazepine, sulfamethoxazole, and trimethoprim as well as the acute aquatic toxicity with different bioindicators showed in special over 1 values of hazard quotients for sulfamethoxazole and acetaminophen (6.3 and 1.8, respectively) suggesting their potential for environmental risk (KIM, Y. *et al.*, 2007).

Carbamazepine and diclofenac have known impact in the ecosystem, including to species as rainbow trout (*Oncorhynchus mykiss*) and zebrafish, respectively, as well as much to be evaluated regarding their chronic impact and synergistic interactions with other substances in environmental matrixes (CAPODAGLIO; BOJANOWSKA-CZAJKA; TROJANOWICZ, 2018). Caffeine, a substance present in several products besides pharmaceuticals including food and beverages, has shown to induce effects on different aquatic organisms *Corbicula fluminea*, *Ruditapes philippinarum*, *Diopatra neapolitana* and *Arenicola marine* (AGUIRRE-MARTÍNEZ; DELVALLS; LAURA MARTÍN-DÍAZ, 2015; CRUZ *et al.*, 2016; PIRES *et al.*, 2016). Acetaminophen showed to trigger the onset of deleterious effects in edible clams *Venerupis decussata* and *Venerupis philippinarum*, as well as chromic effects on rainbow trout (*Oncorhynchus mykiss*) (ANTUNES *et al.*, 2013; CHOI; ALSOP; WILSON, 2018). Sulfamethoxazole and trimethoprim are usually combined as antibiotic prescription drug, and results suggest that sulfamethoxazole may cause genetic toxicity in fish tissues (YANG; SONG; LIM, 2020). While trimethoprim might not have shown considerable biological effect on four evaluated freshwater organisms (*Pseudokirchneriella subcapitata*, *Lemna minor, Daphnia magna* and *Poecilia reticulata*), authors highlight how the co-occurrence and additive effects with other agents should be investigated and considered in environmental risk assessments (DE LIGUORO *et al.*, 2012).

For all experiments with the target compounds, always a mixture of the six MPs was used with the same concentration of each one, 100 µg L^{-1} or 20 µg L^{-1}, totalizing 600 µg L^{-1} or 120 µg L^{-1} of MPs, respectively. The lower value (120 µg L^{-1}) was also investigated since it is closer to the reality of MPs concentrations found in real EMWWTPs. This value usually varies accordingly to location, due to factors such as regional consumption pattern and raw influent concentrations, but also due to sampling and analytical methods applied in the study (TRAN; REINHARD; GIN, 2018). Nevertheless, different studies around the world have identified values usually around this order of magnitude of a few µg L^{-1} up until more than one hundred µg L^{-1} (BOURGIN *et al.*, 2018; GUERRA *et al.*, 2014; MEADOR *et al.*, 2016; PAPAGEORGIOU; KOSMA; LAMBROPOULOU, 2016; YAN *et al.*, 2014).

A stock solution in methanol with 2.5 g L^{-1} of each micropollutant was prepared by dissolving the compounds and left under constant agitation overnight, protected from light, for complete homogenization. After preparation, the stock solution was stored at low temperature (4 ºC) and in darkness. For experiments in lab-scale, an intermediary solution in demineralized water was prepared at a concentration of 1 or 2 mg L^{-1} to make possible the addition of the MPs for the experiments. At a semi-pilot scale, the direct addition from the stock solution in methanol was possible.

Samples from experiments at 100 µg L^{-1} of each micropollutant were analyzed by direct injection with UPLC-UV/DAD, while experiments with 20 µg L^{-1} of each micropollutant were analyzed by combining solid phase extraction (SPE) and UPLC-UV/DAD.

II.3.3.3.Lab-scale experiments with artificial sunlight

For experiments in lab-scale two identical cylindrical PVC vessels (0.19 m of diameter and 0.19 m of height) with opaque walls were used, one of which had a reflexive aluminum surface placed inside, on the bottom (Figure II.3.13). In order to work with different liquid depth levels of 7 cm, 10 cm, and 15 cm, the volume in the reactor was respectively adjusted to 1.6 L, 2.4 L, and 3.9 L.

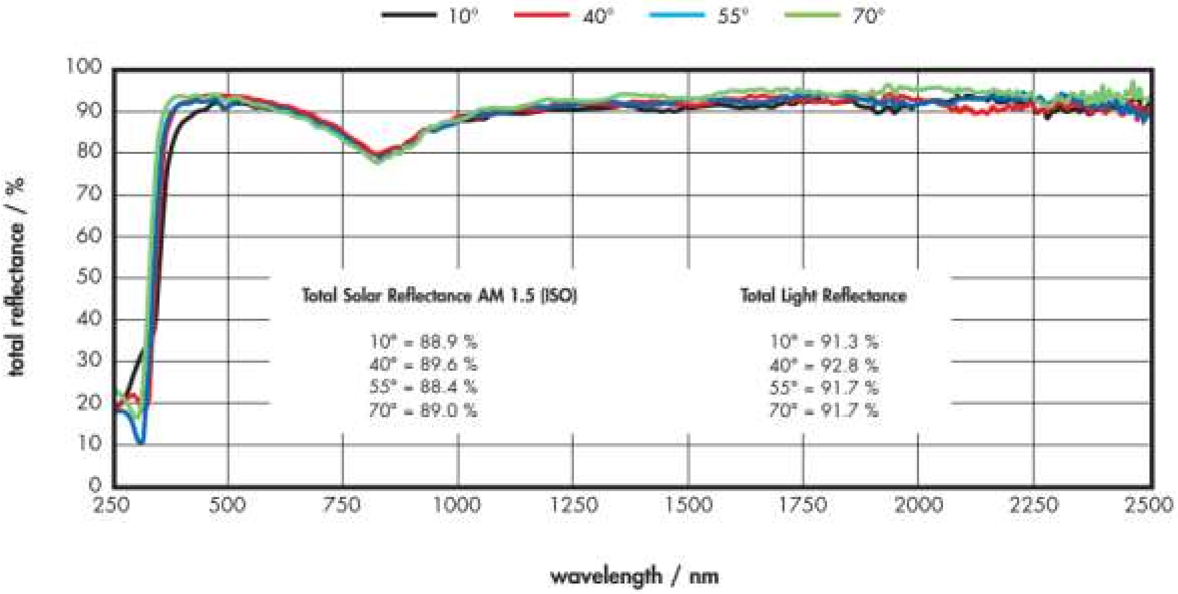
A solar simulator from Atlas - SunTest XLS+ - was used for lab-scale experiments. This equipment had a daylight filter, and it was programmed for a spectrum emission in the range of 300-800 nm, with total radiation of 365 W m^{-2} and total UVA (300 – 400 nm) radiation of 30 W m^{-2}. The cylindrical vessel was placed just inside the solar simulator receiving irradiation from the top directly on the water surface (A_s = 283.4 cm^2) (Figure II.3.14). The reaction medium was continuously mixed with a magnetic stirrer at 350 RPM, and the system operated in batch mode.

FIGURE II.3.13 – Lab-scale reaction vessels used for experiments, with and without a reflective surface

FIGURE II.3.14 – Solar simulator (Sun-Test XLS+, Atlas) equipment used in lab-scale experiments

The aluminum surface used in all experiments was a Miro-Sun® surface, which has a solar reflection coefficient (λ ≥ 300 nm) above 89 % and a total light reflection above 93 % (Figure II.3.15).

FIGURE II.3.15 – Diagram of total solar light AM 1.5 (ISO) reflectance for the reflexive aluminum surface (Miro-Sun®)



Reflectance's accordingly to standards DIN 5036-1 (Radiometric and photometric properties of materials; definitions characteristics) and 5036-3 (Radiometric and photometric properties of materials; methods of measurement for photometric and spectral radiometric characteristics), and solar spectrum standard AM 1.5.

II.3.3.4.Semi-pilot scale experiments with natural sunlight

As for experiments outdoors in semi-pilot scale a PVC-made RPR, with 90 L of capacity at 15 cm of liquid depth, with 0.45 m of width and 0.97 m of length was used (Figure II.3.16).

TABLE II.3.8 – Raceway pond reactor dimensions

<table>
<tr><td>Width: 45 cm</td><td>Length: 97 cm</td><td>Half circles radius:
22.5 cm</td><td>Water depth:
15 cm</td></tr>
<tr><td colspan="4">Total reactor surface area: (width ×length) + (π ×radius^2) = 0.5955 m^2</td></tr>
<tr><td colspan="2">Shadow area at midday: 0.19 m^2</td><td colspan="2">Volume of shadow area: 0.15 m x 0.19 m^2
= 28.5 L</td></tr>
<tr><td colspan="4">Total irradiated volume: 90 L – 28.5 L = 61.50 L</td></tr>
</table>

FIGURE II.3.16 – Raceway pond reactors, with and without the aluminum surface on the bottom.

The RPR reactor had a short mixing time, lower than 2 minutes, and was operated in batch mode. The mixing time was determined experimentally with a saline pulse test by monitoring the concentration of ions Na^+ and Cl^- by HPLC/IC every 2 minutes, for a total time of 30 minutes for the reactor filled with 72 L of demineralized water (12 cm of water depth). A volume of around 50 mL of NaCl 36.6 g L^{-1} was added before the mixing mechanism of the RPR (Figure II.3.17) so that the expected concentrations in the reactor of Na^+ and Cl^- would be approximately 10 and 15 mg L^{-1}, respectively. In less than 2 minutes, both ions' concentrations were stabilized, indicating a homogeneous distribution of reagents within this time (Table II.3.9).

FIGURE II.3.17 – Raceway pond reactor mixing time determination with saline pulse test

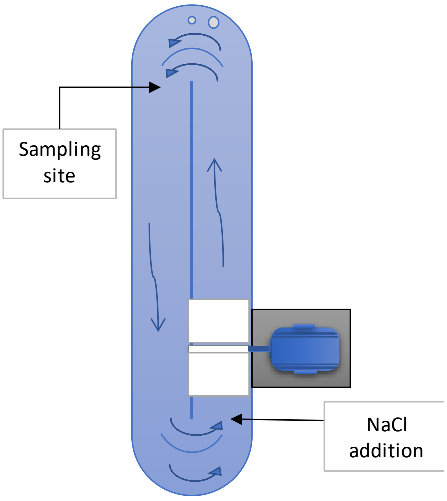


TABLE II.3.9 – Raceway pond reactor saline pulse test determination of mixing time

Time (min)	Cl^- (mg L^{-1})	Na^+ (mg L^{-1})
2	15.59	9.30
4	15.65	9.30
6	15.55	9.33
8	15.65	9.34
10	15.65	9.38

The incident UV radiation was monitored with a horizontally positioned global UV radiometer (CUV3 Kipp & Zonen, a 290 – 400 nm range, 264 mV W^{-1} m^{-2} sensibility) positioned. Radiation data was constantly sent to a server, where it could be accessed for further use.

For the accumulated energy per volume unity (Q_{UV}, kJ L^{-1}) calculation (Equation II.9), reactor's volume (V_r, L) and irradiated area (A_r, m^2) were considered, as well the average incident irradiation ($\overline{UV}_{G,n}$, W m^{-2}) and the energy accumulated up to the start of the current reaction time period ($Q_{UV,n}$, J L^{-1}), with the appropriate unit conversion for kJ L^{-1} in the end.

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t \, . \overline{UV}_{G,n} \, . \frac{A_r}{V_r}; \; \Delta t = t_n - t_{n-1} \qquad \text{(Eq. II.9)}$$

Another option is to report result as a function of the normalized illumination time (t_{30W}) (Equation II.10). This corresponds to the reaction time normalized with a constant UV solar irradiance of 30 W m^{-2} (typical for a sunny day around noon with clear sky) (MALATO *et al.*, 2009). Both illuminated volume (V_i) and total reactor volume (V_T) are taken in account, as well as the average incident irradiation ($\overline{UV}_n$ W m^{-2}) during the sampling time (Δt).

$$t_{30W,n} = t_{30W,n-1} + \Delta t \, . \frac{\overline{UV}_n}{30} \, . \frac{V_i}{V_T}; \; \Delta t = t_n - t_{n-1} \qquad \text{(Eq. II.10)}$$

However, the use of Q_{UV} was chosen as preference in this work because all geometry of the reactor is considered in this unity (A_r and V_r) in comparison to the t_{30W}.

The treatment capacity (TC) of experiments was calculated (Equation II.11) considering the sum of MPs initial concentration (C_0, mg L^{-1}), the volume of liquid (V, L), the irradiated surface of the reactor (S_r, m^2) and treatment time for attaining 80 % ($t_{80\,\%}$, min) considering as a reference the Swiss legislation for MWWTP effluent advanced treatment (BOURGIN *et al.*, 2018). Also, TC was obtained in mg kJ^{-1} considering the average incident irradiation ($\overline{UV}$ W m^{-2}) (Equation II.12).

$$\mathrm{TC(mg\,m^{-2}min^{-1})} = \frac{0.8 \times C_0 \times V}{S_r \times t_{80\,\%}} \qquad \text{(Eq. II.11)}$$

$$\mathrm{TC(mg\,kJ^{-1})} = \frac{\mathrm{TC(mg\,m^{-2}\,min^{-1})} \times 1000}{\overline{UV} \times 60} \qquad \text{(Eq. II.12)}$$

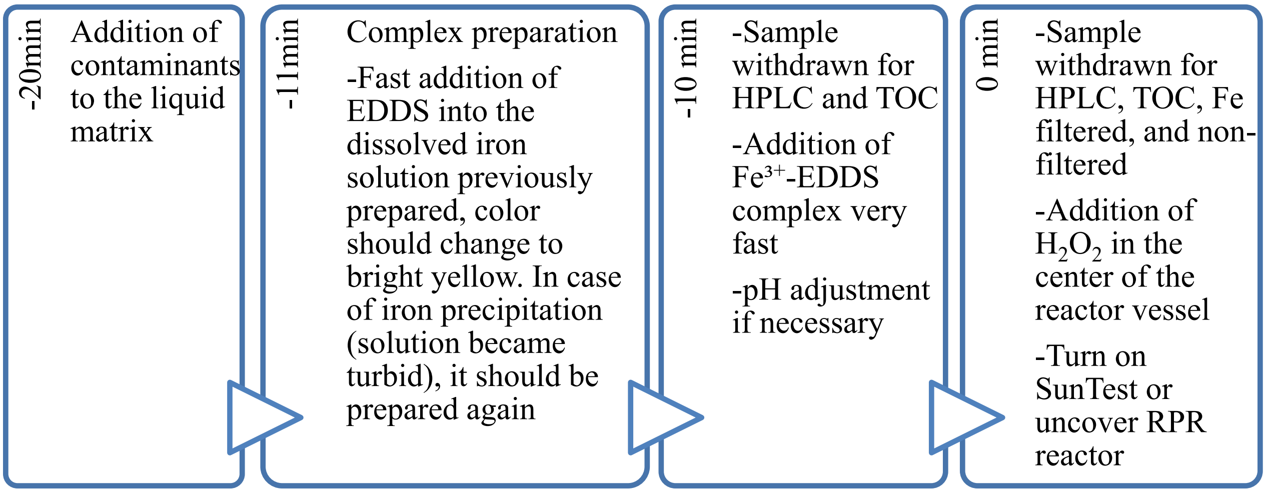
II.3.3.5.Experiments routine

All reactions were performed at natural pH (6.5 – 8.5). For all experiments, the hydrogen peroxide concentration was 50 mg L^{-1} (1.47 mM), which is enough to complete the degradation of all the micropollutants. Fe^{3+}-EDDS complex ratio 1:2 for all experiments, an optimum proportion for MPs degradation in secondary EMWWTP (KLAMERTH *et al.*, 2012, 2013).

The complex was prepared in the laboratory and used immediately after preparation. $Fe_2(SO_4)_3.xH_2O$ was previously dissolved in 50 mL of demineralized water at pH 3, followed by a quick addition of EDDS under agitation (Figure II.3.18).

Experiments were performed considering a combination of the variables: iron concentration (1, 2, 3 and 5.5 mg L^{-1}, respectively in molar concentration, 0.018 mM, 0.036 mM, 0.054 mM and 0.1 mM), liquid depth (7 cm, 10 cm, and 15 cm), each micropollutant initial concentration (100 μg L^{-1} and 20 μg L^{-1}), water matrixes (natural or real effluent), with or without an aluminum reflexive surface. The maximum experimental time was 120 minutes. The number of samples, and therefore volume withdrawn, varied accordingly to this time, but not exceeding 10 % of the total volume in reaction. In general, 8 to 12 samples were analyzed per experiment, with 5 minutes interval during first 30 minutes of reaction, followed by 15 or 30 minutes interval up until the end.

FIGURE II.3.18 – Experiment's protocol with Fe^{3+}-EDDS complex



-20min

Addition of contaminants to the liquid matrix

-11min

Complex preparation

-Fast addition of EDDS into the dissolved iron solution previously prepared, color should change to bright yellow. In case of iron precipitation (solution became turbid), it should be prepared again

-10 min

-Sample withdrawn for HPLC and TOC

-Addition of Fe^{3+}-EDDS complex very fast

-pH adjustment if necessary

0 min

-Sample withdrawn for HPLC, TOC, Fe filtered, and non-filtered

-Addition of H_2O_2 in the center of the reactor vessel

-Turn on SunTest or uncover RPR reactor

Control experiments were performed only in lab-scale for 100 μg L^{-1} MPs concentration in demineralized water (pH 5.7±0.2) without the reflexive aluminum surface. Photolysis (7 cm and 15 cm) and photolysis-H_2O_2 were tested at different liquid depths (7 cm, 10 cm, and 15 cm), while dark Fenton reaction was performed with Fe 0.054 mM and at 10 cm liquid depth.

At first, experiments at lab-scale were tested with all investigated iron concentrations in all three liquid depths, for 100 μg L^{-1} MPs in natural water without the reflexive aluminum surface (Figure II.3.19). For some selected iron concentrations were executed experiments using the reflexive aluminum surface. In sequence, experiments with relevant results were performed with a lower MPs concentration (20 μg L^{-1}), with and without the aluminum surface. Then, the best results were tested at semi pilot-scale in the RPR, with and without the reflexive aluminum surface with both concentrations of MPs.

Later, the best conditions obtained previously were tested at lab-scale in the solar simulator with both MPs concentration (100 μg L^{-1} and 20 μg L^{-1}) spiked to the real secondary EMWWTP (Figure II.3.20). Finally, at semi pilot-scale (RPR), the degradation of compounds identified on the real effluent was evaluated during the treatment.

FIGURE II.3.19 – Flowchart of experiments executed with natural water

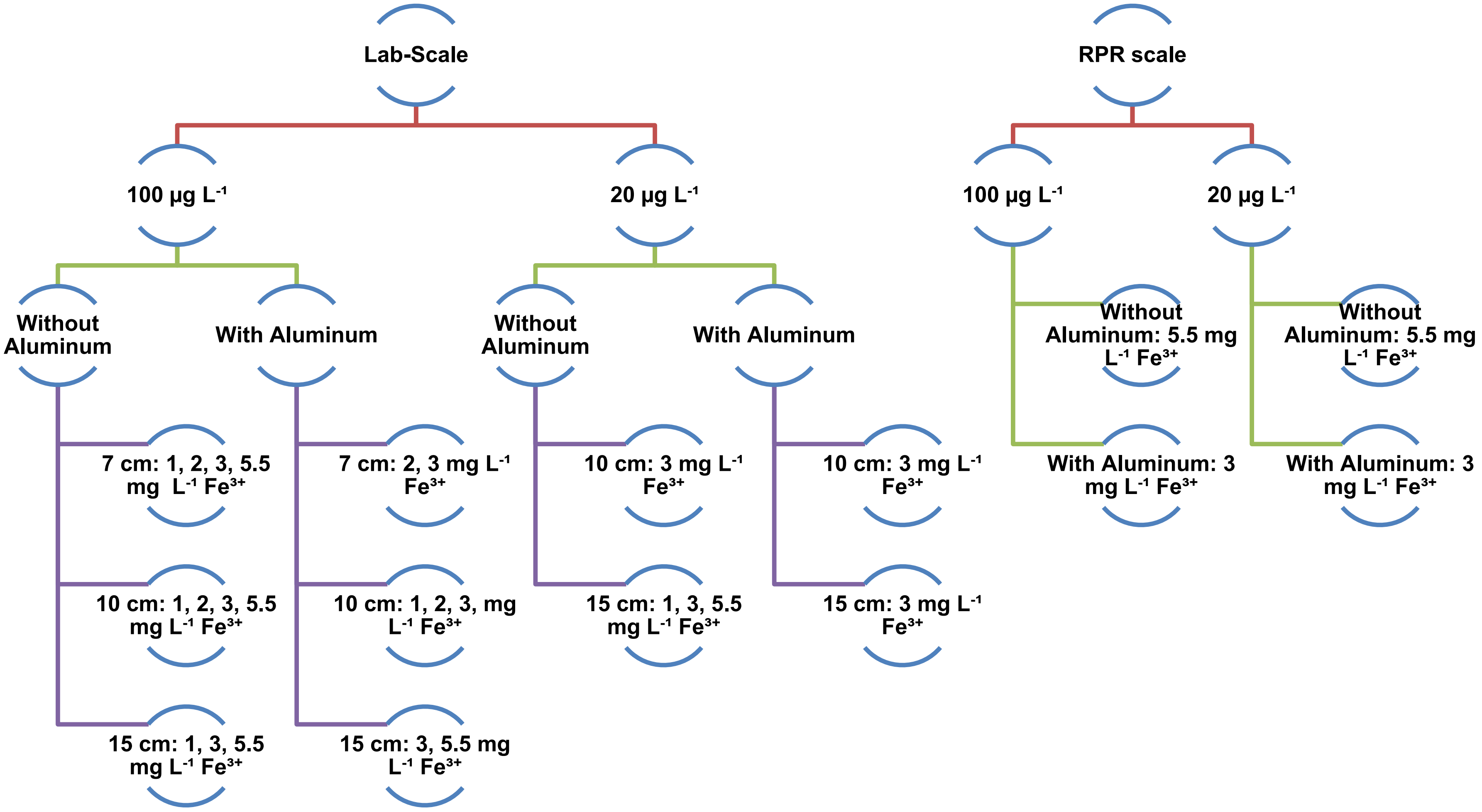
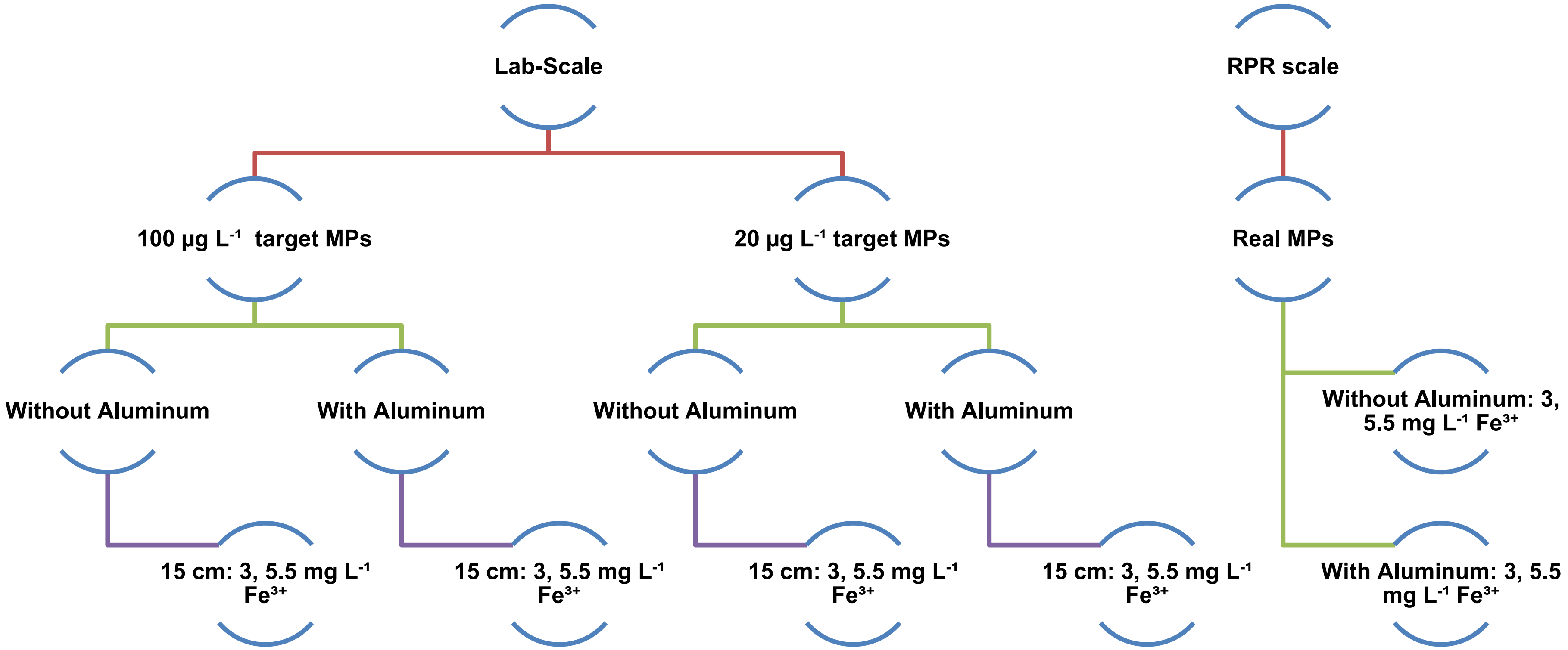


FIGURE II.3.20 – Flowchart of experiments executed in real secondary effluent with target contaminants or identified MPs



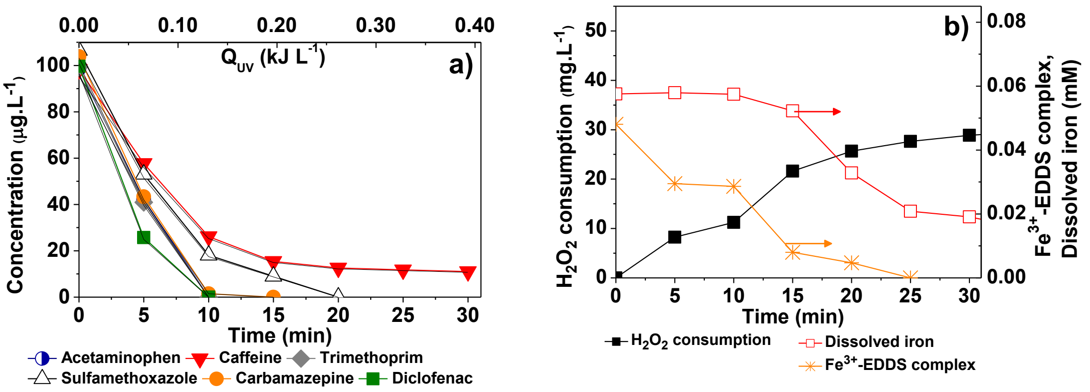
II.4.RESULTS AND DISCUSSION

II.4.1.1.Lab-scale results with natural water

At first, experiments were performed with two iron initial concentrations (0.1 mM and 0.054 mM) at lab-scale in the solar simulator, at different liquid depths and without the aluminum reflexive surface. The 0.1mM concentration has been proven to be effective in the removal of MPs (PAPOUTSAKIS *et al.*, 2015; SORIANO-MOLINA; PLAZA-BOLAÑOS; *et al.*, 2019). A lower concentration iron (0.054 mM) was tested for comparison.

For all experiments, degradation of MPs occurs mostly during the first minutes with a fast consumption of H_2O_2 and while enough Fe^{3+}-EDDS complex was available (Figure II.4.1) to keep iron in the dissolved form on the solution. Iron concentration remained stable during the first 10 minutes due to the excess of EDDS (ratio 1:2), maintaining the iron complexed while Fe^{3+}-EDDS was degraded (Equation II.12). Thus, dissolved iron decrease could be measured at the same time Fe^{3+}-EDDS concentration started to decrease, too (Figure II.4.1b). As discussed in detail by other authors (SORIANO-MOLINA; GARCÍA SÁNCHEZ; ALFANO; *et al.*, 2018), this phenomenon begins with the Fe^{3+}-EDDS complex decomposition into EDDS radical species and ferrous iron (Equation II.13), which is later oxidized in the Fenton reaction (Equation II.14) forming ferric iron, that could be complexed again if EDDS is still available, or ferric hydroxide, which would immediately precipitate.

FIGURE II.4.1 – a) Degradation of six MPs (100 µg L^{-1} each) by solar photo-Fenton with 0.054 mM of iron and 15 cm liquid depth; b) hydrogen peroxide consumption, Fe^{3+}-EDDS complex, and dissolved iron concentration evolution.



$$[Fe^{3+}\text{-EDDS}]^{-}_{(aq)} \xrightarrow{h\upsilon} Fe^{2+}_{(aq)} + EDDS^{\cdot 3-}_{(aq)} \qquad \text{(Eq.II.13)}$$

$$Fe^{2+}_{(aq)} + H_2O_{2(aq)} \rightarrow Fe^{3+}_{(aq)} + HO^{\cdot}_{(aq)} + OH^{-}_{(aq)} \qquad \text{(Eq. II.14)}$$

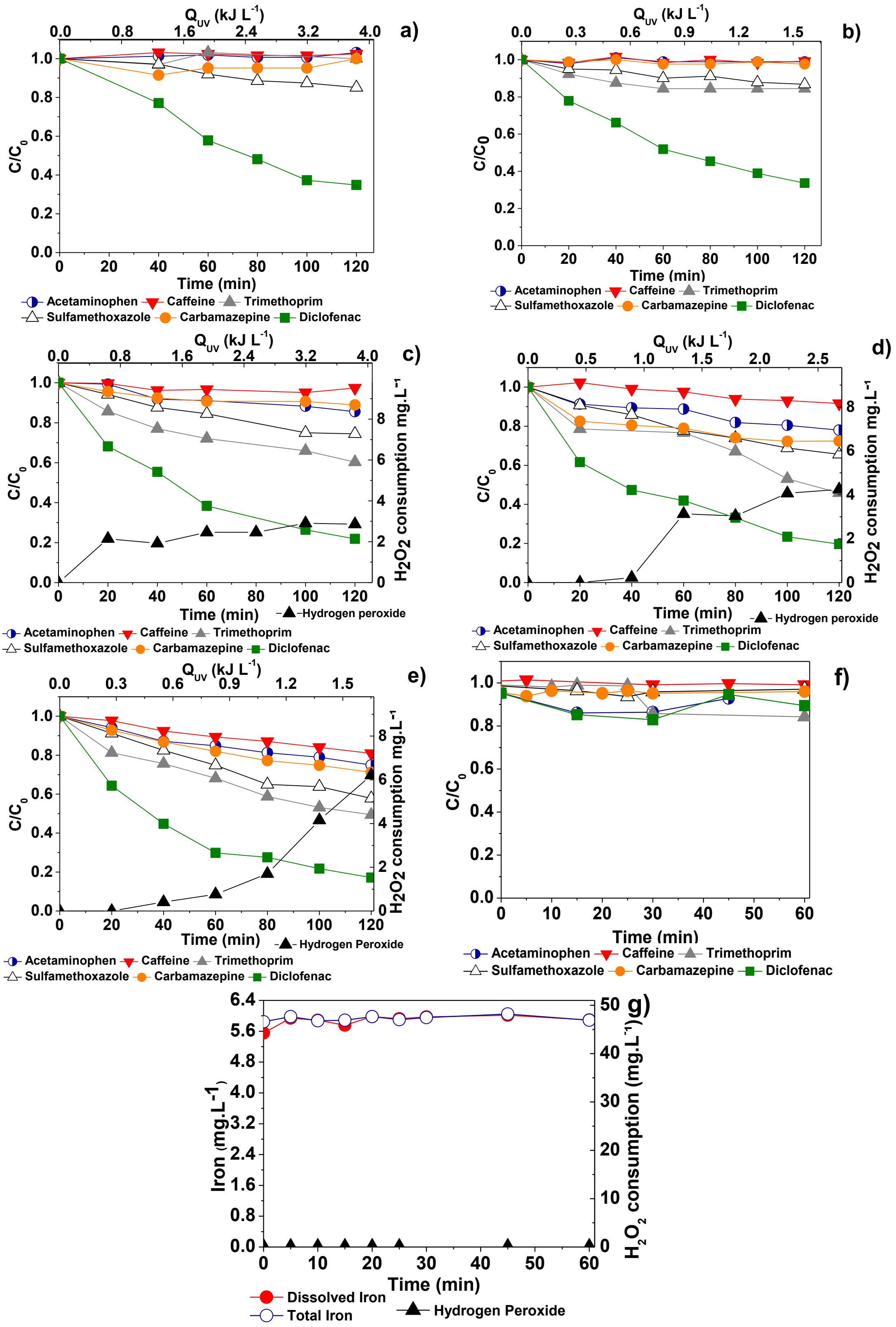
Cuervo Lumbaque *et al.* (2019) have demonstrated with cyclic voltammetry the formation of the Fe^{3+}-EDDS complex at pH 3 with Fe^{3+}:EDDS ratio above 1:1, and they confirmed a higher stabilization of the complex for ratios above 1:2. The stabilization of the complex was not affect in different pH values (3.0 – 9.0). The complex was not altered within 10 minutes during solar exposition at pH 7.0 using Fe^{3+}:EDDS ratio 1:2 and 0.5 mM-Fe, with maximum exposure time indicated as 120 min. During solar photo-Fenton reactions (0.28 mM-Fe and 5.0 mM of H_2O_2) an initial faster degradation of pharmaceuticals occurred simultaneously to a faster decomposition of the complex and a faster H_2O_2 consumption, followed by a slower reaction afterwards (t_{30W} of 15.8 min) (CUERVO LUMBAQUE *et al.*, 2019). This pattern is in accordance to results shown in this work (Figure II.4.1) but using lower reactant concentrations that might have resulted in a slower reaction, and final lower remaining concentration of H_2O_2.

Control experiments in demineralized water with photolysis achieved the highest degradation efficiency for diclofenac (around 65 % in 120 min), while trimethoprim and sulfamethoxazole showed a smaller variation during photolysis (around 13 – 15%) for both liquid depths tested (Figure II.4.2 a and b).

During all photolysis-H_2O_2 experiments in the solar simulator, again diclofenac presented the highest degradation (around 80 % in 120 min), followed by trimethoprim (between 40 % – 51 %), and sulfamethoxazole (between 26 % – 42 % of degradation) (Figure II.4.2 c, d, and e). The other three compounds (acetaminophen, caffeine, and carbamazepine) showed removal efficiencies between 3 % – 26 % (at 7 cm) and 25 % – 42 % (at 15 cm). The slow and low hydrogen peroxide consumption achieved during photolysis-H_2O_2 experiments (between 3 – 6 mg L^{-1}) indicates the predominance of photolysis contribution for degradation of contaminants over the effect of the oxidant used (H_2O_2).

In contrast to irradiated control experiments, during dark Fenton reaction no appreciable degradation was observed for the studied compounds (Figure II.4.2 f). This highlights the importance of irradiation for the removal of contaminants with photolysis and photolysis-H_2O_2 processes together with the production of radical species after the Fe^{3+}-EDDS complex decomposition in the Fenton process (Equation 4.1 and Equation 4.2).

FIGURE II.4.2 – Control experiments with 100 µg L^{-1} of each micropollutant: photolysis a) at 7cm and b) at 15 cm liquid depth; MPs and H_2O_2 consumption in photolysis-H_2O_2 c) at 7 cm, d) at 10 cm, and e) at 15 cm liquid depth; f) MPs in dark Fenton, g) H_2O_2 consumption and Fe-dissolved in dark Fenton with 0.054 mm of iron and 10 cm liquid depth



The dissolved iron concentration was stable throughout the reaction, which might indicate that the Fe^{3+}-EDDS complex did not decompose and was constant during reaction (Figure II.4.2 g). In this way, no radical reaction occurred, and MPs could not be degraded. There was not H_2O_2 consumption, and this result associated with the constant dissolved iron concentration corroborates this idea (Figure II.4.2 f).

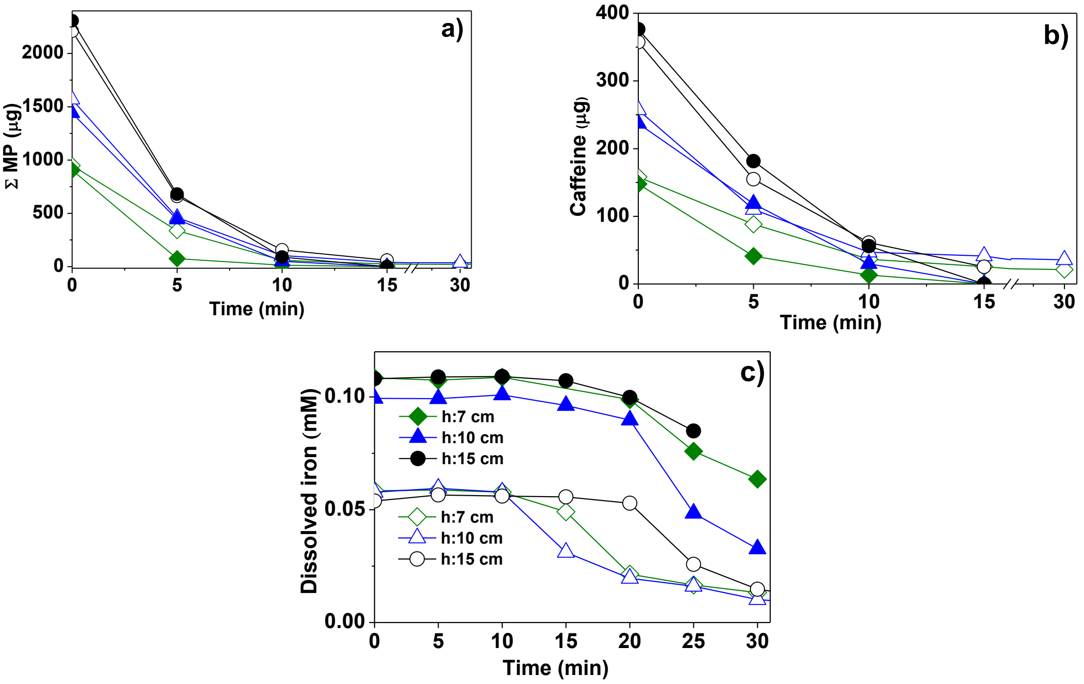
In this way, control experiments (< 120 min) with photolysis, photolysis-H_2O_2 and dark Fenton reaction showed no appreciable MPs degradation (Figure II.4.2) in 30 min. On the other hand, as show previously, a fast degradation of all MPs occurred (Figure II.4.1). Among the studied compounds, caffeine demonstrated to be the most persistent one, always the last to be degraded (Figure II.4.1a). On the opposite side, diclofenac was the first one to be removed. In agreement with other studies which have described diclofenac as an MP easy to degrade by photolysis and AOPs (ALHARBI *et al.*, 2017; CAPODAGLIO; BOJANOWSKA-CZAJKA; TROJANOWICZ, 2018).

Trimethoprim and acetaminophen were secondly removed, followed later by carbamazepine and sulfamethoxazole. This degradation pattern occurred under all experimental conditions tested. In this way, further discussion in this work is focused on the degradation of the sum of all compounds' mass (ΣMP, where the photoreactor volume was considered), as well on the degradation of caffeine, as the most persistent contaminant.

When a higher initial iron concentration was tested, the decomposition of the photoactive Fe-EDDS complex occurred later during the reaction (Figure II.4.3c), keeping iron available in the system and allowing the progress of the reaction. In this way, H_2O_2 consumption was around 80% and 50% at 0.1 mM and 0.054 mM of Fe, respectively, and MPs were almost totally degraded (data not shown). H_2O_2 was consumed up these values when dissolved iron was > 0.02 mM, indicating that the presence of enough Fe:EDDS plays a fundamental role in the process (PAPOUTSAKIS *et al.*, 2015).

Concerning MPs removal, an increase in initial iron concentration from 0.054 mM to 0.1 mM led to a slightly faster degradation of ΣMP at 7 cm liquid depth, as well as for caffeine (Figure II.4.3 a and b) because the higher photon availability increased the efficiency of the oxidation process by producing higher amount of radicals. At 10 cm and 15 cm liquid depth, degradation of MPs was similar at both 0.054 mM and 0.1 mM of Fe, as MP consumption of oxidizing radical species was marginal compared with the consumption of organic matter in the mg L^{-1} range, including EDDS, present in water at the same time. In addition, when lower amount of radicals is generated due to the lower photon availability, the positive effect than an increase in iron concentration could show is buffered.

FIGURE II.4.3 – Solar photo-Fenton with Fe:EDDS using 0.054 mm (empty symbols) and 0.1 mm (full symbols) of iron, for different liquid depths (green, blue and black colors for 7 cm, 10 cm and 15 cm, respectively) and MPs initial concentration of 100 μgL^{-1} each: a) ΣMP mass evolution, b) caffeine mass evolution and c) dissolved iron profile.



Whether working at 7 cm, 10 cm or 15 cm of liquid depth, the efficiency of ΣMP and caffeine degradation was very similar for the same iron concentration. In fact, within 15 minutes of reaction, all experimental conditions achieved maximum efficiency for all the different liquid depths tested. Nevertheless, when analyzing the initial degradation rate for each compound (Table II.4.1), it can be noticed a higher initial degradation rate for all MPs at 15 cm of liquid depth with both initial iron concentrations tested. In this way, working at 15 cm of liquid depth attained a considerably higher treatment capacity within the tested conditions. (Table II.4.1).

The same reaction conditions were also studied at 15 cm liquid depth with a lower initial concentration of each micropollutant (20 $\mu g\ L^{-1}$), which is closer to the real concentration of MPs usually found in actual EMWWTP (Figure II.4.4). Similar conclusions could be observed, despite a slightly faster initial degradation of ΣMP and caffeine when using 0.1mM of dissolved iron in comparison to 0.054 mM (Table II.4.1 and Figure II.4.4) was measured. The degradation efficiency achieved was similar, and the reactions stabilized when dissolved iron was very low. In general, 80% degradation of ΣMP was reached within a shorter treatment time in comparison to experiments with a higher MPs initial concentration (100 μg L^{-1}).

FIGURE II.4.4 – Solar photo-Fenton with 0.054 mM and 0.1 mM of iron, at 15 cm of liquid depth for MPs initial concentration of 20 μg L^{-1} each: a) profile of the degradation of MP mass and b) caffeine mass.

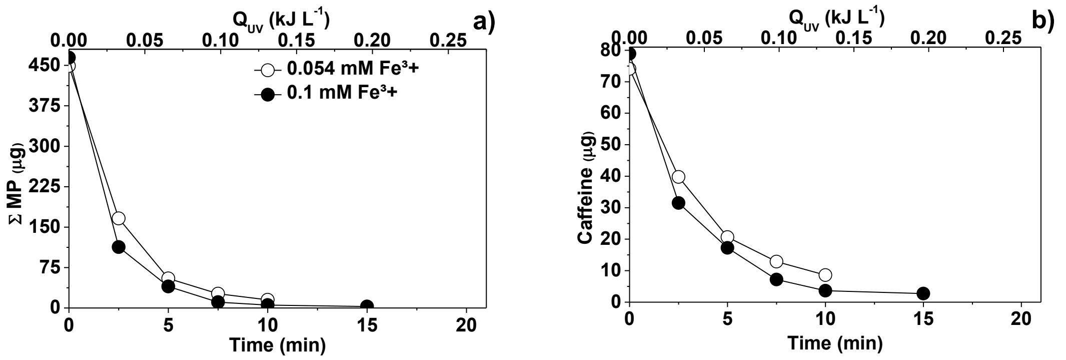


Table II.4.1 presents the results of TCs at 100 and 20 μg L^{-1} initial concentration of each micropollutant. When analyzing TCs for both concentrations of iron, higher TC could be reached at 15 cm liquid depth. Also, TC was similar for both iron concentrations in experiments at 100 μg L^{-1} MPs initial concentration, but relatively higher when using 0.1 mM of Fe-dissolved in comparison to 0.054 mM for experiments at 20 μg L^{-1} MP concentration. Remarkably, at 20 μg L^{-1} lower TC was attained, highlighting the need of confirming MPs degradation rate of any new process or new operation condition as close as possible to real MP concentration.

TABLE II.4.1 – Initial degradation rate (r_0, µg min^{-1}) and treatment time for attaining 80% ($t_{80\%}$, min) degradation of MPs by solar photo-Fenton reactions with Fe:EDDS using 0.054 mm and 0.1 mm of iron, for each liquid depth (7 cm, 10 cm and 15 cm) and MPs initial concentration of 100 µg L^{-1} each. Treatment Capacity for 100^1 and 20^2 µg L^{-1} is also included.

	r_0	$t_{80\%}$	r_0	$t_{80\%}$	r_0	$t_{80\%}$	r_0	$t_{80\%}$	r_0	$t_{80\%}$	r_0	$t_{80\%}$
Acetaminophen	16	6.8	26	5.6	34	6.0	30	4.0	24	6.4	39	6.4
Caffeine	12	11.2	21	10.0	30	8.8	13	5.8	21	8.8	32	9.0
Trimethoprim	16	6.8	27	5.6	37	5.8	31	4.0	25	6.0	39	5.8
Sulfamethoxazole	13	8.8	23	7.2	23	7.2	15	5.2	22	8.0	34	7.8
Carbamazepine	16	7.2	22	8.0	35	6.4	31	4.0	23	6.6	40	6.4
Diclofenac	32	4.0	27	5.6	64	4.2	29	4.0	49	4.0	76	4.0
	7 cm		**10 cm**		**15 cm**		**7 cm**		**10 cm**		**15 cm**	
	0.054 mM Fe^{3+}						**0.1 mM Fe^{3+}**					
TC (mg m^{-2} min^{-1})	3.8^1		$6.8^1/2.7^2$		$9.6^1/3.2^2$		6.4^1		6.3^1		$10.0^1/4.8^2$	
TC (mg kJ^{-1})	2.1^1		$3.8^1/1.5^2$		$5.3^1/1.8^2$		3.5^1		3.5^1		$5.6^1/2.6^2$	

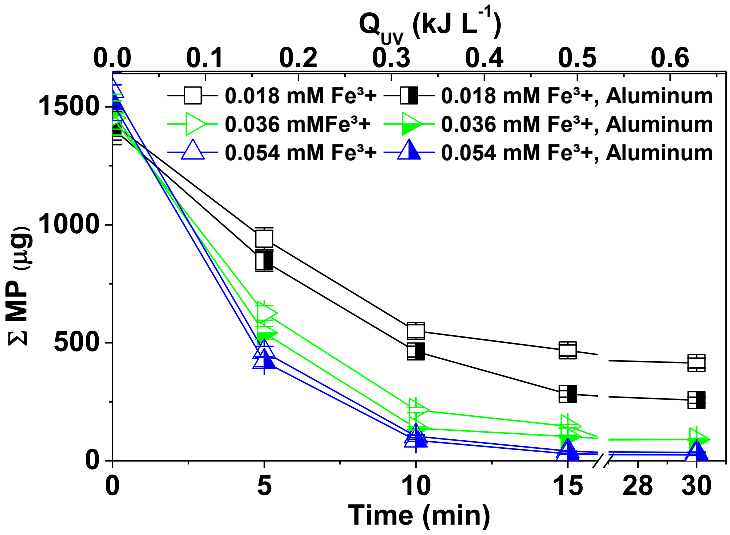
When working with open solar photoreactors such as RPR, lower treatment times are required to reduce the possibility of weather exposition and evaporation. Besides, faster reaction times combined with higher liquid depths might lead to a higher TC and lower hydraulic retention times (HRT). These two factors combined can result in a reduced surface area, provoking a decrease in overall capital costs relative to the reactor's construction and land area requirements. Treating large flows of MWTP effluents (around 0.25 m^3 $habitant^{-1}$ day^{-1}) requires AOPs with short treatment times.

In this way, increasing iron concentration to attain faster reactions should be one possibility. However, iron (and therefore EDDS) should be minimized to avoid extra organic carbon contribution and to allow easy effluent reuse, for example in crops irrigation. Another option would be to enhance the photon absorption within the reactor by increasing the liquid depth (SORIANO-MOLINA; GARCÍA SÁNCHEZ; MALATO; *et al.*, 2018). It is necessary to highlight that solar irradiation also affects TC, changing it throughout the day and seasonally. In this way, one strategy is to increase the light path inside the RPR without excessively increasing the reactor liquid depth. The new trend proposed in this work was installing a reflexive surface on the bottom of the photoreactor, enabling the return of non-absorbed photons to the bulk of the photoreaction, which also allows the reduction of iron concentration.

II.4.1.2.Lab-scale results with natural water: effect of an aluminum reflexive surface

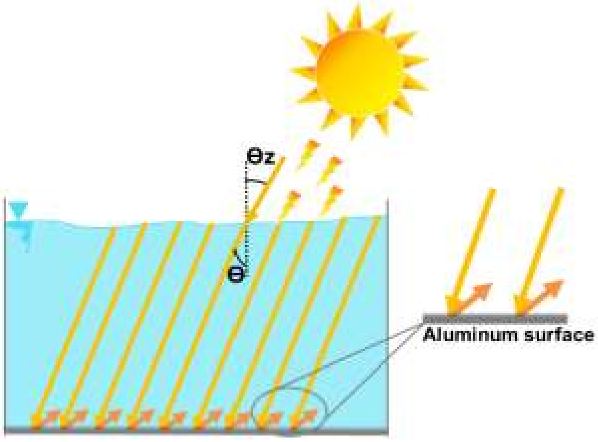
In order to confirm the influence of the aluminum surface applied to the bottom of the reactor, three very low and different iron concentrations were tested at 10 cm of liquid depth: 1, 2 and 3 mg L^{-1} (0.018 mM, 0.036 mM, and 0.054 mM). The initial iron concentration of 0.054 mM, with and without the aluminum reflexive surface, showed the highest degradation rate for the sum of MPs (Figure II.4.5). The use of the reflexive surface improved the degradation of MPs in all cases, showing a higher difference for the lower iron initial concentrations (0.018 mM and 0.036 mM).

FIGURE II.4.5 – ΣMP mass degradation profile comparison with (half-full symbols) and without (empty symbols) aluminum surface for MPs initial concentration of 100 µg L^{-1} each, 10 cm of liquid depth and iron initial concentration of 0.018 mM, 0.036 mM and 0.054 mM



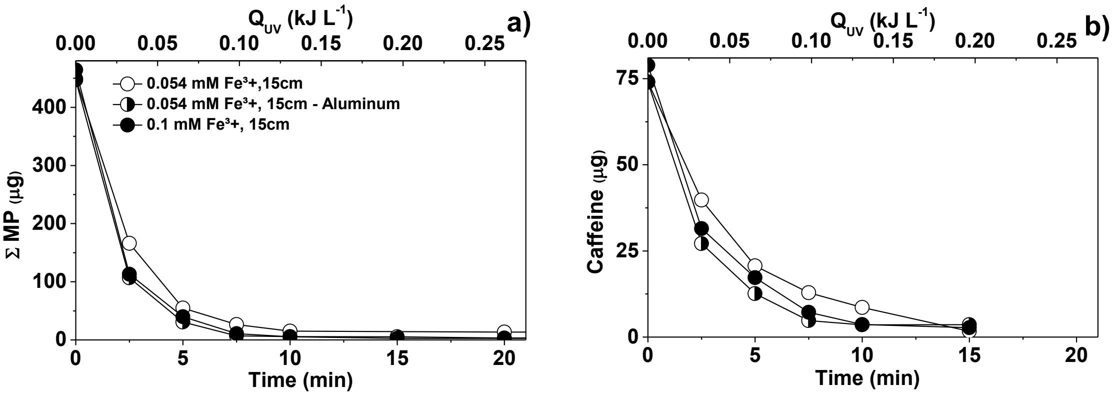
The photon absorption process within the reactor depends on several factors, including the iron concentration, the UV-visible light absorption from the water matrix and the liquid depth, among others. In this case, 100 % return of all the photons reaching the bottom of the photoreactor is not expected even when using the aluminum reflective surface. Only some of the photons can return to the system because of light attenuation, which explains the moderate improvement while using the aluminum surface (Figure II.4.6). In this way, the positive influence of the reflexive surface on TC is more apparent with lower initial iron concentrations due to the solution's lower optical density that might reduce the probability of photons to reach the iron catalyst. Thus, the reflexive surface could allow those photons that were not absorbed to be returned to the reaction bulk, thus leading to faster reaction rates at the same irradiance, liquid depth, and iron concentration.

FIGURE II.4.6 – Schematic of light reflection inside the reactor when using an aluminum surface in the bottom of the reactor.



The experiments carried out with 0.054 mM of iron, with the initial concentration of each MP of 100 µg L^{-1} and at 15 cm of liquid depth, showed an increase in the reaction rate by applying an aluminum surface in the bottom of the photoreactor (data not shown). Tests with lower MP's initial concentration (20 µg L^{-1} of each MP and total concentration of 120 µg L^{-1}) showed better degradation results compared to those obtained with 0.1 mM of iron without the aluminum surface (Figure II.4.7 a and b). As a result, iron concentration could be lower with the use of a reflective surface, besides reducing the required dose of EDDS.

FIGURE II.4.7 – Solar photo-Fenton with 0.054 mM or 0.1 mM of iron, at 15 cm of liquid depth for MPs initial concentration of 20 µg L^{-1} each with and without aluminum surface in the reactor: a) profile of the degradation of MP mass and b) caffeine mass.



II.4.1.3. Semi-pilot plant scale results with natural water: effect of an aluminum reflexive surface in RPR under solar irradiation

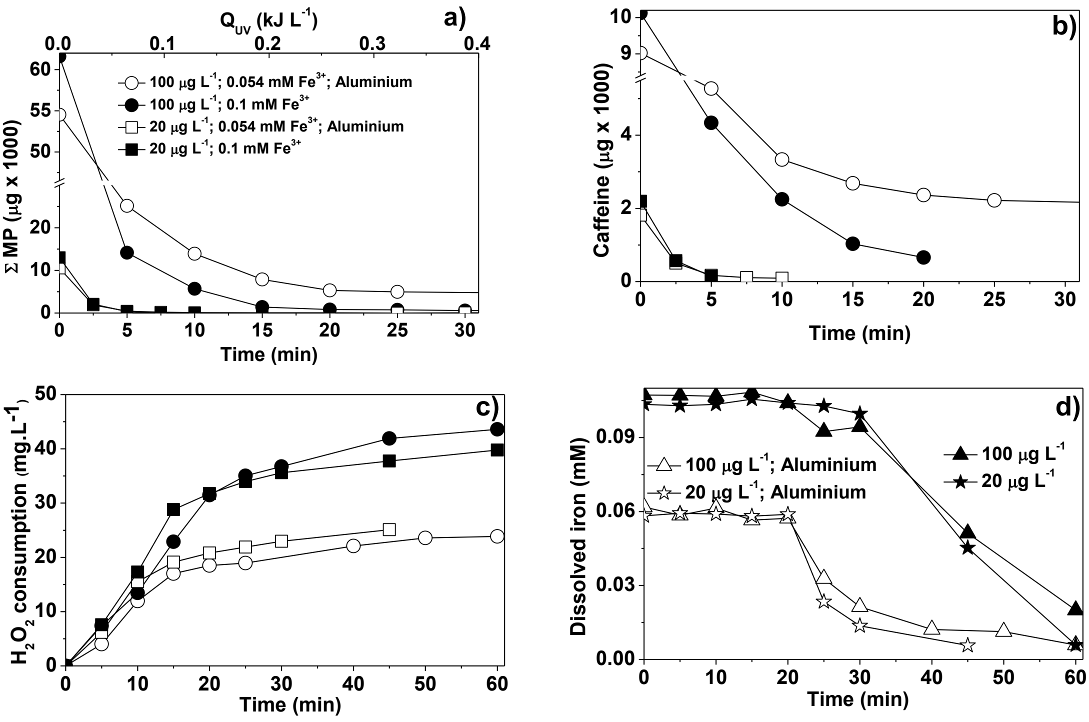
Results obtained at lab-scale within the solar simulator were checked outdoors at semipilot-plant scale in an RPR (90 L total volume), at 15 cm liquid depth with both initial concentrations of MPs (100 µg L^{-1} and 20 µg L^{-1}, each). Iron concentrations of 0.054 mM and 0.1 mM, with and without aluminum surface, were compared (Figure II.4.8).

Dissolved iron results indicated that the Fe^{3+}-EDDS complex remained in reaction for about 20 – 30 minutes, while at lab-scale it lasted between 15 – 20 minutes (Figure II.4.3 c). There was a notable difference in dissolved iron stability between 0.054 mM of iron (with the aluminum surface) compared to 0.1 mM of iron (without the aluminum surface), lasting longer in solution with higher iron concentration (Figure II.4.8 d).

Degradation of MPs was slower under natural solar irradiation in the RPR than in solar simulator for 100 µg L^{-1} initial concentration (Figure II.4.8 a), while for 20 µg L^{-1} initial MP concentration, treatment time was similar for both experimental set-ups. In addition, treatment time to achieve a substantial elimination (> 90 %) of MPs at 20 µg L^{-1} in the RPR with 0.054 mM of iron and the aluminum surface was very similar to 0.1 mM of iron (Figure II.4.8 a and b). The same did not occur with 100 µg L^{-1} of MPs. Dissolved iron stability lasted shorter time with 0.054 mM than with 0.1 mM of iron, not enough for a substantial degradation of MPs at 100 µg L^{-1}, but enough for MPs at 20 µg L^{-1}, also confirmed by the lower consumption rate of H_2O_2 (Figure II.4.8 c).

Similar solar accumulated UV energy was enough to reach 80% of degradation of the $\sum$MPs for both iron concentrations tested: 0.045 kJ L^{-1} (2.5 min) for 0.054 mM of iron with the aluminum surface and 0.039 kJ L^{-1} (2.5 min) for 0.1 mM of iron without aluminum surface.

FIGURE II.4.8 – Solar photo-Fenton in the RPR with 0.054 mM of iron and using the aluminum surface and with 0.1 mM of iron without using the aluminum surface: profile of the degradation of a) ΣMP mass; b) caffeine mass; c) hydrogen peroxide consumption; and d) dissolved iron concentration. MPs initial concentration of 20 µg L^{-1} and 100 µg L^{-1} each, at 15 cm of liquid depth. Average solar irradiation of 41 W m^{-2} and 46 W m^{-2} for experiments with 100 µg L^{-1} of each MP with and without aluminum surface, respectively, and 47 W m^{-2} and 50 W m^{-2} for experiments with 20 µg L^{-1} of each MP, with and without aluminum surface, respectively.



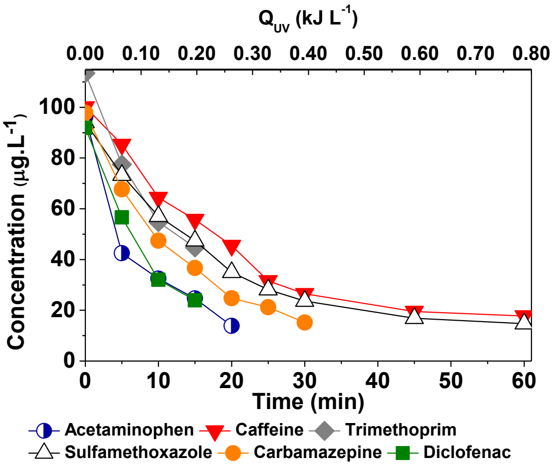
II.4.1.4.Lab-scale results with spiked real secondary EMWWTP: effect of an aluminum reflexive surface

At first, experiments with a real secondary EMWWTP were performed at the lab-scale with 0.054 mM or 0.1 mM Fe concentration, with and without the aluminum reflexive surface. For all experiments, the same liquid depth was used (15 cm), which obtained higher treatment capacity previously in the investigation with natural water matrix. At lab-scale, the real secondary EMWWTP matrix was spiked with both initial concentrations of MPs (100 μg L^{-1} and 20 μg L^{-1}, each).

Results with the higher initial concentration of MPs (100 μg L^{-1}) in the real secondary effluent indicated that with 0.1 mM of Fe over 80 % removal for ΣMPs was reached promptly (30 minutes, results not shown), with and without the aluminum surface. Nonetheless, the experiments with lower iron concentration (0.054 mM-Fe) reached a maximum removal with and without the aluminum surface, of 76 % and 75 % respectively, after 60 minutes of reaction (Q_{UV} of 0.59 kJ L^{-1}). In experiments with 0.1mM-Fe, only caffeine and sulfamethoxazole slightly persisted, and their final removal efficiency ranged between 78 % and 88 % (results not shown). For experiments with 0.054mM-Fe, acetaminophen and diclofenac were removed over 99 % within 30-45 minutes (Q_{UV} of 0.39 – 0.59 kJ L^{-1}).

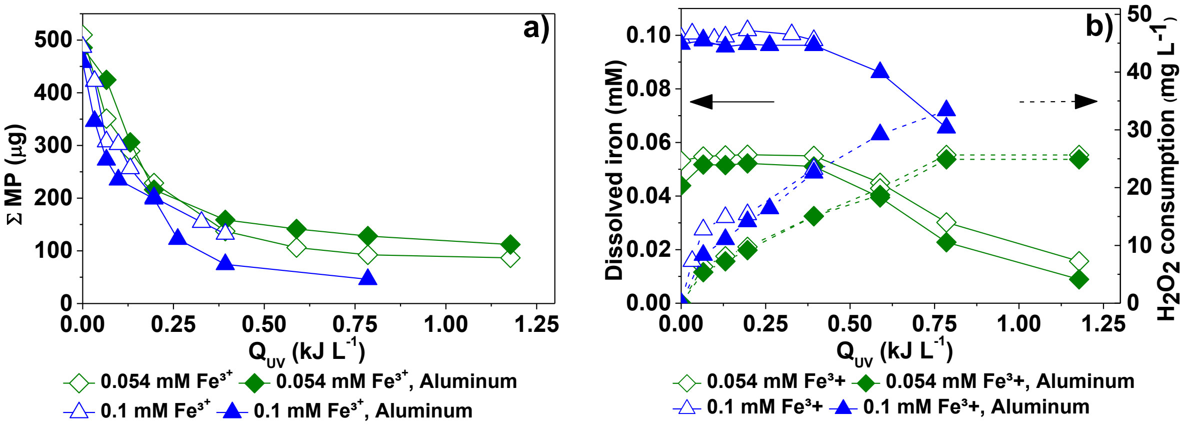
The final removal efficiencies of caffeine, trimethoprim, sulfamethoxazole, and carbamazepine were, respectively, 51 %, 71 %, 59 %, and 67 % without aluminum surface and of 53 %, 75 %, 59 %, and 70 % with the aluminum surface. Caffeine and sulfamethoxazole were the most persistent compounds in all the experiments (Figure II.4.9).

FIGURE II.4.9 – Degradation of six MPs (100 µg L^{-1} each) in spiked real secondary effluent by solar photo-Fenton with 0.1 mM of iron and 15 cm liquid depth.



When similar experiments were performed using a lower initial concentration of each MPs (20 µg L^{-1}), that is closer to real MPs concentration in EMWWTP, the ΣMPs removal efficiency was improved with the aluminum surface for both iron concentrations, and values above 80 % could be achieved (Figure II.4.10). The results with the real EMWWTP indicate a higher time required for the degradation of compounds (ΣMPs), and slower consumption of hydrogen peroxide in comparison with the results obtained with natural water matrix, regardless of the aluminum surface presence and initial iron concentration (Figure II.4.10).

FIGURE II.4.10 – Solar modified photo-Fenton reactions with Fe(III):EDDS 1:2 at 15 cm of liquid depth in spiked real secondary effluent from MWWTP at lab-scale for MPs initial concentration of 20 µg L^{-1}: a) degradation of ΣMP mass, b) dissolved iron concentration and hydrogen peroxide consumption.



Dissolved iron concentration was more stable for longer times on the reactions with real EMWWTP than with natural water for both initial iron concentration and both MPs initial concentration. Dissolved iron was very persistent even after 25-30 min of reaction (Q_{UV} of 0.33 – 0.39 kJ L^{-1}), contrasting with 10–15 minutes of reaction (Q_{UV} of 0.13 – 0.20 kJ L^{-1}) previously obtained with natural water, indicating that Fe^{3+}-EDDS complex was also stable in real

EWWTP experiments, and remained at least 50 % of the initial concentration up to approximately 50 minutes of reaction (Q_{UV} of 0.6 – 0.7 kJ L^{-1}). The main reason is the complex composition of EMWWTP, including humic substances (HS). Although there are differences in HS from different sources, they contain carboxylic acids, phenolic, alcoholic quinine, and amino and amido groups which enable them to form complexes (LIPCZYNSKA-KOCHANY; KOCHANY, 2008). Fe-HS complexes have recently attracted much attention in photo-Fenton process at natural pH (CLARIZIA *et al.*, 2017; NDOUNLA; PULGARIN, 2014). However, such remaining levels of dissolved iron were not enough when was used a lower iron initial concentration (0.054 mM) and might have caused the reduced efficiency of the modified photo-Fenton process.

H_2O_2 consumption was more similar for the same initial iron concentration with or without the aluminum surface. Nevertheless, reactions were initially faster with higher iron concentration, with higher associated H_2O_2 consumption. During the first 30 minutes of the reaction, hydrogen peroxide consumption reached an average (with and without the aluminum surface) of 30 % and 46 %, respectively, for 0.054 mM or 0.1 mM of Fe concentration (Figure II.4.10b), while with natural water matrix these values were up to 59 % and 91 %, respectively.

Under the same conditions, the treatment time required for real EMWWTP (over 30 minutes – Figure II.4.10a) was increased in comparison to the natural water (about 15 minutes), which is expected due to the complexity of the matrix (real secondary effluent from MWWTP). Different effects are well known and reported about the parameters that could interfere in this process (LADO RIBEIRO *et al.*, 2019). About the experiments discussed here, the main effect on the treatment time required was the dissolved organic matter (DOM) and turbidity.

Lado Ribeiro *et al.* (2019) reviewed the effects for different AOPs of the main components present in water matrices, including wastewater. The constitution of DOM in water and wastewater matrices depends on several factors regarding its location, MWWTP technology and operation and seasonality, that results in its complex composition (carbohydrates, proteins, trace recalcitrant MPs, among others). While being complex, DOM is not usually completely characterized and only mostly evaluated in terms of its DOC content. The other relevant constituents of real wastewater that might interfere with AOPs are inorganic substances (e.g., carbonate/bicarbonate, sulfate, chloride, nitrate/nitrite/ammonium, bromide, and others). Both organic and inorganic components might present either positive, negative, or neutral effects on

AOPs. In the case of Fenton-based reactions, the DOM can present inhibitory effects by light attenuation and reactive oxygen species (ROS) scavenging. In contrast, photosensitization of DOM and the formation of photoactive iron complexes with higher molar absorption than Fe^{3+}- EDDS are examples of promoting effects.

About the inorganic constituents, only adverse effects were pointed out for Fenton-based reactions (LADO RIBEIRO *et al.*, 2019), including scavenging of radicals and ROS, the formation of complexes with iron interfering with the Fe^{2+}/Fe^{3+} regeneration cycling, and formation of less reactive radicals than hydroxyl (for example, $SO_4^{\bullet -}$ and $Cl_2^{\bullet -}$). However, a recent work evaluated the effect of different inorganic ions and their concentration in the solar photo-Fenton process at circumneutral pH (1 mg L^{-1}-Fe and 10 mg L^{-1} of H_2O_2) (ROMMOZZI *et al.*, 2020). Results showed a more significant inhibiting effect for bicarbonate ions, but the adverse effects of bicarbonate and chloride occurred only at "higher" concentrations (10 mg L^{-1} HCO_3^- or higher, and above 100 mg L^{-1} Cl^-). Even though this work was applied for disinfection in natural water matrices, these results are valuable since the experiments were conducted in the presence of organic matter and, again, bicarbonate ions was the most interferer on the oxidative efficiency of the photo-Fenton process. In this way, the control of this parameter is essential for the promotion of effective treatment at real-scale conditions. Indeed, the control of this parameter was reached by keeping it at less than 75 mg L^{-1} in both matrices (EMWWTP and natural water). Therefore, in the present work bicarbonate ions concentrations were so similar in both matrices and then should be not responsible for differences in the reaction rate between natural water and EMWWTP in the photo-Fenton process.

About other constituents, chloride and sulfate are other predominant anions identified in EMWWTP at high concentration (> 100 mg L^{-1}) that could interfere in photo-Fenton reactions. However, it is not possible to directly associate any interference of these anions in the MPs removal, considering the slight difference between the chloride and sulfate average concentration in both matrices studied (natural water and EMWWTP). Regarding chloride anions, average values in natural water (324 mg L^{-1}) and in the EMWWTP (427 mg L^{-1}) are close to the range value (386 – 481 mg L^{-1}) reported that could not interfere in the reaction (SORIANO-MOLINA; PLAZA-BOLAÑOS; *et al.*, 2019). For sulfate anion, according to the average values in natural water (220 mg L^{-1}) and EMWWTP (140 mg L^{-1}), a slight improvement of the reactions could occur. Soriano-Molina; Plaza-Bolaños *et al.* (2019) observed a small increase in the removal of contaminants using effluents with sulfate concentration increasing from 160 mg L^{-1} to 240 mg L^{-1}, but only significantly higher removal of contaminants for sulfates concentration over 600 mg L^{-1}.

In the light of these results, it seems that chloride and sulfate would most likely equally not affect or equally improve reactions on both matrixes, in contrast to detrimental effects as usually reported by other authors (LADO RIBEIRO *et al.*, 2019).

About turbidity, pre-treatment of the effluent with sand and cartridge filters (Figure II.3.11) leads to a substantial reduction of suspended solids, which could actively interfere with irradiated processes. In the case of natural water, the DOC content was lower (2.5 ±1.4 mg L^{-1}), and the turbidity was insignificant (not detected) when compared to real secondary effluent of MWWTP (DOC = 12.0 mg L^{-1} and turbidity = 11.9 N.T.U.) even after pre-treatment steps. Thus, the predominant effect here could be mainly associated with the DOC concentration and turbidity in the real effluent due to the light attenuation and scavenging of radical species.

Regardless of all these discussed effects for organic and inorganic contents on the real matrices, high efficiency can still be achieved treating wastewater matrices with solar photo-Fenton process, as presented in this current work and other (SORIANO-MOLINA; MIRALLES-CUEVAS; *et al.*, 2019). Values above 80 % for the degradation of the sum of the six investigated MPs could be achieved at low contaminants concentration, indicating the possibility of using low iron concentration with the aluminum surface for real EMWWTP, with low turbidity, treatment.

In case of an initial faster rate for degradation would be necessary, a higher iron concentration could be used, with the treatment in sequence following at lower iron doses, in a similar strategy as indicated for other parameters. An example of this kind of operation strategy is indicated for the HRT, which points out that the continuous operation for disinfection on RPR should begin with a 60 min-HRT during the first day, and subsequently being reduced to 30 min the following operation days in winter. This was suggested because during winter the low average irradiation associated to the lower HRT (30 min) resulted in a lower accumulated irradiation and inefficient disinfection in the first day in comparison to a higher HRT (60 min) that was efficient in the first day. While during summer with 30 min of HRT the system was efficient from the first day of continuous operation (DE LA OBRA JIMÉNEZ, I. *et al.*, 2019).

II.4.1.5.Semi-pilot scale results with real secondary EMWWTP: effect of an aluminum reflexive surface in RPR under solar irradiation

Experiments were performed on the real secondary MWWTP effluent without the addition of the selected mix of micropollutants, in order to evaluate the degradation of compounds that occur at real concentration in this effluent. The two previously optimized iron concentrations (0.054 mM and 0.1 mM) were tested in an RPR (90 L) at 15 cm liquid depth, with and without the aluminum surface, respectively.

Regarding the MPs naturally found on the real secondary effluent from MWWTP, of the 150 compounds analyzed, a maximum of 60 substances could be identified. The initial concentration reached a total MPs load of 24 800 ±4 900 ng L^{-1} (Table II.4.2). Nevertheless, this total MPs load agrees within the total load identified in the literature of MPs in real effluent from MWWTP, and it does not have a stable concentration or composition, since it depends on variable factors and it is always in the range of tens of µg L^{-1} (7 – 90 µg L^{-1}) (CHÁVEZ *et al.*, 2019; MEADOR *et al.*, 2016; MIJANGOS *et al.*, 2018; PAPAGEORGIOU; KOSMA; LAMBROPOULOU, 2016; WANG, J. *et al.*, 2018).

TABLE II.4.2 – Initial concentrations and respective statistics of compounds identified on the real secondary effluent from MWWTP

#	MPs (ng L^{-1})	Average	Maximum	Minimum
1	4-FAA[a]	6 730	10 000	4 750
2	Antipyrine	2 780	5 970	950
3	Imidacloprid	1 620	1 870	1,350
4	4-AA[b]	1 420	2 050	760
5	Gabapentin	1 330	1 440	1 220
6	O-Venlafaxine	1 310	1 530	1 070
7	4-AAA[c]	1 130	1,360	860
8	Caffeine	980	1 300	410
9	Levofloxacin[d]	880	1 590	510
10	Tramadol	730	810	550
11	O-Desmethyltramadol	710	770	590
12	Sulfapyridine	680	1 380	20
13	Ciprofloxacin	630	780	360
14	Atenolol	620	640	590
15	Trimethoprim	420	550	330
16	Amitriptyline	290	800	20
17	Azithromycin	290	550	140
18	Acetamiprid	270	300	220
19	Citalopram	260	280	200

#	MPs (ng L^{-1})	Average	Maximum	Minimum
20	Naproxen	210	340	100
21	Venlafaxine	200	240	170
22	Ketoprofen	180	260	130
23	Acetaminophen	170	220	120
24	Lidocaine	150	170	140
25	Carbamazepine	140	210	90
26	Ranitidine	140	180	40
27	Primidone	130	150	120
28	Sulfadiazine	130	200	50
29	Flumequine	110	290	50
30	Pentoxifylline	80	100	50
31	Propamocarb	70	90	60
32	Dimethomorph	70	90	50
33	Pyrimethanil	70	160	10
34	Erythromycin	70	70	60
35	Salbutamol	60	80	40
36	Clarithromycin	60	80	50
37	Acetanilide	60	90	50
38	Cyprodinil	60	70	60
39	Metoprolol	60	60	50
40	Pirimicarb	50	50	40
41	Fenofibric acid	50	70	40
42	Propranolol	50	60	30
43	Fenhexamid	40	40	40
44	Metronidazole	40	50	30
45	Indomethacin	30	40	30
46	Azoxystrobin	30	40	20
47	Thiabendazole	30	40	30
48	Sotalol	30	30	30
49	Diuron	30	40	20
50	Famotidine	30	30	20
51	Chlorfenvinphos	30	30	30
52	Metoclopramide	20	30	20
53	Methadone	20	20	20
54	Tebuconazole	20	20	20
55	Carbendazim	20	20	20
56	Terbutaline	20	20	20
57	Isoproturon	20	20	20
58	Mepivacaine	20	20	10
59	Mefenamic acid	10	20	10
60	Fluoxetine	10	10	10
	Total Load	**24 800**	**30 800**	**19 300**

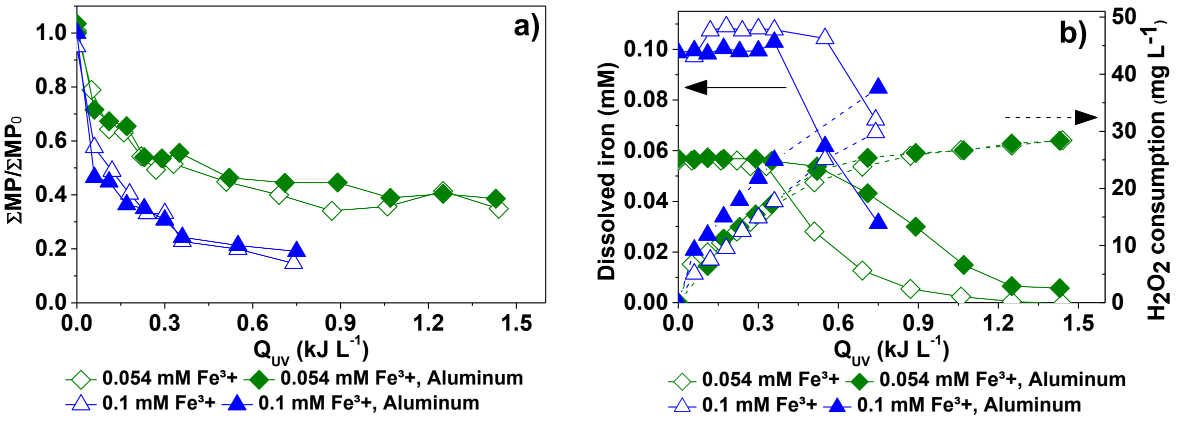
[a]4-FAA: 4-formylaminoantipyrine; [b]4-AA: 4-aminoantipyrine; [c]4-AAA: 4-acetamidoantipyrine; [d]sum of levofloxacin and ofloxacin.

Among the identified MPs, the highest concentrations were observed for pharmaceuticals, including the analgesics/antipyretics antipyrine, tramadol, and its metabolite O- desmethyltramadol, and the metabolites of dipyrone 4-FAA (4-formylaminoantipyrine), 4-AA (4-aminoantipyrine) and 4-AAA (4-acetylaminoantipyrine). Other classes of MPs identified were anti-inflammatory (naproxen), antidepressants (O-venlafaxine [R-(-)-O-Desmethyl Venlafaxine] a metabolite of venlafaxine, amitriptyline, and citalopram), antiepileptic/treatment of neuropathic pain (gabapentin), beta-blocker (atenolol), and antibiotics (trimethoprim, azithromycin, ciprofloxacin, levofloxacin and sulfapyridine). Pesticides were also identified as imidacloprid and acetamiprid (neonicotinoid insecticides). The pollution marker caffeine was identified, which is also present in some pharmaceuticals' composition.

In general, the aluminum surface in RPR enhanced the degradation of the compounds at the beginning of the reactions, but this effect was not very clear after 20-30 minutes (Q_{UV} of 0.24 – 0.36 kJ L^{-1}) of the reaction (Figure II.4.11a) when iron concentration tended to decrease. Final degradation of the total load of MPs was above 80 % only for experiments with 0.1 mM of Fe (82-90 %) with a Q_{UV} of 0.55 kJ L^{-1}, while for 0.054 mM of Fe experiments it remained 63-65 % for Q_{UV} > 0.87 kJ L^{-1}.

The average irradiation during experiments ($\overline{UV}$, W m^{-2}) in RPR at pilot-scale, was very similar between all the tested conditions, ranging in between $\overline{UV}$ = 43 and 46 W m^{-2}. Temperature varied from 17-23 °C during experiments.

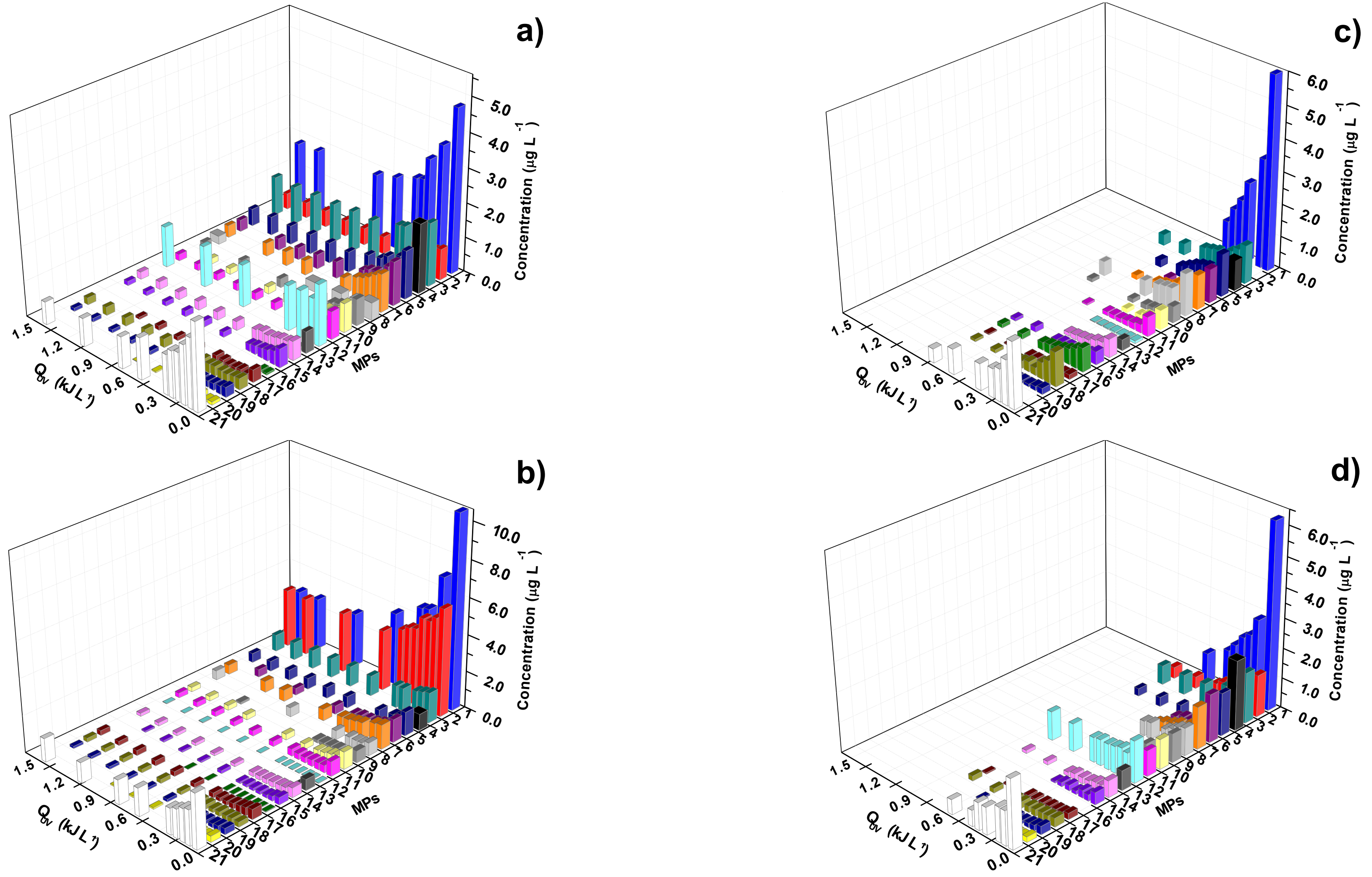
FIGURE II.4.11 – Solar modified photo-Fenton reactions with Fe(III):EDDS 1:2 at 15 cm of liquid depth in real secondary effluent from MWWTP in RPR at different iron concentrations: a) degradation of ΣMP mass, b) dissolved iron concentration and hydrogen peroxide consumption.



The dissolved iron concentration profiles showed that this catalyst was very stable in the solution until 30-45 min of the reaction (around 0.4 kJ L^{-1}). After this time, it decreased until 75 - 90 minutes of the reaction (0.7 – 0.8 kJ L^{-1}), when the hydrogen peroxide consumption achieved its maximum value and stabilized (Figure II.4.11b). These results agree with the results at the lab-scale experiments. An initially faster consumption of hydrogen peroxide on the experiments with the aluminum surface could be observed. Final hydrogen peroxide consumption was around 57 % for both 0.054 mM-Fe experiments (with and without the aluminum surface), while it reached 75 % and 90 %, respectively, without and with the aluminum surface for 0.1 mM of Fe.

For each MPs detected at a concentration higher than 1,000 ng L^{-1} (Figure II.4.12), the effect of the aluminum surface on the efficiency removal was different.

FIGURE II.4.12 – Solar modified photo-Fenton reactions with Fe(III):EDDS 1:2 at 15 cm of liquid depth in real secondary effluent from MWWTP in RPR: concentration of most identified compounds with: a) 0.054 mM-Fe without the aluminum surface, b) 0.054 mM-Fe with the aluminum surface, c) 0.1 mM-Fe without the aluminum surface, and d) 0.1 mM-Fe with the aluminum surface.



Notation 1-20 corresponds to Table II.4.2 compounds. Notation “21” corresponds to the sum of compounds 21-60 of Table II.4.2.

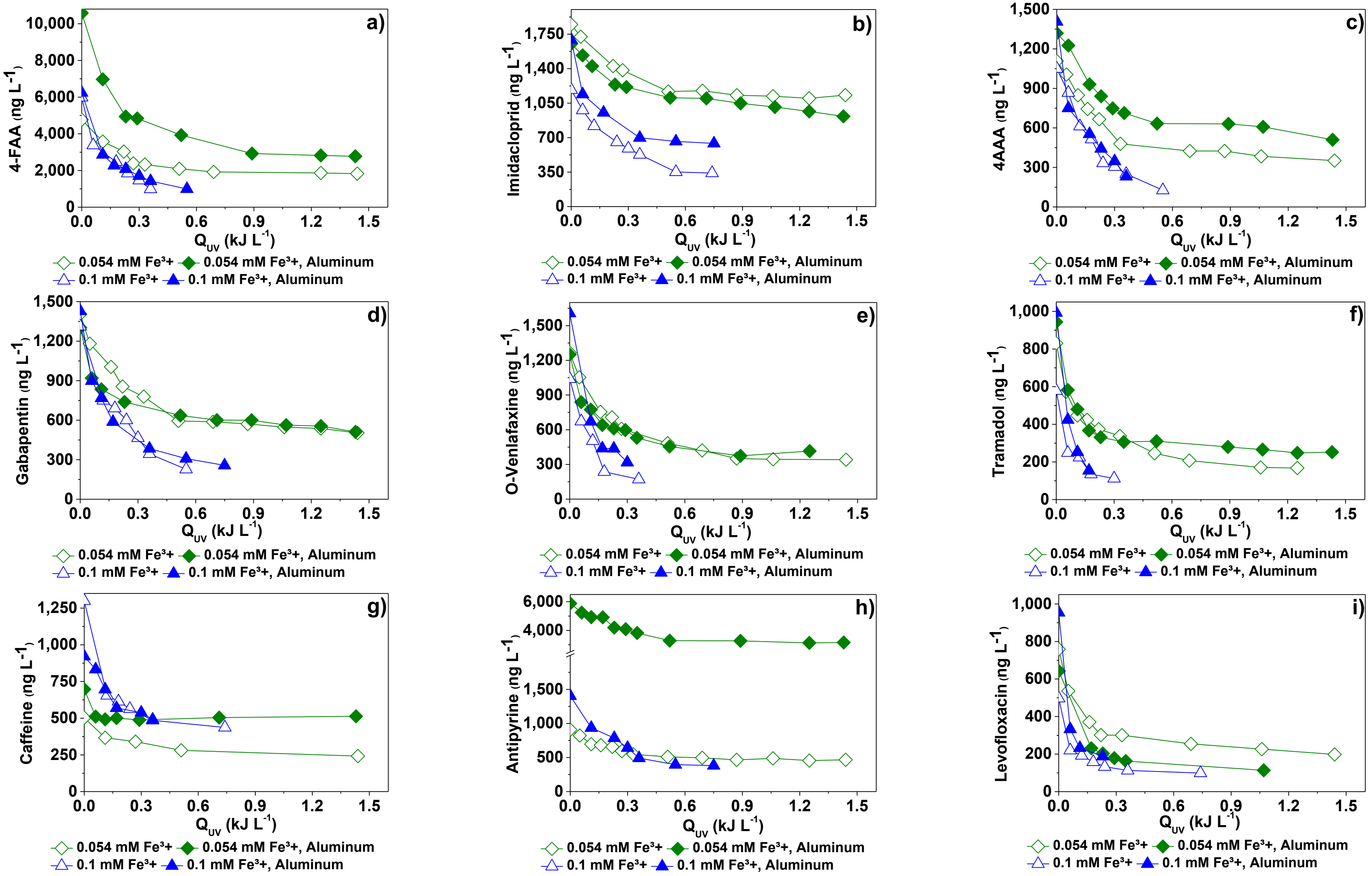
Higher efficiency removal of compounds was achieved with a higher iron initial concentration (0.1 mM). Figure II.4.13 includes detailed results of the MPs detected at higher concentration in the real EMWWTP, including compounds as 4-FAA, imidacloprid, 4-AAA, gabapentin, O- venlafaxine, tramadol, caffeine, antipyrine, and levofloxacin, with exception to 4-AA (n. º 4), which was removed under detection limit in less than 5 minutes for all the experiments. Even though the majority of the compounds achieved over 80% of removal with 0.1 mM of Fe (Figure II.4.12), some compounds (levofloxacin - n. º 9, tramadol - n. º 10, ciprofloxacin - n. º 13, amitriptyline - n. º 16, azithromycin n. º 17, and naproxen n. º 20) also achieved this efficiency of removal, but with lower iron initial concentration (0.054 mM).

For some individual compounds, it was possible to verify the aluminum surface influence on the initial rate of the reactions. However, considering the experiments for removal of antipyrine (n. º 2), amitriptyline, and naproxen (n. º 20), at the initial iron concentration of 0.1 mM, it was not possible to compare the aluminum surface influence, due to absence of these compounds in some of the real EMWWTP samples (Figure II.4.12). Experiments with the initial iron concentration of 0.054 mM-Fe, the aluminum surface presence leading the increase in the initial degradation of antipyrine, achieved an almost five times higher initial reaction rate (Table II.4.3). While for caffeine - n. º 8 and 4-FAA n. º 1, the effect was predominant mostly in the initial rate of the reactions (Table II.4.3) with the lower iron concentration of 0.054 mM of Fe. On another way, for imidacloprid (n. º 3) and 4-AAA (n. º 7), the effect of the aluminum surface on the initial removal was more effective at a higher initial iron concentration (0.1 mM-Fe).

TABLE II.4.3 – Initial degradation rate (r0, ng min^{-1}) and treatment time for attaining 80 % (t80%, min) degradation of MPs (4-FAA, imidacloprid, 4AAA, gabapentin, O-venlafaxine, tramadol, caffeine, antipyrine, and levofloxacin) by modified photo-Fenton reactions with Fe(III):EDDS 1:2 at 15 cm of liquid depth in real secondary effluent from MWWTP in RPR at different iron concentrations.

MPs	0.054 mM Fe^{3+}		0.054 mM Fe^{3+}, Aluminum		0.1 mM Fe^{3+}		0.1 mM Fe^{3+}, Aluminum	
	r_0, ng min^{-1}	$t_{80\%}$, min	r_0, ng min^{-1}	$t_{80\%}$, min	r_0, ng min^{-1}	$t_{80\%}$, min	r_0, ng min^{-1}	$t_{80\%}$, min
4-FAA	87	>120	282	>120	520	28	338	35
caffeine	14	>120	37	>120	64	>120	24	>120
antipyrine	21	>120	96	>120	[1]	[1]	29	>120
imidacloprid	21	>120	21	>120	37	45	111	>120
4AAA	23	>120	24	>120	44	34	131	28
gabapentin	45	>120	77	>120	56	39	106	49
O-venlafaxine	34	>120	82	>120	54	18	80	25
tramadol	38	105	46	>120	66	18	114	12
levofloxacin	22	>120	27	40	55	60	124	19

FIGURE II.4.13 – Solar modified photo-Fenton reactions in real secondary effluent in the RPR with Fe(III):EDDS 1:2 at 15 cm of liquid depth: evolution of the concentration of a) 4-FAA, b) imidacloprid, c) 4AAA, d) gabapentin, e) O-venlafaxine, f) tramadol, g) caffeine, h) antipyrine, and i) levofloxacin.



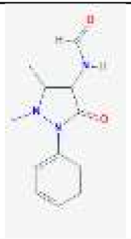
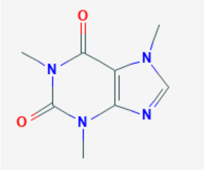
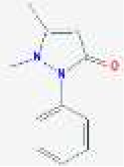
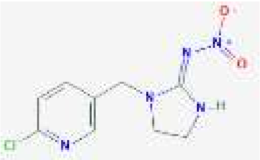
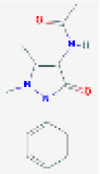
The aluminum surface effect on the initial rate of the reactions could be observed for both initial iron concentrations for some compounds, including gabapentin (n. º 5), tramadol, levofloxacin (n. º9), and the metabolite O-venlafaxine (n. º 6) (Figure II.4.12). Mechanisms of reaction for hydroxyl radical with organic molecules might include electrophilic addition of the radical to an unsaturated or aromatic structure, hydrogen abstraction with the hydroxyl radical reacting with a saturated structure, and by direct electron transfer with reduction of the hydroxyl radical to a hydroxyl anion (TANG, 2003). Besides, effects such as steric hindrance may also affect the reactivity with radicals and other oxidants (ZHANG, S. *et al.*, 2015). A combination of such possible mechanisms and molecular structure (Table II.4.4) might explain the higher reactivity of some compounds regardless of iron concentration. Also, it probably explains how some compounds (e. g. imidacloprid) would be more difficult to remove at low concentration but have a higher removal at higher iron initial concentration, whereas radical formation increases with more catalyst.

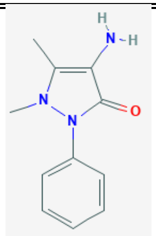
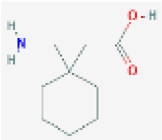
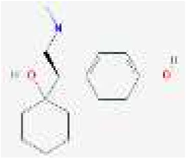
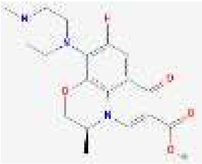
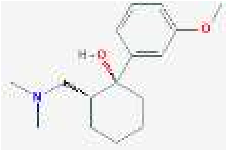
Hydroxyl radicals usually react at high pseudo-second-order rates ($4.1 \times 10^9 - 9.1 \times 10^9$ M^{-1} s^{-1}) with most of each MP and with the DOM (MANDAL, 2018). Different competitive reactions occur in complex matrixes in the presence of DOM, and the degradation efficiency of each compound cannot be predicted solely with their properties (Table II.4.4). In this way, when DOM is at a much higher concentration than that of MPs, the competition for oxidant species (in this case predominantly hydroxyl radicals) is enhanced, thus leading to the differences observed on the degradation rate of each MPs (ZHANG, S. *et al.*, 2015).

As discussed in the previous section, regardless of the real secondary effluent from MWWTP complexity, the primary inhibiting effect could be associated with its DOM content due to the light attenuation and scavenging of ROS. In this way, this inhibitory effect of the organic matter could be responsible for the higher treatment times required with the real EMWWTP, in contrast to the previous results with natural water. However, with lower liquid depth, DOM inhibitory light attenuation effect would be minimized, and the light would be able to reach the aluminized surface on the bottom of the reactor improving the photo-Fenton reaction.

It is important to highlight that this circumneutral modified photo-Fenton, with Fe^{3+}:EDDS complex, does not aim at promoting higher mineralization in EMWWTP, once the low levels of DOC within these effluents are usually in accordance with the environmental protection laws for final disposal.

TABLE II.4.4 – Main properties of micropollutants detected at the higher concentration on the EMWWTP (4-FAA, imidacloprid, 4AA, gabapentin, O-venlafaxine, 4AAA, tramadol, caffeine, antipyrine, and levofloxacin)

Micropollutant	Category	CAS Number #	Molecular formula	Molecular weight (g.mol^{-1})	Water solubility [1] (mg.L^{-1})	Log P	pKa	Structure	$k^{\bullet}OH$ (M^{-1}s^{-1}) [6]
4-FAA (4-formylaminoantipyrine)	metabolite of dipyrone - analgesics/antipyretics	1672-58-8	$C_{12}H_{13}N_3O_2$	231.25	2.1 – 377 [2]	-0.410 – 1.24 [2] -0.14[3]	5.0 [3]		-
Caffeine	central-nervous-system stimulant, analgesic adjuvant	58-08-2	$C_8H_{10}N_4O_2$	194.19	21,600	-0.07	14.0		4.10 x 10^9 at pH 7 6. 9 x 10^9
Antipyrine	analgesic	60-80-0	$C_{11}H_{12}N_2O$	188.23	51,900	0.38	1.4		5.2 x 10^9 5.3 x 10^9 4.86 x 10^9 at pH 7
Imidacloprid	insecticide	138261-41-3	$C_9H_{10}ClN_5O_2$	255.66	62	0.57	1.56; 11.12		2.65-3.79 at pH 6.02-8.64 [7]
4AAA (4-Acetamidoantipyrine)	metabolite of dipyrone - analgesics/antipyretics	83-15-8	$C_{13}H_{15}N_3O_2$	245.28	1,590 [4]	-0.13 [3,4]	4.6 [3]		8.4 ± 0.7 × 10^9 [8]

Micropollutant	**Category**	**CAS Number #**	**Molecular formula**	**Molecular weight (g.mol^{-1})**	**Water solubility [1] (mg.L^{-1})**	**Log P**	**pKa**	**Structure**	**$k^{\bullet}OH$ ($M^{-1}s^{-1}$) [6]**
4AA (4-aminoantipyrine)	metabolite of dipyrone - analgesics/antipyretics	83-07-8	$C_{11}H_{13}N_3O$	203.24	50,000 [4] - 727,599	0.588 [4]	-		-
Gabapentin	anticonvulsant	60142-96-3	$C_9H_{17}NO_2$	171.24	4,490	-1.10	3.7		9.1 x 10^9
O-Venlafaxine (R-(-)-O-Desmethyl Venlafaxine)	metabolite of venlafaxine - antidepressant	142761-11-3	$C_{16}H_{25}NO_2$	263.37	3,670 [4]	2.72 [4]	8.87 - 10.11 [5]		- (of venlafaxine = 8.8 x 10^9)
Levofloxacin	antibiotic	100986-85-4	$C_{18}H_{20}FN_3O_4$	361.40	54.2 ; 1.1 – 28,261[2]	-0.39	6.25		6. 6 x 10^9
Tramadol	analgesics/antipyretics	27203-92-5	$C_{16}H_{25}NO_2$	263.37	1,151	3.01	9.41		6.3 x 10^9

Source: National Center for Biotechnology Information. PubChem Database. https://pubchem.ncbi.nlm.nih.gov (main information source, with exceptions wherever mentioned).
[1] Solubility at 25 °C (with exception: imidacloprid, at 20 °C) [2] Predicted range. EPA. United States Environmental Protection Agency. https://comptox.epa.gov/dashboard (WILLIAMS *et al.*, 2017) [3] (MARTÍNEZ-PIERNAS *et al.*, 2018) [4] ChemSpider. http://www.chemspider.com/ [5] DrugBank. https://www.drugbank.ca/ (WISHART *et al.*, 2018) [6] (MANDAL, 2018) [7] (CHEN *et al.*, 2019) [8] (ZHANG, S. *et al.*, 2015)

II.5.CONCLUSIONS

Dissolved iron concentration and liquid depth are major parameters in solar photo-Fenton reactions. When the dissolved iron concentration was too low (<0.02 mM) the oxidative reactions stopped. Extremely high iron concentrations are usually undesirable for domestic wastewater treatment. At the same time, some reaction parameters (reaction rate, treatment capacity, and treatment time) were not different between experiments with very close low iron initial concentrations (0.1 mM and 0.054 mM), special at higher liquid depth (15 cm).

In this way, there are limitations to enhance treatment considering the increase in these two parameters. The proposed new strategy of using a reflexive aluminum surface to return to reaction non-absorbed photons showed to increase the degradation of the investigated MPs at different initial concentration levels in natural water (20 and 100 µg L^{-1} initial concentration of each micropollutant).

The aluminum reflexive surface effect was noted particularly within lower iron initial concentrations due to a reduction in the light attenuation effect. Results with 20 µg L^{-1} initial concentration of each micropollutant (closer to concentrations detected in real EMWWTPs), in semi-pilot-scale experiments, showed a similar treatment time for 80% removal of ΣMP with 0.054 mM of iron using the aluminum surface and for 0.1 mM of iron without the surface.

Caffeine was the most recalcitrant MP in this study, and it could be used to control the results obtained with the sum of MP. That would mean that monitoring removal of most recalcitrant MPs only would give the key design and efficiency parameters for a reaction system or photoreactor without the necessity of monitoring a massive amount of MPs. This possibility should be evaluated in future studies in depth to see if it applies in general application or not.

Experiments at lab-scale in real secondary EMWWTP with the mix of investigated MPs at both concentrations (20 and 100 µg L^{-1}) corroborated the results obtained in natural water, even though the treatment time and the Fe^{3+}-EDDS complex decomposition were slower. An average load of about 25 ± 5 µg L^{-1} in total of 60 MPs was detected in the real secondary effluent. Reactions were even slower at semi pilot-scale with the RPR, leading to slower Fe^{3+}-EDDS complex decomposition and hydrogen peroxide consumption, which resulted in a treatment time of around 60 minutes with a total consumption of 30 mg L^{-1} H_2O_2 in less than 45 min.

Only experiments with 0.1 mM of iron with and without the aluminum reflexive surface reached 82 % - 90 % removal efficiency, but with 0.054 mM of iron, a maximum of 65 % could be achieved.

Dissolved iron was more persistent in secondary EMWWTP than in natural water, indicating that Fe^{3+}-EDDS complex remained at least 50% up to approximately 50 minutes of the reaction due to the presence of DOM. It lead the higher treatment time required (over 30 minutes) once the reactions were inhibited by light attenuation and ROS scavenging. Results indicated that chloride and sulfate (main inorganic anions in EMWWTP and natural water) would most likely equally or not affect the efficiency of the photo-Fenton process.

The results of this work indicated that the use of an aluminized surface inside these reactors had been confirmed as a suitable option to improve the photo-Fenton reactions in open solar reactors with low doses of iron and for the MPs degradation in secondary EMWWTP, with low turbidity. This suggests that the aluminized RPR could be indicated as an alternative to improve the secondary effluent treatment without increasing iron concentration using less colored effluents or lower liquid depths. Otherwise, reflection properties of the aluminized surface inside water, treated by photo-Fenton at circumneutral pH, during prolonged usage should be evaluated.

Chemical Engineering Journal 385 (2020) 123982

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

New trend on open solar photoreactors to treat micropollutants by photo-Fenton at circumneutral pH: Increasing optical pathway

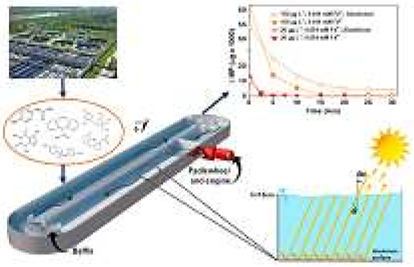
Elizangela P. Costa[a], Melina Roccamante[b,d], Camila C. Amorim[a], Isabel Oller[b,d],
José A. Sánchez Pérez[b,c], Sixto Malato[b,d,*]

[a] *Department of Sanitary and Environmental Engineering, Research Group on Environmental Applications of Advanced Oxidation Processes, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, Belo Horizonte, Minas Gerais 31270-901, Brazil*
[b] *Solar Energy Research Centre (CIESOL), Joint Centre University of Almería-CIEMAT, Carretera de Sacramento s/n, E-04120 Almería, Spain*
[c] *Chemical Engineering Department, University of Almería, Ctra de Sacramento s/n, E-04120 Almería, Spain*
[d] *Plataforma Solar de Almería, CIEMAT, Carretera Senés Km. 4, E-04200, Tabernas, Almería, Spain*

HIGHLIGHTS

- Al to return to reaction non-absorbed photons was desired in Raceway Pond Reactor.
- Iron < 0.1 mM is necessary for reusing in irrigation treated municipal wastewater.
- Studying micropollutants removal at actual concentrations is of utmost importance.
- Removal of most recalcitrant pollutants would give the key design parameters.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Contaminant of emerging concern
EDDS
Photo-Fenton
Raceway pond reactor
Solar light

ABSTRACT

Raceway Pond Reactors (RPRs) have arisen as an interesting and feasible scaling-up option for treating substantial amount of wastewater by solar photo-Fenton process, a technology with short-term perspective due to its high contaminants of emerging concern (CEC) removal efficiency associated with a low reagents' consumption (Fe and H_2O_2) and different strategies to work at near-neutral pH. This work proposes to modify the RPR optical pathway by using a reflexive surface of aluminum at the bottom of it. In this study, modified neutral solar photo-Fenton process with EDDS (Ethylenediamine-N,N'-disuccinic acid) has been applied for the elimination of a mixture of six micropollutants (acetaminophen, caffeine, carbamazepine, diclofenac, sulfamethoxazole, and trimethoprim) at 20 and 100 μg L^{-1} in natural water with different low iron concentrations (0.018-0-1 mM) and liquid depths (7–15 cm). Results showed a similar treatment time for 80% removal of micropollutants with 0.054 mM of iron using the aluminum surface and for 0.1 mM of iron without the surface. Utilizing a reflexive aluminum surface to return to reaction non-absorbed photons permitted to lower the consumption of iron and EDDS without losing efficiency.

---

[*] Corresponding author at: Plataforma Solar de Almería, CIEMAT, Carretera Senés Km. 4, E-04200, Tabernas, Almería, Spain.
E-mail address: Sixto.malato@psa.es (S. Malato).

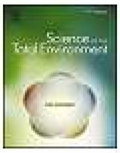
https://doi.org/10.1016/j.cej.2019.123982
Received 4 September 2019; Received in revised form 9 December 2019; Accepted 27 December 2019

Science of the Total Environment 755 (2021) 142624

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv



Aluminized surface to improve solar light absorption in open reactors: Application for micropollutants removal in effluents from municipal wastewater treatment plants

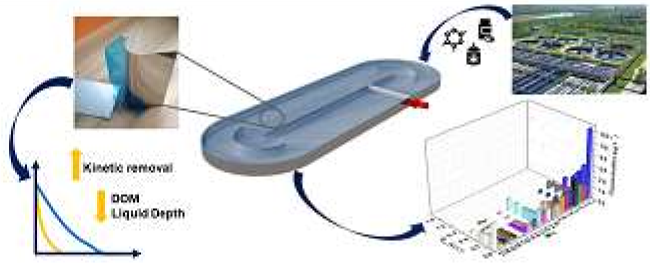
Elizangela P. Costa [a], Melina Roccamante [b,d], Patricia Plaza-Bolaños [b,c], Isabel Oller [b,d], Ana Agüera [b,c], Camila C. Amorim [a], Sixto Malato [b,d,*]

[a] *Department of Sanitary and Environmental Engineering, Research Group on Environmental Applications of Advanced Oxidation Processes, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, Belo Horizonte, Minas Gerais 31270-901, Brazil*
[b] *Solar Energy Research Centre (CIESOL), Joint Centre University of Almería-CIEMAT, Carretera de Sacramento s/n, E-04120 Almería, Spain*
[c] *Department of Chemistry and Physics, University of Almería, Carretera de Sacramento s/n, E-04120 Almería, Spain*
[d] *Plataforma Solar de Almería, CIEMAT, Carretera Senés Km. 4, E-04200 Tabernas, Almería, Spain*

HIGHLIGHTS

- Near-neutral photo-Fenton at low iron concentration on open reactors.
- Low contaminant level simulation approximates kinetic values to real effluents.
- Higher treatment time on real MTWWP effluent than on natural water
- Reaction's inhibition mainly to DOM's light attenuation than inorganic scavenging
- Aluminized surface would improve treatment at low liquid depth and with less DOM.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 July 2020
Received in revised form 28 August 2020
Accepted 22 September 2020
Available online 30 September 2020

Guest Editor: Vítor Jorge Vilar

Keywords:
EDDS
Neutral photo-Fenton reactions
Organic micropollutants
Raceway pond reactor
Real secondary effluent

ABSTRACT

This work proposes the evaluation of an aluminized surface on the bottom of open reactors to perform a photo-Fenton process, at circumneutral pH (using Fe III-Ethylenediamine-N,N'-disuccinic acid complex), for elimination of micropollutants (MPs) in real effluents from municipal wastewater treatment plants (EMWWTP). Firstly, the strategy was to initially investigate the real EMWWTP spiked with several MPs (acetaminophen, diclofenac, carbamazepine, caffeine, trimethoprim and sulfamethoxazole) with 20 and 100 μg L^{-1} in a laboratory scale (evaluated by HPLC-UV) using a solar simulator. Finally, the removal of all MCs present in the real EMWWTP was monitored (evaluated by HPLC-MS) in a pilot-scale (90 L) in a raceway pond reactor (RPR). The treatment time required for degradation above 80% for the investigated MPs was over 30 min, and the predominant effect could be mainly associated with organics present in the real EMWWTP due to the light attenuation and scavenging of radical species. Moreover, the results confirmed that chloride and sulfate would most likely equally not affect the process. The use of an aluminized surface on the bottom of RPRs has been confirmed as a suitable option to improve the photo-Fenton reaction, enabling the use of lower doses of iron. Up to 60 different MPs found in EMWWTP have been successfully degraded using 0.1 mM of Fe at circumneutral pH with a consumption of 30 mg L^{-1} H_2O_2 with less than 45 min.

---

[*] Corresponding author at: Solar Energy Research Centre (CIESOL), Joint Centre University of Almería-CIEMAT, Carretera de Sacramento s/n, E-04120 Almería, Spain.
E-mail address: Sixto.malato@psa.es (S. Malato).

https://doi.org/10.1016/j.scitotenv.2020.142624
0048-9697/© 2020 Elsevier B.V. All rights reserved.

CHAPTER III – MODIFIED CIRCUMNEUTRAL PHOTO-FENTON REACTIONS ON THE REMOVAL OF SELECTED CECS AND DISINFECTION IN REAL SECONDARY EFFLUENTS FROM UASB+ SBTF SYSTEM

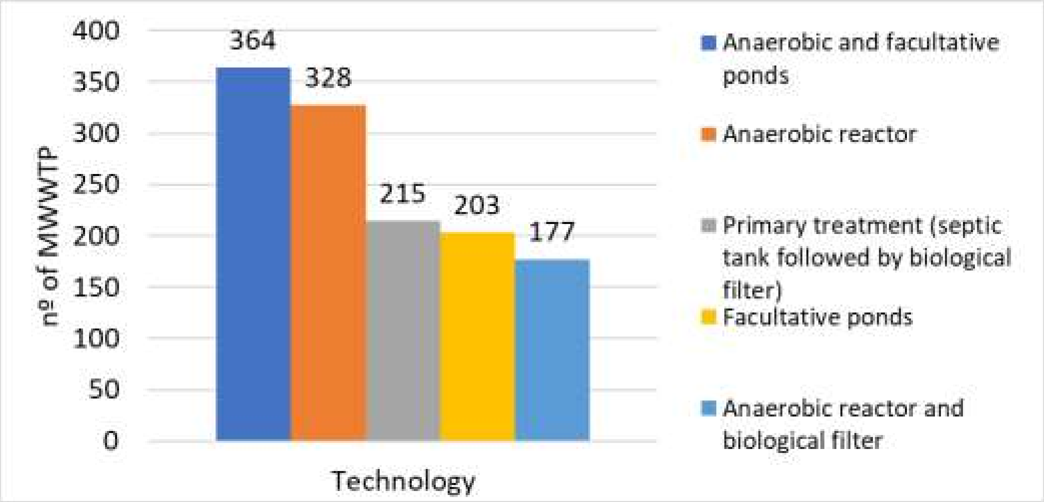
III.1.INTRODUCTION

Biological treatment has been widely used for domestic and industrial wastewater worldwide since it is a technology able to degrade organic matter at relatively low energy and operational costs, usually with low chemical reagent and able to treat a large flow of wastewater. Among the different biological treatments available, the conventional activated sludge system (CAS) is a widely applied technology. Most studies on the removal of CECs in MWWTP, particularly with detailed removal mechanisms, are regarding aerobic processes (ALVARINO *et al.*, 2014, 2018), as also pointed out in Chapter I.

Several parameters influence the performance of the biological treatment not only for organic matter removal but also for CECs removal, including the temperature, hydraulic retention time (HRT), solids retention time (SRT), pH, redox conditions, microbial community, and CECs characteristics (toxicity and physicochemical properties) (ALVARINO *et al.*, 2014; TRAN; REINHARD; GIN, 2018). Considering redox potentials, hybrid biological reactors with distinct conditions have received much attention for their ability to work with a more complex microbial diversity and degrade a larger variety of CECs compounds (LIU; ZHANG; CHANG, 2018; TRAN; REINHARD; GIN, 2018).

In Brazil, the most applied wastewater treatment technologies in terms of number of MWWTP are facultative ponds (anaerobic followed by facultative or just facultative), primary treatment (septic tank followed by biological filter - BF), and anaerobic reactors, that together are used in 1 287 (Figure III.1.1) out of a total of 2 768 MWWTP present in the country a few years ago (ANA, 2017). Those anaerobic processes present lower BOD (biological oxygen demand) removal efficiency (< 60 %) against the CAS system (60 – 80 %) but are a technological choice in the favorable and hot Brazilian climate due to lower operational costs in comparison to the CAS. In this way, in terms of served population, CAS responds to around 16.5 million people (23 % of the 71.7 million in total that is served in Brazil with wastewater treatment), and it is the most frequently used system for larger cities, with 110 MWWTPs in the country (ANA, 2017). Also, most MWWTP in the country are considered very small (35 % of MWWTP with flow lower than 5 L s^{-1}) to the small size (27% of MWWTP with flow between 5.1 – 10 L s^{-1}) (NOYOLA *et al.*, 2012).

FIGURE III.1.1 – Most frequently used treatment processes in Brazil by number of MWWTP. Source: Adapted from **(ANA, 2017).**



Small-sized MWWTP might show more operational problems due to their reduced technical and financial resources (NOYOLA *et al.*, 2012). In the case of stabilization ponds, these might present variable and medium level removal efficiencies for non-polar organic compounds such as endocrine disruptors hormones (estrone, E1; 17-β-estradiol, E2; and 17-α-ethinylestradiol, EE2) (PESSOA *et al.*, 2014). UASB reactors have shown low efficiency for hydrophobic and hydrophilic compounds, while those units followed by post-treatment (polishing ponds, submerged constructed wetlands, and trickling filter) have been able to remove CECs at levels compatible with CAS systems (BRANDT *et al.*, 2013; CHERNICHARO *et al.*, 2015). It is important to highlight how higher removal efficiency for these compounds has been related to higher HRT in both biological and physical-chemical systems, such as ozonation (BOURGIN *et al.*, 2018; BRANDT *et al.*, 2013).

Characteristics of effluents originated from MWWTP with different biological systems can vary depending on the operation and configuration of the systems. In general, CAS has shown better performances for BOD and COD removal in comparison to UASB reactors. However, the association of post-treatment units to UASB enhances the treatment efficiency of these units (SPERLING, 2016). Even though the removal of nutrients and disinfection might not be the main target in these systems, they can present some efficiency (Table III.1.1), which are, in fact, sometimes higher when real systems are monitored (SPERLING, 2016).

TABLE III.1.1 – Average quality of effluent in treatment processes of MWWTP in Brazil. Source: Adapted from (SPERLING, 2016).

Parameter	System			
	Facultative pond	**UASB reactor**	**UASB + high rate trickling filter**	**Conventional activated sludge**
BOD_5 ($mg\ L^{-1}$)	50-80	70-100	20-60	15-40
COD ($mg\ L^{-1}$)	120-200	180-270	70-80	45-120
Suspended Solids ($mg\ L^{-1}$)	60-90	60-100	20-40	20-40
Ammonia ($mg\ L^{-1}$)	>15	>15	>15	<5
Total Nitrogen ($mg\ L^{-1}$)	>20	>20	>20	>20
Total Phosphorus ($mg\ L^{-1}$)	>4	>4	>4	>4
Thermotolerant Coliforms (FC 100 mL^{-1})	10^6-10^7	10^6-10^7	10^6-10^7	10^6-10^7
Helminth eggs (eggs L^{-1})	<1	>1	>1	>1

In this way, the differences in composition and contaminants load among the effluents from different biological systems should be taken into consideration for the investigation of advanced treatments such as the AOP – photo-Fenton, UV/H_2O_2, etc. Different effects have been associated with the composition of aqueous matrixes, such as natural organic matter (NOM), color, turbidity, and inorganic ions.

During the irradiated process, some of the real matrixes' compositions have high optical density and reduce the possibility of photons reaching the catalyst (light attenuation), slowing down the reaction. Also, these substances could act as scavengers, such as inorganic anions (carbonate/bicarbonate, sulfate, chloride, nitrate/nitrite/ammonium, among others) for the radicals formed during the reaction and lead to the formation of less active radical species themselves, which will also slow down the reactions. On the other hand, some ROS could be formed, enhancing the oxidative reaction such as hydroxyl, hydroperoxyl, and superoxide radicals. Another positive effect of substances present in the matrix that can form complexes and help the catalyst regeneration, as well as the degradation of the organic matrix into intermediates that can also act as complex, for example, with carboxylic or phenolic groups (LADO RIBEIRO *et al.*, 2019).

Some secondary effluents might require a pre-treatment prior to AOP technologies in order to reduce possible matrix interference. One example is the case of the El Ejido MWWTP from El Ejido (Almería, Spain). This MWWTP treats the wastewater from a population equivalent to 100 000 with a treatment capacity of 12 459 $m^3\ day^{-1}$. It is characterized by significant inputs from different sources such as greenhouses, the plastic industry, and hospital wastewater. It employs a pre-treatment for solids removal, a primary treatment to remove suspended materials, an activated sludge biological treatment, and a final clarification. The aerobic secondary effluent from this MWWTP presents high inorganic carbon concentration and high ionic content (calcium, magnesium, chloride, sulfates) (Table III.1.2) due to local geological characteristics. Such high inorganic carbon concentration requires a pre-treatment with carbonates neutralization by partial acidification before applying an AOP treatment.

Comparatively, Table III.1.2 also presents physical-chemical characteristics of aerobic and anaerobic effluents from an MWWTP in Brazil, located in the metropolitan region of a big city, and receives contributions of the urban area, including hospitals, landfill leachate, and eventually from industries. It treats the wastewater from an equivalent population of 1 600 000 with a treatment capacity of 388 800 m^3 day^{-1} and employs pre-treatment for solids removal, a primary treatment to remove suspended materials, a conventional activated sludge biological treatment with final clarification after secondary treatment. Lower inorganic carbon and ionic content on this effluent can be observed (Table III.1.2) in comparison to the exemplified effluent from the Spanish MWWTP. In this way, the effluent from the Brazilian MWWTP would not require a pre-treatment prior to any AOP.

In Belo Horizonte city is located the center of research and training on sanitation "*Centro de Pesquisa e Treinamento em Saneamento UFMG / COPASA" – CePTS*, which is one of the most important centers in Latin America for the research on domestic wastewater treatment. The CePTS has several pilot-scale and demonstration-scale units of different technologies, including UASB, biofilters, stabilization ponds, wetlands, UV disinfection, among others. All of these systems receive the wastewater from a local MWWTP after the preliminary treatment (screening, sedimentation tank, and flow measurement – Parshall flume channel).

One of these systems is constituted of a UASB reactor followed by two sponge-bed trickling filters (SBTF) operated in parallel (Figure III.1.2). These one m^3 reactors operate with an organic load of 10 m^3 m^{-2} d^{-1}. The improved quality of the effluent is noteworthy after the combined system of the UASB and trickling filters (Table III.1.2), with lower TSS, alkalinity, COD, and $N\text{-}NH_3^+$ (BRESSANI-RIBEIRO, T; CHERNICHARO; VOLCKE, 2020). According to the physical-chemical characterization (Table III.1.2), this final effluent can be appropriate for the application of advanced irradiated treatment with a lower concentration of suspended solids as well as lower alkalinity, reducing, in this case, the need for application of pre-treatment, such as partial acidification of carbonates.

TABLE III.1.2 – Comparison of secondary effluent quality in different biological treatment processes of two MWWTP from Brazil and Spain.

Parameter	MWWTP - Spain		MWWTP - Brazil				
	Pre-filtered CAS[1]	Filtered CAS[1]	CAS[2]	CAS[3]	Influent[4]	UASB[4]	UASB+TF[4]
pH	7.08	7.46	7.00	6.60	7.70 (0.20)[5]	7.23 (0.15)	7.39 (0.40)
Temperature (°C)	22.2	21.0	25.5	27.2	25.4 (2.7)	25.5 (2.2)	24.3 (2.3)
Cond. (mS cm^{-1}) at 25 °C	2.18	2.27	0.53	0.43	-	-	-
Total COD (mg L^{-1})	-	-	73	70	514 (176)	153 (59)	62 (30)
Filtered COD (mg L^{-1})	-	-	-	-	-	70 (25)	46 (33)
TOC (mg L^{-1})	17.3	16.2	-	14.8	-	-	-
TC (mg L^{-1})	97.6	109.0	-	-	-	-	-
IC (mg L^{-1})	84.7	97.0	-	22.6	-	-	-
Total alkalinity (mg $CaCO_3$ L^{-1})	431	493	89	80	207 (43)	237 (38)	19 (15)
TSS (mg L^{-1})	-	-	41	75	251 (110)	43 (29)	12 (15)
Turbidity (N.T.U.)	342	12	23	-	-	-	-
Na^+ (mg L^{-1})	247	279	-	-	-	-	-
NH_4^+/ N-NH_4^+ (mg L^{-1})	16	16	7	49	30 (9)	30 (9)	6 (3)
K^+ (mg L^{-1})	22	28	-	15	-	-	-
Ca^{2+} (mg L^{-1})	103	98	22	26	-	-	-
Mg^{2+} (mg L^{-1})	64	66	-	3	-	-	-
Total phosphorus (mg L^{-1})	-	-	3.6	-	-	-	-
Cl^- (mg L^{-1})	432	427	63	-	-	-	-
Br^- (mg L^{-1})	6	3	-	-	-	-	-
NO_2^- (mg L^{-1})	3	5	-	-	-	-	0.2 (1.0)
NO_3^- (mg L^{-1})	17	15.5	6	-	-	0 (2)	27 (4)
SO_4^{2-} (mg L^{-1})	131	140	52	-	-	-	-

[1]Effluent after real-scale conventional activated sludge treatment, one sample. [2]Effluent after real-scale conventional activated sludge treatment, an average of 2015's monitoring. [3]Effluent after real-scale conventional activated sludge treatment, an average of three samples was collected in 2017. [4]Averages of Influent, Effluent after UASB treatment, and Effluent after UASB+TF treatment samples during a monitoring period in 2019/2020. [5]Standard deviation from the monitoring period in 2019/2020 in brackets.

FIGURE III.1.2 – UASB reactor (green to the left size) and biological filters (blue in the right)

The presence of alkalinity and other known scavengers of hydroxyl radicals might vary among aerobic and anaerobic effluents. In special for anaerobic processes, due to the control of volatile acids through the buffering capacity of alkalinity, essential to avoid pH shock on these systems and avoid disturbing the microorganisms (CHERNICHARO *et al.*, 2015). In general, it should not exceed a relation of 0.3 between volatile fatty acids (VFA) and bicarbonate alkalinity, which can lead to alkalinity values up to a few hundred mg L^{-1} as $CaCO_3$ depending on the system. For example, values around 200 – 250 mg L^{-1} were obtained for a UASB pilot scale (population equivalent of 500 habitants) (ALMEIDA, 2007). The combination of a post-treatment such as trickling filters can improve the removal of nitrogen, further removal of carbon, suspended solids, as shown previously for the demonstration-scale reactors (BRESSANI-RIBEIRO *et al.*, 2018). After the complete treatment in the system of USAB + SBTF the alkalinity reduced from 237 ± 38 mg L^{-1} in the UASB effluent to 19 ± 15 mg L^{-1} (Table III.1.2).

The high availability of solar irradiation throughout the year and in a vast majority of the country (MARCELINO *et al.*, 2014) makes very interesting the investigation of solar-based technologies for the advanced treatment of EMWWTP in Brazil towards both removal of CECs and disinfection. A recent investigation applied the solar modified Fenton reactions for the tertiary treatment of the effluent from the CAS system of an MWWTP in Brazil, monitoring a mixture of CECs (caffeine, carbendazim, and losartan potassium) spiked at a concentration of 100 µg L^{-1} each (STARLING, 2018; STARLING *et al.*, 2021). Different strategies to work at circumneutral pH with different oxidants (H_2O_2 and $S_2O_8^{2-}$) were evaluated and compared to the conventional process at acidic pH, including single addition (5.5 or 55 mg L^{-1} of dissolved- Fe) and intermittent additions with two doses of 20 mg L^{-1} followed by three doses of 5 mg L^{-1} of dissolved-Fe. Removal of contaminants was around 50 % at solar pilot-scale, while on a solar simulator, removal efficiency reached 80 %. None of the investigated systems generated acute toxicity in the final effluent, and there was a higher disinfection efficiency in the persulfate system (*E. coli* 3 log units, ARB 3-4 log units within a Q_{UV} of 1.9 kJ L^{-1}) than in the solar/Fe/H_2O_2 system. It is important to highlight that in that study, no pre-treatment was necessary once the effluent already had a low inorganic carbon value (Table III.1.2), and the solution pH remained neutral through all the experiments, showing a promising technology without the need for pH adjustment before nor after the treatment. Lower costs were identified for the persulfate system (0.6 € m^{-3}) compared to the hydrogen peroxide system (1.2 € m^{-3}).

Regarding the application of the solar AOP reactions in EMWWTP from the anaerobic process in Brazil, there are almost no published studies. Just more recently published studies were obtained regarding the application of photo-Fenton with different complexing agents and using solar or artificial black light irradiation. However, all these studies focused on a tertiary effluent from an MWWTP that applies a UASB process followed by a combination of physical-chemical treatment (coagulation-flocculation with ferric chloride and flotation) (AMILDON RICARDO *et al.*, 2018; GONÇALVES *et al.*, 2020; SILVA *et al.*, 2021). Modified photo-Fenton reaction with oxalate as a complexing agent was applied for the removal of an antibiotic (650 µg L^{-1} of chloramphenicol) in surface water and the tertiary effluent (AMILDON RICARDO *et al.*, 2018). A high removal efficiency was obtained in both matrixes and irradiation sources, efficiently reducing acute toxicity (91 % to 34 % in the treated effluent evaluating *Vibrio fischeri*). For the tertiary effluent, the best conditions were 192 µmol L^{-1} of ferrioxalate, 1500 µmol L^{-1} of hydrogen peroxide, and at a pH of 6.0. In another study, different complexing agents were investigated (oxalate, citrate, NTA, EDTA, and EDDS) for the removal of an anti- inflammatory (1 µmol L^{-1} of naproxen) also using two oxidants (H_2O_2 and $S_2O_8^{2-}$) (SILVA *et al.*, 2021). The treatment using persulfate as an oxidant agent achieved a higher efficiency for removing naproxen in the tertiary effluent.

Higher efficiency was obtained for Fe/EDDS (1:1) and Fe/NTA (1:1), and the complex Fe/EDDS has also shown an efficient removal on the same effluent for a mixture of pesticides (5 µmol L^{-1} of each ametrine, atrazine, imidacloprid, and tebuthiuron) (GONÇALVES *et al.*, 2020). All processes showed, in general, higher efficiency in less complex matrices (distilled or surface water) in comparison to the tertiary effluent, which showed a high conductivity (0.846 mS cm^{-1}), alkalinity (269 mg $CaCO_3$ L^{-1}), and chloride values (174 mg L^{-1}).

After treatment, effluents might be disposed of or redirected for reuse applications. Regarding effluent disposal in Brazil, it is not established a limit for Total coliforms, *E. coli,* or other fecal indicators organisms in the Brazilian legislation for effluent disposal at the national level, the National Council on the Environment – CONAMA resolution 357 of March 17, 2005 (modified later by CONAMA resolution 430 of May 13, 2011).

There are limits preconized in these resolutions only for the quality of superficial inland water bodies with different salinity levels (fresh, brackish, and saline) accordingly to a classification established on the same legislation and complemented with local legislation for each State. Water bodies are usually classified into different classes, and each one must attend water quality parameters limits according to the predominant desired uses (e.g., human consumption, irrigation, dilution of effluents, etc.). For the specific use of bathing, another legislation establishes more strict limits for Total coliforms, or *E. coli* or *Enterococcus* organisms in the water body (natural or artificial) for this end (CONAMA resolution 274 of November 29, 2000). In this way, studies are usually required to demonstrate that the disposal of treated effluents does not negatively affect the water quality of the receiving water body.

In the case of effluent reuse applications in Brazil, there is not yet specific legislation at the national level in the country. Some resolutions from the National Council on Water Resources (CNRH resolution n.º 54 of November 28, 2005, and resolution n.º 121 of December 16, 2010) define reuse water and also give some very general guidelines. However, these do not specify appropriate technologies or recommended values for water quality parameters. One exception is the Brazilian Technical Normative for the elaboration of projects, construction, and operation for septic tanks, complementary units, and effluent disposal (ABNT NBR 13.969 of September 1997). However, in Brazil, there are many other technologies applied in MWWTP than just septic tanks (Figure III.1.1). This normative recommends using the effluent of septic tanks after a post-treatment (aerobic + conventional filtration - sand or activated carbon + disinfection) according to the desired use shown in Table III.1.3.

TABLE III.1.3 – Some recommended uses for MWWTP effluent reuse in Brazil

Recommended use	Legislation			
	ABNT NBR 13.969 (09/ 1997) (septic tanks)	**São Paulo State Resolution SSRH/SMA/SS n. º 01 06/28/2017**	**Campinas city Resolution SVDS/SMS n. º 09 07/31/2014**	**Ceará State Resolution COEMA n. º 02 of 02/28/2017**
Irrigation of landscaped areas	Yes	Yes	Yes	Yes
Irrigation of agriculture activities and planted forestry				Yes
Orchard, cereal, pastures, and other cultures irrigation	Yes			
Floor washing of public spaces	Yes	Yes	Yes	Yes
Civil construction		Yes	Yes	Yes
Removal of hindrance in sewage and pluvial water drainage		Yes	Yes	Yes
Car washing	Yes	Yes	Yes	Yes
Firefighting		Yes	Yes	Yes
Industrial activities			Yes	Yes
Sanitary discharge	Yes			
Implantation of environmental recuperation projects				Yes
Aquaculture for animals or aquatic vegetables				Yes

Only some local legislation from States or cities provides more detailed recommendations, including different reuse classifications, appropriate use, and limits for the effluent quality parameter for each classification. Some examples are the in the city of São Paulo (Law n. º 16.171 of April 22, 2015), the city of Campinas (Resolution SVDS/SMS n. º 09 of July 31, 2014), the State of São Paulo (Resolution SSRH/SMA/SS n. º 01 of June 28, 2017), and the State of Ceará (Law n. º 16.033 of June 2, 2016, and Resolution COEMA n. º 02 of February 28, 2017).

In the State of São Paulo and Campinas city, some uses are indicated, with the addition of industrial activities in Campinas city (Table III.1.3). In the State of São Paulo, it is recommended to use the effluent after secondary treatment, disinfection, and filtration. In the Ceará state, detailed legislation is presented, with more categories for reuse (aquaculture and agriculture activities), and in the industrial activities reuse recommendation, there is a list for specific inorganic parameters accordingly to different industrial processes.

A summarized comparison of some parameters recommended threshold values for reuse from these legislations are presented in the Table III.1.4.

TABLE III.1.4 – Some recommended parameters values for treated municipal wastewater reuse in Brazil.

Parameter	Legislation			
	ABNT NBR 13.969 (09/ 1997)[1]	**São Paulo State Resolution SSRH/SMA/SS n. º 01 06/28/2017**	**Campinas city Resolution SVDS/SMS n. º 09 07/31/2014**	**Ceará State Resolution COEMA n. º 02 of 02/28/2017**
BOD$_5$ (mg L^{-1})	-	≤10 - ≤30	5 – 30	20-60
pH	6.0 – 8.0	6 - 9	-	6.0 – 8.5
Turbidity	<5 - <10	≤0.2 (membrane filtration) - ≤2	1 - 5	-
Total Suspended Solids (mg L^{-1})	-	≤0.5 (membrane filtration) - ≤30	5 - 30	-
Total Dissolved Solids (mg L^{-1})	<200 – not applicable	<450 - <2000	-	-
Conductivity (µS cm^{-1})	-	<700 - <3000	-	<3000
Sodium (mg L^{-1})	-	[2]	200 – 200	[2] RAS=15 for agriculture
Residual chlorine (mg L^{-1})	0.5 – 1.5	<1 - <1	Max. 1.5 – 3.0 (free Max. 1.0 – 2.0)	-
Chloride (mg L^{-1})	-	<106 - <350	250 - 250	-
Boron (mg L^{-1})	-	<0.7 - <2.0	-	-
Thermotolerant Coliforms (CFU 100 mL^{-1})	(Fecal coliforms MPN 100 mL^{-1} <200, <500 or <5000)	Not detectable - <200 (<120 in the case of *E. coli*)	<100 - <200 (or *E. coli*)	Not detectable (direct irrigation of vegetables eatable parts) 1000, 5000, 10000
Helminth eggs (eggs L^{-1})	-	<1 - <1 (<0.1 in the case of *Ascaris sp*)	- <1	Not detectable (direct irrigation of vegetables eatable parts) - <1
Giardia and *Cryptosporidium* (cysts or oocysts L^{-1})	-	-	- <0.05	-

[1] DO - Not applicable - >2 mg L^{-1}. [2] Not applicable, but instead is defined a sodium adsorption ratio (RAS 0-12 accordingly to conductivity ranges), RAS = $Na^{+}/ [(Ca^{2+} Mg^{2+})/2]^{1/2}$

Around the world, several localities/ organizations have specific legislation or recommendations for reuse applications, including California, Nevada, Washington, and Texas States in the USA, USA-EPA, Australia, Israel, Singapore, Mediterranean countries, European Union, and the World Health Organization (WHO) (VOULVOULIS, 2018).

Even though several countries have implemented reuse to solve water scarcity problems, there is still a great potential to be explored, and the global movement towards a circular economy is expected to expand the global reuse. One example is the recently implemented regulation for agricultural water reuse in the EU (Regulation EU 2020/741 of the European Parliament and the Council of 25 May 2020) according to United Nations Sustainable Development Goal on Water (SDG 6) by 2030. In Europe, this priority for the incentive of reuse in agriculture considers urban wastewater treatment plants as a reliable and less variable water supply (independent from seasonal phenomena such as droughts) and able to provide nutrients reducing the need for fertilizers (EUROPEAN COMISSION, 2021). Therefore, reuse is considered beneficial for both the environment and agriculture.

Applying an overall and brief comparison of some of these reuse legislations around the world (VOULVOULIS, 2018) with some of the local Brazilian recommendations (Table III.1.4), it is possible to see that only the resolution from Ceará state is closer to foreign recommendations in terms of reuse possibilities and detailed directions. There are recommended values for different reuse categories, with less or more strict values for different parameters in accordance with each use. On the other hand, only legislations from São Paulo state bring other organisms into the recommendations (Giardia and *Cryptosporidium*). There is a lack of recommendations for viruses and CECs, for example.

Considering this global perspective of increasing the potential of reuse, Brazil should soon progress to a national level recommendation for reuse, particularly with incentives towards water reuse in agriculture, a major consumer of water in the country. A national guideline on the topic would likely be constructed upon both local legislation and the successful international experience.

In this way, considering the high and continuous availability of solar radiation in most of Brazil's territory and the urgency for studies with advanced alternative treatments with lower costs, the application of the circumneutral solar photo-Fenton in open reactors such as the RPR becomes an interesting proposal. Since most studies with solar photo-Fenton for CECs and disinfection on RPR did not focus on anaerobic and other secondary EMWWTP, this work aims to apply a modified solar photo-Fenton with EDDS for disinfection (*E. Coli* and Total Coliforms) and the removal of a group of selected CECs (acetaminophen, caffeine, carbamazepine, diclofenac, sulfamethoxazole, and trimethoprim) spiked in secondary effluent from a UASB + STBF system in Brazil, at lab-scale.

III.2.OBJECTIVES

III.2.1.General objective

The main objective of this chapter is to evaluate the efficiency of circumneutral solar photo-Fenton reactions on the removal of a group of CECs (acetaminophen, caffeine, carbamazepine, diclofenac, sulfamethoxazole, and trimethoprim) and disinfection (*E. Coli* and Total Coliforms) in secondary anaerobic+aerobic EMWWTP from a demonstration-scale UASB+STBF system.

III.2.2.Specific objectives

The specific objectives of this work are as follows:

- Evaluate a modified photo-Fenton reaction with complexing agent EDDS at circumneutral pH in bench-scale with artificial solar irradiation for the removal of selected CECs in a secondary EMWWTP from a demonstration-scale UASB+STBF system.
- Evaluate a modified photo-Fenton reaction with complexing agent EDDS at circumneutral pH in bench-scale with artificial solar irradiation for the disinfection (*E. Coli* and Total Coliforms) in a secondary EMWWTP from a demonstration-scale UASB+STBF system.

III.3.MATERIALS AND METHODS

III.3.1.Chemicals

All reagents used for liquid chromatography analysis were HPLC-grade and acquired from Sigma-Aldrich or J.T. Baker, including methanol, acetonitrile, and formic acid. Acetaminophen (Sigma-Aldrich), caffeine (Fluka), carbamazepine (Sigma-Aldrich), diclofenac (Sigma-Aldrich), sulfamethoxazole (Sigma-Aldrich), and trimethoprim (Sigma-Aldrich). All reagents used during experiments and analysis were of analytical grade, including Sulphuric acid (98 %; Neon), hydrogen peroxide (35 %; Neon), ferric sulfate (75 %; Synth), ethylenediamine disuccinic acid (EDDS, 35 %; Sigma-Aldrich), ortho-phenanthroline (Vetec), ammonium acetate (Neon), acetic acid (Neon), ascorbic acid (Dinâmica), ammonium metavanadate (Nuclear).

III.3.2.Analytical methods

III.3.2.1.Sample preparation

All samples for chromatographic analysis were mixed with acetonitrile in a 90:10 proportion to stop oxidative reactions and filtered through a 0.22 µm PVDF Filtrilo® filter. For all other analyses, samples were filtered with a 0.45 µm PVDF Filtrilo® filter.

In samples for Total Coliforms, *E. coli*, DOC, and COD analyses, the catalase enzyme (18.4 mg L^{-1} at 460 mg L^{-1} 0.04 M phosphate buffer, pH 7, SIGMA CAT. Nº. C9322, Steinheim am Albuch, Germany) was added to consume remains of hydrogen peroxide (1 mL for each 24 mL of the sample).

III.3.2.2.Micropollutants monitoring

Quantification of target MPs was performed by ultra-performance liquid chromatography with an ultraviolet diode array detector (UPLC-UV/DAD) (Shimadzu, model NEXERA-i LC-2040C 3D Plus). All UPLC analyses were executed with a reverse-phase column Shim-pack GIST-HP (C18 3 µm, 150 mm x 3.0 mm) (Part Number 227-30040-05) connected previously to a pre-column Shim-pack GIST-HP(G) (C18 3 µm, 10 mm x 3.0 mm) (Part Number 227-30047-02), with a flow of 0.6 mL min^{-1} and volume of injection of 50 µL. Solvent A consisted of Milli- Q® water with 0.1% formic acid, and solvent B was acetonitrile. A gradient flux was applied by varying solvents A and B accordingly to Table III.3.1. Total analysis time was 16 minutes, including 1.5 minutes at the beginning and end of analysis for re-equilibrium of the column to initial conditions. The maximum pressure applied was 300 bar, while the oven temperature was set to 40 °C.

TABLE III.3.1 – Gradient flux of solvents during HPLC analysis in Brazil

Time (minutes)	Solvent A (%)	Solvent B (%)
0	90	10
1.50	90	10
11.50	0	100
13.50	0	100
14.50	90	10
16.00	90	10

Standard solutions of 10, 20, 40, 60, 80, 100 and 120 µg L^{-1} of the mix of the 6 MPs (acetaminophen, caffeine, trimethoprim, sulfamethoxazole, carbamazepine, and diclofenac) were prepared in 90 % matrix (demineralized water or filtered secondary effluent) with 10 % acetonitrile and filtered with 0.22 µm PVDF syringe filters. Standard solutions for the calibration curve were prepared in each matrix from a standard intermediary solution of 1 mg L^{-1} also in each matrix. The intermediary solution was prepared from a stock solution of 0.5 g L^{-1} in methanol. Standards were injected 5 times, and all parameters of each calibration curve were analyzed. All solutions were prepared in glassware previously rinsed with both Milli-Q® water and acetonitrile, including volumetric glass flasks and glass pipettes.

Each compound's retention time, maximum quantification wavelength, and calibration curve (10 – 120 µg L^{-1}) are presented in Table III.3.2 for the demineralized water matrix and Table III.3.3 for filtered secondary effluent matrix. Calibration curves for each compound were obtained using a linear equation. In APPENDIX IV is shown a chromatogram from an injection of a standard solution of 100 µg L^{-1}, and details of caffeine spectrum and peak purity.

TABLE III.3.2 – UPLC-UV/DAD wavelength of maximum absorbance, retention time, and calibration curve parameters for each investigated compound at 50 µL injection volume in demineralized water matrix (n =5)

Micropollutant	λ_{max} (nm)	R_t (min)	a	b	R^2
Acetaminophen	3.437	243	1017	333	0.9990
Caffeine	4.825	272	625	233	0.9997
Trimethoprim	5.109	269	108	92	0.9993
Sulfamethoxazole	6.765	269	957	344	0.9997
Carbamazepine	7.912	285	495	237	0.9979
Diclofenac	10.108	269	244	140	0.9963

TABLE III.3.3 – UPLC-UV/DAD wavelength of maximum absorbance, retention time, and calibration curve parameters for each investigated compound at 50 µL injection volume in filtered secondary effluent matrix (n =5)

Micropollutant	λ_{max} (nm)	R_t (min)	a	b	R^2
Acetaminophen	243	3.447	457	340	0.9996
Caffeine	272	4.780	200	230	0.9997
Trimethoprim	269	5.097	42	93	0.9996
Sulfamethoxazole	269	6.752	731	361	0.9999
Carbamazepine	285	7.893	495	237	0.9991
Diclofenac	269	10.081	210	164	0.9998

III.3.2.3.Chemical Oxygen Demand analyses

For Chemical Oxygen Demand (COD) analyses the method 5220 D. (APHA, 2005) closed reflux and colorimetric determination. A calibration curve was prepared in two ranges: 0-100 (Eq.III.1) and 0-1000 mg L^{-1} of COD (Eq.III.2) with potassium hydrogen phthalate standard (Merck®).

$$[COD, mg\ L^{-1}] = 0.0017857 + (0.000156 \times Absorbance) \quad R^2 = 0.983 \qquad \text{(Eq.III.1)}$$

$$[COD, mg\ L^{-1}] = 0.0015714 + (0.00016 \times Absorbance) \quad R^2 = 0.999 \qquad \text{(Eq.III.2)}$$

III.3.2.4.Total and dissolved iron analyses

Total and dissolved iron concentration was measured spectrophotometrically (Hach® spectrophotometer DR 6000) at 510 nm according to ISO 6332 (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 1988) with the 1,10-phenanthroline method.

The buffer solution was prepared with 250 g ammonium acetate, 150 mL of deionized water, and 700 mL glacial acetic acid, while the 1,10-phenanthroline solution was prepared by dissolving 100 mg 1,10-phenanthroline monohydrate ($C_{12}H_8N_2.H_2O$) in 100 mL water.

Always 2.5 mL of samples (diluted if necessary) were mixed with 1 mL of the 1,10- phenanthroline solution, 1 mL of the buffer solution, and one tip of a micro spatula of ascorbic acid. After homogenization and 5 minutes stabilization, samples were measured in the spectrophotometer, and the concentration calculated from absorbance results against the calibration curve. A calibration curve from 0.4 up to 9 mg L^{-1} was prepared, which was linear on this interval (Equation III.3).

$$[Fe^{2+}, mg\ L^{-1}] = 0.0517 + (6.5847 \times Absorbance) \quad R^2 = 0.9995 \qquad \text{(Eq.III.3)}$$

III.3.2.5.Hydrogen peroxide analyses

Residual concentration of hydrogen peroxide during experiments was quantified using the ammonium metavanadate method accordingly to Nogueira; Oliveira; Paterlini (2005). This method consists of a fast and stable formation of a red-orange complex between H_2O_2 and ammonium metavanadate in an acidic pH medium (Equation III.4).

$$VO_3^- + 4H^+ + H_2O_2 \rightarrow VO_2^{3+} + 3\,H_2O \qquad \text{(Eq. III.4)}$$

Samples (2 mL) are mixed with the 9 mol L^{-1} ammonium metavanadate solution (1 mL) and a 0.058 mol L^{-1} sulfuric acid solution (7 mL). Then absorbance is measured on the wavelength of maximum absorption of 450 nm. The concentration is obtained against a calibration curve (Equation III.5, 1.4 – 136 mg L^{-1}).

$$[H_2O_2, mg\ L^{-1}] = 13.976 - (405.08 \times Absorbance) \quad R^2 = 0.9998 \qquad \text{(Eq. III.5)}$$

III.3.2.6.Sulfate’s analyses

The concentration of total sulfates during effluent characterization and after the investigated treatment were analyzed by the turbidimetric method 4500 (APHA, 2005) using precipitation with barium chloride. This method consists of forming barium sulfates that precipitate and can be analyzed by modifying the solution turbidity or absorbance determination at a wavelength of 420 nm.

Samples and blank with demineralized water are analyzed in duplicate (50 mL) in Erlenmeyers (125 mL). Samples or blank are mixed with the buffer solution “A” (10 mL), and absorbance is measured on the wavelength of 420 nm. After adding one tip of a micro spatula of barium chloride (20-30 mesh) the sample is immediately mixed for 60 ± 2 s. In sequence, the solution is left resting 5 ± 0.5 min for the precipitate formation. Then absorbance is measured again on the wavelength of 420 nm. The concentration is obtained against a calibration curve (Equation III.6, 5– 40 mg L^{-1}) by subtracting the absorbance from each sample after the barium chloride addition from the absorbance before its addition.

$$[SO_4^{2-}, mg\ L^{-1}] = 1.17 + \left(165.6 \times Absorbance_{After-Before\ BaCl_2}\right);\ R^2 = 0.9953 \quad \text{(Eq.III.6)}$$

III.3.2.7.Nitrate and orthophosphate analyses

The concentration of total nitrates and orthophosphates in samples was analyzed by a Hach® DR 6000 spectrophotometer using commercial kits and standardized pre-programmed methods. For orthophosphates, the Molybdovanadate Method 8114 was applied (0.3 – 45 mg L^{-1} PO_4^{3-}). This method is based on the reaction of orthophosphates with molybdate anions at an acidic pH, forming phosphates/molybdate complexes. In the presence of vanadium, the yellow-colored molybdovanadophosphoric acid is produced, which can be read at a wavelength of

430 nm in the spectrophotometer. The dissolved or filterable ortophosphates were determined after filtration with a 0.45 µm PVDF Filtrilo® filter.

As for nitrates, the NitraVer® 5 cadmium reduction method (Method 8039) was applied (0.3 – 30 mg L^{-1} NO_3^-). In this method, the nitrate present in the sample is reduced to nitrates with cadmium metal. Nitrite anions produced then react with sulfanilic acid in an acidic pH medium to form the diazonium salt as an intermediate. In combination with gentisic acid, this salt forms a colored amber solution that can be measured at the wavelength of 500 nm in the spectrophotometer.

III.3.2.8.Total coliforms and *E. coli*

Escherichia coli and Total Coliforms were evaluated with Colilert (IDEXX®) 24 hours direct test approved by USEPA (APHA, 2005). The method is based on the use of two substrates for the simultaneous identification of total coliforms and *E. coli*. For this, two nutrient-indicators, ONPG (o-nitrophenyl) and MUG (4-methyl-umbelliferyl), work as the primary source of carbon and are metabolized by specific enzymes (coliform enzyme β-galactosidase and the *E. coli* enzyme β-glucuronidase). The metabolization of these nutrients by each enzyme produces a change in the medium: β-galactosidase metabolize ONPG and changes it from colorless to yellow, while β-glucuronidase metabolize MUG and create fluorescence. Other components in the substrate work to suppress non-targeting organisms and assure the method's selectivity.

Samples were diluted (10^{-2} to 10^{-1}) to 100 mL volume using sterile pipettes and sterile unbuffered water. One packet of reagent powder was added to the sample in a sterile flask, properly mixed, and transferred to a Quanti-Tray, sealed according to instructions. In sequence, the Quanti-Tray was incubated at 35 °C for 24 h. After this period, results were read: if there was no yellow color, the test was negative. If the sample had a yellow color, the presence of total coliforms was confirmed. In this case, it was checked for blue fluorescence by placing a 6 W (365 nm) UV light within 10 cm of the sample. If blue fluorescence was present, the presence of *E. coli* was confirmed. By counting the number of positive yellow wells and the number of yellow and blue-fluorescent wells, the MPN $100mL^{-1}$ was determined using the table provided with the Quanti-Tray. This method detection limit (DL) is 10 MPN $100mL^{-1}$ (inferior limit) and 2420 MPN $100mL^{-1}$ (superior limit, samples with a higher level of bacteria counting can be diluted before analysis). No filtration step was used for these samples.

III.3.3.Experimental set-up

III.3.3.1.Investigated matrix

Experiments were performed with a real secondary anaerobic+aerobic effluent from the UASB+SBTF system previously described (Figure III.1.2), located in Brazil. The effluent was collected after the trickling filter in five samplings of about 20 L, transported in polystyrene boxes with ice, and characterized soon after the arrival at the UFMG facilities.

All effluent was pre-treated to remove suspended solids with stainless steel mesh filters of 100 µm and 25 µm followed by the quantitative paper filter (medium flow; 4-7 µm particles' retention), in this respective order (Figure III.3.1 and Figure III.3.2). A sample of the effluent after this process was also characterized (Table III.3.4).

FIGURE III.3.1 – Pre-treatment filtering process: stainless steel mesh filters (100 µm and 5 µm) and medium flow quantitative paper

FIGURE III.3.2 – Secondary effluent from the UASB + SBTF system aspect before and after filtration

TABLE III.3.4 – Characterization of effluent from the secondary treatment of UASB+SBTF system (n = 4)

Parameter	UASB + SBTF - Brazil			
	Secondary effluent (one sample)	**Filtered secondary effluent (one sample)**	**Secondary effluent Average of all samples**	**Filtered secondary effluent Average of all samples**
pH^{1}	7.84	7.89	6.47±0.97	7.76±0.09
Temperature (ºC) ^{1}	21.4	22.2	23.2±2.2	20.8±0.8
Cond. (mS cm^{-1}) at 25 ºC^{1}	0.60	0.60	0.61±0.05	0.54±0.08
DO (mgO_2 L^{-1}) ^{1}	7.03	7.39	6.47±0.40	8.2±0.57
ORP (mV) ^{1}	202	200	280±55	327±90
Total Coliforms (MPN 100mL^{-1})	1.30x10^{6}	1.99x10^{5}	1.18x10^{5}±5.92 x10^{5}	1.17x10^{5}± 5.96x10^{4}
E coli (MPN 100mL^{-1})	1.99x10^{4}	1.48x10^{4}	9.68x10^{4}±1.14 x10^{5}	2.41x10^{4}± 4.69x10^{3}
DOC (mg L^{-1})^{2}	7.6	11.0	-	-
TC (mg L^{-1})^{2}	41.0	41.9	-	-
IC (mg L^{-1})^{2}	33.4	30.9	-	-
TN (mg L^{-1})^{2}	35.4	35.1	-	-
Total alkalinity (mg $CaCO_3$ L^{-1})	-	30.1	-	-
Turbidity (N.T.U.)^{1}	11.9	3.9	14.6±6.3	1.2±1.4
TSS (mg L^{-1})	16.9	-	-	-
TDS (mg L^{-1}) ^{1}	419	414	414±4	301±80
COD (mgO_2 L^{-1})	58	60	-	-
Total - PO_4^{2-} (mg L^{-1})^{3}	-	-	15±2	16±2
Dissolved - PO_4^{2-} (mg L^{-1})^{3}			14±0	14±1
NO_3^- (mg L^{-1})^{3}	-	-	12±4	15±9
SO_4^{2-} (mg L^{-1})^{4}	20 ^{2}	-	35±8	38±4

^{1}Multiparameter probe YSI ProDDS ^{2} For Dissolved Organic Carbon (DOC), Total Inorganic Carbon (TIC), Total Carbon (TC), and Total Nitrogen (TN) measurement, a Shimadzu TOC-VCPN Total Organic Carbon Analyzer was used ^{3}Hach DR 6000 spectrophotometer kits ^{4}Turbidimetric Method 4500 from the Standard Methods (APHA, 2005)

III.3.3.2.Target micropollutants (MPs)

The same six pharmaceuticals selected in Chapter II were used as target compounds for this chapter: acetaminophen (ACE), caffeine (CAF), carbamazepine (CARBA), diclofenac (DIC), sulfamethoxazole (SULF), and trimethoprim (TRI) (Table II.3.7). Characterization of their spectrum in demineralized water at three pH values (3.0, natural, and 9.0) were evaluated with a Shimadzu spectrophotometer model UV-2600 using a 10 mm quartz cuvette (APPENDIX V).

For all experiments with the target compounds, always a mixture of the six MPs was used with a concentration of each one around 100 µg L^{-1} (80 - 110 µg L^{-1}), totalizing approximately 600 µg L^{-1} of MPs.

A stock solution in methanol with 2.5 g L^{-1} of each micropollutant was prepared by dissolving the compounds and left under constant agitation overnight, protected from light, for complete homogenization. After preparation, the stock solution was stored at a low temperature (4 ºC) and in darkness. For experiments in lab-scale, an intermediary solution in the investigated matrix was prepared at a concentration of 2 mg L^{-1} to make possible the addition of the MPs for the experiments. Samples from experiments were analyzed by direct injection with UPLC-UV/DAD.

III.3.3.3.Lab-scale experiments with artificial sunlight

A solar simulator from Atlas - SunTest CPS+ - was used for lab-scale experiments (Figure III.3.3). This equipment had a daylight filter, and it was programmed for a spectrum emission in the range of 300-800 nm, with total radiation of 268 W m^{-2} and total UVA (300 – 400 nm) radiation of 30 W m^{-2}. A rectangular glass vessel was used (0.193 m x 0.098 m; 0.13 m of height) with covered opaque walls (Figure III.3.4). For a liquid depth level of 10 cm, the volume in the reactor was adjusted to 1.88 L.

FIGURE III.3.3 – SunTest CPS+ (ATLAS) and covered glass reactor (right side)

FIGURE III.3.4 – Glass covered reactor in the inside and as positioned in the SunTest CPS+ (ATLAS)

The reaction vessel was placed just inside the solar simulator receiving irradiation from the top directly on the liquid surface (A_s = 189 cm^2) (Figure III.3.4). The reaction medium was continuously mixed with a magnetic stirrer at a fixed position (60 %), and the system was operated in batch mode.

The UASB+SBTF secondary effluent was evaluated after the complete pre-treatment (Figure III.3.1 and Figure III.3.2), which reduced on average 92 % of the effluent's turbidity. The effluent was evaluated without spiking and spiked with a concentration of around 100 $\mu g\ L^{-1}$ of each MP.

All reactions were performed at the natural matrix pH value (7.5 – 8.5) without acidification. Considering the lower content of alkalinity and inorganic carbon of this secondary effluent (Table III.1.2 and Table III.3.4) there was no need to reduce carbonates by partial acidification.

Fe^{3+}-EDDS complex ratio 1:2 was applied for all experiments. The Fe^{3+}-EDDS complex was prepared in the laboratory and used immediately after mixing $Fe_2(SO_4)_3.5H_2O$ (previously dissolved in acidic pH) and EDDS, as described in the previous Chapter II (Figure II.3.18). The iron concentration applied was 5.5 mg L^{-1} (0.1 mM) because it was the condition that previously resulted in the highest MPs removal efficiency. In the same way, the hydrogen peroxide concentration used in experiments was 50 mg L^{-1} (1.47 mM), as previously evaluated.

Control experiments of photolysis and photolysis-H_2O_2 were performed for the spiked UASB+SBTF secondary effluent. A dark reaction with the Fe^{3+}-EDDS complex and H_2O_2 was not performed since, as demonstrated in the previous chapter, there is no decomposition of the Fe^3+-EDDS complex without UV-light, no formation of radicals, neither iron species are available for promoting coagulation in the system.

The maximum experimental time was 120 minutes. The number of samples, and therefore volume withdrawn, varied accordingly to this time but not exceeding 10 % of the total volume in reaction. In general, 8 to 12 samples were analyzed per experiment, with 5 minutes intervals during the first 30 minutes of reaction, followed by 10 or 30 minutes intervals until the end.

Accumulated energy per volume unity (Q_{UV}, kJ L^{-1}) was calculated as previously demonstrated (Equation II.8).

III.4.RESULTS AND DISCUSSION

III.4.1.Removal of MPs in the UASB+SBTF secondary effluent by modified circumneutral photo-Fenton reaction

The specific order of degradation of each MPs in the UASB+SBTF secondary effluent was the same as obtained in previous results with natural water and with the CAS secondary effluent (Chapter II). Diclofenac and acetaminophen were the first to be removed, followed by trimethoprim and carbamazepine with an intermediary removal efficiency, and finally sulfamethoxazole and caffeine as the most resistant to the treatment (Figure III.4.1). This pattern was observed in all experiments, except the photolysis and photolysis-H_2O_2, with no substantial degradation for all compounds (except diclofenac) (Figure III.4.2).

The removal efficiency for ΣMPs was 86 % on average for 0.1 mM-Fe and 1.47 mM (50 mg L^{-1}) of H_2O_2 at 10 cm liquid depth (Figure III.4.2). The control experiments of photolysis and photo-H_2O_2 at 10 cm showed low removal of MPs (11 % and 14%, respectively) (Figure III.4.2). Almost no consumption (2 %) of H_2O_2 occurred in the photo-H_2O_2 system, in accordance with such low removal of contaminants (Figure III.4.3).

Diclofenac was the MP most sensible to photolysis, as also shown in the discussion of results of Chapter II. This pharmaceutical is known to be degraded by photolysis and AOPs (ALHARBI *et al.*, 2017; CAPODAGLIO; BOJANOWSKA-CZAJKA; TROJANOWICZ, 2018).

FIGURE III.4.1 – Degradation of six MPs (100 µg L^{-1} each) in spiked real secondary UASB+SBTF effluent by solar photo-Fenton modified with Fe^{3+}:EDDS 1:2, 0.1 mM of iron, 1.47 mM H_2O_2, and 10 cm liquid depth.

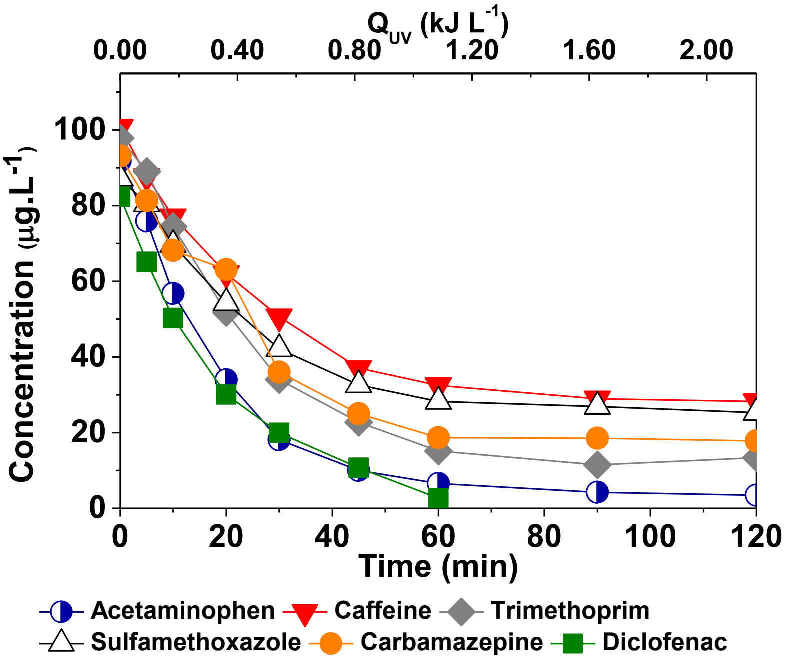
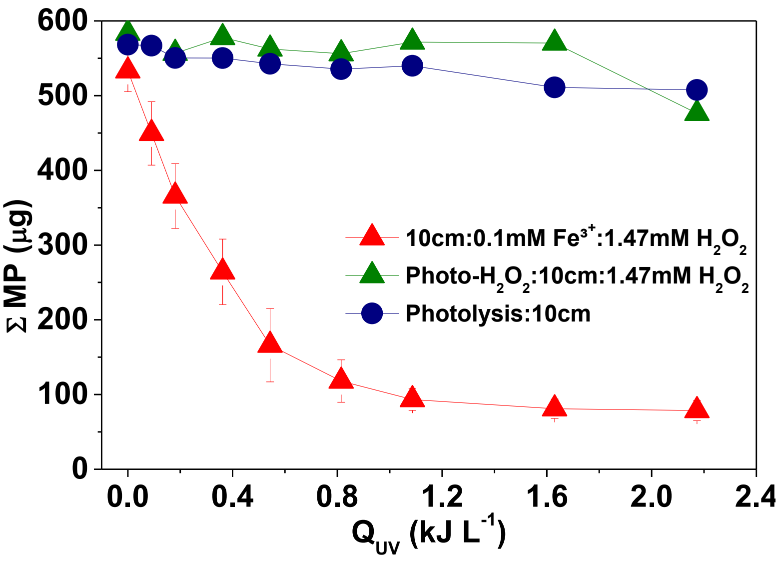


FIGURE III.4.2 – ΣMPs removal in spiked (100 µg L^{-1} each MP) real secondary UASB+SBTF effluent by solar modified photo-Fenton, photolysis and photo-H_2O_2. Fe^{3+}:EDDS 1:2.



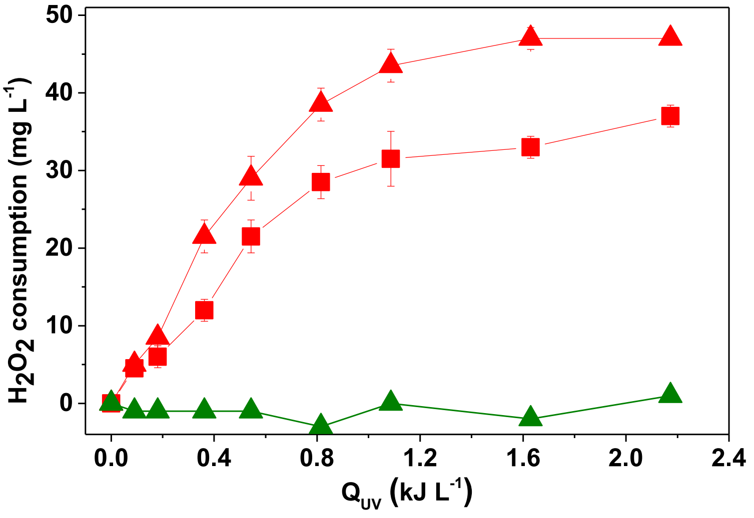
Results with the initial average degradation rate of reactions are shown in Table III.4.1. Treatment time to achieve 80 % of MP removal was 48 minutes, resulting in an overall bit longer treatment time for the degradation of ΣMPs in the UASB+SBTF in comparison to results in the secondary CAS effluent in Chapter II (around 30 min, Q_{UV} of 0.40 kJ L^{-1} at liquid depth of 15 cm). This was not expected since the reactor used in experiments from this Chapter III presents lower liquid depth (10 cm) and smaller surface area that, consequently, result in a smaller reaction volume and a higher accumulation of energy in the system (Q_{UV} of 0.87 kJ L^{-1} at 48 min). Once these matrices did not differ much on alkalinity and DOC content, and turbidity on the filtered UASB+SBTF (1.2±1.4 N.T.U.) was even lower than in the secondary CAS effluent (11.9 N.T.U.), a hypothesis is a different composition in the type of organic substances from these matrices (humic, fulvic, and protein- like/soluble microbial products). Different substances can be more or less reactive towards hydroxyl radicals and, therefore, a distinct composition could make an effluent more or less susceptible to reaction (LI *et al.*, 2013).

TABLE III.4.1 – Initial degradation rate (r_0, µg min^{-1}) and treatment time for attaining 80 % ($t_{80\%}$, min) degradation of MPs by modified photo-Fenton reaction with Fe^{3+}:EDDS 1:2 in spiked (100 µg L^{-1} each MP) real secondary UASB+SBTF effluent.

MPs	10 cm: 0.1 mM Fe^{3+}: 1.47 mM H_2O_2	
	r_0, µg min^{-1}	**$t_{80\%}$, min**
ΣMP	22.5	48
ACE	4.6	27
CAF	3.2	>120
TRI	4.2	39
SUL	3.1	>120
CARB	3.8	52
DIC	3.7	28

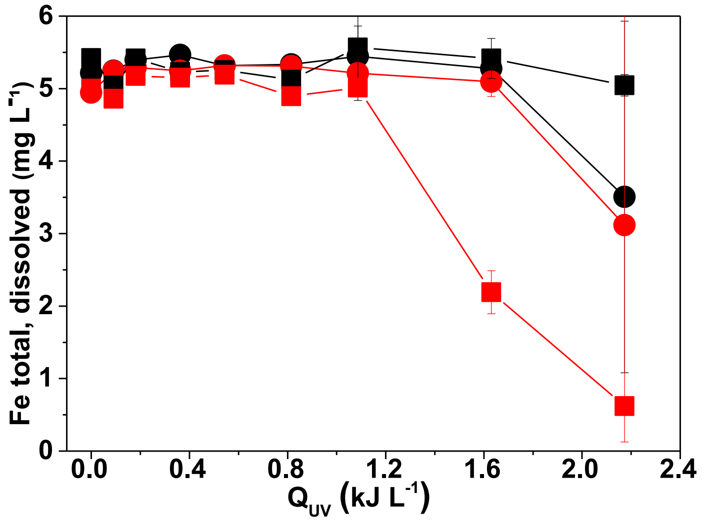
In the case of the photo-Fenton system, a fast initial hydrogen peroxide consumption occurred for both effluents (spiked with MP and not spiked) (Figure III.4.3), but afterward, the final H_2O_2 consumption was 94 % and 74 %, respectively. This lower consumption of hydrogen peroxide in the not spiked effluent might be related to earlier precipitation of iron (reduction of dissolved iron at the end of reaction) in the not spiked effluent comparatively to the spiked effluent (Figure III.4.4).

FIGURE III.4.3 – Hydrogen peroxide consumption during —▲— solar photo-H_2O_2 treatment and solar modified photo-Fenton in real secondary UASB+SBTF effluent —▲— spiked (S) at MPs 100 µg L^{-1} each or ■ not spiked (NS), at 10 cm liquid depth with Fe^{3+}:EDDS 1:2, 0.1 mM of iron, and 1.47 mM H_2O_2.



The total and dissolved iron concentrations during all treatments remained constant during most of the time, and only after 60 - 90 minutes of reaction iron precipitation start to occur (Figure III.4.4). The precipitation started earlier in the not spiked effluent (around 60 min, QUV of 1.1 kJ L^{-1}).

FIGURE III.4.4 – Total (black symbols) and dissolved (red symbols) iron during modified solar photo-Fenton in real secondary UASB+SBTF effluent —●— —●— spiked (S) at MPs 100 µg L^{-1} each or -■- -■- not spiked (NS) at 10 cm liquid depth with Fe^{3+}:EDDS 1:2, 0.1 mM of iron, and 1.47 mM H_2O_2.



Fe^{3+}-EDDS complex might decompose into EDDS radical and ferrous iron (Equation II.12), which is later oxidized in the Fenton reaction (Equation II.13), forming ferric iron. As previously discussed, ferric iron could be complexed again if EDDS is still available (ratio 1:2) (PAPOUTSAKIS *et al.*, 2015), or ferric hydroxide, which would immediately precipitate. Since dissolved iron concentration remained constant throughout the experiment and only decreased after 60 - 90 min of reaction, the precipitation of ferric hydroxide took place only at the end of reactions.

After treatment, the inorganic composition of effluent undergoes few modifications (Table III.4.2), and these parameters values are within an appropriate range for discharge or reuse. There was a reduction of the pH values after modified photo-Fenton processes, which did not occur for the photo-H_2O_2 treatment and photolysis. It is an indication of the oxidate reactions that took place, leading to the production from NOM of intermediates relatively strong acids such as carboxylic acids (*e.g.*, oxalic acid) (MACHULEK; QUINA; GOZZI, 2012; STARLING; CASTRO; *et al.*, 2017). Regarding orthophosphates, in the presence of iron, different species of precipitates can be formed, including either ferric phosphate ($FePO_4$), ferric hydroxide ($Fe(OH)_3$ and metal-hydroxy-phosphate precipitates ($Fe_{2.5}PO_4(OH)_{4.5}$) (FULAZZAKY *et al.*, 2014; METCALF & EDDY, 2013). Considering that total and dissolved iron concentration reduced during modified photo-Fenton spiked experiments (Figure III.4.4), the precipitation with orthophosphates is most probably.

TABLE III.4.2 – Sulfates, total and filtrable orthophosphates, nitrates, and pH in the effluent before and after treatment after solar photo-H_2O_2, solar photolysis, and solar photo-Fenton treatments in real secondary UASB+SBTF effluent spiked (S) at 100 µg L^{-1} each MP and not spiked (NS).

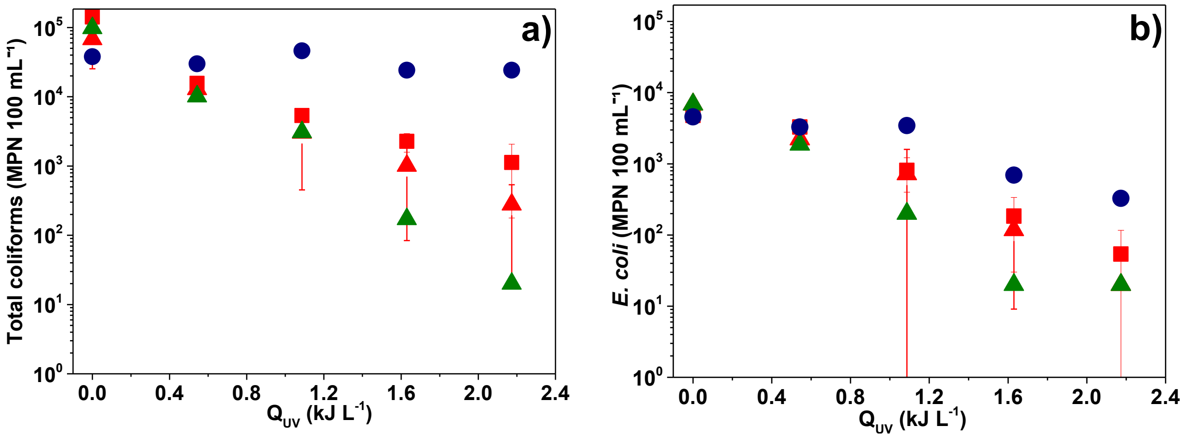
Condition	Not spiked 10 cm: 0.1 mM Fe^{3+}: 1.47 mM H_2O_2. Fe^{3+}:EDDS 1:2		Spiked 10 cm: 0.1 mM Fe^{3+}: 1.47 mM H_2O_2 Fe^{3+}:EDDS 1:2		Photo-H_2O_2 10 cm: 1.47 mM H_2O_2		Photolysis 10 cm:	
Time (min)	0	120	0	120	0	120	0	120
SO_4^{2-} (mg L^{-1})	23.0	42.0±1.4	23.0	48.5±9.2	23.0	23.0	23.0	26.0
o-PO_4^{3-} (mg L^{-1})	13.8	18.5±0.4	13.8	13.1±0.3	13.8	29.9	13.8	14.0
Filtrable o-PO_4^{3-} (mg L^{-1})	12.7	12.5±1.1	12.7	7.9±1.0	12.7	29.5	12.7	12.7
N-NO_3^- (mg L^{-1})	16.7	29.1±3.0	16.7	19.5±1.4	16.7	15.8	16.7	13.9
pH	6.80±0.09	6.44±0.00	6.91±0.25	6.09±0.39	6.76	6.99	7.04	7.16

III.4.2.Disinfection in the UASB+SBTF secondary effluent by modified circumneutral photo-Fenton reaction

Among the tested conditions, the highest removal of total coliforms and *E. coli* occurred with the solar photo-H_2O_2 treatment with 1.47 mM (50 mg L^{-1}) of H_2O_2 (Figure III.4.5) after 2 hours or 2.2 kJ L^{-1} of accumulated energy. The removal efficiency of total coliforms and *E. coli*, in this case, was, respectively, 99.98 % (3.69 log units) and 99.71 % (2.53 log units).

The modified photo-Fenton reaction was also effective on the disinfection of both effluents (spiked and not spiked with MPs). The removal efficiency of total coliforms and *E. coli* was, respectively, 99.34±0.80 % (2.47±0.78 log units) and 99.71 % (2.53 log units) for spiked effluent, and 99.20±0.67 % (2.19±0.42 log units) and 98.78±1.45 % (2.18±0.75 log units) for the effluent not spiked. After 2 hours of reaction, the reaction had also achieved its highest MPs removal efficiency and stabilized (Figure III.4.2), while there was very little hydrogen peroxide remaining in the system (Figure III.4.3). This difference in the disinfection efficiency among the spiked and not spiked effluent is slight and within the variation of the experiments.

FIGURE III.4.5 – a) Total coliforms and b) *E. coli* results during ▲ solar photo-H_2O_2, ● solar photolysis, and modified solar photo-Fenton in real secondary UASB+SBTF effluent ▲ spiked (S) at 100 µg L^{-1} each MP and ■ not spiked (NS), at 10 cm liquid depth with Fe^{3+}:EDDS 1:2, 0.1 mM of iron, and 1.47 mM H_2O_2



The solar photolysis showed no removal for total coliforms (Figure III.4.5), while the removal efficiency for *E. coli* after 120 min of reaction was small, only 92.87 % (1.15 log units' removal). Within 90 min of reaction, the solar photo-H_2O_2 treatment was also able to substantially remove the fecal indicator in the effluent, achieving a removal efficiency of

99.83 % (2.76 log units) for total coliforms, and the same efficiency for *E. coli* than at the end of the reaction, 99.71 % (2.53 log units).

However, the solar photo-H_2O_2 treatment could not achieve efficient removal of MPs (removal efficiency of 14 %). In contrast, the solar-modified photo-Fenton treatment was able to remove total coliforms and *E. coli* and degrade MPs (>80 % removal efficiency). This higher efficiency for MPs removal in modified photo-Fenton than with photo-H_2O_2 treatment, besides a disinfection potential of both of them, was also obtained in an investigation of MWWTP secondary effluent treatment with modified photo-Fenton reaction with EDDS (MANIAKOVA *et al.*, 2021).

In a solar/Fe/H_2O_2 system at semi-pilot scale (5 cm liquid depth) at circumneutral pH, but treating a secondary effluent from CAS treatment plant, authors obtained 49 % of removal efficiency for CECs and 2.5 log units removal efficiency for *E. coli* with a Q_{UV} of 2.5 kJ L^{-1} (STARLING, 2018; STARLING *et al.*, 2021). The authors applied a higher concentration of iron (55 mg L^{-1} of dissolved-Fe, 1.0 mM) and used an intermittent iron dosage to maintain a neutral pH without the need for complexing agents. These results are not far from the current obtained in this study with the modified photo-Fenton reaction for 0.1 mM-Fe and 1.47 mM (50 mg L^{-1}) of H_2O_2 at 10 cm liquid depth, that achieved higher removal efficiency for CECs (86 %) and 2.47±0.78 log unit's removal for total coliforms and 2.53 log unit's removal for *E. coli* using a Q_{UV} of 2.2 kJ L^{-1}. In the study of Starling *et al.* (2021), the treatment using persulfate as an oxidant agent achieved a higher efficiency for the removal of contaminants and disinfection (CECs 54 %; *E. coli* 3 log units) with a lower Q_{UV} of 1.9 kJ L^{-1}, and that performance was associated with a higher selectivity of ROS species formed from sulfate towards the CECs in comparison to hydroxyl radicals, which also aim the organic matter in the matrix.

In this way, the use of the Fe^{3+}-EDDS complex could be evaluated as an alternative to promote a faster circumneutral reaction using a lower initial iron concentration. Such results should also be future evaluated on semi-pilot scale with natural solar light to compare total costs with the higher iron and intermittent addition strategy used in other studies.

During photo-Fenton reactions, the disinfection of water and wastewater is based on the solar disinfection process enhanced with additional concentrations of Fe^{2+} and H_2O_2 reagents (DE

LA OBRA JIMÉNEZ, IRENE *et al.*, 2020; GIANNAKIS; LÓPEZ; *et al.*, 2016; GIANNAKIS; POLO LÓPEZ; *et al.*, 2016). These processes have been detailed in the literature. They involve a combination of both intracellular (accumulation of internal damages induced by solar light, UVA, UVB) and extracellular (oxidation of membrane cells of organisms by ROS formed in oxidative reactions and by the photo excitation of NOM) mechanisms (GIANNAKIS, 2018). In fact, the intracellular mechanism has been highlighted as the primary process responsible for bacterial inactivation (FENG *et al.*, 2020).

A recent review has detailed several manuscripts that applied the neutral photo-Fenton reaction for the removal of different microorganisms (including bacteria and ARB, fungi, viruses, and parasites), as well as discussed the influence of the main parameters including pH, temperature, irradiance levels, the concentration of reagents, and the use of chelating agents (DOWD; PILLAI, 2020). *E. coli* was present in most reported investigations and was shown very susceptible to the photo-Fenton under different conditions.

Higher disinfection kinetic for both *E. coli* and *E. faecalis* was achieved by applying just solar photo-H_2O_2 with 0.3 mM of H_2O_2 in water and MWWTP effluent (GARCÍA-FERNÁNDEZ *et al.*, 2019). The use of EDDS did not enhance the photo-Fenton reaction in the effluent, which was also obtained by another study (MANIAKOVA *et al.*, 2021), and the authors indicate a possible effect of the matrix organic and inorganic components. Nonetheless, from the different investigated proportions, the best disinfection results for the Fe^{3+}-EDDS complex were achieved with a 1:2 ratio, applying 0.1 mM of Fe^{3+} and 0.3 mM of H_2O_2. All reactions could achieve disinfection below the method's detection limit for both organisms. However, higher accumulated energy was observed than in this current work (10.2 kJ L^{-1} for *E. coli* and 29 kJ L^{-1} for *E. faecalis*).

The results for total coliforms and *E. coli* were low at the end of the reaction and appropriate for discharge once after dilution in receiving freshwater bodies values would most not likely extrapolate permitted values (CONAMA resolutions 357 of March 17 and resolution 430 of May 13, 2011). Values were in the range of 10^1 - 10^2 MPN $100mL^{-1}$ for *E. coli*, and 10^2 - 10^3 MPN $100mL^{-1}$ for total coliforms.

Such results demonstrate the possibility of applying the circumneutral modified photo-Fenton with the Fe^{3+}-EDDS complex for disinfection of secondary effluent from a combined UASB +

SBTF biological treatment. These values of 10^1 - 10^2 MPN $100mL^{-1}$ for *E. coli* would allow even the application of the final treated effluent for most uses described in some local Brazilian reuse legislations (Table III.1.3) from the city of Campinas (Resolution SVDS/SMS n. º 09 of July 31, 2014), the state of São Paulo (Resolution SSRH/SMA/SS n. º 01 of June 28, 2017), and the State of Ceará (Resolution COEMA n. º 02 of February 28, 2017). However, these values would not allow some stricter applications that require not detectable levels of coliforms, such as direct human contact and irrigation in agriculture of plants that are eaten raw, for which the reuse water could have direct contact with those eatable parts. These stricter recommendations from the State of Ceará, the State of São Paulo, and Campinas city follow international guidelines for direct contact with the public and the food (VOULVOULIS, 2018).

For stricter use and faster treatment, reactions could be enhanced by reducing liquid depth in the reactor and increasing the light availability, which plays an essential part in the modified photo-Fenton system.

Recently, it has been shown that the combined application of solar modified circumneutral photo-Fenton treatment with the photo-H_2O_2 system in the sequence was able to enhance a removal efficiency for MPs (80 % removal) and disinfection of different organisms (*E. coli*, *S. enteritidis,* and *E. faecalis*) within 60 min of reaction (0.70 kJ L^{-1}) (MANIAKOVA *et al.*, 2021).

Another important aspect when evaluating the disinfection process of water for reclamation is the formation of disinfection byproducts (DBPs) due to the reaction of disinfectant agents with DOM from the water source (natural water or treated wastewater) (DU *et al.*, 2017). A process widely applied around the world for the disinfection process is chlorination (Cl_2). In this process, there is the formation of chlorinated disinfection byproducts like trihalomethanes (THMs) and haloacetic acids (HAAs), among others, which can be present serious toxic and human health effects (BOND; TEMPLETON; GRAHAM, 2012; RICHARDSON *et al.*, 2007).

Different other DBPs have been discovered in the last decades, including bromate and nitrosamines, which are of concern for ozonation and chloramination, respectively. These processes are considered alternatives to chlorination due to the control on formation of firstly known DBPs as THMs and HAAs (BOND; TEMPLETON; GRAHAM, 2012; RICHARDSON *et al.*, 2007). However, all these byproducts raise concern, and treatments have been evaluated not only in terms of disinfection and CECs' degradation capacity but also on the control of the formation of DBPs and their detrimental toxic effects. In this line, the combination of different oxidants without or with UV light irradiation has been compared. These might be a solution, in special when combining different oxidants and UV light that would attenuate the lower efficiency of individual treatments in either disinfection or removing contaminants and also would enhance the control on DBPs (SGROI; SNYDER; ROCCARO, 2021; SUN *et al.*, 2016; WANG, J. *et al.*, 2018; WANG, W. L. *et al.*, 2016). Even when applying UV radiation, the chlorination process can increase toxicity, and an alternative oxidant as H_2O_2 can be advantageous (MIKLOS *et al.*, 2019).

Regarding the modified photo-Fenton reaction at circumneutral pH, a study with the treatment of secondary MWWTP effluent at pilot scale performed several bioassays, including *in vivo* (algal growth inhibition test) and *in vitro*, endocrine disruptor tests (androgenic/glucocorticoid activity and estrogenicity), and cytotoxicity tests, showing a final high removal of CECs present in the effluent (over 99 %) and also efficient elimination or attenuation in toxicity parameters (RIVAS IBÁÑEZ *et al.*, 2017). Thus, the modified photo-Fenton process seems not to produce toxic oxidation products. Nonetheless, future work using this process on different effluents should monitor both toxicity and formation of DBPs.

III.5.CONCLUSIONS

The circumneutral modified Fe^{3+}-EDDS complex photo-Fenton reaction was able to achieve 86 % of removal efficiency for ΣMPs, 2.47±0.78 log unit's removal for total coliforms, and 2.53 log unit's removal for *E. coli* in a secondary effluent from a demonstration-scale UASB+SBTF. These efficiencies were reached at Q_{UV} of 2.2 kJ L^{-1} using 0.1 mM-Fe and 1.47 mM (50 mg L^{-1}) of H_2O_2 at 10 cm liquid depth.

The solar peroxidation (photo-H_2O_2) treatment using 1.47 mM (50 mg L^{-1}) of H_2O_2 was able to achieve higher disinfection (3.69 log unit's removal for total coliforms and 2.53 log unit's removal for *E. coli*) at the same accumulated energy. However, it was very inefficient in the removal of spiked MPs (14 %).

The final levels of total coliforms and *E. coli* after the advanced treatment indicated that the effluent would be adequate for final disposal and reduce impact in the receiving freshwater bodies, with lower levels of microorganisms compared to the secondary treated effluent.

Furthermore, the advanced treatment would allow several reuse applications in urbanistic and agriculture uses. For stricter reuse applications, including those that implicate direct contact with food and humans, the final disinfection efficiency should be improved in the system. Some alternatives could be to reduce the liquid depth or associate a combined treatment with both photo-Fenton and photo- H_2O_2 reactions.

5. CONCLUSIONS

The main goal was to investigate the applicability of the circumneutral solar photo-Fenton reactions modified with iron-EDDS complex for the treatment of domestic secondary effluent from different biological processes considering the removal of CECs and disinfection.

Initially, using an investigation with a literature review methodology, it was possible to obtain a relevant selection of manuscripts regarding advanced treatments for simultaneous removal of CECs and pathogens (disinfection) from domestic wastewaters. In fact, most studies published over the last 11 years about the tertiary treatment of effluents from the secondary biological treatment in MWWTP do no present information on the simultaneous removal of CECs and pathogens. Most information is presented separately for each contaminant, except during ARB and antibiotics studies, which presented more simultaneous results.

Furthermore, during the literature review, it was detected that most studies focus on secondary effluents from conventional activated sludge (CAS) systems, and there is less information about other secondary biological treatments. Considering the Brazilian scenario where CAS systems are mostly applied to larger cities, different biological systems, including UASB, trickling filters, and stabilization ponds, are used in the country and represent the majority in MWWTP.

There is still much to do for improvement and scale-up investigation of AOPs, including the photo-Fenton reaction, and they might be an alternative with lower costs and reduced energy application in comparison to other more established technologies as ozonation. Research with solar photoreactors might be an interesting application for lower-income countries with high and well-distributed solar light availability.

Finally, the literature review pointed out how costs and efficiency in tertiary/quaternary treatment could be improved and balanced by associating different treatment technologies (combined treatment).

To improve the application of the photo-Fenton reaction in lower costs reactors such as the RPR, this work investigated the use of a reflexive aluminum surface in the bottom of the reactor to promote a higher treatment capacity with a lower concentration of reagents.

Iron concentration and liquid depth are the major operational parameters in the photo-Fenton treatment in the RPR. In fact, it was initially observed that some reaction parameters (reaction rate, treatment capacity, and treatment time) were not different between two different but low iron initial concentrations (0.1 mM and 0.054 mM, Fe: EDDS 1:2), especially at higher liquid depth (15 cm). Extremely low (<0.02 mM) or high iron concentrations (> 0.3 mM) are undesirable because they either slow down MPs reaction or result in an effluent with inadequate iron concentration for further reuse. Low liquid depths can improve reaction rates and considerably reduce the treatment capacity in an open reactor.

In this way, the proposed new strategy of using a reflexive aluminum surface to return to reaction non-absorbed photons showed to increase the degradation of the investigated MPs (acetaminophen, caffeine, carbamazepine, diclofenac, sulfamethoxazole, and trimethoprim) in natural water, in particular within lower iron initial concentrations, due to a reduction in the light attenuation effect. In semi-pilot-scale experiments with natural water, there was a similar treatment time for 80% removal of ΣMP with 0.054 mM of iron using the aluminum surface and for 0.1 mM iron without the surface.

The results obtained in the spiked (100 or 20 µg L^{-1}) secondary effluent corroborated the results obtained in natural water, even though the treatment time and the Fe^{3+}-EDDS complex decomposition were slower in the secondary effluent, due to the presence of DOM in this matrix that led the higher treatment time required (over 30 minutes), once the reactions were inhibited by light attenuation and ROS scavenging. Results indicated that chloride and sulfate (main inorganic anions present in the effluent from MWWTP and the natural water) would most likely equally or not affect the efficiency of the photo-Fenton process.

Results were slower at semi pilot-scale with the RPR evaluated without spiking the real secondary effluent. There was a slower Fe^{3+}-EDDS complex decomposition (around 50 minutes of the reaction) in the effluent compared to natural water and a slower hydrogen peroxide consumption of 30 mg L^{-1} (0.88 mM) H_2O_2, leading to a treatment time of around 60 minutes. Only experiments with 0.1 mM of iron and 50 mg L^{-1} (1.47mM) H_2O_2 with and without the aluminum reflexive surface reached 82 % - 90 % removal efficiency (Q_{UV} of 0.55 kJ L^{-1}). With 0.054 mM of iron, only a maximum of 65 % could be achieved (Q_{UV}>0.87 kJ L^{-1}).

These results indicate that the aluminum surface inside open solar reactors is a suitable option for water and wastewater treatment with low color and turbidity values. The use of the aluminum surface might allow to reduce iron concentration and improve light pathway without reducing treatment capacity.

Regarding the removal of CECs in effluent from an anaerobic reactor followed by a biological filter (UASB+SBTF), disinfection was evaluated considering total coliforms and *E. coli*.

Previously investigated conditions (Fe^{3+}-EDDS complex 1:2, 0.1 mM-Fe and 1.47 mM of H_2O_2), but at 10 cm liquid depth was able to achieve relevant levels of MPs removal (86 %) and disinfection (2.47±0.78 log unit's removal for total coliforms and 2.53 log unit's removal for *E. coli*) using a Q_{UV} of 2.2 kJ L^{-1}. The photo-H_2O_2 process was efficient for disinfection purposes (3.69 log unit's removal for total coliforms and 2.53 log unit's removal for *E. coli*), but not for MPs removal (14 %).

The efficiency in the system can be improved by lowering the liquid depth or combining the treatments (of photo-Fenton and photo- H_2O_2) as reported in the literature. The final levels of total coliforms and *E. coli* already allow final disposal with less impact in receiving freshwater bodies or less strict reuse applications than those that involve direct human contact.

Regarding the investigated MPs, caffeine was the most recalcitrant throughout this study, and this could indicate the relevance for monitoring a recalcitrant contaminant in secondary wastewaters during photo-Fenton treatment as an indicator of overall efficiency for the system.

6. RECOMMENDATIONS

- The bibliometric analysis and systemic review of the literature should be applied with some additional modification selection factors besides the number of citations for each article. For example, it can be applied the strategy to read titles and abstracts of recently published papers and include papers relevant to the search but with few citations.

- The continuous operation of the modified photo-Fenton at neutral pH in RPR should be tested within different weather conditions (cloudy and lower UV-irradiation) and seasons of the year (summer and winter), with and without the aluminum reflexive surface, to enable an appropriate cost evaluation of this system operation and durability of material under constant oxidative conditions at a larger scale.

- The modified photo-Fenton at neutral pH and photo-H_2O_2 should be tested in detail in a semi-pilot scale in the RPR for the UASB+SBTF secondary effluent, which would enable an evaluation of costs for this system application.

- Reactions in the UASB+SBTF secondary effluent should be evaluated at lower MPs initial concentration, closer to the real concentration of contaminants, as demonstrated in Chapter II.

- The treatment of the UASB+SBTF secondary effluent should be evaluated without the filtration pre-treatment to evaluate a simplified possible application in a larger scale of this system without previous filtration unit, directly from the biological treatment.

- A risk assessment considering the remaining concentration of CECs and pathogen indicators in the final treated effluent should be performed for evaluation and comparison of each treatment condition investigated;

- Other combinations of AOPs and biological treatments commonly applied in Brazil could be tested, UASB+solar AOPs, UASB+AOPs+stabilization ponds (to evaluate the possibility of reducing areas of stabilization ponds), etc.

- Considering that in RPRs for algal production, the energy for mixing corresponds to 69% of the system total cost (HREIZ *et al.*, 2014), a change from mixing with the paddlewheels to a hydraulic mixing design could reduce even more the costs for implementation of this reactor. An example of hydraulic mixing is the well-known unit used for flocculation in water treatment plants (WTP), with horizontal or vertical baffles.

- Another mixing design would be based on the distributed addition of reagents to each of the different channels that form the baffled reactor. In this way, the applicability of a modified photo-Fenton at neutral pH could be investigated without the complex agent but instead with sequential or intermittent dose addition of iron. This strategy of sequential addition has been tested by different authors and has shown to work well for CECs removal and disinfection, even with different oxidants - hydrogen peroxide and persulfate - (STARLING, 2018). Even so, higher catalyst (iron) concentration might be required to achieve a desirable efficiency on the system, eventually ten times higher than concentration applied at acidic pH (CARRA *et al.*, 2013; CLARIZIA *et al.*, 2017).

REFERENCES

AGUIRRE-MARTÍNEZ, G. V.; DELVALLS, A. T.; LAURA MARTÍN-DÍAZ, M. Yes, caffeine, ibuprofen, carbamazepine, novobiocin and tamoxifen have an effect on Corbicula fluminea (Müller, 1774). *Ecotoxicology and Environmental Safety*, v. 120, p. 142–154, 2015. Available at: <http://dx.doi.org/10.1016/j.ecoenv.2015.05.036>.

AHMED, M. B. *et al.* Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: A critical review. *Journal of Hazardous Materials*, v. 323, p. 274–298, 2017. Available at: <http://www.sciencedirect.com/science/article/pii/S0304389416303867>.

ALHARBI, S. K. *et al.* Photolysis and UV/H2O2 of diclofenac, sulfamethoxazole, carbamazepine, and trimethoprim: Identification of their major degradation products by ESI–LC–MS and assessment of the toxicity of reaction mixtures. *Process Safety and Environmental Protection*, v. 112, p. 222–234, 2017. Available at: <https://doi.org/10.1016/j.psep.2017.07.015>.

ALMEIDA, P. G. S. *Efeito de diferentes meio suporte no desempenho de filtros biológicos percoladores aplicados ao pós-tratamento de efluentes de reatores UASB, com ênfase na nitrificação*. 2007. 156 f. 2007.

ALVARINO, T. *et al.* Trends in organic micropollutants removal in secondary treatment of sewage. *Reviews in Environmental Science and Bio/Technology*, v. 17, n. 3, p. 447–469, 2018. Available at: <http://link.springer.com/10.1007/s11157-018-9472-3>.

ALVARINO, T. *et al.* Understanding the removal mechanisms of PPCPs and the influence of main technological parameters in anaerobic UASB and aerobic CAS reactors. *Journal of Hazardous Materials*, v. 278, p. 506–513, 2014. Available at: <http://dx.doi.org/10.1016/j.jhazmat.2014.06.031>.

AMILDON RICARDO, Ivo *et al.* Chloramphenicol photo-Fenton degradation and toxicity changes in both surface water and a tertiary effluent from a municipal wastewater treatment plant at near-neutral conditions. *Chemical Engineering Journal*, v. 347, n. January, p. 763–770, 2018. Available at: <https://doi.org/10.1016/j.cej.2018.04.169>.

ANA. *Agência Nacional de Águas (ANA) - Atlas Esgotos - Despoluição de bacias hidrográficas*. . Brasília-DF: [s.n.], 2017.

ANDERSON, J. C. *et al.* Reducing nutrients, organic micropollutants, antibiotic resistance, and toxicity in rural wastewater effluent with subsurface filtration treatment technology. *Ecological Engineering*, v. 84, p. 375–385, 1 nov. 2015.

ANDREOZZI, R. Advanced oxidation processes (AOP) for water purification and recovery. *Catalysis Today*, v. 53, n. 1, p. 51–59, 1999. Available at: <http://www.sciencedirect.com/science/article/pii/S0920586199001029>.

ANTUNES, S. C. *et al.* Biochemical effects of acetaminophen in aquatic species: edible clams Venerupis decussata and Venerupis philippinarum. *Environmental Science and Pollution Research*, v. 20, n. 9, p. 6658–6666, 2013. Available at: <http://link.springer.com/10.1007/s11356-013-1784-9>.

APHA. *Standard methods for the examination of water and wastewater*. 21. ed. Washington, DC: APHA-AWWA-WEF, 2005.

ARZATE, S. *et al.* Effect of residence time on micropollutant removal in WWTP secondary effluents by continuous solar photo-Fenton process in raceway pond reactors. *Chemical*

Engineering Journal, v. 316, p. 1114–1121, 2017. Available at: <http://dx.doi.org/10.1016/j.cej.2017.01.089>.

BALAKRISHNA, K. *et al.* A review of the occurrence of pharmaceuticals and personal care products in Indian water bodies. *Ecotoxicology and Environmental Safety*, 2017.

BARBOSA, M. O. *et al.* Occurrence and removal of organic micropollutants: An overview of the watch list of EU Decision 2015/495. *Water Research*, v. 94, p. 257–279, 2016. Available at: <http://dx.doi.org/10.1016/j.watres.2016.02.047>.

BIANCULLO, F. *et al.* Heterogeneous photocatalysis using UVA-LEDs for the removal of antibiotics and antibiotic resistant bacteria from urban wastewater treatment plant effluents. *Chemical Engineering Journal*, v. 367, p. 304–313, 2019. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S1385894719302293>.

BOLZONELLA, D. *et al.* Application of membrane bioreactor technology for wastewater treatment and reuse in the Mediterranean region: Focusing on removal efficiency of non-conventional pollutants. *Journal of Environmental Management*, v. 91, n. 12, p. 2424–2431, 2010.

BOND, T.; TEMPLETON, M.R.; GRAHAM, N. Precursors of nitrogenous disinfection by-products in drinking water--A critical review and analysis. *Journal of Hazardous Materials*, v. 235–236, p. 1–16, 2012. Available at: <http://dx.doi.org/10.1016/j.jhazmat.2012.07.017>.

BOURGIN, M. *et al.* Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: Abatement of micropollutants, formation of transformation products and oxidation by-products. *Water Research*, v. 129, p. 486–498, 2018. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0043135417308734>.

BRANDT, E. M. F. *et al.* Behaviour of pharmaceuticals and endocrine disrupting chemicals in simplified sewage treatment systems. *Journal of Environmental Management*, v. 128, p. 718–726, 2013. Available at: <https://www.sciencedirect.com/science/article/pii/S0301479713004052>.

BRESSANI-RIBEIRO, T; CHERNICHARO, C.; VOLCKE, E. Anammox prevalence in sponge-bed trickling filters treating anaerobic effluents - just a matter of time? 2020, Notre Dame: IWA Publishing, 2020.

BRESSANI-RIBEIRO, T. *et al.* Trickling filters following anaerobic sewage treatment: state of the art and perspectives. *Environmental Science: Water Research & Technology*, v. 4, n. 11, p. 1721–1738, 2018. Available at: <http://xlink.rsc.org/?DOI=C8EW00330K>.

BRIENZA, M. *et al.* Combining micelle-clay sorption to solar photo-Fenton processes for domestic wastewater treatment. *Environmental Science and Pollution Research*, v. 26, n. 19, p. 18971–18978, 2019.

CABRERA REINA, A. *et al.* The influence of location on solar photo-Fenton: Process performance, photoreactor scaling-up and treatment cost. *Renewable Energy*, v. 145, p. 1890–1900, 2020. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0960148119311334>.

CAMPOS-MAÑAS, M. C. *et al.* Fast determination of pesticides and other contaminants of emerging concern in treated wastewater using direct injection coupled to highly sensitive ultra-high performance liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A*, v. 1507, p. 84–94, 2017.

CAPODAGLIO, A. G.; BOJANOWSKA-CZAJKA, A.; TROJANOWICZ, M. Comparison of different advanced degradation processes for the removal of the pharmaceutical compounds diclofenac and carbamazepine from liquid solutions. *Environmental Science and Pollution*

Research, v. 25, n. 28, p. 27704–27723, 2018. Available at: <http://link.springer.com/10.1007/s11356-018-1913-6>.

CARRA, I. *et al.* Degradation and monitoring of acetamiprid, thiabendazole and their transformation products in an agro-food industry effluent during solar photo-Fenton treatment in a raceway pond reactor. *Chemosphere*, v. 130, p. 73–81, 2015. Available at: <http://dx.doi.org/10.1016/j.chemosphere.2015.03.001>.

CARRA, I. *et al.* Iron dosage as a strategy to operate the photo-Fenton process at initial neutral pH. *Chemical Engineering Journal*, v. 224, n. 1, p. 67–74, 2013. Available at: <http://dx.doi.org/10.1016/j.cej.2012.09.065>.

CARRA, I. *et al.* New approach to solar photo-Fenton operation. Raceway ponds as tertiary treatment technology. *Journal of Hazardous Materials*, v. 279, p. 322–329, 2014. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0304389414005718>.

CASSANO, A. . *et al.* Photocatalysis in water environments using artificial and solar light. *Catalysis Today*, v. 58, n. 2–3, p. 199–230, 2002.

CASTILLO-VALENZUELA, J.; MARTINEZ-GUERRA, E.; GUDE, V. G. Wetlands for Wastewater Treatment. *Water Environment Research*, v. 89, n. 10, p. 1163–1205, 2017. Available at: <https://onlinelibrary.wiley.com/doi/abs/10.2175/106143017X15023776270269>.

CHÁVEZ, A. M. *et al.* Removal of Organic Micropollutants from a Municipal Wastewater Secondary Effluent by UVA-LED Photocatalytic Ozonation. *Catalysts*, v. 9, n. 5, p. 472, 2019. Available at: <https://www.mdpi.com/2073-4344/9/5/472>.

CHEN, S. *et al.* Influencing factors and kinetic studies of imidacloprid degradation by ozonation. *Environmental Technology*, v. 40, n. 16, p. 2127–2134, 2019. Available at: <https://www.tandfonline.com/doi/full/10.1080/09593330.2018.1439105>.

CHERNICHARO, C. A. L. *et al.* Anaerobic sewage treatment: state of the art, constraints and challenges. *Reviews in Environmental Science and Bio/Technology*, v. 14, n. 4, p. 649–679, 2015. Available at: <http://link.springer.com/10.1007/s11157-015-9377-3>.

CHINNAIYAN, P. *et al.* Pharmaceutical products as emerging contaminant in water: relevance for developing nations and identification of critical compounds for Indian environment. *Environmental Monitoring and Assessment*, v. 190, n. 5, p. 288, 2018. Available at: <http://link.springer.com/10.1007/s10661-018-6672-9>.

CHISTI, Y. Algae Biotechnology. In: BUX, F.; CHISTI, Y. (Org.). . *Algae Biotechnology, Green Energy and Technology*. Switzerland: Springer, Cham, 2016. p. 21–40. Available at: <http://link.springer.com/10.1007/978-3-319-12334-9>.

CHOI, E.; ALSOP, D.; WILSON, J. Y. The effects of chronic acetaminophen exposure on the kidney, gill and liver in rainbow trout (Oncorhynchus mykiss). *Aquatic Toxicology*, v. 198, p. 20–29, 2018. Available at: <https://doi.org/10.1016/j.aquatox.2018.02.007>.

CHONG, M. N. *et al.* Recent developments in photocatalytic water treatment technology: A review. *Water Research*, v. 44, n. 10, p. 2997–3027, 2010. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0043135410001739>.

CLARIZIA, L. *et al.* Homogeneous photo-Fenton processes at near neutral pH: A review. *Applied Catalysis B: Environmental*, v. 209, p. 358–371, 2017. Available at: <https://www.sciencedirect.com/science/article/pii/S0926337317302084>.

COGGINS, L. X.; CROSBIE, N. D.; GHADOUANI, A. The small, the big, and the beautiful: Emerging challenges and opportunities for waste stabilization ponds in Australia. *WIREs*

Water, v. 6, n. 6, p. e1383, 2019. Available at: <https://onlinelibrary.wiley.com/doi/abs/10.1002/wat2.1383>.

COOPER, I. D. What is a "mapping study?" *Journal of the Medical Library Association : JMLA*, v. 104, n. 1, p. 76–78, 2016.

COSTA, E.P. *et al.* New trend on open solar photoreactors to treat micropollutants by photo-Fenton at circumneutral pH: Increasing optical pathway. *Chemical Engineering Journal*, v. 385, n. December 2019, p. 123982, 2020. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S1385894719333972>.

CRUZ, D. *et al.* Caffeine impacts in the clam Ruditapes philippinarum: Alterations on energy reserves, metabolic activity and oxidative stress biomarkers. *Chemosphere*, v. 160, p. 95–103, 2016.

CUERVO LUMBAQUE, E. *et al.* Solar photo-Fenton-like process at neutral pH: Fe(III)-EDDS complex formation and optimization of experimental conditions for degradation of pharmaceuticals. *Catalysis Today*, v. 328, n. January, p. 259–266, 2019. Available at: <https://doi.org/10.1016/j.cattod.2019.01.006>.

DA COSTA, ELIZÂNGELA PINHEIRO *et al.* Degradation of carbendazim in water via photo-Fenton in Raceway Pond Reactor: assessment of acute toxicity and transformation products. *Environmental Science and Pollution Research*, p. 1–13, 2018. Available at: <http://link.springer.com/10.1007/s11356-018-2130-z>.

DE LA CRUZ, N. *et al.* Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. *Water Research*, v. 46, n. 6, p. 1947–1957, 2012.

DE LA CRUZ, N. *et al.* Degradation of emergent contaminants by UV, UV/H2O2 and neutral photo-Fenton at pilot scale in a domestic wastewater treatment plant. *Water Research*, v. 47, n. 15, p. 5836–5845, 2013.

DE LA OBRA, I. *et al.* Microcontaminant removal in secondary effluents by solar photo-Fenton at circumneutral pH in raceway pond reactors. *Catalysis Today*, v. 287, p. 10–14, 2017. Available at: <http://dx.doi.org/10.1016/j.cattod.2016.12.028>.

DE LA OBRA JIMÉNEZ, I. *et al.* Continuous flow disinfection of WWTP secondary effluents by solar photo-Fenton at neutral pH in raceway pond reactors at pilot plant scale. *Applied Catalysis B: Environmental*, v. 247, n. February, p. 115–123, 2019. Available at: <https://doi.org/10.1016/j.apcatb.2019.01.093>.

DE LA OBRA JIMÉNEZ, IRENE *et al.* Unfolding the action mode of light and homogeneous vs. heterogeneous photo-Fenton in bacteria disinfection and concurrent elimination of micropollutants in urban wastewater, mediated by iron oxides in Raceway Pond Reactors. *Applied Catalysis B: Environmental*, v. 263, n. May 2019, p. 118158, 2020. Available at: <https://doi.org/10.1016/j.apcatb.2019.118158>.

DE LIGUORO, M. *et al.* Sublethal effects of trimethoprim on four freshwater organisms. *Ecotoxicology and Environmental Safety*, v. 82, p. 114–121, 2012. Available at: <http://dx.doi.org/10.1016/j.ecoenv.2012.05.016>.

DENG, Y.; ZHAO, R. Advanced Oxidation Processes (AOPs) in Wastewater Treatment. *Current Pollution Reports*, v. 1, n. 3, p. 167–176, 2015.

DEZOTTI, M. *Processos e técnicas para o controle ambiental de efluentes líquidos*. 1st. ed. Rio de Janeiro: Editora E-papers, 2008.

DOWD, K. O.; PILLAI, S. C. Photo-Fenton disinfection at near neutral pH : Process , parameter optimization and recent advances. *Journal of Environmental Chemical Engineering*, v. 8, n. 5, p. 104063, 2020. Available at: <https://doi.org/10.1016/j.jece.2020.104063>.

DU, Y *et al.* Formation and control of disinfection byproducts and toxicity during reclaimed water chlorination: A review. *Journal of Environmental Sciences (China)*, v. 58, p. 51–63, 2017.

DULAR, M. *et al.* Use of hydrodynamic cavitation in (waste)water treatment. *Ultrasonics Sonochemistry*, v. 29, p. 577–588, 2016.

ENSSLIN, L.; ENSSLIN, S. R. Uma análise bibliométrica da literatura sobre estratégia e avaliação de desempenho. *Gestão & Produção*, v. 19, n. 1, p. 59–78, 2012.

ESTEBAN GARCÍA, B. *et al.* Wild bacteria inactivation in WWTP secondary effluents by solar photo-fenton at neutral pH in raceway pond reactors. *Catalysis Today*, v. 313, p. 72–78, set. 2018. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0920586117307289>.

EUROPEAN COMISSION. *Water reuse*. Available at: <https://ec.europa.eu/environment/water/reuse.htm>.

FAUST, B. C.; HOIGNÉ, J. Photolysis of Fe (III)-hydroxy complexes as sources of OH radicals in clouds, fog and rain. *Atmospheric Environment Part A, General Topics*, v. 24, n. 1, p. 79–89, 1990.

FENG, L. *et al.* Employing bacterial mutations for the elucidation of photo-Fenton disinfection: Focus on the intracellular and extracellular inactivation mechanisms induced by UVA and H2O2. *Water Research*, v. 182, 2020.

FERRO, G. *et al.* Cross-Contamination of Residual Emerging Contaminants and Antibiotic Resistant Bacteria in Lettuce Crops and Soil Irrigated with Wastewater Treated by Sunlight/H 2 O 2. *Environmental Science & Technology*, v. 49, n. 18, p. 11096–11104, 2015. Available at: <http://pubs.acs.org/doi/10.1021/acs.est.5b02613>.

FREITAS, A. M. *et al.* Ecotoxicity evaluation of a WWTP effluent treated by solar photo-Fenton at neutral pH in a raceway pond reactor. *Environmental Science and Pollution Research*, v. 24, n. 2, p. 1093–1104, 2017. Available at: <http://link.springer.com/10.1007/s11356-016-7101-7>.

FULAZZAKY, M. A. *et al.* Precipitation of iron-hydroxy-phosphate of added ferric iron from domestic wastewater by an alternating aerobic–anoxic process. *Chemical Engineering Journal*, v. 253, p. 291–297, 2014. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S138589471400624X>.

GANI, K. M.; KAZMI, A. A. Contamination of Emerging Contaminants in Indian Aquatic Sources: First Overview of the Situation. *Journal of Hazardous, Toxic, and Radioactive Waste*, v. 21, n. 3, p. 04016026, jul. 2017. Available at: <http://ascelibrary.org/doi/10.1061/%28ASCE%29HZ.2153-5515.0000348>.

GARCÍA-FERNÁNDEZ, I. *et al.* Inactivation of E. coli and E. faecalis by solar photo-Fenton with EDDS complex at neutral pH in municipal wastewater effluents. *Journal of Hazardous Materials*, v. 372, n. February 2018, p. 85–93, 2019. Available at: <https://doi.org/10.1016/j.jhazmat.2018.07.037>.

GHIMIRE, U. *et al.* Wetlands for wastewater treatment. *Water Environment Research*, v. 91, n. 10, p. 1378–1389, 2019. Available at: <https://onlinelibrary.wiley.com/doi/abs/10.1002/wer.1232>.

GIANNAKIS, S. Analogies and differences among bacterial and viral disinfection by the photo-Fenton process at neutral pH: a mini review. *Environmental Science and Pollution Research*,

v. 25, n. 28, p. 27676–27692, 2018.

GIANNAKIS, S.; VOUMARD, M.; *et al.* Micropollutant degradation, bacterial inactivation and regrowth risk in wastewater effluents: Influence of the secondary (pre)treatment on the efficiency of Advanced Oxidation Processes. *Water Research*, v. 102, p. 505–515, 2016.

GIANNAKIS, S.; LÓPEZ, M. I. P.; *et al.* Solar disinfection is an augmentable, in situ-generated photo-Fenton reaction-Part 2: A review of the applications for drinking water and wastewater disinfection. *Applied Catalysis B: Environmental*, v. 198, p. 431–446, 2016.

GIANNAKIS, S.; POLO LÓPEZ, M. I.; *et al.* Solar disinfection is an augmentable, in situ-generated photo-Fenton reaction—Part 1: A review of the mechanisms and the fundamental aspects of the process. *Applied Catalysis B: Environmental*, v. 199, p. 199–223, 2016.

GONÇALVES, Bárbara R. *et al.* Reducing toxicity and antimicrobial activity of a pesticide mixture via photo-Fenton in different aqueous matrices using iron complexes. *Science of The Total Environment*, v. 740, p. 140152, 2020. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0048969720336731>.

GOSSET, A. *et al.* Ecotoxicological risk assessment of contaminants of emerging concern identified by "suspect screening" from urban wastewater treatment plant effluents at a territorial scale. *Science of the Total Environment*, v. 778, p. 146275, 2021. Available at: <https://doi.org/10.1016/j.scitotenv.2021.146275>.

GRANDCLÉMENT, C. *et al.* From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: A review. *Water Research*, v. 111, p. 297–317, mar. 2017. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0043135417300052>.

GUERRA, P. *et al.* Occurrence and fate of antibiotic, analgesic/anti-inflammatory, and antifungal compounds in five wastewater treatment processes. *Science of the Total Environment*, v. 473–474, p. 235–243, 2014. Available at: <http://dx.doi.org/10.1016/j.scitotenv.2013.12.008>.

GWENZI, W.; CHAUKURA, N. Organic contaminants in African aquatic systems: Current knowledge, health risks, and future research directions. *Science of the Total Environment*, v. 619–620, p. 1493–1514, 2018. Available at: <https://doi.org/10.1016/j.scitotenv.2017.11.121>.

HREIZ, R. *et al.* Experimental and numerical investigation of hydrodynamics in raceway reactors used for algaculture. *Chemical Engineering Journal*, v. 250, n. January, p. 230–239, 2014. Available at: <http://www.sciencedirect.com/science/article/pii/S1385894714003027>.

JIANG, J.-Q. Advances in the development and application of ferrate(VI) for water and wastewater treatment. *Journal of Chemical Technology & Biotechnology*, v. 89, n. 2, p. 165–177, 2014. Available at: <http://doi.wiley.com/10.1002/jctb.4214>.

KARAOLIA, P. *et al.* Removal of antibiotics, antibiotic-resistant bacteria and their associated genes by graphene-based TiO2 composite photocatalysts under solar radiation in urban wastewaters. *Applied Catalysis B: Environmental*, v. 224, p. 810–824, 2018. Available at: <http://www.sciencedirect.com/science/article/pii/S0926337317310755>.

KIM, I.; YAMASHITA, N.; TANAKA, H. Performance of UV and UV/H2O2 processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. *Journal of Hazardous Materials*, v. 166, n. 2–3, p. 1134–1140, 2009. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0304389408018505>.

KIM, Y. *et al.* Aquatic toxicity of acetaminophen, carbamazepine, cimetidine, diltiazem and six major sulfonamides, and their potential ecological risks in Korea. *Environment*

International, v. 33, n. 3, p. 370–375, 2007.

KLAMERTH, N. *et al.* Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: A comparison. *Water Research*, v. 47, n. 2, p. 833–840, 2013.

KLAMERTH, N. *et al.* Treatment of municipal wastewater treatment plant effluents with modified photo-fenton as a tertiary treatment for the degradation of micro pollutants and disinfection. *Environmental Science and Technology*, v. 46, n. 5, p. 2885–2892, 2012.

KRZEMINSKI, P. *et al.* Occurrence of UV filters, fragrances and organophosphate flame retardants in municipal WWTP effluents and their removal during membrane post-treatment. *Journal of Hazardous Materials*, v. 323, p. 166–176, 2017. Available at: <http://www.sciencedirect.com/science/article/pii/S030438941630704X>.

KRZEMINSKI, P. *et al.* Performance of secondary wastewater treatment methods for the removal of contaminants of emerging concern implicated in crop uptake and antibiotic resistance spread: A review. *Science of the Total Environment*, v. 648, p. 1052–1081, 2019.

KUMAR, K. *et al.* Recent trends in the mass cultivation of algae in raceway ponds. *Renewable and Sustainable Energy Reviews*, v. 51, p. 875–885, 2015. Available at: <http://dx.doi.org/10.1016/j.rser.2015.06.033>.

KUSIAK-NEJMAN, E.; MORAWSKI, A. W. TiO2/graphene-based nanocomposites for water treatment: A brief overview of charge carrier transfer, antimicrobial and photocatalytic performance. *Applied Catalysis B: Environmental*, v. 253, p. 179–186, 2019.

LADO RIBEIRO, A. R. *et al.* Impact of water matrix on the removal of micropollutants by advanced oxidation technologies. *Chemical Engineering Journal*, v. 363, n. October 2018, p. 155–173, 2019. Available at: <https://doi.org/10.1016/j.cej.2019.01.080>.

LI, W. *et al.* Changes of excitation / emission matrixes of wastewater caused by Fenton- and Fenton-like treatment and their associations with the generation of hydroxyl radicals , oxidation of effluent organic matter and degradation of trace-level organic pollutants. *Journal of Hazardous Materials*, v. 244–245, p. 698–708, 2013. Available at: <http://dx.doi.org/10.1016/j.jhazmat.2012.10.064>.

LIPCZYNSKA-KOCHANY, E.; KOCHANY, J. Effect of humic substances on the Fenton treatment of wastewater at acidic and neutral pH. *Chemosphere*, v. 73, n. 5, p. 745–750, out. 2008. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0045653508008096>.

LIU, B.; ZHANG, S.; CHANG, C.-C. Emerging Pollutants - Part II: Treatment. *Water Environment Research*, v. 90, n. 10, p. 1792–1820, 2018. Available at: <http://doi.wiley.com/10.2175/106143018X15289915807443>.

LUO, Y. *et al.* A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of the Total Environment*, v. 473–474, p. 619–641, 2014. Available at: <http://dx.doi.org/10.1016/j.scitotenv.2013.12.065>.

LUUKKONEN, T. *et al.* Comparison of organic peracids in wastewater treatment: Disinfection, oxidation and corrosion. *Water Research*, v. 85, p. 275–285, 2015.

MACHULEK, A.; QUINA, F. H.; GOZZI, F. Fundamental Mechanistic Studies of the Photo-Fenton Reaction for the Degradation of Organic Pollutants. *Organic pollutants. Intech Publisher Inc., Rijeka*, p. 271–292, 2012.

MACÍAS-QUIROGA, I. F. *et al.* Bibliometric analysis of advanced oxidation processes (AOPs) in wastewater treatment: global and Ibero-American research trends. *Environmental Science and Pollution Research*, n. Wwap 2017, 2020.

MACKUĽAK, T. *et al.* Hospital wastewaters treatment: Fenton reaction vs. BDDE vs. ferrate(VI). *Environmental Science and Pollution Research*, v. 26, n. 31, p. 31812–31821, 2019. Available at: <http://link.springer.com/10.1007/s11356-019-06290-9>.

MADIKIZELA, L. M.; TAVENGWA, N. T.; CHIMUKA, L. Status of pharmaceuticals in African water bodies: Occurrence, removal and analytical methods. *Journal of Environmental Management*, v. 193, p. 211–220, 2017. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0301479717301305>.

MALATO, S. *et al.* Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today*, v. 147, n. 1, p. 1–59, 2009.

MANDAL, S. Reaction Rate Constants of Hydroxyl Radicals with Micropollutants and Their Significance in Advanced Oxidation Processes. *Journal of Advanced Oxidation Technologies*, v. 21, n. 1, 2018.

MANENTI, D. R. *et al.* Performance evaluation of different solar advanced oxidation processes applied to the treatment of a real textile dyeing wastewater. *Environmental science and pollution research international*, v. 22, n. 2, p. 833–845, 2015.

MANIAKOVA, G. *et al.* Simultaneous removal of contaminants of emerging concern and pathogens from urban wastewater by homogeneous solar driven advanced oxidation processes. *Science of the Total Environment*, v. 766, p. 144320, 2021. Available at: <https://doi.org/10.1016/j.scitotenv.2020.144320>.

MARCELINO, R. B. P. *et al.* Solar energy for wastewater treatment: review of international technologies and their applicability in Brazil. *Environmental Science and Pollution Research*, v. 22, n. 2, p. 762–773, 2014.

MARGOT, J. *et al.* Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? *Science of The Total Environment*, v. 461–462, p. 480–498, 2013. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0048969713005779>.

MARTINEZ-GUERRA, E. *et al.* Wetlands for Wastewater Treatment. *Water Environment Research*, v. 87, n. 10, p. 1095–1126, 2015. Available at: <https://onlinelibrary.wiley.com/doi/abs/10.2175/106143015X14338845155426>.

MARTÍNEZ-PIERNAS, A. B. *et al.* Validation and application of a multiresidue method based on liquid chromatography-tandem mass spectrometry for evaluating the plant uptake of 74 microcontaminants in crops irrigated with treated municipal wastewater. *Journal of Chromatography A*, v. 1534, p. 10–21, 2018.

MEADOR, J. P. *et al.* Contaminants of emerging concern in a large temperate estuary. *Environmental Pollution*, v. 213, p. 254–267, 2016. Available at: <https://www.sciencedirect.com/science/article/pii/S0269749116300884?via%3Dihub#appsec1>.

METCALF & EDDY, I. *Wastewater Engineering: Treatment and Resource Recovery*. 5th. ed. New York, NY, US: McGraw-Hill, 2013.

MICHAEL-KORDATOU, I. *et al.* Dissolved effluent organic matter: Characteristics and potential implications in wastewater treatment and reuse applications. *Water Research*, v. 77, p. 213–248, 2015. Available at: <http://www.sciencedirect.com/science/article/pii/S0043135415001931>.

MICHAEL, I. *et al.* Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: A review. *Water Research*, v. 47, n. 3, p. 957–995, 2013. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0043135412008391>.

MIJANGOS, L. *et al.* Occurrence of emerging pollutants in estuaries of the Basque Country: Analysis of sources and distribution, and assessment of the environmental risk. *Water Research*, v. 147, p. 152–163, 2018. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0043135418307486>.

MIKLOS, D. B. *et al.* Comparison of UV-AOPs (UV/H2O2, UV/PDS and UV/Chlorine) for TOrC removal from municipal wastewater effluent and optical surrogate model evaluation. *Chemical Engineering Journal*, v. 362, p. 537–547, 2019.

MOREIRA, N. F. F. *et al.* Solar treatment (H2O2 , TiO2 -P25 and GO-TiO2 photocatalysis, photo-Fenton) of organic micropollutants, human pathogen indicators, antibiotic resistant bacteria and related genes in urban wastewater. *Water Research*, v. 135, p. 195–206, 2018. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S004313541830085X>.

NASUHOGLU, D. *et al.* Chemical, microbial and toxicological assessment of wastewater treatment plant effluents during disinfection by ozonation. *Chemical Engineering Journal*, v. 346, p. 466–476, 2018. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1385894718305862>.

NATIONAL HEALTH AND MEDICAL RESEARCH COUNCIL. *How to review the evidence: systematic identification and review of the scientific literature*. 1st. ed. Canberra: Biotext, 2000.

NDOUNLA, J.; PULGARIN, C. Evaluation of the efficiency of the photo Fenton disinfection of natural drinking water source during the rainy season in the Sahelian region. *Science of The Total Environment*, v. 493, p. 229–238, 2014. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0048969714008316>.

NOGUEIRA, R. F. P.; OLIVEIRA, M. C.; PATERLINI, W. Simple and fast spectrophotometric determination of H2O2 in photo-Fenton reactions using metavanadate. *Talanta*, v. 66, n. 1, p. 86–91, 2005.

NOYOLA, A. *et al.* Typology of Municipal Wastewater Treatment Technologies in Latin America. *Clean - Soil, Air, Water*, v. 40, n. 9, p. 926–932, 2012.

ORT, C. *et al.* Sampling for PPCPs in Wastewater Systems: Comparison of Different Sampling Modes and Optimization Strategies. *Environmental Science & Technology*, v. 44, n. 16, p. 6289–6296, 2010. Available at: <https://doi.org/10.1021/es100778d>.

PAPAGEORGIOU, M.; KOSMA, C.; LAMBROPOULOU, D. Seasonal occurrence, removal, mass loading and environmental risk assessment of 55 pharmaceuticals and personal care products in a municipal wastewater treatment plant in Central Greece. *Science of the Total Environment*, v. 543, p. 547–569, 2016. Available at: <http://dx.doi.org/10.1016/j.scitotenv.2015.11.047>.

PAPOUTSAKIS, S. *et al.* Microcontaminant degradation in municipal wastewater treatment plant secondary effluent by EDDS assisted photo-Fenton at near-neutral pH: An experimental design approach. *Catalysis Today*, 8th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications, v. 252, p. 61–69, 2015. Available at: <http://www.sciencedirect.com/science/article/pii/S092058611500070X>.

PESSOA, G. P. *et al.* Occurrence and removal of estrogens in Brazilian wastewater treatment plants. *Science of The Total Environment*, v. 490, p. 288–295, 2014. Available at: <http://www.sciencedirect.com/science/article/pii/S0048969714006664>.

PHILIPPE, K. K. *et al.* Photocatalytic Disinfection and Removal of Emerging Pollutants from Effluents of Biological Wastewater Treatments, Using a Newly Developed Large-Scale Solar

Simulator. *Industrial & Engineering Chemistry Research*, v. 55, n. 11, p. 2952–2958, 2016. Available at: <https://doi.org/10.1021/acs.iecr.5b04927>.

PINTOR, A. M. A.; VILAR, V. J. P.; BOAVENTURA, R. A. R. Decontamination of cork wastewaters by solar-photo-Fenton process using cork bleaching wastewater as H2O2 source. *Solar Energy*, v. 85, n. 3, p. 579–587, 2011.

PIRES, A. *et al.* Long-term exposure of polychaetes to caffeine: Biochemical alterations induced in Diopatra neapolitana and Arenicola marina. *Environmental Pollution*, v. 214, p. 456–463, 2016.

PRIETO-RODRÍGUEZ, L. *et al.* Application of solar AOPs and ozonation for elimination of micropollutants in municipal wastewater treatment plant effluents. *Water Research*, v. 47, n. 4, p. 1521–1528, 2013.

RICHARDSON, S D. *et al.* Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutation Research - Reviews in Mutation Research*, v. 636, n. 1–3, p. 178–242, 2007.

RIVAS, G. *et al.* Modelling of the operation of raceway pond reactors for micropollutant removal by solar photo-Fenton as a function of photon absorption. *Applied Catalysis B: Environmental*, v. 178, n. April 2016, p. 210–217, 2015. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0926337314005426>.

RIVAS IBÁÑEZ, G. *et al.* Does micropollutant removal by solar photo-Fenton reduce ecotoxicity in municipal wastewater? A comprehensive study at pilot scale open reactors. *Journal of Chemical Technology and Biotechnology*, v. 92, n. 8, p. 2114–2122, 2017. Available at: <http://doi.wiley.com/10.1002/jctb.5212>.

RIZZO, L. *et al.* Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater. *Science of The Total Environment*, v. 655, n. October 2018, p. 986–1008, 2019. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0048969718346229>.

RODRÍGUEZ-CHUECA, J. *et al.* Assessment of full-scale tertiary wastewater treatment by UV-C based-AOPs: Removal or persistence of antibiotics and antibiotic resistance genes? *Science of the Total Environment*, v. 652, p. 1051–1061, 2019.

RODRÍGUEZ-CHUECA, J. *et al.* Intensification of UV-C tertiary treatment: Disinfection and removal of micropollutants by sulfate radical based Advanced Oxidation Processes. *Journal of Hazardous Materials*, abr. 2018. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0304389418302760>.

ROMMOZZI, E. *et al.* Detrimental vs. beneficial influence of ions during solar (SODIS) and photo-Fenton disinfection of E. coli in water: (Bi)carbonate, chloride, nitrate and nitrite effects. *Applied Catalysis B: Environmental*, v. 270, n. February, 2020.

SÁNCHEZ PÉREZ, J. A. *et al.* Effect of temperature and photon absorption on the kinetics of micropollutant removal by solar photo-Fenton in raceway pond reactors. *Chemical Engineering Journal*, v. 310, p. 464–472, 2017. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1385894716308622>.

SÁNCHEZ PÉREZ, J. A. *et al.* Neutral or acidic pH for the removal of contaminants of emerging concern in wastewater by solar photo-Fenton? A techno-economic assessment of continuous raceway pond reactors. *Science of the Total Environment*, v. 736, p. 139681, 2020. Available at: <https://doi.org/10.1016/j.scitotenv.2020.139681>.

SCHWARZENBACH, R. P. The Challenge of Micropollutants in Aquatic Systems. *Science*, v.

313, n. 5790, p. 1072–1077, 2006. Available at: <http://www.sciencemag.org/cgi/doi/10.1126/science.1127291>.

SGROI, M.; SNYDER, S.A.; ROCCARO, P. Comparison of AOPs at pilot scale: Energy costs for micro-pollutants oxidation, disinfection by-products formation and pathogens inactivation. *Chemosphere*, v. 273, p. 128527, 2021.

SHARMA, S. K.; KENNEDY, M. D. Soil aquifer treatment for wastewater treatment and reuse. *International Biodeterioration & Biodegradation*, v. 119, p. 671–677, 2017. Available at: <http://www.sciencedirect.com/science/article/pii/S0964830516303973>.

SHARMA, V. K.; ZBORIL, R.; VARMA, R. S. Ferrates: Greener Oxidants with Multimodal Action in Water Treatment Technologies. *Accounts of Chemical Research*, v. 48, n. 2, p. 182–191, 2015. Available at: <https://doi.org/10.1021/ar5004219>.

SILVA, Gizele D. et al. Contrasting the performance of photo-Fenton at neutral pH in the presence of different organic iron-complexes using hydrogen peroxide or persulfate as oxidants for naproxen degradation and removal of antimicrobial activity. *Process Safety and Environmental Protection*, v. 147, p. 798–807, 1 mar. 2021. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0957582021000069>.

SIMON, R. G. *et al.* Current to Clean Water – Electrochemical Solutions for Groundwater, Water, and Wastewater Treatment. *Chemie Ingenieur Technik*, v. 90, n. 11, p. 1832–1854, 2018. Available at: <https://onlinelibrary.wiley.com/doi/abs/10.1002/cite.201800081>.

SKOOG, D. A.; HOLLER, F. J.; CROUCH, S. R. *Princípios de analise instrumental*. 6th. ed. Porto Alegre: Bookman, 2009.

SORIANO-MOLINA, P.; PLAZA-BOLAÑOS, P.; *et al.* Assessment of solar raceway pond reactors for removal of contaminants of emerging concern by photo-Fenton at circumneutral pH from very different municipal wastewater effluents. *Chemical Engineering Journal*, v. 366, n. February, p. 141–149, 2019. Available at: <https://doi.org/10.1016/j.cej.2019.02.074>.

SORIANO-MOLINA, P.; GARCÍA SÁNCHEZ, J.; MALATO, S.; *et al.* Effect of volumetric rate of photon absorption on the kinetics of micropollutant removal by solar photo-Fenton with Fe3+-EDDS at neutral pH. *Chemical Engineering Journal*, v. 331, p. 84–92, 2018. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1385894717314377>.

SORIANO-MOLINA, P.; GARCÍA SÁNCHEZ, J.; ALFANO, O.; *et al.* Mechanistic modeling of solar photo-Fenton process with Fe 3+ -EDDS at neutral pH. *Applied Catalysis B: Environmental*, v. 233, n. March, p. 234–242, 2018. Available at: <https://doi.org/10.1016/j.apcatb.2018.04.005>.

SORIANO-MOLINA, P.; GARCÍA SÁNCHEZ, J.; *et al.* On the design and operation of solar photo-Fenton open reactors for the removal of contaminants of emerging concern from WWTP effluents at neutral pH. *Applied Catalysis B: Environmental*, v. 256, p. 117801, 2019. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0926337319305478>.

SORIANO-MOLINA, P.; MIRALLES-CUEVAS, S.; *et al.* Two strategies of solar photo-Fenton at neutral pH for the simultaneous disinfection and removal of contaminants of emerging concern. Comparative assessment in raceway pond reactors. *Catalysis Today*, 2019. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0920586119306443>.

SOUZA, B. S. *et al.* Evaluation of UV/H2O2 for the disinfection and treatment of municipal secondary effluents for water reuse. *Journal of Chemical Technology & Biotechnology*, v. 88, n. 9, p. 1697–1706, 2013. Available at: <http://doi.wiley.com/10.1002/jctb.4021>.

SPASIANO, D. *et al.* Solar photocatalysis: Materials, reactors, some commercial, and preindustrialized applications. A comprehensive approach. *Applied Catalysis B: Environmental*, v. 170–171, p. 90–123, 2015.

SPERLING, M. VON. *Urban wastewater treatment in Brazil. IDB - Inter-American Development Bank*. Belo Horizonte:, 2016. Available at: <www.iadb.org>.

STAEDELE, A. E.; ENSSLIN, S. R.; FORCELLINI, F. A. Knowledge building about performance evaluation in lean production: An investigation on international scientific research. *Journal of Manufacturing Technology Management*, v. 30, n. 5, p. 798–820, 2019.

STARLING, M. C. V. M.; DOS SANTOS, P. H. R.; *et al.* Application of solar photo-Fenton toward toxicity removal and textile wastewater reuse. *Environmental Science and Pollution Research*, v. 24, n. 14, p. 12515–12528, 2017. Available at: <http://dx.doi.org/10.1007/s11356-016-7395-5>.

STARLING, Maria Clara V. M. *Degradation of Contaminants of Emerging Concern in Different Matrices By Advanced Oxidation Processes : Evolution of Toxicity and disinfection*. 2018. 194 f. UFMG, 2018.

STARLING, M. C. V. M. *et al.* Intensification of UV-C treatment to remove emerging contaminants by UV-C/H 2 O 2 and UV-C/S 2 O 82−: Susceptibility to photolysis and investigation of acute toxicity. *Chemical Engineering Journal*, n. xxxx, p. 0–1, 2019. Available at: <https://doi.org/10.1016/j.cej.2019.01.135>.

STARLING, M. C. V. M.; CASTRO, L. A. S.; *et al.* Optimized treatment conditions for textile wastewater reuse using photocatalytic processes under UV and visible light sources. *Environmental Science and Pollution Research*, v. 24, n. 7, p. 6222–6232, 2017.

STARLING, M. C. V. M. *et al.* Persulfate mediated solar photo-Fenton aiming at wastewater treatment plant effluent improvement at neutral PH: emerging contaminant removal, disinfection, and elimination of antibiotic-resistant bacteria. *Environmental Science and Pollution Research*, 2021. Available at: <http://link.springer.com/10.1007/s11356-020-11802-z>.

STARLING, M. C. V. M.; AMORIM, C. C.; LEÃO, M. M. D. Occurrence, control and fate of contaminants of emerging concern in environmental compartments in Brazil. *Journal of Hazardous Materials*, v. 372, p. 17–36, 2019. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0304389418302759>.

SUN, P. *et al.* Degradation of DEET and caffeine under UV/Chlorine and simulated sunlight/Chlorine conditions. *Environmental Science and Technology*, v. 50, n. 24, p. 13265–13273, 2016.

TANG, W. Z. *Physicochemical Treatment of Hazardous Wastes*: CRC Press, 2003. Available at: <https://books.google.com.br/books?id=0pWGmybyyH4C>.

TAOUFIK, N. *et al.* Removal of emerging pharmaceutical pollutants: A systematic mapping study review. *Journal of Environmental Chemical Engineering*, v. 8, n. 5, p. 104251, 2020. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S221334372030600X>.

TASCA, J. E. *et al.* An approach for selecting a theoretical framework for the evaluation of training programs. *Journal of European Industrial Training*, v. 34, n. 7, p. 631–655, 2010. Available at: <https://www.emerald.com/insight/content/doi/10.1108/03090591011070761/full/html>.

TERNES, T. A. *et al.* Integrated Evaluation Concept to Assess the Efficacy of Advanced Wastewater Treatment Processes for the Elimination of Micropollutants and Pathogens. *Environmental Science & Technology*, v. 51, n. 1, p. 308–319, 2017. Available at:

<https://doi.org/10.1021/acs.est.6b04855>.

TRAN, N. H.; REINHARD, M.; GIN, K. Y. H. Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review. *Water Research*, v. 133, p. 182–207, 2018. Available at: <https://doi.org/10.1016/j.watres.2017.12.029>.

TSIHRINTZIS, V. A. The use of Vertical Flow Constructed Wetlands in Wastewater Treatment. *Water Resources Management*, v. 31, n. 10, p. 3245–3270, 2017. Available at: <http://link.springer.com/10.1007/s11269-017-1710-x>.

VAN ECK, N. J.; WALTMAN, L. Software survey: VOSviewer, a computer program for bibliometric mapping. *Scientometrics*, v. 84, n. 2, p. 523–538, 2010. Available at: <http://link.springer.com/10.1007/s11192-009-0146-3>.

VANDERFORD, B. J. *et al.* Assessment of sample preservation techniques for pharmaceuticals, personal care products, and steroids in surface and drinking water. *Analytical and Bioanalytical Chemistry*, v. 399, n. 6, p. 2227–2234, 2011. Available at: <https://doi.org/10.1007/s00216-010-4608-5>.

VERLICCHI, P.; AL AUKIDY, M.; ZAMBELLO, E. What have we learned from worldwide experiences on the management and treatment of hospital effluent? — An overview and a discussion on perspectives. *Science of The Total Environment*, v. 514, p. 467–491, 2015. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0048969715001564>.

VILLEGAS- GUZMAN, P. *et al.* A green solar photo-Fenton process for the elimination of bacteria and micropollutants in municipal wastewater treatment using mineral iron and natural organic acids. *Applied Catalysis B: Environmental*, v. 219, p. 538–549, 2017. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0926337317307154>.

VOULVOULIS, N. Water reuse from a circular economy perspective and potential risks from an unregulated approach. *Current Opinion in Environmental Science and Health*, v. 2, p. 32–45, 2018. Available at: <https://doi.org/10.1016/j.coesh.2018.01.005>.

WANG, J. *et al.* Monitoring of 943 organic micropollutants in wastewater from municipal wastewater treatment plants with secondary and advanced treatment processes. *Journal of Environmental Sciences (China)*, v. 67, p. 309–317, 2018. Available at: <https://doi.org/10.1016/j.jes.2017.09.014>.

WANG, W. L. *et al.* Synergistic effect between UV and chlorine (UV/chlorine) on the degradation of carbamazepine: Influence factors and radical species. *Water Research*, v. 98, p. 190–198, 2016. Available at: <http://dx.doi.org/10.1016/j.watres.2016.04.015>.

WANG, W.L. *et al.* Light-emitting diodes as an emerging UV source for UV/chlorine oxidation: Carbamazepine degradation and toxicity changes. *Chemical Engineering Journal*, v. 310, p. 148–156, 2017. Available at: <http://www.sciencedirect.com/science/article/pii/S1385894716315078>.

WHO. WORLD HEALTH ORGANIZATION. *Antibiotic resistance*. Available at: <https://www.who.int/news-room/fact-sheets/detail/antibiotic-resistance>. Acessed in 25 June 2020.

WILLIAMS, A. J. *et al.* The CompTox Chemistry Dashboard: a community data resource for environmental chemistry. *Journal of Cheminformatics*, v. 9, n. 1, p. 61, 2017. Available at: <https://jcheminf.biomedcentral.com/articles/10.1186/s13321-017-0247-6>.

WISHART, D. S. *et al.* DrugBank 5.0: a major update to the DrugBank database for 2018. *Nucleic Acids Research*, v. 46, n. D1, p. D1074–D1082, 2018. Available at:

<http://academic.oup.com/nar/article/46/D1/D1074/4602867>.

WU, Y.-H. *et al.* Microalgal species for sustainable biomass/lipid production using wastewater as resource: A review. *Renewable and Sustainable Energy Reviews*, v. 33, p. 675–688, maio 2014. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1364032114001476>.

YAN, Q. *et al.* Occurrence, fate and ecotoxicological assessment of pharmaceutically active compounds in wastewater and sludge from wastewater treatment plants in Chongqing, the Three Gorges Reservoir Area. *Science of The Total Environment*, v. 470–471, p. 618–630, 2014. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S004896971301070X>.

YANG, C.; SONG, G.; LIM, W. A review of the toxicity in fish exposed to antibiotics. *Comparative Biochemistry and Physiology Part - C: Toxicology and Pharmacology*, v. 237, p. 108840, 2020. Available at: <https://doi.org/10.1016/j.cbpc.2020.108840>.

ZHANG, J. *et al.* Ceramic membrane separation coupled with catalytic ozonation for tertiary treatment of dyestuff wastewater in a pilot-scale study. *Chemical Engineering Journal*, v. 301, p. 19–26, 2016. Available at: <http://www.sciencedirect.com/science/article/pii/S1385894716306088>.

ZHANG, S. *et al.* Dual roles of hydroxyl radicals and effects of competition on ozonation kinetics of two phenazone-type pollutants. *Emerging Contaminants*, v. 1, n. 1, p. 2–7, 2015. Available at: <http://dx.doi.org/10.1016/j.emcon.2015.05.004>.

ZHAO, Y.; YE, L.; ZHANG, X.-X. Emerging Pollutants–Part I: Occurrence, Fate and Transport. *Water Environment Research*, v. 90, n. 10, p. 1301–1322, 2018. Available at: <http://doi.wiley.com/10.2175/106143018X15289915807236>.

ZIMMERMANN, S. G. *et al.* Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: Micropollutant oxidation, by-product formation and disinfection. *Water Research*, v. 45, n. 2, p. 605–617, 2011. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0043135410005634>.

APPENDICES

APPENDIX I – FINAL PORTFOLIO OF PEER-REVIEWED MANUSCRIPTS WITH RESPECTIVE NUMBER OF CITATIONS

Title	Reference	Number of citations
Recent developments in photocatalytic water treatment technology: A review	(CHONG *et al.*, 2010)	3626
Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: A review	(MICHAEL *et al.*, 2013)	1050
Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon?	(MARGOT *et al.*, 2013)	478
Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: A critical review	(AHMED *et al.*, 2017)	321
Advanced Oxidation Processes (AOPs) in Wastewater Treatment	(DENG; ZHAO, 2015)	308
Performance of UV and UV/H2O2 processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan	(KIM, I.; YAMASHITA; TANAKA, 2009)	288
Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: Micropollutant oxidation, by-product formation and disinfection	(ZIMMERMANN *et al.*, 2011)	218
Dissolved effluent organic matter: Characteristics and potential implications in wastewater treatment and reuse applications	(MICHAEL-KORDATOU *et al.*, 2015)	207
From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: A review	(GRANDCLÉMENT *et al.*, 2017)	196
Ferrates: Greener Oxidants with Multimodal Action in Water Treatment Technologies	(SHARMA, V. K.; ZBORIL; VARMA, 2015)	165
What have we learned from worldwide experiences on the management and treatment of hospital effluent? — An overview and a discussion on perspectives	(VERLICCHI; AL AUKIDY; ZAMBELLO, 2015)	147
Treatment of Municipal Wastewater Treatment Plant Effluents with Modified Photo-Fenton As a Tertiary Treatment for the Degradation of Micro Pollutants and Disinfection	(KLAMERTH *et al.*, 2012)	128
Use of hydrodynamic cavitation in (waste)water treatment	(DULAR *et al.*, 2016)	118
Advances in the development and application of ferrate(VI) for water and wastewater treatment	(JIANG, 2014)	115

Title	**Reference**	**Number of citations**
Performance of secondary wastewater treatment methods for the removal of contaminants of emerging concern implicated in crop uptake and antibiotic resistance spread: A review	(KRZEMINSKI *et al.*, 2019)	69
Application of membrane bioreactor technology for wastewater treatment and reuse in the Mediterranean region: Focusing on removal efficiency of non-conventional pollutants	(BOLZONELLA *et al.*, 2010)	57
Micropollutant degradation, bacterial inactivation and regrowth risk in wastewater effluents: Influence of the secondary (pre)treatment on the efficiency of Advanced Oxidation Processes	(GIANNAKIS; VOUMARD; *et al.*, 2016)	56
Comparison of organic peracids in wastewater treatment: Disinfection, oxidation, and corrosion	(LUUKKONEN *et al.*, 2015)	48
Solar treatment (H2O2 , TiO2 -P25 and GO-TiO2 photocatalysis, photo-Fenton) of organic micropollutants, human pathogen indicators, antibiotic resistant bacteria and related genes in urban wastewater	(MOREIRA *et al.*, 2018)	48
Ceramic membrane separation coupled with catalytic ozonation for tertiary treatment of dyestuff wastewater in a pilot-scale study	(ZHANG, J. *et al.*, 2016)	36
Cross-Contamination of Residual Emerging Contaminants and Antibiotic Resistant Bacteria in Lettuce Crops and Soil Irrigated with Wastewater Treated by Sunlight/H 2 O 2	(FERRO *et al.*, 2015)	36
A green solar photo-Fenton process for the elimination of bacteria and micropollutants in municipal wastewater treatment using mineral iron and natural organic acids	(VILLEGAS- GUZMAN *et al.*, 2017)	30
Occurrence of UV filters, fragrances and organophosphate flame retardants in municipal WWTP effluents and their removal during membrane post-treatment	(KRZEMINSKI *et al.*, 2017)	28
Evaluation of UV/H2O2 for the disinfection and treatment of municipal secondary effluents for water reuse	(SOUZA *et al.*, 2013)	27
Integrated Evaluation Concept to Assess the Efficacy of Advanced Wastewater Treatment Processes for the Elimination of Micropollutants and Pathogens	(TERNES *et al.*, 2017)	27
Soil aquifer treatment for wastewater treatment and reuse	(SHARMA, S. K.; KENNEDY, 2017)	26
Photocatalytic Disinfection and Removal of Emerging Pollutants from Effluents of Biological Wastewater Treatments, Using a Newly Developed Large-Scale Solar Simulator	(PHILIPPE *et al.*, 2016)	23

Title	Reference	Number of citations
Reducing nutrients, organic micropollutants, antibiotic resistance, and toxicity in rural wastewater effluent with subsurface filtration treatment technology	(ANDERSON *et al.*, 2015)	19
Heterogeneous photocatalysis using UVA-LEDs for the removal of antibiotics and antibiotic resistant bacteria from urban wastewater treatment plant effluents	(BIANCULLO *et al.*, 2019)	16
Intensification of UV-C tertiary treatment: Disinfection and removal of micropollutants by sulfate radical based Advanced Oxidation Processes	(RODRÍGUEZ-CHUECA *et al.*, 2018)	15
Assessment of full-scale tertiary wastewater treatment by UV-C based-AOPs: Removal or persistence of antibiotics and antibiotic resistance genes?	(RODRÍGUEZ-CHUECA *et al.*, 2019)	14
TiO2/graphene-based nanocomposites for water treatment: A brief overview of charge carrier transfer, antimicrobial and photocatalytic performance	(KUSIAK-NEJMAN; MORAWSKI, 2019)	14
The use of Vertical Flow Constructed Wetlands in Wastewater Treatment	(TSIHRINTZIS, 2017)	12
Chemical, microbial and toxicological assessment of wastewater treatment plant effluents during disinfection by ozonation	(NASUHOGLU *et al.*, 2018)	10
Wetlands for Wastewater Treatment	(MARTINEZ-GUERRA *et al.*, 2015)	8
Wetlands for Wastewater Treatment	(CASTILLO-VALENZUELA; MARTINEZ-GUERRA; GUDE, 2017)	5
Combining micelle-clay sorption to solar photo-Fenton processes for domestic wastewater treatment	(BRIENZA *et al.*, 2019)	2
Current to Clean Water – Electrochemical Solutions for Groundwater, Water, and Wastewater Treatment	(SIMON *et al.*, 2018)	2
Hospital wastewaters treatment: Fenton reaction vs. BDDE vs. ferrate(VI)	(MACKUĽAK *et al.*, 2019)	1
Wetlands for wastewater treatment	(GHIMIRE *et al.*, 2019)	1
The total sum of citations in the portfolio		7,995

APPENDIX II – COMPLETE SYSTEMIC ANALYSIS: FINAL MANUSCRIPTS

Manuscript	Description of method (tool, instrument, methodology, etc.) used in the paper. In case there is no description, develop a quick description of the evaluation performance carried out in the paper	Reference
A green solar photo-Fenton process for the elimination of bacteria and micropollutants in municipal wastewater treatment using mineral iron and natural organic acids	Evaluation of alternative and natural iron sources and organic complexing agents for photo-Fenton reaction disinfection and CECs removal	(VILLEGAS-GUZMAN *et al.*, 2017)
Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon?	Evaluation of two pilot-scale plants of ozonation and activated carbon for MP removal, estrogenicity, toxicity, disinfection, etc., over 1 year in a MWWTP in Switzerland	(MARGOT *et al.*, 2013)
Solar treatment (H_2O_2, TiO_2-P25 and GO-TiO_2 photocatalysis, photo-Fenton) of organic micropollutants, human pathogen indicators, antibiotic resistant bacteria and related	Evaluation of MP removal in a semi-pilot scale reactor evaluating disinfection for solar AOP treatments (photo-Fenton, photocatalysis, and peroxidation)	(MOREIRA *et al.*, 2018)
What have we learned from worldwide experiences on the management and treatment of hospital effluent? — An overview and a discussion on perspectives	A review of 48 works exploring treatment of hospital effluent from 2005-2015, comparing different technologies, MP removal and other conventional parameters, from different countries around the world	(VERLICCHI; AL AUKIDY; ZAMBELLO, 2015)
Intensification of UV-C tertiary treatment: Disinfection and removal of micropollutants by sulfate radical based Advanced Oxidation Processes	Evaluation of UVC treatment alone or combined with persulfate in semi-pilot scale for MP removal and disinfection	(RODRÍGUEZ-CHUECA *et al.*, 2018)

Article: A green solar photo-Fenton process for the elimination of bacteria and micropollutants in municipal wastewater treatment using mineral iron and natural organic acids (VILLEGAS- GUZMAN *et al.*, 2017)

Lens	The research lens (concept) is dealt with in the paper?	If yes, highlight how this lens (concept) is dealt with in the paper	MAIN STRENGTHS Concept	MAIN WEAKNESSES Concept
Monitored parameters	Yes	Physical-chemical: dissolved iron, hydrogen peroxide, COD, DOC, and 21 MP (analytical method had up to 28 MP). Many drugs and chemicals, no hormones. Microbiological: bacteria by spread plate	Both MP and disinfection evaluation through all reactions. In experiments with real WW not only E.coli, but heterotrophic bacteria was analyzed	Maybe quantification of scavengers species (carbonate, sulfates, chloride, etc.), a better description of pH evolution within the different acids tested
Studied matrixes	Yes	Initially, simulated municipal secondary effluent (39ppm COD, 9.8ppmDOC, pH 7.5 E.coli K-12 strain) and real effluents from MWWTP Vidy treated by AS or coagulation/flocculation	Simulated effluent contained bacteria. Real effluent not just AS, but also C/F pre-treatment. Real MP content in real effluent (not doped).	Some parts of a study performed on simulated effluent, with no MP dosage (perhaps the MP in the real effluent can produce byproducts, or make more difficult the disinfection?)
Treatment process parameters	Yes	With a description of the parameters	Evaluation after 24 h in the dark not only for bacteria regrowth but also MP removal: increase in the dark at a slow rate (Fenton)	Small volume, batch lab-scale test, solar-box with no variation of radiation intensity, no variation of doses of reagents or ligand/iron
Toxicity and other possible effects	No	-	-	-

Lens	The research lens (concept) is dealt with in the paper?	If yes, highlight how this lens (concept) is dealt with in the paper	MAIN STRENGTHS Concept	MAIN WEAKNESSES Concept
Treatment process efficiency	Yes	It is described on graphs (disinfection), and MP is shown each % and also a global weighted % removal	No regrowth. Fast disinfection (270 min, real effluent) but slow MP (40%), mineralization (40%) and EfOM removal (COD 50%) (24 h)	Not all experiments reached complete inactivation, perhaps a table with all log removals
Costs analysis	No	-	-	-

Article: Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? (MARGOT *et al.*, 2013)

Lens	The research lens (concept) is dealt with in the paper?	If yes, highlight how this lens (concept) is dealt with in the paper	MAIN STRENGTHS Concept	MAIN WEAKNESSES Concept
Analytical parameters	Yes	Physical-chemical: Standard wastewater quality parameters (TSS, DOC, COD, BOD_5, NH_4, NO_3, NO_2, P_{total}, and $P_{soluble}$), pH, temperature, conductivity (online). and 58 MP (and two seasonal up to 120). Microbiological: indicator bacteria (Escherichia coli, intestinal enterococci, and total viable bacteria) and coliphages (F-specific (RNA) and somatic phages. Bioassays: YES, Combined Algal Assay, fish early life stage with rainbow trout	More than one bioassay, and microbiological indicator, as well as many different MP with different characteristics were analyzed. Composite samples from different campaigns	No weaknesses
Studied matrices	Yes	Complete description of the real wastewater and also of treatment facilities.	Pilot-scale of real municipal wastewater over 1 year	No weaknesses
Treatment conditions	Yes	Brings a description of the parameters	Continuous pilot-scale reactors, investigation with different ozone doses, nitrification on biological process, organic matter concentration for the coagulation stage	Mostly results for MP removal only and related to different operational parameters. But for disinfection only results for the main operational conditions and presented briefly at the end of the article

Lens	The research lens (concept) is dealt with in the paper?	If yes, highlight how this lens (concept) is dealt with in the paper	MAIN STRENGTHS Concept	MAIN WEAKNESSES Concept
Toxicity and other possible effects	Yes	Brings the description of the assays, with a good variety of assays	Estrogenicity study with YES, toxicity in different trophic levels (with combined algal and also early life stage rainbow trout). Also, bromate and toxic bromide byproducts investigated	No weaknesses
Efficiency of proposed treatment	Yes	Described in graphs, tables. Very complete. Arithmetic Average for MP %	Comparison of MP efficiencies with specific characteristics	Few results and combined in graphs with SD for the disinfection, not able to compare it in different situations
Costs analysis	Yes	Described in a table, including operating (staff, reagents, electricity), investment, interest rate, and amortization	Includes operational and investment, amortization rates different for different types of equipment (mechanical, or structural for ex.)	No details of the calculation method! Few results in a table, for just some of the operational conditions (80% average removal MP).

Article: Solar treatment (H_2O_2, TiO_2 -P25 and GO-TiO_2 photocatalysis, photo-Fenton) of organic micropollutants, human pathogen indicators, antibiotic resistant bacteria and related (MOREIRA *et al.*, 2018)

Lens	The research lens (concept) is dealt with in the paper?	If yes, highlight how this lens (concept) is dealt with in the paper	MAIN STRENGTHS Concept	MAIN WEAKNESSES Concept
Analytical parameters	Yes	Physicochemical: DOC, DIC, turbidity, H_2O_2 concentration, Fe, and 3 MP (carbamazepine, diclofenac, sulfamethoxazole). Microbiological: fecal coliforms, enterococci, and their tetracycline and ciprofloxacin-resistant counterparts selected ARGs (DNA extraction and PCR)	Bacteria diversity. Inactivation and MP removal over time, ABR and ARG analysis	Not much information on inorganic substances, and nor on the mentioned parameters over time pH, temperature, H_2O_2 consumption, and Fe concentration
Studied matrices	Yes	Complete description of real wastewater, but very brief of the treatment facilities.	Spiked real effluent, semi-pilot study	Only three MP evaluated
Treatment conditions	Yes	Brings a description of the parameters	Different AOPs, optimized from previous works, batch semi-pilot study, regrowth after 3 days	No variation of parameters, more detail on reaction time besides accumulated energy,
Toxicity and other possible effects	Yes	ARB and ARG, and bacteria diversity	ARB and ARG study, also for the regrowth after 3 days in the dark	ARG and bacteria diversity not evaluated for the photo-Fenton process because it was not efficient on the MP removal. But, MPs were at high concentration (100 ppb each) and were spiked to the effluent.

Lens	The research lens (concept) is dealt with in the paper?	If yes, highlight how this lens (concept) is dealt with in the paper	MAIN STRENGTHS Concept	MAIN WEAKNESSES Concept
Efficiency of proposed treatment	Yes	Described on graphs, and in the text.	Many results for bacteria inactivation and ARB and ARG over time	No table with a summary of results in % or concentrations, just information on graphs
Costs analysis	No	-	-	-

Article: What have we learned from worldwide experiences in the management and treatment of hospital effluent? — An overview and a discussion on perspectives (VERLICCHI; AL AUKIDY; ZAMBELLO, 2015)

Lens	**The research lens (concept) is dealt with in the paper?**	**If yes, highlight how this lens (concept) is dealt with in the paper**	**MAIN STRENGTHS Concept**	**MAIN WEAKNESSES Concept**
Analytical parameters	Yes	A table with the parameters evaluated for all 48 papers of the review	Many parameters (since conventional physical-chemical ones, microbiological and MP).	Not all parameters analyzed in all the papers or not indicated by the review (just one or two with analysis of both MP and disinfection; usually, the disinfection was evaluated together with just conventional parameters). Focused on MP removal throughout the paper and disinfection just at the end and very briefly
Studied matrices	Yes	A table of the review summarized all works, and mostly real effluents were studied	Real hospital effluents from different places around the world, sampled from different technologies (CAS, MBR, AOP, ponds, membrane, ozonation, etc.)	No weaknesses
Treatment conditions	Yes	Summarized briefly in a table with a description of the processes for each paper, or some parameters mentioned during the discussion	Many different technologies, from membrane separation and biological treatment to coagulation, filtration, disinfection with ozone, chlorine, AOP, etc.	Absence of a summary table with the best operational parameters of each technology in the reviewed papers
Toxicity and other possible effects	Yes	Mentioned very briefly studies with risk assessment, Microtox, D.	It was mentioned that hospital effluents are 5-15 more toxic	Few results for toxicity in the studies in general and focus more

Lens	The research lens (concept) is dealt with in the paper?	If yes, highlight how this lens (concept) is dealt with in the paper	MAIN STRENGTHS Concept	MAIN WEAKNESSES Concept
		magna. Also, one paragraph mentioned ARB and ARG.	than domestic WW. Interesting Risk assessment for (RQ of measured MP concentration and predicted no-effect concentration PNEC).	on conventional parameters. No investigation of possible byproducts.
Efficiency of proposed treatment	Yes	MP efficiency is discussed throughout the paper for each technology group. And just in the end, disinfection and conventional parameters are discussed.	AOPs seem to be the most promising technologies to remove a great diversity of compounds, including those that are not removed by other processes. AOP has fast reaction rates, leading to compact reactors, and also lower doses of reagents and lower residuals.	The necessity of toxicity evaluation after AOPs treatments. Wide range of efficiencies obtained for all technologies, necessity of definition of the best operational conditions.
Costs analysis	Yes	Summarized briefly in a table with description of operational, investment and maintenance costs	Even though some technologies as PAC and GAG seem efficient and competitive towards some AOPs if the EfOM increases operational costs increase very much with changes of filter and disposal of these technologies. The treatment of HWW is more expensive than UHH (euros/m^3), but the treated volume is lower.	Few studies presented costs, and some did not break into investment, operational, and maintenance costs.

Article: Intensification of UV-C tertiary treatment: Disinfection and removal of micropollutants by sulfate radical based Advanced Oxidation Processes (RODRÍGUEZ-CHUECA *et al.*, 2018)

Lens	**The research lens (concept) is dealt with in the paper?**	**If yes, highlight how this lens (concept) is dealt with in the paper**	**MAIN STRENGTHS Concept**	**MAIN WEAKNESSES Concept**
Analytical parameters	Yes	MPs (11 tested and 7 detected) in real wastewater and bacterial indicators on both (E. coli strain K12 and E. faecalis for simulated and wild for real) and fungi (Yeast Malt Extract Aga)	Both MP and disinfection in real wastewater. Also, fungi analyses	No description of pH, organic matter, other parameters, residual persulfate
Studied matrices	Yes	Simulated municipal secondary effluent and real effluents from MWWTP	Two strains in simulated wastewater. Use of real wastewater semi-pilot study	Some parts of the study performed with simulated effluent, with no MP dosage (perhaps the MP in the real effluent can produce byproducts, or limit disinfection?)
Treatment conditions	Yes	Brings a description of the parameters	Different flow rates and contact times (with different irradiation doses), regrowth after 24 and 48hs. Different concentrations of oxidant and Fe	Perhaps a comparison with other lamps than no UVC (LED) for sulfate activation?
Toxicity and other possible effects	No	-	-	-
Efficiency of proposed treatment	Yes	Described in graphs and tables.	Bacteria and fungi removal in Log (better to comprehend). Very complete on MP and disinfection discussion	Absence of other parameters (H_2O_2, persulfate consumption).
Costs analysis	No			

APPENDIX III – INFORMATION FOR THE FINAL FIVE SELECTED MANUSCRIPTS OF THE SYSTEMIC ANALYSIS: TREATMENT TECHNOLOGY, EVALUATED MATRIX, TREATMENT SCALE, MICROPOLLUTANTS, AND DISINFECTION EFFICIENCY, TOXICITY AND OTHER EFFECTS, AND TREATMENT COSTS

Manuscript	(VILLEGAS- GUZMAN *et al.*, 2017)	(MARGOT *et al.*, 2013)	(MOREIRA *et al.*, 2018)	(RODRÍGUEZ-CHUECA *et al.*, 2018)	(VERLICCHI; AL AUKIDY; ZAMBELLO, 2015)
Technology	Solar photo-Fenton	Ozonation + sand post-filtration or PAC + Membrane separation (UF) or sand post-filtration	Solar-H_2O_2, heterogeneous photocatalysis (TiO_2, TiO_2/H_2O_2, composite graphene GO/TiO_2; 0.2 g/L catalysts and 20 mg/L H_2O_2), solar photo-Fenton (10 mg L^{-1} Fe^{2+} and 20 mg L^{-1} H_2O_2, pH 5.5)	Sulfate Radical-based AOPs: H_2O_2/UVC, UVC/OS, UVC/PMS, UVC/PMS/Fe(II)	Membrane separation and biological treatment (CAS, MBR, MBBR, ponds among others) to coagulation, filtration, disinfection with ozone, chlorine, AOP
Treatment scale	Lab-scale	Pilot scale	Semipilot-scale	Lab-scale	Lab-scale and pilot scale (69 %), and full-scale (31 %)
Matrix	Real and synthetic wastewater, secondary effluent from the aerobic process, activated sludge or coagulation/flocculation process	Real secondary effluent, CAS	Real secondary effluent, CAS (spiked 100 µg L^{-1} each: carbamazepine-CBZ, sulfamethoxazole-SMX, and diclofenac-DFC)	Real secondary effluent, CAS (1-10^2 CFU mL^{-1}) and synthetic (spiked with *E. coli* strain K12 and *E. faecalis* each 10^6 CFU mL^{-1})	Real hospital wastewater (raw and pre-treated effluent)
MP removal efficiency	~35 – 40 % MP removal after 6 hours in the real effluent after CAS, using	80 % MPs (over 70 compounds detected) average ozone dose 5.7	MP removal <LOQ in 4 h (<40 kJ L^{-1}) for TiO_2 and TiO_2/H_2O_2.	Dose of oxidant: 0.5 mM and low UV-C contact time (9 s), 19 J L^{-1} led to	Pharmaceuticals were detected and evaluated in 60 % of the studies. The

Manuscript	(VILLEGAS- GUZMAN *et al.*, 2017)	(MARGOT *et al.*, 2013)	(MOREIRA *et al.*, 2018)	(RODRÍGUEZ-CHUECA *et al.*, 2018)	(VERLICCHI; AL AUKIDY; ZAMBELLO, 2015)
	the Lime juice extract, 5 ppm [M-Fe], 25 ppm H_2O_2. Mineralization (40 %) and EfOM removal (COD 50 %) after 24 h.	mg O_3 L^{-1} or PAC 10-20 mg L^{-1}. PAC-UF: DOC (54 ± 10 %), phosphorus (>90 %), NH_4 (85 ± 20 %) and BOD_5 (72 ± 18 %), and complete removal of TSS. PAC-SF: similar COD, TOC, DOC, and NH_4, but lower TSS and Phosphorus. Ozonation: no phosphorus removal, absence of DOC removal, and a significant increase in BOD_5 (49 ± 54 %). Sand filter was responsible for most of the macropollutant removals after ozonation, with 80 ± 13 % of TSS, 79 ± 10 % of P_{total}, 59 ± 21 % of BOD_5, 44 ±34 % NH_4, and 20 ± 8 % of DOC		complete MP removal, and microbial inactivation, except sucralose (SCL) that was at a high initial concentration in the effluent (ranging 20–24 µg L^{-1}), with 50 % removal achieved only under strongest conditions (5 mM PS/Fe(II)/UV-C at 1 L min^{-1}; 57 J L^{-1}; 28 s). Lower dosages (0.01 mM) were enough to inactivate microbial populations completely but insufficient to degrade MPs. PMS/Fe(II)/UV-C and PS/Fe(II)/UV-C reached mineralization >50 %	most investigated technologies are MBR, PAC, ozonation, and UV. Best removal results by MBR (secondary step) and PAC (tertiary step) (for MP> 80 %). 1.08 g O_3 g DOC^{-1}, 23 mg L^{-1} PAC and 2400 J m^{-2} UV
Disinfection removal efficiency	Total bacterial inactivation in 270 min (4.5 h) in the real effluent after CAS, using the Lime	Microbiological: indicator bacteria (Escherichia coli, intestinal enterococci, and total viable bacteria)	Total fecal coliforms and enterococci and ARB (tetracycline and ciprofloxacin) values<= DL (0.01 CFU mL^{-1}) for		Secondary treatment (CAS and UASB) not efficient for virus removal (rotavirus A, human adenovirus,

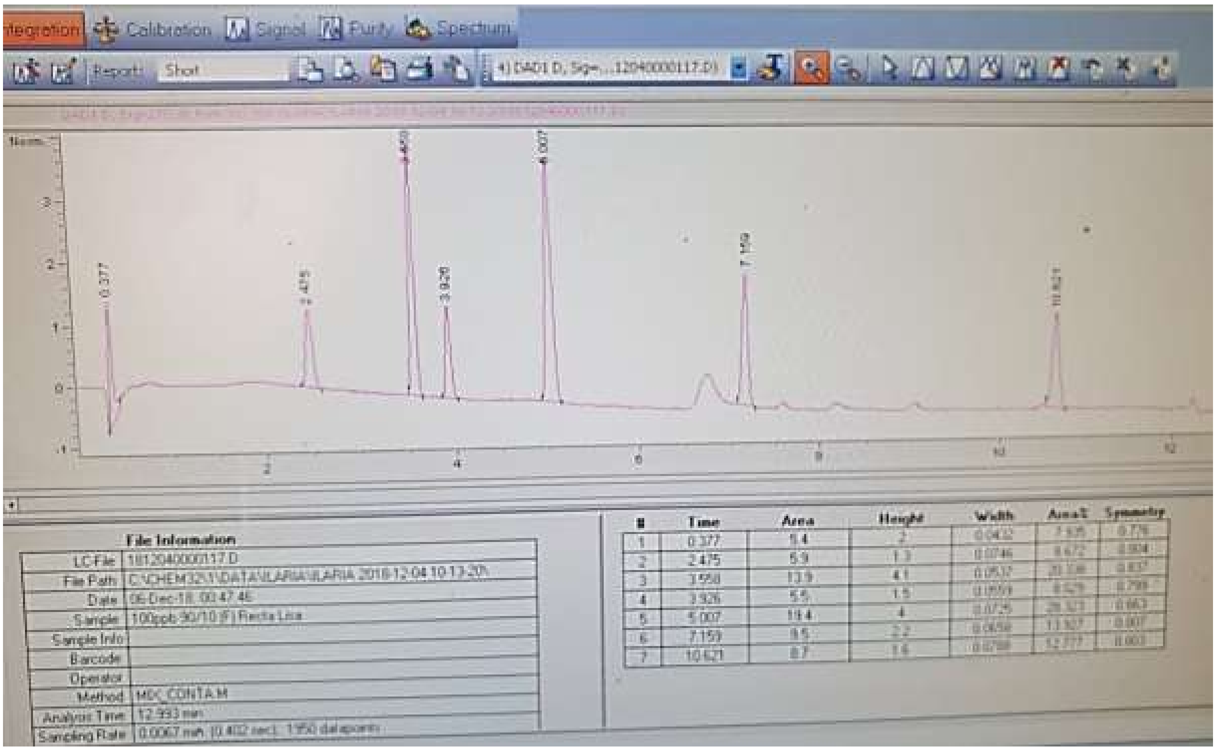
Manuscript	(VILLEGAS- GUZMAN *et al.*, 2017)	(MARGOT *et al.*, 2013)	(MOREIRA *et al.*, 2018)	(RODRÍGUEZ-CHUECA *et al.*, 2018)	(VERLICCHI; AL AUKIDY; ZAMBELLO, 2015)
	juice extract, 5 ppm [M-Fe], 25 ppm H_2O_2	and coliphages (F-specific (RNA) and somatic phages. PAC-UF: complete removal of intestinal bacteria and coliphages (b5 UFP ml^{-1}, an indicator of human viruses). PAC-SF: only 11 % *E. coli* removal, 79 % enterococci. Ozonation: coliphage virus below the detection limit (5 UFP ml^{-1}) (>95 % removal) and >97 % in the concentration of fecal bacteria	all treatments employing H_2O_2, even upon storage of the treated wastewater for 3-days.		norovirus genogroups I and II, and hepatitis A viruses). Efficient for bacteria removal (Thermotolerant coliforms, among other bacteria): MBR + post-chlorination, ozonation, UV, AOPs ($UV/TiO_2/O_3$ the best, UV/TiO_2, UV/O_3, O_3/TiO_2, TiO_2). For UV irradiated, higher fluence necessary for virus and oocysts removal.
Toxicity, ARG, and other effects	-	Bioassays: YES, Combined Algal Assay, fish early life stage with rainbow trout. Removal of toxicity with 5.7 mgO_3 L^{-1} or 0.86 gO_3 $gDOC^{-1}$. PAC-UF was slightly more effective than ozone in reducing toxicity to algae (PAC: 84 % [79–88 %], OZ:75 % [67–81 %]), photosynthesis inhibition	$P25/H_2O_2$ and solar-H_2O_2 had the most reduction in abundance (gene copy number per volume of wastewater) for genes. However, this was transient for 16S and some genes, with regrowth after 3-days storage.	The total fungi population was also analyzed. Photolytic activation of PMS led to the total inactivation of bacteria (≈ 5.70 logs) with the highest UV-C dose (57 J L^{-1}) low dosage of reagents enough for bacteria inactivation is not suitable for fungi. HP/UV-C reach DL at 1 - 3 L min^{-1} and values higher than 3-log with	Mentioned in some studies very brief with risk assessment, Microtox, D. magna. One paragraph also mentioned ARB and ARG: advanced biological and chemical processes show between 1–5 log units of efficiency. Hospital effluent is 5–15 more toxic than urban

Manuscript	(VILLEGAS- GUZMAN *et al.*, 2017)	(MARGOT *et al.*, 2013)	(MOREIRA *et al.*, 2018)	(RODRÍGUEZ-CHUECA *et al.*, 2018)	(VERLICCHI; AL AUKIDY; ZAMBELLO, 2015)
		(PAC: 87 % [77–99 %], OZ:82 % [77–92 %]) and fish development impact (PAC: similar to control, OZ: delay in the development). On the other hand, ozone was slightly better in reducing estrogenic activity (PAC: 77 % [58–90 %], OZ: 89 % [85–92 %]). No genotoxicity or mutagenicity was detected in OZ effluents despite the formation of bromate.		photolysis of PMS and PS, when 1 L min^{-1} was used, and higher than 2-log at 3 L min^{-1}	wastewater due to the presence of detergents, disinfectants, free chlorine, AOX, ethanol, propanol, and metals, including Zn, Cu, As, and Pb.
Costs	-	0.16–0.18 € m^{-3} for ozonation or PAC with sand post-filtration, a 30 % increase in WWTP in Switzerland (0.54 € m^{-3}, 0.33 kWh m^{-3}). PAC-UF higher costs (0.80 € m^{-3}) could be reduced if optimized. Data from 2010 prices.	-	-	Even though some technologies as PAC and GAG seem efficient and competitive towards some AOPs, if the EfOM increases, operational costs increase very much with changes in these technologies' filter and disposal. The treatment of HWW is more expensive than UHH (euros m^{-3}), but the

Manuscript	(VILLEGAS-GUZMAN *et al.*, 2017)	(MARGOT *et al.*, 2013)	(MOREIRA *et al.*, 2018)	(RODRÍGUEZ-CHUECA *et al.*, 2018)	(VERLICCHI; AL AUKIDY; ZAMBELLO, 2015)
					treated volume is lower. Photo-Fenton (O&M 0.38 € m^{-3}), MBR (O&M 0.45-0.163 € m^{-3}), MBR+ O_3 + UV (Investment 3.6 € m^{-3}), MBR + GAC (total 4.1 € m^{-3}), MBR+ O_3 + GAC (O& M 1.45 € m^{-3}, total 4.7 € m^{-3}), MBR+ MBR + PAC (O&M 1.65 € m^{-3}, total 5 € m^{-3}), MBR+ O_3 (O& M 1.85 € m^{-3}, total 5.5 € m^{-3}), O_3 (O&M 0.22-0.4 € m^{-3}), O_3 + H_2O_2 (O&M 0.34-1.08 € m^{-3}), PAC (O&M 1.08 € m^{-3}), ClO_2 (O&M 0.3 € m^{-3}), MBR+ O_3 (O&M 1 € m^{-3})

APPENDIX IV – CHROMATOGRAM OF 100 μg L^{-1} STANDARD SOLUTION INJECTION

Results from the injection of a 100 μg L^{-1} standard solution of the mixture of target micropollutants in 90 % matrix (filtered natural tap water) with 10 % acetonitrile, using an (UPLC-UV/DAD) (Agilent Technologies, Infinity Series 1200): chromatogram for channel of the wavelength of 270 nm.

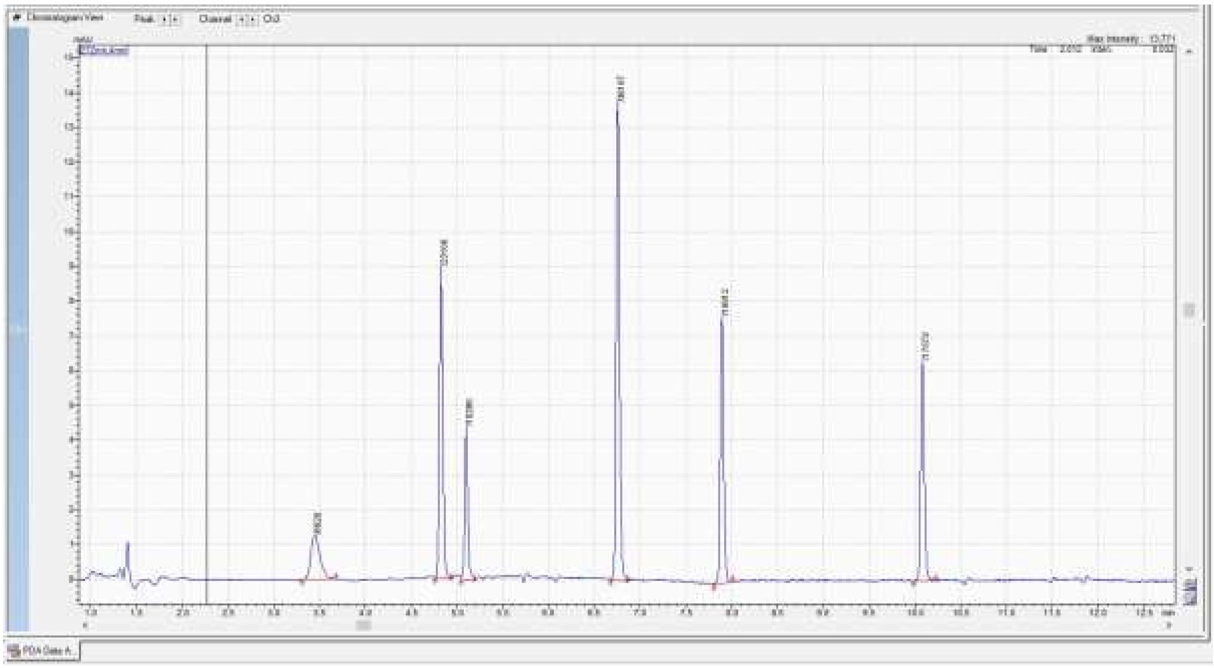


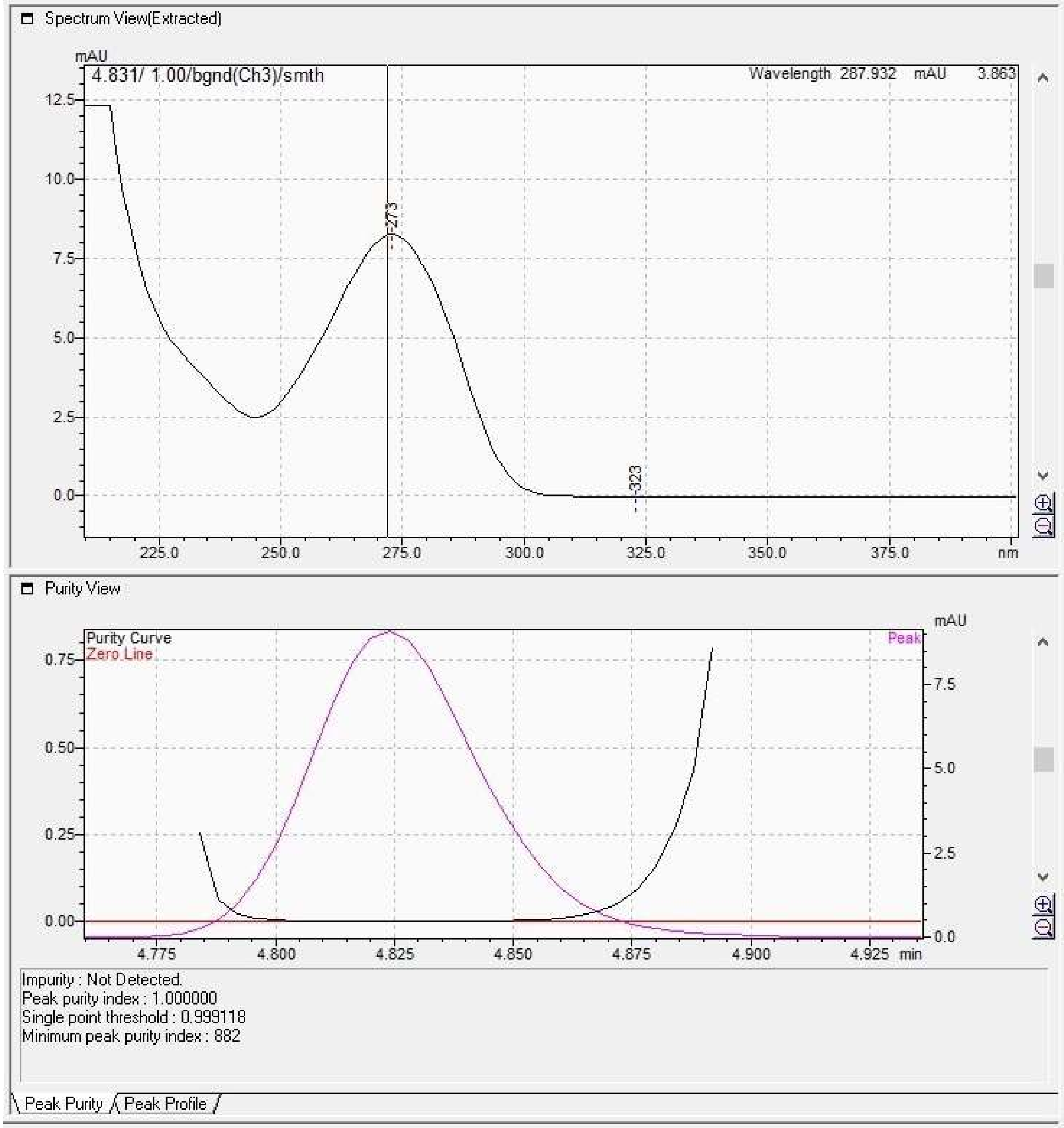
File Information

LC File	1812040000117.D
File Path	C:\CHEM32\1\DATA\ILARIA\ILARIA 2018-12-04 10-13-20\
Date	06-Dec-18, 00:47:46
Sample	100ppb 90/10 (F) Recta Lisa
Sample Info	
Barcode	
Operator	
Method	MIC_CONTA.M
Analysis Time	12.993 min
Sampling Rate	0.0067 min (0.402 sec), 1950 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	0.377	5.4	2	0.0432	7.635	0.776
2	2.475	5.9	1.3	0.0746	8.672	0.904
3	3.558	13.9	4.1	0.0537	20.336	0.837
4	3.926	5.5	1.5	0.0559	8.029	0.799
5	5.007	19.4	4	0.0725	28.523	0.663
6	7.159	9.5	2.2	0.0658	13.927	0.807
7	10.621	8.7	1.6	0.0788	12.777	0.803

Results from the injection of a 100 µg L^{-1} standard solution of the mixture of target micropollutants in 90 % matrix (filtered secondary effluent) with 10 % acetonitrile, using an UPLC-UV/DAD (Shimadzu®, model NEXERA-i LC-2040C 3D Plus): chromatogram for channel of the wavelength of 272 nm, and details with spectrum and the peak purity of caffeine (retention time of 4.83 min).





```
Impurity : Not Detected.
Peak purity index : 1.000000
Single point threshold : 0.999118
Minimum peak purity index : 882
```

APPENDIX V – SELECTED MICROPOLLUTANTS SPECTRUM UNDER DIFFERENT pH VALUES

Measurements in 10 mm quartz cuvette, in demineralized water using a Shimadzu® spectrophotometer model UV-2600.