EVALUATION AND COMPARISON OF ADVANCED TREATMENT TECHNOLOGIES TO ENHANCE THE REMOVAL OF PHARMACEUTICAL ACTIVE COMPOUNDS FROM WWTP SECONDARY EFFLUENT

Luca Sbardella

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DOCTORAL THESIS

EVALUATION AND COMPARISON OF ADVANCED TREATMENT TECHNOLOGIES TO ENHANCE THE REMOVAL OF PHARMACEUTICAL ACTIVE COMPOUNDS FROM WWTP SECONDARY EFFLUENT

Luca Sbardella

2019

DOCTORAL PROGRAME IN WATER SCIENCE AND TECHNOLOGY

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Tutor: Ignasi Rodriguez-Roda

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WE DECLARE:

That the thesis “Evaluation and comparison of advanced treatment technologies to enhance the removal of pharmaceutical active compounds from WWTP secondary”, presented by Luca Sbardella to obtain a doctoral degree, has been completed under our supervision and meets the requirements to opt for an International Doctorate.

For all intents and purposes, we hereby sign this document.

Ignasi Rodriguez-Roda

Joaquim Comas Matas

Alessio Fenu

Girona, April of 2018

DECLARATION OF AUTHORSHIP

I, Luca Sbardella, declare that this thesis titled, “Evaluation and comparison of advanced treatment technologies to enhance the removal of pharmaceutical active compounds from WWTP secondary” and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.

Luca Sbardella

Luca Sbardella

Girona, April of 2018

…and in the End

the Love you take

is equal to the Love…you make!

-The Beatles, 1969-

Do! Or do not!

There is no try!

- Jedi Master Yoda -

Acknowledgements

This was a long journey during which I was not alone. I had indeed the luck to have people who supported me along the way. There was Family, there were friends, colleagues and other people who worked with me, or just shared a coffee, a beer or a chat. Without them it wouldn’t have been the same, and therefore it is also because of them that I have managed to achieve this goal.

To my Friends and Family!

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List of acronyms and abbreviations

WWTPs: Wastewater Treatment Plants
DWTPs: Drinking Water Treatment Plants
GAC: Granular Activated Carbon
BAC: Biological Activated Carbon
PhACs: Pharmaceutically Active Compounds
MPs : Micropollutants
EBCT: Empty Bed Contact Time
BV: Bed Volumes
UF: Ultrafiltration
TOC: Total Organic Carbon
COD: Chemical Oxygen Demand
DO : Dissolved Oxygen
SPE: Solid Phase Extraction
ATP: Adenosine Triphosphate
AOPs :Advanced oxidation processes
PDS : peroxydisulfate
PMS : peroxymonosulfate
UV : Ultraviolet
LCA : Life Cycle Assessment
LCIA : Life Cycle Impact Assessment
SHA : Specific Heterotrophic Activity
SNA : Specific Nitrifying Activity
EEO : Electrical Energy per Order
CC : climate change
OD : ozone depletion
TA : terrestrial acidification
FE : freshwater eutrophication
ME : marine eutrophication
HT : human toxicity
POF : photochemical oxidant formation
PMF : particulate matter formation
TET : terrestrial ecotoxicity
FET : freshwater ecotoxicity
MET : marine ecotoxicity

IR : ionising radiation
ALO : agricultural land occupation
ULO : urban land occupation
NLT : natural land transformation
WD : water depletion
MRD : mineral resource depletion
FD : fossil fuel depletion
HH : human health
ED : ecosystem diversity
RA : resource availability

PhACs acronyms :

sulfamethoxazole (SMX), azithromycin (AZIT), ofloxacin (OFLX), trimethoprim (TRIM) and ciprofloxacin (CIPX), metoprolol (MTP), atenolol (ATN), propanolol (PROP), nadolol (NDL), carbamazepine (CBZ), venlafaxine (VNLX), diazepam (DZP), hydrochlorothiazide (HDCT), irbesartan (IRB) and bezafibrate (BZF).

Abbreviations :

C1: Column 1 = Biologically active column
C2: Column 2 = Biologically inhibited column
SPI-P: Sampling Point Influent-Pilot
SPE-P: Sampling Point Effluent-Pilot
SPI-C: Sampling Point Influent-Columns
SPE-C1: Sampling Point Effluent Column 1
SPE-C2: Sampling Point Effluent Column 2
P1: Phase 1 (0-9,200 BV)
P2: Phase 2 (9,200-13,800 BV)
log K_{ow}: octanol water coefficient
pKa: acid dissociation constant
log D: distribution coefficient
K_{obs} : fluence based degradation rate constant

List of publication

L. Sbardella, J. Comas, A. Fenu, I. Rodriguez-Roda, M. Weemaes, Advanced biological activated carbon filter for removing pharmaceutically active compounds from treated wastewater, Sci. Total Environ. 636 (2018). doi:10.1016/j.scitotenv.2018.04.214.

Abstract book : L. Sbardella, A. Fenu, J. Comas, I. Rodriguez-Roda, M. Weemaes. 2017. Removal of Pharmaceuticals from WWTP Secondary Effluent with Biofilters. Mannina, G., 2017. Proceedings of Frontiers International Conference on Wastewater Treatment. May 21-14, 2017, Palermo, ITALY.

L. Sbardella, I. Velo Gala, J. Comas, I. Rodriguez-Roda, A. Fenu, W. Gernjak, Impact of wastewater matrix on degradation of PhACs during UV sulfate-based oxidation processes, (Accepted to Journal of Hazardous Material).

L. Sbardella, I. Velo Gala, J. Comas, I. Rodriguez-Roda, W. Gernjak, Holistic evaluation of PhACs degradation during UV sulfate-based oxidation processes as advanced wastewater treatment, (Submitted to Journal of Cleaner Production).

Summary

During the last 20 years, the presence of several pharmaceutical active compounds (PhACs) in water bodies has garnered increasing attention and worldwide concern. The effluents from wastewater treatment plants (WWTPs) are one of the main sources of PhACs in aquatic environments. In fact, most WWTPs are designed to comply with conventional pollutant thresholds such as those for nutrients, organic matter and solids, but they are not efficient enough at eliminating organic compounds at trace levels. Advanced tertiary treatments are required to improve the quality of WWTP effluents discharged into sensitive receiving water bodies and those utilized for potable reuse, industrial reuse and irrigation purposes. Advanced wastewater treatment can be classified according to the following main groups: advanced oxidation processes (AOPs), adsorption/filtration, ozone and membranes. Some of those (such as granular activated carbon adsorption and ozonation) have been applied at large scale. Nevertheless there are some promising alternative technologies that have to be explored before their full scale application as tertiary treatment. This thesis has focused on the combination of advanced biological, adsorption, filtration and oxidation processes. In particular the studied technologies were biological activated carbon coupled with ultrafiltration (BAC-UF) and UV-C activated peroxydisulfate and peroxymonosulfate (UV/PDS and UV/PMS). Due to their novelty, several research gaps with regard to the removal mechanisms, efficiency under real-case circumstances, operational costs and environmental impacts, remain unsolved and have to be studied in detail. In this context, the main objective of this thesis is to assess the application of former mentioned advanced treatment technologies for an effective elimination of PhACs from secondary effluents of WWTPs. The strategy to evaluate these techniques as tertiary treatments is based on assessing their removal capacity, identifying the main removal mechanisms, calculating the costs required for the effective PhACs removal (80%) and finally to assess their environmental footprint. The BAC-UF technology has been evaluated at pilot-scale during one year of operation, assessing the removal of 15 PhACs at environmentally relevant concentration. On the other hand, the removal mechanisms involved in the BAC-UF technology, have been investigated in a lab-scale column set-up fed with the same WWTP secondary effluent as the pilot-plant. The evaluation carried out with the BAC-UF pilot plant allowed to identify a clear evolution in the removal capacity of this system, in according to which two differentiated phases were identified. The first phase (I) was characterized by removal efficiencies in the range of 80%, while in the second phase (II) the system was not able to achieve similar efficiencies mostly due to the loss of adsorption capacity. Although the biodegradation proved to have a net contribution on the overall PhACs removal, especially during phase II, this bio/filtration system relied mostly on adsorption capacity of the granular activated carbon particles. With respect to UV/PDS and UV/PMS technologies, they were preliminarily assessed with a set of lab-scale experiments treating both synthetic mineral water and real WWTP secondary effluent. Then, these technologies were validated at pilot-scale simulating real operating conditions. In both lab-and pilot-scale investigations, removals and degradation rate constants of 9 PhACs were calculated. On the other hand, the AOPs based on the UV-C activation of PDS or PMS were efficient in removing PhACs from secondary effluent of WWTPs, even though their efficiency was clearly influenced by several factors either improving or limiting their capacity to degrade PhACs. Among the improving factors, higher UV fluence values allowed to achieve removal values ranging between 70% and 80%, while effluent organic matter was the factor with the greatest negative impact in terms of kinetics and removal efficiencies. As a whole, these two oxidation processes resulted to be compound-specific for each of the investigated experimental conditions. The validation of these results during pilot-scale experiments clearly indicated the potential for these novel techniques to be applied as tertiary wastewater treatment, since average removal values greater than 80% for both systems were obtained with 416 mJ/cm^2 of UV fluence and 0.4 mM of oxidant. Moreover, assessing the kinetics (Kobs - apparent degradation rate constant), we found 8.7 cm^2/J, 8.8 cm^2/J and 1.4 cm^2/J respectively for UV/PMS, UV/PDS and UV alone. At the same time, the energy needed to effectively remove PhACs (90% average removal), resulted to be 0.8 kWh/m^3, 0.9 kWh/m^3 and 5.3 kWh/m^3, respectively for UV/PMS, UV/PDS and UV alone. Therefore, the addition of either PDS or PMS resulted key in order to achieve efficient PhACs degradation, since direct photolysis only had a minor role. Finally the comprehensive evaluation of the advanced treatment technologies studied in this thesis identified some of the practical factors limiting the potential application of BAC-UF, UV/PDS and UV/PMS technologies. Among them, with regard to the BAC-UF technology, the energetic consumption of the UF (6.6 x 10-1 kWh/m^3) and the need to regenerate spent activated carbons, were the factors with the greatest environmental and economic footprint. The impact of the BAC-UF technology, assessed through climate change midpoint category, was calculated to be 0.371 kg CO2 equivalent. The factors contributing the most were indeed electricity and GAC reactivation, respectively with a contribution of 49.1% and 27.4%. On the other hand, the two AOP alternatives, although showing similar removal efficiency, significantly differed when operating cost and environmental sustainability were considered. With respect to this analysis, PMS production resulted to be a critical factor having a negative impact on the environment and on operating costs. Keeping in mind the framework outlined by these considerations, UV/PDS technology can have the potential for real-case applications, although it requires further investigations for its optimization.

To sum up, the present thesis contributes to cast a wide net on advanced wastewater treatment alternatives for the removal of PhACs. The current work provides information regarding the applicability of the studied technologies, insights on their removal mechanism and calculation of the operating costs required. These findings have been then broadened with an environmental sustainability assessment of each treatment option and compared among state-of-the-art technologies.

Resum

Durant els últims 20 anys, la presència de diversos compostos actius farmacèutics (PhACs) a les masses d’aigua ha guanyat una atenció creixent i preocupació arreu del món. Els efluents de les depuradores són una de les fonts principals de PhACs en entorns aquàtics. De fet, la major part de les depuradores són dissenyades per complir només amb llindars de contaminants convencionals, com són els nutrients, la matèria orgànica i els sòlids, però aquestes no són suficientment eficaços per eliminar compostos orgànics a nivells de traça. Es requereixen tractaments terciaris avançats per millorar la qualitat dels efluents de les depuradores que aboquen en masses d’aigua receptores sensibles, així com per a la reutilització d’aigua per a consum humà, per a la indústria i regadius. Els tractaments avançats d’aigües residuals poden ser classificats en els següents grups principals: processos d’oxidació avançada (AOPs), adsorció/filtració, ozó i membranes. Alguns d’aquests (com ara adsorció de carbó actiu granular i ozó) ja s’han aplicat a gran escala. No obstant això, hi ha algunes tecnologies alternatives prometedores que encara han de ser més explorades abans de la seva aplicación a gran escala com a tractament terciari. Aquesta tesi es focalitza en la combinació de processos avançats biològics, d’adsorció, filtració i oxidació. En particular, s’examinen les tecnologies de carbó actiu biològic combinat amb l’ultrafiltració (BAC-UF) i UV-C peroxidisulfat i peroximonosulfat actiu (UV/PDS i UV/PMS). A causa de la seva novetat, alguns buits de recerca encara no estan resolts i han de ser estudiats més en detall en relació amb els mecanismes d’eliminació, eficàcia en condicions reals, costos operacionals i impactes mediambientals. En aquest context, l'objectiu principal d'aquesta tesi és avaluar l’aplicació de les anteriors tecnologies de tractament avançat per a l’eliminació efectiva dels PhACs dels efluents secundaris de les depuradores. L’estratègia per avaluar aquestes tècniques com a tractaments terciaris es basa en avaluar les seves capacitats d’eliminació, identificar els mecanismes principals d’eliminació, calcular els costos associats a una eliminació de PhACs efectiva (80%) i, finalment, avaluar les seues petjades mediambientals. La tecnologia BAC-UF s’ha avaluat a escala pilot durant un any d’operació, avaluant l’eliminació de 15 PhACs a concentracions mediambientals rellevants. D’altra banda, els mecanismes d’eliminació de la tecnologia BAC-UF s’han investigat en laboratori amb una columna alimentada amb el mateix efluent secundari que la planta pilot. L’avaluació amb la planta pilot BAC-UF va permetre identificar una clara evolució en la capacitat d’eliminació d’aquest sistema, segons la qual es van poder identificar dos fases diferenciades. La primera fase (I) es va caracteritzar per eficàcies d’eliminació al voltant de 80% mentre que en la segona fase (II), el sistema no va ser capaç d’assolir eficàcies semblants degut majoritàriament a la pèrdua de capacitat d’adsorció. Malgrat que la biodegradació va resultar tenir una contribució neta en l’eliminació global de PhACs, especialment durant la fase II, aquest sistema de biofiltració depenia fonamentalment de la capacitat d’adsorció de les partícules de carbó actiu granular. Respecte a les tecnologies UV/PDS, aquestes van ser avaluades, en primera instància, amb un conjunt d’experiments en el laboratori, utilitzant tant aigua mineral sintètica

com efluent secundari real. Després, aquestes tecnologies van ser validades a escala pilot simulant condicions d'operació reals. Tant en les investigacions a escala pilot com en el laboratori, les eliminacions i les constants de degradació de 9 PhACS van ser calculades. D'altra banda, els AOP's basats en UV-C peroxidisulfat i peroximonosulfat actiu van eliminar eficaçment PhACs procedents d'efluents secundaris, malgrat que diversos factors influeixen en aquesta eficàcia, bé millorant-la o bé limitant la capacitat per degradar PhACs. Entre els factors de millora, una fluència UV més alta va permetre assolir valors d'eliminació entre 70% i 80%, mentre que la matèria orgànica va ser el factor amb el major impacte negatiu en termes cinètics i eficàcia d'eliminació. En conjunt, aquests dos processos d'oxidació van resultar compost-específics en cadascuna de les condicions experimentals investigades. La validació d'aquests resultats durant els experiments a escala pilot van indicar clarament el potencial d'aquestes dues tecnologies per ser aplicades com a tractament terciari, ja que es va obtenir una mitjana d'eliminació major de 80% per ambdós sistemes amb 416 mJ/cm² de fluència UV i 0.4 mM d'oxidant. A més, respecte a la cinètica (constant de degradació aparent de K_{obs}), vam obtenir 8.7 cm²/J, 8.8 cm²/J i 1.4 cm²/J per a UV/PMS, UV/PDS i UV a soles, respectivament. Tanmateix, l'energia necessària per eliminar eficaçment PhACs (mitjana de 90%), va resultar 0.8 kWh/m³, 0.9 kWh/m³ i 5.3 kWh/m³ per UV/PMS, UV/PDS i UV a soles, respectivament. Per tant, l'addició de bé PDS ó bé PMS va resultar crucial per tal d'assolir una degradació eficaç de PhACs, ja que la fotòlisi directa només va tenir una funció menor. Finalment, l'avaluació exhaustiva de les tecnologies de tractament avançat estudiades en aquesta tesi va identificar aquells factors pràctics que limiten el potencial d'aplicació de les tecnologies BAC-UF, UV/PDS i UV/PMS. Entre aquests, en relació amb la tecnologia BAC-UF, els factors amb la major petjada mediambiental i econòmica van ser el consum energètic de la UF (6.6 x 10-1 kWh/m³) i la necessitat de regenerar els carbons actius gastats. L'impacte de la tecnologia BAC-UF, calculada a través de la categoria "midpoint"de canvi climàtic, va resultar 0.371 kg CO2 equivalents. Els factors que van contribuir més van ser, en efecte, electricitat i reactivació del GAC, respectivament, amb una contribució de 49.1% i 27.4%. D'altra banda, les dues alternatives AOP, encara que mostren una eficàcia d'eliminació semblant, es van diferenciar significativament quan es va considerar el cost operacional i la sostenibilitat ambiental. Respecte a aquest anàlisi, la producció PMS va resultar un factor crític, tenint un impacte negatiu sobre el medi ambient i els costos operacionals. Tenint en compte el marc perfilat per aquestes consideracions, la tecnologia UV/PDS pot tenir potencial per aplicacions reals, malgrat que requereix més recerca per la seva optimització.

Per resumir, aquesta tesi contribueix a ampliar la cerca d'alternatives de tractament avançat d'aigües residuals per a l'eliminació de PhACs. Aquest treball proporciona informació sobre l'aplicabilitat de les tecnologies, els diferents mecanismes d'eliminació i el càlcul dels costs operacionals. Finalment, els resultats s'han ampliat utilitzant una avaluació de sostenibilitat mediambiental de cadascuna de les opcions de tractament i comparats amb les tecnologies d'última generació.

Resumen

Durante los últimos 20 años, la presencia de varios compuestos activos farmacéuticos (PhACs) en las masas de agua ha ganado una atención creciente y preocupación en todo el mundo. Los efluentes de las depuradoras son una de las fuentes principales de PhACs en entornos acuáticos. De hecho, la mayor parte de las depuradoras están diseñadas para cumplir sólo con umbrales de contaminantes convencionales, como son los nutrientes, la materia orgánica y los sólidos, pero éstas no son suficientemente eficaces para eliminar compuestos orgánicos a niveles de traza. Se requieren tratamientos terciarios avanzados para mejorar la calidad de los efluentes de las depuradoras que abocan en masas de agua receptoras sensibles, así como para la reutilización de agua para consumo humano, para la industria y regadíos. Los tratamientos avanzados de aguas residuales pueden ser clasificados en los siguientes grupos principales: procesos de oxidación avanzada (AOPs), adsorción/filtración, ozono y membranas. Algunos de estos (como por ejemplo adsorción de carbón activo granular y ozono) ya se han aplicado a gran escala. Sin embargo, algunas tecnologías alternativas prometedoras aún tienen que ser más exploradas antes de su aplicación a gran escala como tratamiento terciario. Esta tesis se focaliza en la combinación de procesos avanzados biológicos, de adsorción, filtración y oxidación. En particular, se examinan las tecnologías de carbón activo biológico combinado con la ultrafiltración (BAC-UF) y UV-C peroxidisulfato y peroximonosulfato activo (UV/PDS y UV/PMS). Debido a su novedad, algunos vacíos de investigación aún no están resueltos y tienen que ser estudiados más en detalle en relación con los mecanismos de eliminación, eficacia en condiciones reales, costes operacionales e impactos medioambientales. En este contexto, el objetivo principal de esta tesis es evaluar la aplicación de las anteriores tecnologías de tratamiento avanzado para la eliminación efectiva de los PhACs de los efluentes secundarios de las depuradoras. La estrategia para evaluar estas técnicas como tratamientos terciarios se basa en evaluar sus capacidades de eliminación, identificar los mecanismos principales de eliminación, calcular los costes asociados a una eliminación de PhACs efectiva (80%) y, finalmente, evaluar sus huellas medioambientales. La tecnología BAC-UF se ha evaluado a escala piloto durante un año de operación, evaluando la eliminación de 15 PhACs a concentraciones medioambientales relevantes. Por otro lado, los mecanismos de eliminación de la tecnología BAC-UF se han investigado en laboratorio con una columna alimentada con el mismo efluente secundario que la planta piloto. La evaluación con la planta piloto BAC-UF permitió identificar una clara evolución en la capacidad de eliminación de este sistema, según la cual se pudieron identificar dos fases diferenciadas. La primera fase (I) se caracterizó por eficacias de eliminación alrededor del 80% mientras que en la segunda fase (II), el sistema no fue capaz de lograr eficacias parecidas debido, mayoritariamente, a la pérdida de capacidad de adsorción. A pesar de que la biodegradación resultó tener una contribución neta en la eliminación global de PhACs, especialmente durante la fase II, este sistema de biofiltración dependía fundamentalmente de la capacidad de adsorción de las partículas de carbón activo granular. Respecto a

las tecnologías UV/PDS, estas fueron evaluadas, en primera instancia, con un conjunto de experimentos en el laboratorio, utilizando tanto agua mineral sintética como efluente secundario real. Después, estas tecnologías fueron validadas a escala piloto simulando condiciones de operación reales. Tanto en las investigaciones a escala piloto como en el laboratorio, las eliminaciones y las constantes de degradación de 9 PhACS fueron calculadas. Por otro lado, los AOP's basados en UV-C peroxidisulfato y peroximonosulfato activo eliminaron eficazmente PhACs procedentes de efluentes secundarios, a pesar de que varios factores influyen en esta eficacia, bien mejorándola o bien limitando la capacidad para degradar PhACs. Entre los factores de mejora, una fluencia UV más alta permitió lograr valores de eliminación entre 70% y 80%, mientras que la materia orgánica fue el factor con el mayor impacto negativo en términos cinéticos y eficacia de eliminación. En conjunto, estos dos procesos de oxidación resultaron compuesto-específicos en cada una de las condiciones experimentales investigadas. La validación de estos resultados durante los experimentos a escala piloto indicaron claramente el potencial de estas dos tecnologías para ser aplicadas como tratamiento terciario, puesto que se obtuvo una media de eliminación mayor de 80% por ambos sistemas con 416 mJ/cm^2 de fluencia UV y 0.4 mm de oxidante. Además, respecto a la cinética (constante de degradación aparente de K_{obs}), obtuvimos 8.7 cm^2/J, 8.8 cm^2/J y 1.4 cm^2/J para UV/PMS, UV/PDS y UV sólo, respectivamente. Aun así, la energía necesaria para eliminar eficazmente PhACs (media de 90%), resultó 0.8 kWh/m^3, 0.9 kWh/m^3 y 5.3 kWh/m^3 por UV/PMS, UV/PDS y UV sólo, respectivamente. Por lo tanto, la adición de bien PDS o bien PMS resultó crucial para lograr una degradación eficaz de PhACs, puesto que la fotólisis directa sólo tuvo una función menor. Finalmente, la evaluación exhaustiva de las tecnologías de tratamiento avanzado estudiadas en esta tesis identificó aquellos factores prácticos que limitan el potencial de aplicación de las tecnologías BAC-UF, UV/PDS y UV/PMS. Entre estos, en relación con la tecnología BAC-UF, los factores con la mayor huella medioambiental y económica fueron el consumo energético de la UF (6.6 x 10-1 kWh/m^3) y la necesidad de regenerar los carbones activos gastados. El impacto de la tecnología BAC-UF, calculada a través de la categoría "midpoint" de cambio climático, resultó 0.371 kg CO2 equivalentes. Los factores que contribuyeron más fueron, en efecto, la electricidad y reactivación del GAC, respectivamente, con una contribución de 49.1% y 27.4%. Por otro lado, las dos alternativas AOP, aunque muestran una eficacia de eliminación parecida, se diferenciaron significativamente cuando se consideró el coste operacional y la sostenibilidad ambiental. Respecto a este análisis, la producción PMS resultó un factor crítico, teniendo un impacto negativo sobre el medio ambiente y los costes operacionales. Teniendo en cuenta el marco perfilado por estas consideraciones, la tecnología UV/PDS puede tener potencial para aplicaciones reales, a pesar de que requiere más investigación para su optimización.

Para resumir, esta tesis contribuye a ampliar la búsqueda de alternativas de tratamiento avanzado de aguas residuales para la eliminación de PhACs. Este trabajo proporciona información sobre la aplicabilidad de las tecnologías, los diferentes mecanismos de eliminación y el cálculo de los costes operacionales. Finalmente, los resultados se han ampliado utilizando una evaluación de sostenibilidad medioambiental de cada una de las opciones de tratamiento y comparados con las tecnologías de última generación.

Introduction

Wastewater reuse and regulations

The management of water resources in many arid and semi-arid regions of the planet has been a big challenge for a long time due to water scarcity problems. Scarcity refers to the situation when the balance between the availability of usable water and the demand reaches a critical point. In many regions under water scarcity, intensive industrial and urban development, along with a large population growth especially in the cities, has caused severe pressure on local water resources [1]. In addition, climate change is expected to further compromise the water quality and availability for supply as well as the functioning of aquatic ecosystems, increasing the need to find sustainable solutions to this compelling problem. In order to cope with water scarcity, one of the most promising supply-management practices to be explored is the reuse of wastewater [2]. Although irrigation is the traditional and more feasible reuse purpose for reclaimed wastewater, technological advances in the treatment field have enabled treatment facilities to obtain reclaimed water quality suitable for urban and even potable supply [3,4]. Wastewater can be reused after treatment for a variety of beneficial purposes [5]. The two main configurations of wastewater reuse are : potable reuse and non-potable reuse. In either cases, the reuse can be direct or indirect, and requires a treatment train specific for each final purpose of the treated effluent [6,7].

Treatment of urban and industrial wastewater must meet the requirements of increasingly stronger regulations [8]. The main objective of the Urban Wastewater Treatment Directive (Directive /EEC) of European Union (EU) is to protect the environment from the adverse effects of discharges of urban wastewater from settlements areas and industrial operations. This Directive require Member States to ensure that such water is collected and properly treated. Wastewater generated by the population of the 27 Member States of the EU and by the industry is a major source of pollution of European waters including groundwater, rivers, lakes and seas. Wastewater discharges can lead and affect drinking water supplies or bathing water sites, and thereby have important links to public health concerns [9]. Around 80% of the population from countries from north and south of Europe apply conventional systems for urban wastewater treatment. This percentage varies among the different geographical areas of the EU. Both industries and domestic water generate a wide variety of waste daily, which can be classified as hazardous. The discharge of hazardous wastes generates contaminations which may extend hundreds of kilometers from where the waste was initially discharge and is commonly found in the environment at concentrations in the range of µg/L [10]. The regulations in the water reuse sector are increasing worldwide [11]. It is the case of Europe, where some States have already their own regulation, while at European level the Joint Research Center (JRC) has published a report on the “minimum quality requirements for the use of treated wastewater for agricultural purposes” to support the proposal of EU legislation on water reuse. However, a lot of discussion is still opened on the target contaminants to be included as water quality standards for safe wastewater reclamation.

Emerging MPs : Pharmaceutical Active Compounds (PhACs)

Besides the regulated contaminants, there are emerging micropollutants (MPs) which have not been regulated yet including pharmaceuticals and personal care products, flame retardants and many others. These have been found in surface water, groundwater, wastewater and even in drinking water [12]. Recent studies demonstrated that the presence of some of these substances in the environment, has been linked to the pollution of groundwater and soils as well as the loss of biodiversity and some signs of their possible adverse effects on human health, such as neurotoxicity, endocrine disruption and cancer [13]. Emerging MPs (MPs) are found at concentration in the range of ng/L to µg/L. Such concentration in the aquatic environment may cause ecological risks such as interference with endocrine system of high organisms, microbiological resistance, and accumulation in soil, plants and animals. In the past years, the main focus was on detecting the severe, direct effects of individual contaminants and the short-term negative impact on ecosystems. But, as scientific understanding has advanced, and the concentrated emissions have been lowered, environmental evaluation reveals a considerable number of chronic effects that can usually only be detected after a long period of time. Evaluation was focused mostly on the effect of individual substances, whereas we are now beginning to study and understand interactions in mixtures of these substances. However, there are substantial knowledge gaps in terms of chronic, long-term exposure or non-exposure of non-target aquatic organisms and the effects on ecosystem functioning. Data are available to suggest that some compounds may display chronic effects at or close to the levels detected in the environment [14]. Among the vast set of emerging contaminant of concern, the presence of several pharmaceutically active compounds (PhACs) in water bodies has garnered increasing attention and worldwide concern. PhACs include analgesic, lipid regulators, antibiotics, diuretics, non-steroid anti-inflammatory drugs, stimulant drugs, antiseptics, analgesic, beta blockers and antimicrobials [15]. Recent studies proved that this class of contaminant can affect water quality and potentially affect drinking water supplies, ecosystem and human health. As it is the case for other classes of emerging contaminant, PhACs are continuously released into the environment in extremely large quantities and on a regular basis through different ways like human activities, waste from pharmaceutical industries, residues and waste from hospitals, use of illicit drugs and veterinary drugs, and agribusiness [16](Figure 1). With regard to their negative effect on the environment, their bioaccumulation exacerbates the abnormal hormonal control causing reproductive impairments, decreased fecundity, increased incidence of breast and testosterone cancers, and persistent antibiotic resistance. Of particular concern are antibiotic residues which can induce the development of antibiotic resistant genes potentially favoring superbugs. As stated before, the potential long-term effects of PhACs in water are still uncertain and need further investigation. At present, different government and non-government organizations including the European Union, the North America Environmental Protection Agency (EPA), the World Health Organization (WHO), or the International Program of

Chemical Safety (IPCS) are considering these problems and setting up directives and legal frameworks to protect and improve the quality of freshwater resources. Nevertheless, the limits for PhACs in wastewater discharge are still not regulated. Directive 2008/105/EC has established a list of 33 Priority Substances (PS) for surface water and their associated Environmental Quality Standards (EQS). The recently updated EU directive (Decision 2015/495/EU of 20 March 2015 and updated in Decision 2018/840/EU of 5 June 2018) included three hormones (EE2, E2 and E1), diclofenac and three antibiotics (Erythromycin, Clarithromycin and Azithromycin) in the "Watch List" of substances which require targeted monitoring across the EU [17]. The "Watch List" supports the prioritization process in future reviews of the Priority Substances Directive [18]. The Global Water Research Coalition (GWRC) developed an International Priority List of PhACs relevant for the water cycle, based on the compounds that present a potential risk in water supply. Switzerland (the Swiss Centre for Applied Ecotoxicology Eawag - EPFL) has also proposed EQS for emerging contaminants, including PhACs, that show a risk for aquatic organisms when the annual average concentrations in surface water exceed the chronic EQS.

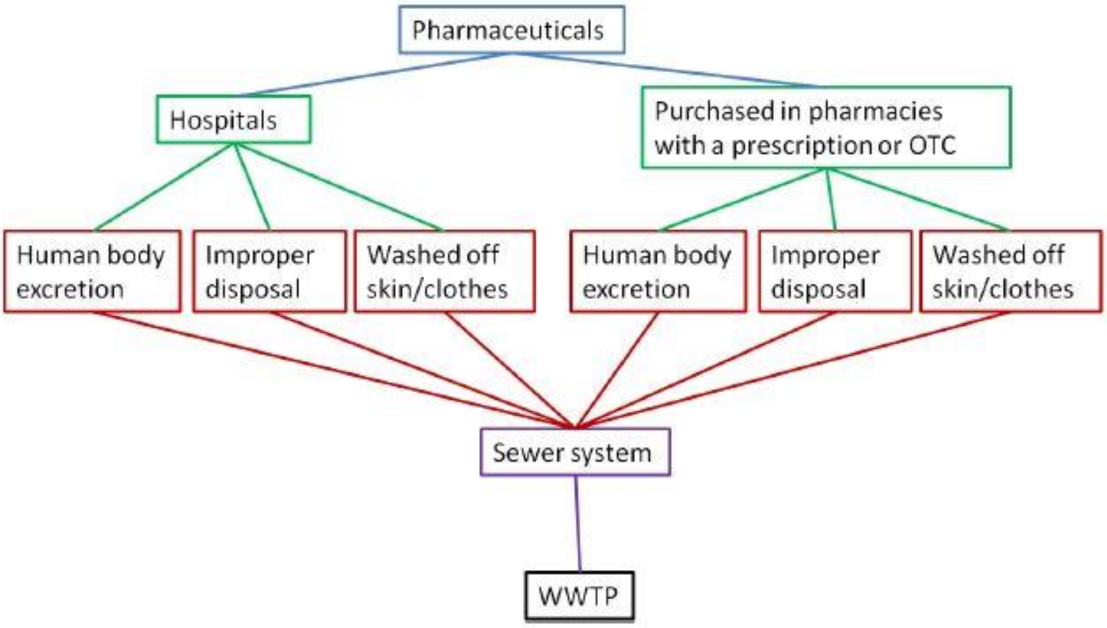


Figure 1 : Sources of pharmaceuticals in WWTP influents

Conventional treatment

The human consumed pharmaceuticals may show the following route, starting from uptake, they are excreted, transported in sewer systems to WWTP where they are partially treated and eventually discharged into surface water. Studies on fate of PhACs showed that the predominant pathway of entry to the aquatic environment is indeed the effluents from wastewater treatment plants (WWTPs) [14]. In fact, most WWTPs are designed to comply with conventional pollutant thresholds such as those for nutrients, organic matter and solids, but they are not efficient at completely eliminating organic compounds at low concentrations ranging from ng/L to µg/L [19]. Generally, conventional WWTPs, including screening, primary sedimentation, aeration tanks and final sedimentation, are ineffective in eliminating PhACs [15]. Removal of PhACs in WWTPs is a complicated process and depends on the chemical and biological properties of pollutants, such as hydrophilicity, solubility, volatility, biodegradability and the adsorption capacity on the activated sludge. Most PhACs are only partially removed in conventional WWTPs equipped with primary and secondary treatment. The capabilities of primary treatment processes in removing PhACs are limited. In fact, since the major removal mechanism in primary treatment is adsorption, most PhACs pass through this step unchanged due to the hydrophilic behavior of most of them [20]. Carbamazepine, metoprolol and other PhACs showed removal <20% in primary sedimentation tanks due to their low water partition coefficient, e.i. hydrophilic characteristics [21], confirming that primary treatment alone may be insufficient to remove most PhACs efficiently. Secondary treatment mostly refer to biological process (e.g. conventional activated sludge, CAS) and may contribute to PhACs removal not only via adsorption but also through biodegradation [22]. PhACs removal in CAS is highly dependent on the nature of compounds, the hydraulic retention time, the solid retention time, adsorption capacity of sludge, and the design of the reactor [23]. Many studies reported that the removal efficiency of some PhACs may reach 40-50% in biological processes. Nevertheless, compounds which are hardly biodegraded, such as carbamazepine, trimethoprim and diazepam showed very low removal efficiencies (<20%) in secondary treatment, regardless of the type of system applied [22,24]. The ineffective removal of PhACs in CAS may be attributed to the transformation of PhACs into by-products or metabolites and the conjugation of target PhACs [15,25]. Yet, an additional problem may rise from the low PhACs removal capabilities of secondary treatments. In particular, the exposure of activated sludge bacteria to antibiotics, antibacterial agents and beta-blockers can induce toxic or inhibitory effects on these bacteria. At the same time, the exposure could also alter the microbial community, resulting in overall malfunctioning of the entire treatment, thereby also in low PhACs removal [26,27]. In order to prevent this exposure, measurements at the source may be needed, aiming at reducing the load of PhACs entering WWTPs. However, preventing PhACs from entering sewage systems and thus WWTPs requires new approaches which not only focus on the end of pipe but also consider the use patterns and fate of chemical substances in the aquatic cycle in the interdisciplinary context [28]. These new approaches will need a special attention in the future. In short, conventional treatment systems are unable to completely remove a large amount of PhACs present in urban wastewaters. More effective and specific treatment are required to reduce the environmental and potential impact of effluents and comply with increasingly strict legislation.

Advanced wastewater treatment technologies

Different advanced wastewater treatment technologies are applied to increase the elimination of PhACs in WWTPs being generally classified in function of the mechanism responsible for the removal of polluting compounds. The technologies successfully applied so far include: adsorption on activated carbon, advanced oxidation processes, membrane filtration and ozonation [29]. This thesis will focus on the first two options, however a brief description of the alternative available, follows below.

Membrane filtration

Membrane technologies provide an important solution in reuse and recovery of water. Microfiltration (MF) and ultrafiltration (UF) membranes are commonly used for the filtration of municipal secondary effluent. The resultant water from these membrane processes may be used for diverse reuse applications after disinfection. The membrane driving force in MF and UF is the hydrostatic pressure difference or vacuum in open vessels. MF and UF membranes are also widely used as a pretreatment step to help prevent fouling of the less permeable nanofiltration (NF) and RO membranes [30]. In contrast to MF and UF, solution/diffusion and exclusion separation mechanisms govern the NF and RO separation. In addition, the hydrostatic pressure difference is the only driving force in NF and RO. In terms of water reuse, NF membranes are commonly used to reduce total dissolved solid (TDS) concentration for specific applications. To this end, NF is also used in conjunction with RO. Both NF and RO are also used to treat pre-filtered effluent (typically with MF or UF) for surface water augmentation or indirect potable reuse applications such as groundwater injection [31]. Filtration and adsorption on the membrane are the key removal mechanisms for membrane processes [32]. The rejection rate depends on both MPs (molecular size and weight, charge and hydrophobicity) and membrane characteristics. With its smallest membrane pore sizes, RO is the most effective membrane process to remove PhACs [33]. However, also nanofiltration has been used to successfully remove low-molecular-weight organic compounds such as pesticides, endocrine disruptors, and various PhACs during water treatment [34].

Ozonation

Ozone is the triatomic form of oxygen, this means that it is composed of three oxygen atoms. Ozone's chemical symbol is O_3. Under normal conditions ozone is unstable and quickly decomposed to the more stable gaseous oxygen O_2. Ozone is capable of oxidizing MPs either by a direct reaction with ozone or indirectly after formation of hydroxyl radicals. As a result, the MPs are transformed into other compounds and not completely removed from the effluent. The ozone is produced from pure oxygen through electrical discharge [35]. The produced ozone can then be mixed with the effluents of WWTP through air diffusers in a contact basin. This contact basin is air-tight as remaining ozone in gaseous form has to be treated. The effluent of the contact basin is then passed through a sand filter to remove any biodegradable metabolites formed during the oxidation of the parent compounds [36]. The effects of ozonation after biological treatment for MPs removal have been widely studied. Similar results are found if MPs are gathered according to their affinity to react with ozone. There is a first group of compounds which are easily removed below detection limits with an average dose of ozone (0.8 gO_3 g^{-1}DOC). Normally, those compounds present second-order rate constants >10 x 4 $M^{-1}s^{-1}$ (regarding to the direct reaction with O_3) such as compounds with aromatic rings, double bonds, or amine moieties, with a high affinity for direct reaction with ozone [37]. There is a second group of compounds with low affinity for O_3 (second-order rate constants <10 x 4 $M^{-1}s^{-1}$) but with high affinity for the strong and unselective hydroxyl radical. An average removal around 60% was achieved for these substances. $HO^{\bullet}$ radical exposure to MPs varies with the EfOM composition (it is sensitive to the addition of coagulants), presence of $HO^{\bullet}$ scavengers (such as carbonate), and pH. Finally, there is a third group which includes those MPs with low affinity to O_3 direct reaction and also to $HO^{\bullet}$. They formed the group of recalcitrant compounds with low removal (below 40%): MPs with amide groups in general [38,39].

Ozonation processes usually require complicated equipment to produce, control and post-treatment of residual ozone in off-gas. Several operational issues such as (i) feed air quality, (ii) a constant and stable coolant supply to counteract ozone generator over-heating, (iii) regular inspection and maintenance of ozone generators necessitate advanced operational skills [40]. Therefore, it may not be feasible in small plants with non-permanent staff [38,41].

Adsorption processes

Adsorption is a technology widely used in wastewater treatment, and several types of materials have been tested as absorbents. However, although there are a large variety of adsorbents in the market, most of the adsorption units in WWTPs use activated carbon due to economic reasons [42]. Activated carbons are produced from materials including wood, coconut shell, peat, lignite, bituminous coal and petroleum residues or lignite. The carbon medium is “activated” by subjecting it to steam and high temperatures (circa 1200°C). The effectiveness of activated carbon for the removal of organic pollutants from water by carbon adsorption is enhanced by its large surface area, an important factor in the adsorption process. The surface area of activated carbon typically can range from 500 to 1400 m^2/g [43]. Activated carbon adsorption is a common method to remove odor, taste and organic compounds in water treatment plants, and currently being extended to remove MPs in WWTPs. Whereas granular activated carbon (GAC) is often utilized as a filtration medium, powdered activated carbon (PAC) is added in activated sludge or coagulation tanks [21].

In an adsorption system, equilibrium between the adsorbent and adsorbate is established between the adsorbate in the bulk phase and the adsorbent. This equilibrium is approached at a certain rate defined as adsorption kinetic. Limitation by mass transport in solution depends on properties of the adsorbent, adsorbate and the surrounding conditions (e.g. hydraulics, solution chemistry and temperature). The main factors influencing the adsorption process are :

i. Carbon pore texture. The extent of adsorption is generally considered proportional to the surface area available for adsorption. The micropore size distribution of adsorbents is one important factor because most of the adsorption on activated carbon takes place in the micropores as a consequence of the enhanced adsorption potential of the pore walls.
ii. Carbon surface chemistry.
iii. Adsorbate properties. Among the characteristics of the adsorbate that mainly influence the adsorption process are its molecular size, polarity, solubility, charge and the nature of the substituent(s) [44][43][45].
iv. Impact of EfOM. In wastewater, EfOM is present at concentrations 103–106 times higher than the MPs of interest. Based on this fact alone, decrease of a MP adsorption capacity is to expect in presence of EfOM.
v. Hydraulics.
vi. Temperature.

The adsorption processes are controlled by contact time (PAC) and empty bed contact time EBCT (GAC). This method is suitable for wastewater with DOC = 10–20 mg/L because higher organic content may interfere the adsorption of targeted contaminants. Activated carbon shows a higher preference towards hydrophobic (log $K_{OW} > 4$), low molecular weight, slightly positively charged compounds (at pH=7–8) and compounds contain aromaticity and N-heterocycles [46]. Activated carbon technologies are preferred by EU countries as an upgrading option for their WWTPs because they can remove most of MPs, including PhACs, in municipal WWTP effluents by 80%. In Germany alone, there are 14 WWTPs already adopting PAC/GAC technologies, six WWTPs under construction and three WWTPs under design [47,48]. Two important parameters of GAC operation are breakthrough capacity and operating time [46,49]. The main drawbacks of GAC applications are (i) the need to properly treat and dispose of both the spent carbon and the sludge generated during the filtration process, and (ii) the need to remove the effluent organic matter before filtration. The effluent organic matter significantly diminishes the adsorption capacity of GAC and thus the operating lifetime. An alternative may be to take advantage of the organic matter retained in the GAC filter to support the growth of autochthonous biomass attached to the GAC particles. This colonization implies the development of biological activity inside the filter bed, and the process can thus be defined as biological activated carbon (BAC) filtration.

Biological activated carbon (BAC) filtration

The application of integrated systems, such as BAC, which combine adsorption and biotransformation has become relevant in the recent years due to their increased enhanced potential for the removal of MPs. The growth of microorganisms on the surface of the adsorbent material is considered a promising solution to increase the lifespan of the filtration system where only adsorption is identified since microorganisms can biodegrade MPs previously adsorbed on the surface of the sorbent since the contact time is increased [50]. As biofilters allow to operate with high biomass concentrations and sludge retention time (SRT), these systems are adequate for the development of slow growth microorganisms such as nitrifying bacteria [51]. The main parameters identified affecting the performance of biofilters in terms of OMPs abatement are the contact time expressed as EBCT, the hydraulic loading rate, the type and concentration of biomass and the concentration of dissolved oxygen [52,53]. BAC filters, compared to other biofiltration systems, have the advantage of presenting a high adsorption capacity, which contributes to the removal of PhACs as well as to biofilm development. It has been demonstrated that the GAC structure with its roughness and high porosity, possesses characteristics that promote microbial growth, thus providing better support compared to other materials such as sand, clay and anthracite [21]. With regard to the abatement of PhACs, BAC filters combine biodegradation with physical adsorption [54]. By combining these two mechanisms, a wider range of PhACs can be addressed, thus increasing the potential of such technology for application as a tertiary treatment [55,56]. Justo et al. [57] showed that during BAC filtration treatment of reverse osmosis brine, approximately 60% of the pharmaceutical content was depleted by the biological treatment. When applied after coagulation and clarification of surface water for drinking purposes, this technique was confirmed to be a sustainable treatment process for PhACs, with removals higher than 75% [58]. In this context, the biofiltration process is often evaluated as a part of larger treatment trains in which BAC filters represent only one step of the entire treatment line, according to the multiple barrier criteria. Few studies have documented situations in which BAC filters, applied as part of wastewater reuse schemes to treat wastewater for reclamation purposes, were proven to effectively remove many PhACs [39,53]. Rattier et al. [13] suggested that biodegradation can enhance the removal of the compounds that are less adsorbed onto GAC. Similarly, BAC filters have also been applied as the last step of an experimental indirect potable reuse treatment train comprising UF and ozone [59]. When preceded by UF and ozone, BAC filtration effectively decreased the concentration of PhACs in the treated WWTP effluent to below the method detection limit (MDL). Nevertheless, to the best of our knowledge, little is known regarding the application of BAC filters as a stand-alone tertiary treatment for the removal of PhACs. Paredes et al. [60] conducted a comparative study of BAC and sand biofiltration, which were both applied as stand-alone tertiary treatments. However, this study was conducted at lab-scale with synthetic water and spiked concentrations of PhACs. Rather than investigating the real operating conditions, the authors mainly focused on the specific removal mechanisms. Understanding the mechanisms shed light on the contributions of the biological processes taking place in these biofiltration systems. To assess whether biodegradation allows for greater removal of PhACs by BAC filters rather than by conventional GAC treatment, gaining insights into the mechanisms involved is key in biofiltration studies. As far as we know, only Rattier et al. [53] and Paredes et al. [60] have distinguished between biodegradation and adsorption during the BAC filtration of wastewater.

BAC-UF process

Studying the BAC filtration of real treated wastewater at pilot scale, Gerrity et al. [15] found higher concentrations of both total coliform and fecal coliform after BAC passage. Since bacteria grow on GAC particles, they can be detached and washed out from the biofilter. Aiming to prevent this escape, an ultrafiltration (UF) step can be performed after the BAC filter. When this BAC-UF combination was applied as a tertiary treatment, total coliforms, E. coli, Enterococci and Somatic coliphages were almost completely removed due to the UF step [17]. On the other hand, single UF is ineffective for the removal of most of the PhACs found in secondary effluents of WWTPs. Several studies have shown limited removal of PhACs by UF membrane alone [18,19]. Ultrafiltration alone is ineffective for PhACs removal because of its high molecular weight cut off and the unavoidable disadvantage of fouling when it is applied to wastewater treatment [20]. Weemaes et al. [17] tested the use of this system for removal of PhACs from secondary effluents in short-term experiments. This concept, applied at the laboratory scale, was able to almost completely remove antibiotics, iodinated contrast media and analgesic anti-inflammatory compounds. Hence, to gain useful information for a real application of this BAC-UF technology, further investigations need to verify this hypothesis at a larger scale. Moreover, the long-term performance of the system after reaching PhACs breakthrough must also be investigated.

Challenge 1

In summary, only a limited number of studies have used BAC filters as advanced technology to remove PhACs from secondary effluents. Furthermore, in these few studies, BAC filters were usually preceded by other treatment units (i.e., the technology was applied to refine tertiary effluents). When this was not the case, the studies were conducted at the laboratory scale and, therefore, within a controlled environment. Moreover, a long-term investigation of the BAC-UF performance, including the start-up phase, a few months of steady operation, and the GAC breakthrough, was not performed in any of the previous studies. To the best of our knowledge, this is the first time that a BAC filter has been evaluated as a stand-alone advanced treatment for the removal of PhACs at pilot scale during one year of operation; the results of this study will provide additional information about the extent to which biological processes can enhance the overall abatement of PhACs. Our hypothesis is that BAC, applied as a stand-alone tertiary treatment, can achieve better performance than other biofiltration systems and guarantee higher short-term levels of PhACs abatement than the conventional GAC treatment while providing the same long-term achievements.

Advanced oxidation processes (AOPs)

Technologies for AOPs involve widely different methods of activation as well as oxidant generation and can potentially utilize a number of different mechanisms for organic destruction [61]. Oxidation methods aim to destruct and transform refractory substances to simpler substances. Since traditional oxidation methods (i.e., Cl_2, HClO, H_2O_2, $KMnO_4$ and ClO_2) are ineffective in tackling MPs, advanced oxidation methods (AOPs) such as O_3,UV/H_2O_2,O_3/ H_2O_2,andUV/O_3 have been proposed as an alternative to overcome this limitation. AOPs presented higher MP removal performance than traditional oxidation methods due to stronger oxidant doses, higher magnitude of free radical compounds, and longer contact time [46,49]. All AOPs comprise of two steps, the in situ formation of reactive oxidative species and the reaction of oxidants with target contaminants. Mechanisms of radical formation depend on process specific parameters and can be affected by system design and water quality. Besides radical scavenging also other parameters (e.g., radical mass transfer in surface based AOPs, hydrodynamics) play an important role for efficiency of contaminant destruction. Several potential applications of AOPs at municipal WWTPs include: (1) pre-oxidation of primary effluent, (2) Sludge conditioning, (3) post-treatment of secondary effluent, (4) treatment of reverse osmosis concentrate, and (5) disinfection of effluent (Figure 2) [62].

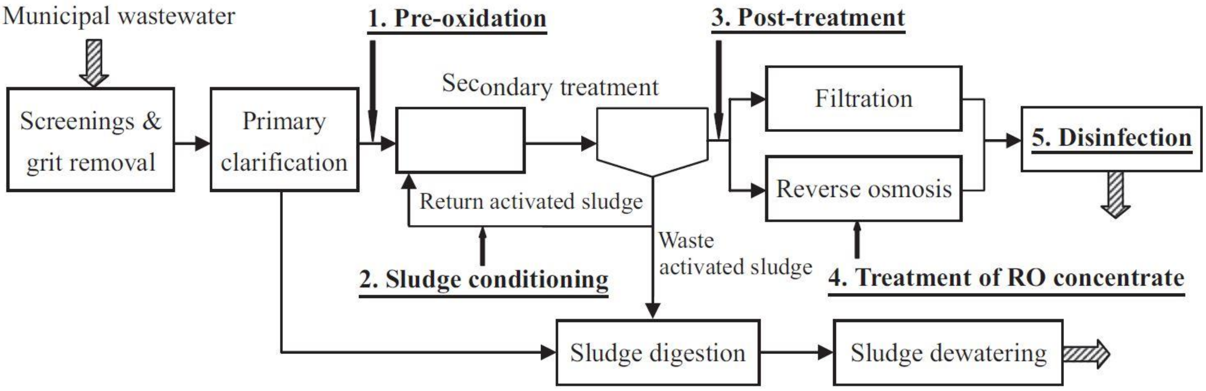


Figure 2 : Potential AOPs applications for municipal wastewater treatment (Adopted from Stefan et al. (2018))

Advanced oxidation processes (e.g., ozonation, photocatalysis, and photo-Fenton) have been proposed as tertiary treatments (position 3. In Figure 2) for municipal WWTP effluents due to their versatility and ability to detoxify effluent streams containing emerging contaminants (e.g., pharmaceuticals, personal-care products, steroid sex hormones, illicit drugs, etc.). Giannakis et al. (2015) have adopted various oxidation processes to treat wastewater from the output of three different secondary treatment facilities for the removal of 6 MPs [63]. These authors observed that the order of MPs degradation rates was: UV/H_2O_2 > UV-C radiation and photo-Fenton > solar radiation > Fenton. Although their efficiency, during the application of advanced oxidation processes, the main concern, relates to the formation of various products as a consequence of the interaction of radicals with both the target compounds and other substances occurring in the wastewater matrix. These interactions may trigger complex reaction pathways. The formation of transformation products (deriving from PhACs) and oxidation by-products (deriving from the wastewater matrix) is therefore a critical factor [64]. During the treatment, the disappearance of the original target compound may therefore not imply that the treatment is efficient and hence further measurements such as come conventional global parameters, including TOC, COD, DOC, adsorbable organic halogen (AOX), and fluorescence measurements can be used to assess the processes which based o, what said before, are not capable to provide solid conclusions on the overall efficiency of the process and the safe use or reuse potential of the treated flow [65]. With regard to UV/H_2O_2, it has been observed in several works that by-products formation from hydroxyl radicals is not critical unless formed at high density on surface areas (e.g; in electrolytic AOPs) [61,66]. However, AOPs involving other oxidants such as ozone, sulfate radicals or chlorine radicals need to be evaluated in more detail since site- and process-specific byproducts might be formed.

As a general classification, AOPs are divided into photochemical and non-photochemical processes. In the following section, focus will be given to photochemical process, e.i. base on light; in particular on UV-C (λ = 254 nm) light.

UV-based AOPs

UV-based AOPs comprise processes based on UV-irradiation (mostly UV-C) and the combination of UV-light with different radical promoters. UV-fluences applied for advanced oxidation are usually >200 mJ/cm² and therefore exceed UV-dose requirements for 4-log inactivation of most pathogens including UV-resistant organisms (e.g. adenovirus) [67]. UV-irradiation sources usually consist of either low (LP) or medium pressure (MP) mercury lamps with mono or polychromatic emission spectra, respectively. While UV alone is not effective in MP elimination, its combination with H_2O_2 or O_3 can boost the formation of free oxidant radicals and thus, significantly improve the removal rate [68,69]. O_3/UV has the highest oxidation potential and exhibits two-tier barriers for contaminants. This is because O_3 has greater UV adsorption capacity by a magnitude of 200 times (at 254 nm) than an equivalent amount of H_2O_2 does [70]. However, its high energy consumption inhibits a widespread application of O_3/UV in reality. To date, UV/H_2O_2 is still the most popular UV-based AOP in large-scale, but other radical promoters such as peroxydisulfate and peroxymonosulfate are also being investigated.

Sulfate based-AOPs

Peroxydisulfate (PDS) and peroxymonosulfate (PMS)

Recently, sulfate radicals ($SO_4^{\bullet -}$)-based technologies have received increasing attention [10]. In comparison to hydroxyl radical, sulfate radicals possess equal or even higher redox potential (2.5~3.1V) based on the activation methods [11]. In addition, sulfate radical has higher selectivity and longer half-life than hydroxyl radical in certain cases [12]. Therefore, sulfate radical could be expected to show similar or better capacity in degrading the emerging contaminants. Peroxydisulfate (PDS) and peroxymonosulfate (PMS), have been investigated as an alternative to generate sulfate radicals.

PDS is colorless or white crystal, and has high stability. It can be easily dissolved in water, with the solubility of 730 g/L [13]. The water solution of PDS is acidic. It has symmetrical structure, the distance of O-O bond is 1.497 Å, and its bond energy is 140 kJ/mol [14, 15]. The common PDS used in the experiments is sodium PDS ($Na_2S_2O_8$) and potassium PDS ($K_2S_2O_8$). Peroxymonosulfate is white solid powder. It is stable when pH is less than 6 or pH is 12. When pH is 9, it showed the poorest stability where half of HSO_5^- decomposes to SO_5^{2-} [16, 17]. PMS can be easily dissolved in water, with the solubility of > 250 g/L. Its water solution is acidic. It has asymmetrical structure, the distance of O-O bond is 1.453 Å. The bond energy is estimated to be in the range of 140 to 213.3 kJ/mol [14, 15, 18]. The common PMS used in the experiments is Oxone ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$). PDS and PMS are strong oxidizer, with the redox potential of 2.01 V and 1.82 V, respectively. However, they reacted directly with the organic contaminants with low reaction rate. To generate the strong oxidizer, sulfate radicals and hydroxyl radicals, appropriate activation is imperative for PDS and PMS.

UV-C activation

PDS and PMS can be activated by a variety of methods, such as heat, UV, alkaline, metal ions and activated carbon [19]. The redox potential of sulfate radical produced through the activation of PDS and PMS depended on the activation methods. Ultraviolet is considered as benign and cost-effective way to activate the PDS and PMS for degrading the organic pollutants in the water and wastewater. The most used wavelength is 254 nm, which is in the energy absorbance of the ultraviolet range. Quantum yield is an important factor for characterizing the activation of PDS and PMS. The UV wavelength has significant influence on the quantum yields. The quantum yields of sulfate radicals decreased with increase of UV wavelength in the range of 248 to 351 nm [57]. The maximal quantum yield was about 1.4 at the wavelength of 248 and 253.7 nm. In general, 254 nm is usually used as the radiation wavelength for persulfate. In comparison, the quantum yield for peroxymonosulfate was 0.12 at the wavelength of 248 nm [57]. In another study the quantum yield for UV-254/PMS was 0.52, when the sink of sulfate radical into hydroxyl radicals was taken into account [57]. For the activation of PDS and peroxymonosulfate by ultraviolet, two mechanisms might be involved. One is the fission of O-O bond by energy input of ultraviolet as presented in equations (1.1) and (1.2).

(1.1) $S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$

(1.2) $HSO_5^{-} \rightarrow SO_4^{\bullet-} + HO^{\bullet}$

The second is that water molecule can produce the electron with the ultraviolet, which activates the PDS or PMS by electron conduction as equations (1.3) to (1.5).

(1.3) $H_2O \rightarrow H^{\bullet} + HO^{\bullet}$

(1.4) $S_2O_8^{2-} + H \rightarrow SO_4^{2-} + H+$

(1.5) $HSO_5^{-} + H^{\bullet} \rightarrow SO_4^{\bullet-} + H_2O$

It is noted that the first mechanism is widely involved in the UV/PDS or UV/PMS process. While for the second mechanism the propagation of radicals was limited due to the extremely short penetration depth of UV-254 nm [71]. Thus, the second activation mechanism is of minor importance in real applications for UV-254 nm. Nevertheless, Under 254 nm UV radiation, PDS and PMS generate two $SO_4^{\bullet-}$ and one $OH^{\bullet}$ plus one $SO_4^{\bullet-}$, respectively. $SO_4^{\bullet-}$ possesses higher reaction rate constants with electron-rich contaminants, and a higher half-life than $OH^{\bullet}$ mainly to its preference to react with organics during electron transfer [18]. On the contrary, hydroxyl radicals due to its non-selectivity, are more prone to be scavenged by effluent organic matter (EfOM) which is a major wastewater matrix component [19]. At this moment, most of investigations regarding UV/PDS and UV/PMS to remove PhACs, have focused on drinking waters and synthetic wastewaters. In WWTPs effluent, being PhACs found at concentrations 3 to 5 orders of magnitude lower than the concentration than of the remaining matrix components, most of the added oxidants are consumed by the matrix [72]. The presence of effluent organic matter (EfOM), nitrate, chloride, sulfate, carbonates and bicarbonates, exert a scavenging effect during AOPs, but they can also contribute to the formation of less reactive oxidant species [73–75]. However these effects have been mostly studied in either pure water or synthetic mineral water [71]. Studies based on real wastewaters are necessary for the future of in-situ applications.

Challenge 2

In summary, to date, very few studies (number of studies = 8)) [72,76–83] investigated the applicability of UV activated PDS or PMS for PhACs degradation in real wastewater. Moreover research literature lacks comparisons between different UV-activated sulfate radical based AOPs. To the best of our knowledge, only Rodríguez-Chueca et al. carried out a comparison of PDS and PMS for PhACs removal from real wastewater [82–84]. The aforementioned work is not fully explanatory, however, as the UV/PDS process could not enhance the removals obtained by UV alone [82]. This fact was attributed to the inadequate contact time between PDS and UV light rather than to wastewater matrix effects. The same authors, together with Nihemaiti et al. (2018), were the only ones providing experimental evidences with regard to UV/PDS and UV/PMS application at large scale wastewater [80,82–84]. Further work is essential if a conclusion has to be reached regarding PDS and PMS efficiencies in this type of water, and could also possibly highlight the impacts of the major wastewater matrix components. Thus keeping these considerations in mind, the current work aim to address the research gaps highlighted above.

Environmental impact assessment of wastewater treatment technologies

In 2005, the US National Decentralized Water Resources Capacity Development project (NDWRCD) published a report entitled “Methods for comparison of wastewater treatment options” [85]. The motivation of this report was the fact that decisions in the US regarding waste and water systems were based primarily on economics and consider a very limited set of treatment options; by doing so, the true environmental and social cost of wastewater treatment were often not included in decision making ” [85]. Nowadays, there are several methodologies for evaluating the environmental impacts particular technologies, products, communities and production processes may have. One of these is the Life Cycle Assessment (LCA). Life cycle thinking is an approach that considers all of the impacts in the different areas of sustainability (environmental, economic and social) that a product or service will produce throughout its life-cycle, i.e. from “cradle-to-grave”. Different areas are dealt within the life cycle thinking approach, such as life cycle assessment, life cycle costing or life cycle management. LCA is a systematic analysis used to assess the environmental impact generated by a product or process throughout all its life-cycle by considering the consumption of energy and materials it makes, along with the emissions it generates. LCA comprises four different phases, namely: goal and scope definition, life cycle inventory, life cycle impact assessment and interpretation, all of which must be carried out in accordance with ISO 14044:2006 [86,87]. LCA is one of the most popular method to evaluate the potential environmental impacts caused by WWTPs. To the best of our knowledge, the first LCA study applied to wastewater treatment plants (WWTPs) published in an international peer reviewed journal was focused on the inventory phase to evaluate different small-scale WWT technologies [88]. They highlighted the importance of including the emission of CO_2 associated with energy production, thus introducing second order (background) impacts in the evaluation of environmental performance.

Electricity use was identified as one of the main contributors to the depletion of fossil resources and the generation of Greenhouse Gas (GHG) emissions. The construction and demolition phases were included in the analysis in addition to the evaluation of operation of the system. Afterwards, a more sophisticated LCA methodology was used to evaluate the societal sustainability of municipal WWT in the Netherlands [89] and the results highlighted the importance of reducing effluent pollution (nitrogen, phosphorus) and minimizing the sludge production. Contrary to the previous study, it was concluded that the contribution of impacts related to energy consumption were very low [86].

LCA of advanced treatment technologies

Emerging technologies for wastewater treatment are being developed and it becomes a common practice to use LCA as the methodology to compare them against conventional technologies. The environmental impact assessment of non-conventional technologies was mostly done in the context of wastewater reclamation practices [5]. Meneses et al. (2010) compared different tertiary treatment processes for wastewater reclamation, traditional treatment for potable water production and desalination process [5]. Desalination appeared as the worst option for non-potable uses due to the high energy consumption. The addition of a tertiary treatment slightly increases the environmental impact of the WWTP, but these impacts are largely offset by the beneficial non-potable use of reclaimed water [1]. LCA has been used as a decision-support tool to compare tertiary treatment options for wastewater reuse in a combination of pilot unit data and models to extrapolate for 20,000 to 10,0000 person equivalents [5,90]. The following treatments were studied to provide a water quality suitable for unrestricted irrigation (depending on the raw wastewater quality): chlorination plus ultraviolet (UV), media filtration plus UV, microfiltration plus UV, ultrafiltration, ozonation, ozonation plus hydrogen peroxide treatment. Scenarios including ozonation have the highest environmental impacts due to the high energy demand for ozone production and the potential ecotoxicity of by-products [5,91]. High quality effluents are produced after ultrafiltration, but at the cost of high electricity and chemical demand with the associated environmental impacts. Media filtration associated with UV disinfection seems to be a good compromise between environmental impacts and effluent quality suitable for unrestricted irrigation [1,5,90,92]. The use of robust technology such as sand filtration followed by UV disinfection (SF-UV) has an environmental impact equivalent to UF alone for most of the mid-point indicators chosen. UF is usually complemented with a sterilization module, to prevent pollution in case of fiber break. If this option is considered, the environmental load is clearly favorable to SF-UV to produce water for unrestricted irrigation according to the French requirements [93].

LCA of advanced treatment technologies for MPs removal

With regard to advanced treatment technologies for MPs removal, there are very few studies using LCA method to evaluate them [87]. Most of the published studies on this topic deal with drinking water conventional and advanced technologies. However, in order to have an overview of LCA studies on advanced treatment technologies to remove MPs, study presenting characteristics similar to this current thesis, will be mentioned in this paragraph (1.5.2). Høibye et al. (2008) evaluated the environmental impact of several advanced treatment technologies for MPs removal [94]. They found that sand filtration has the most advantageous technical and environmental aspects but was ineffective for the removal of MPs and pathogenic microorganisms. At the same time they reported that UV based AOPs, are space-saving and economically advantageous, but they also highlighted that before performing an holistic assessment of advanced treatment technologies, more data must be collected on treatment efficiencies, energy consumption, resource consumption, occupational health and safety aspects and other pros and cons [94]. Wenzel et l. (2008) assessed three alternative of wastewater treatment technologies to remove 9 selected MPs [95]. They found out that the environmental impacts induced by these treatments may be of the same order of magnitude as the impacts avoided by the reduction of the effluent concentration of the selected MPs [95]. Therefore further investigations to evaluate the avoided impact for MPs removal need to be done, and then, directly compared to the induced impacts related to the implementations of advanced treatments. Köhler et al. (2012) studied PhACs removal through UV/H_2O_2 application as advanced treatment technologies, and observed that H_2O_2 had a significant influence on the generated environmental impact due to its production process [96]. Foteinis et al. (2018) estimated the environmental sustainability of a solar photo-Fenton process to remove pharmaceuticals from wastewater [97]. These authors found that the chemical reagents used, mainly H_2O_2, were the main contributors to almost all impact categories with marine and freshwater ecotoxicity categories being mostly affected. To the best of our knowledge, only the work of Zepon Tarpani and Azapagic (2018) evaluated different advanced wastewater treatment technologies for PhACs removal using a LCA methodology [98].

Challenge 3

In summary, several alternatives are available for advanced wastewater treatment technologies, and many of them can achieve high removal efficiencies. Then, an additional evaluation tool, such as LCA methodology, may be key in the process of screening different options. With regard to the technologies studied in this thesis, to the best of our knowledge, they have never been assessed with a multi-criteria approach going beyond their efficiency to remove PhACs, and taking into account the environmental footprint associated to their application. In this framework, this is the first time that environmental impacts of BAC-UF, UV/PDS and UV/PMS technologies have been assessed, and associated to economic and technical feasibility considerations.

Objectives

The main objective of this thesis is to evaluate the application of alternative advanced wastewater treatment technologies to remove pharmaceutical active compounds (PhACs) from secondary effluents of municipal wastewater treatment plants (WWTPs). The two alternative technologies studied and compared among state-of-the-art technologies were a biological activated carbon followed by an ultrafiltration (BAC-UF), and the combination of UV with sulfate-based oxidants such as peroxydisulfate (PDS) and peroxymonosulfate (PMS). The selected strategy followed to evaluate these techniques is based on estimating their removal capacity, identifying the main removal mechanisms, calculating the costs required for the effective PhACs removal and finally assessing their environmental footprint.

To reach the main objective of this thesis, the following specific objectives are considered:

- To evaluate the long-term performance of the BAC-UF technology, operating as stand-alone tertiary treatment, during one year of operation (Chapter 4).
- To identify the main removal mechanisms of PhACs and gain insights into the respective roles of biodegradation and adsorption processes in the BAC-UF technology (Chapter 4).
- To evaluate the feasibility of UV/PDS and UV/PMS technologies and the interference of wastewater matrix (Chapter 5).
- To validate the application of UV/PDS and UV/PMS at larger pilot-scale (Chapter 5).
- To evaluate and compare the energy, economic and the environmental impacts of each studied technology, identifying the main hotspots (Chapter 6).

Materials and Methods

This section contains information about all the materials and chemicals used throughout this thesis. Among the chemicals, emphasis is given to the PhACs which were the main target of the current work. Besides chemicals and materials, the devices used in the different experiments have also been described in order to allow understanding and reproducibility of the experimental work carried out for each studied technology. Finally the methodology followed for the comprehensive comparison of different technologies has been described.

Chemicals

Chemicals used in this study were mostly involved in analysis and samples preparation. Below, a list of all the utilized chemical substances is reported. HPLC grade methanol, was supplied by Merck (Darmstadt, Germany), ammonium hydroxyde, hydrochloric acid and ethylenediaminetetraacetic acid disodium salt solution (Na_2EDTA) at 0.1 mol/l were from Panreac. Nitrogen for drying was from Abelló Linde S.A. (Spain) and it was of 99.9990% purity. A Milli- Q-Advantage system from Millipore Ibérica S.A. (Spain) was used to obtain HPLC-grade water. Potassium peroxydisulfate (PDS; CAS Number: 7727-21-1), sodium bicarbonate, sodium sulfate, sodium chloride and sulfuric acid where purchased by Scharlab. Potassium peroxymonosulfate (Oxone ®, 2KHSO5 KHSO4 K2SO4; PMS; CAS number: 10058-23-8) was provided by Sigma-Aldrich. All PhACs and isotope labeled analytical standards for PhACs analysis were of analytical grade. The PhACs used in this work were: atenolol (ATNL; CAS number: 29122-68-7), carbamazepine (CBZ; CAS number: 298-46-4), ciprofloxacin (CPFX; CAS number: 85721-33-1), diazepam (DZP; CAS number: 439-14-5), metoprolol (MTPL; CAS number: 37350-58-6), sulfamethoxazole (SMX; CAS number: 723-46-6), nadolol (NDL; CAS number: 42200-33-9), ofloxacin (OFLX; CAS number: 82419-36-1), venlafaxine (VLFX; CAS number: 93413-69-5), hydrochlorothiazide (HDCT; CAS number), irbesartan (IRB; CAS number:) and bezafibrate (BZF; CAS number:), trimethoprim (TRIM; CAS number:), azithromycin (AZIT; CAS number:) and propanolol (PROP; CAS number:).

Pharmaceutically active compounds (PhACs)

A total of fifteen PhACs were chosen to assess the removal capacity of the advanced treatment technologies (BAC-UF and AOPs). However, a brief distinction between the two main sections of this work has to be stressed out.

During the BAC-UF study, no spiking of PhACs into the real secondary effluent has been conducted, which was indeed treated as discharged from the WWTP. The entire set of target compounds included thirteen PhACs and the compounds were selected according to the following criteria, which were fulfilled by the selected PhACs:

a. they were found at relevant concentrations in the secondary effluent used to feed the pilot plant;
b. they were reported to have low or very low removals during conventional activated sludge processes [2];
c. they belong to different therapeutic groups and, hence have different physical-chemical properties that should result in different removal behavior;
d. they belong to both the EU Priority and Watch List [21] and finally, when possible;
e. they have not been studied before in BAC filtration units.

This selection resulted in the following list composed of (i) five antibiotics: sulfamethoxazole (SMX), azithromycin (AZIT), ofloxacin (OFLX), trimethoprim (TRIM) and ciprofloxacin (CIPX); (ii) three beta-blockers: metoprolol (MTP), atenolol (ATN) and propanolol (PROP); (iii) two psychiatric drugs: carbamazepine (CBZ) and venlafaxine (VNLX); and (iv) three additional PhACs belonging to other therapeutic groups, i.e., hydrochlorothiazide (HDCT), irbesartan (IRB) and bezafibrate (BZF).

On the other hand, during the experiments conducted with UV/PDS and UV/PMS both at lab-scale and at pilot-scale, PhACs were spiked into the real secondary effluent. The aim was to reach an initial concentration of 10 µg/L for each compound. In this context, spiking working solutions were prepared on weight basis in Milli-Q water. PhACs used in this second branch of this work have been chosen accordingly to the following criteria:

a. they fulfill the above reported criteria (a. – e.);
b. they are poorly photodegraded by 254 nm UV light (e.i. high K_{UV} values; Table);
c. they have not been studied before in UV/PDS and UV/PMS systems.

Therefore the previous selection of thirteen substances was slightly changed and reduced in order to investigate PhACs fulfilling also criteria (f. – g.). The updated selection resulted in the following list composed of (i) three antibiotics: sulfamethoxazole (SMX), ofloxacin (OFLX), and ciprofloxacin (CIPX); (ii) three beta-blockers: metoprolol (MTP), atenolol (ATN) and nadolol (NDL); (iii) three psychiatric drugs: carbamazepine (CBZ) and venlafaxine (VNLX) and diazepam (DZP).

Analytical methods

These thirteen PhACs were analyzed following the analytical procedure developed by Gros et al. [22]. Briefly, wastewater samples were first filtered through 1 µm glass fiber filters followed by 0.45 µm nylon membrane filters (Whatman, U.K.), and then a suitable volume of 0.1 M Na_2EDTA solution, was added to achieve a final concentration of 0.1% (g solute/g solution). Moreover, the water samples were spiked with an appropriate volume of a standard mixture containing surrogate standards to reach a concentration of 100 ng/L in each wastewater sample. Afterwards, the water samples were extracted using Oasis HLB cartridges (60 mg, 3 mL). The cartridges were conditioned with 5 mL of methanol followed by 5 mL of HPLC-grade water at a flow rate of 2 mL/min. A total of 100 mL of wastewater was loaded onto the cartridges at a flow rate of 2 mL/min. After the samples were pre-concentrated, the cartridges were rinsed with 6 mL of HPLC grade water and air dried to remove the excess water. Finally, analytes were eluted with 6 mL of pure methanol at a flow rate of 1 mL/min. The extracts were evaporated to dryness under a gentle nitrogen stream and reconstituted with 1 mL of methanol/water (10:90, v/v). Finally, 10 µL of a 1 ng/µL standard mixture containing all isotopically labeled standards was added to the extract to provide internal standards. Chromatographic separation was carried out with an ultra-performance liquid chromatography (UPLC) system (Waters Corp. Mildford, MA, USA) using an Acquity HSS T3 column (50 mm× 2.1 mmi.d., 1.7 µm particle size) for the compounds analyzed under positive electrospray ionization (PI) and an Acquity BEH C18 column (50 mm× 2.1 mmi.d., 1.7 µm particle size) for the compounds analyzed under negative electrospray ionization (NI), both from the Waters Corporation. The UPLC instrument was coupled with a 5500QqLit, triple quadrupole–linear ion trap mass spectrometer (5500 QTRAP, Applied Biosystems, Foster City, CA, USA) with a Turbo V ion spray source. Two multiple reaction monitoring (MRM) transitions per compound were recorded by using the Scheduled MRM™ algorithm, and the data were acquired and processed using Analyst 2.1 software.

Conventional pollutants

Nitrogen compounds such as NH_4^+, NO_2^- and NO_3^-, were analyzed via ion chromatography (ICS5000, DIONEX.). Total suspended solids were analyzed according to the standard methods (APHA, 1998) by the difference in weight of a dried filter (Macherey-Nagel Filter Paper Circles MN 640 90mm) without biomass and after heating at 105°C for ≥ 24h and of the filter with biomass and after heating at 105°C for ≥ 24h [99]. The soluble Chemical Oxygen Demand concentration (CODs) was determined following the method 5220C of the Standard Methods for the Examination of Water and Wastewater (APHA-AWWA-WPCF, 1999) [99]. Organic carbon in liquid samples may include a variety of organic compounds in different oxidation states. To determine the quantity of organically bound carbon, the organic molecules must be broken down and converted to a single carbon molecular form that can be measured quantitatively. The DOC concentration is determined by a Shimadzu analyzer (TOC-5000) as the difference between the Total Carbon (TC) and the Inorganic Carbon (IC) concentrations.

BAC-UF process

In the following paragraphs (3.4.1 and 3.4.2) the description of the installations referred to the first part of this thesis are presented. Moreover, with regard to the BAC-UF process, all the analytical procedures carried out are also introduced.

Pilot plant

The BAC-UF pilot plant setup coupled two separate units, the biological activated carbon filter and the ultrafiltration tank, as shown in Figure 3. The pilot plant was fed by secondary effluent (the wastewater characteristics are reported in Table 1) from a municipal WWTP designed for biological nutrient removal. The BAC filter was filled with ORGANOSORB ® 10-CO coconut shell-based GAC (Table 2) to an operating volume of 2 m^3. This resulted in an empty bed contact time (EBCT) of 50 minutes. The BAC bed, operated in downstream mode, was maintained submerged by a control valve placed at the outlet of the filter. In order to face clogging problems of the bed filter, backwash was operated. The backwash of the BAC bed filter was controlled on-line when reaching a head loss threshold in the filter. The secondary effluent was pumped into the fixed bed BAC filter in a downstream configuration with a flow rate of 48 m^3/day. The BAC filter operating conditions are reported in Table 3. Taking into account this influent flow, one day of operation corresponded to 38.3 bed volumes (BV [m^3_{water}/m^3_{GAC}]) of wastewater treated by the pilot plant. Considering that this system was operated and monitored for one year, at the end of the experimental period, 13,800 BV were filtered through the BAC filter bed.

Table 1 : Conventional parameters of secondary effluent used as influent of both pilot plant and lab-scale set-up.

Wastewater characteristics (mg/L)	
BOD	4.8 ± 2.9
COD	31.9 ± 7.3
SS	9.1 ± 7.3
TKN	2.3 ± 1.1
NH_4^+	0.8 ± 0.7
NH_3^-	4.8 ± 1.4
NO_2^-	0.1 ± 0.1
N tot	6.5 ± 1.3
P tot	0.4 ± 0.2

Number of samples n=20

Table 2 : GAC specifications

Iodine number	1.2 (mg/g)
Particle size	2.36-4.75 (mm)
Sieve analysis	
< 4.75	90 (%)
> 2.36	93 (%)
Bed density	360 (kg/m³)
CTC value	72 (%W/W)
BET surface area	1.250 (m²/g)
Hardness	96
Material	Coconut shell
Supplier	Desotec

Table 3 : BAC filter operating conditions

Feeding mode	Downstream
Influent Flow	2 m³/h
EBCT	50 min
Backwash (BW)	Automatic Water + Air pulse
BW activating head loss	24.5 millibar
BW duration	10 sec
BW velocity	31.6 m/h
GAC replacement	After 8000 – 9000 BV

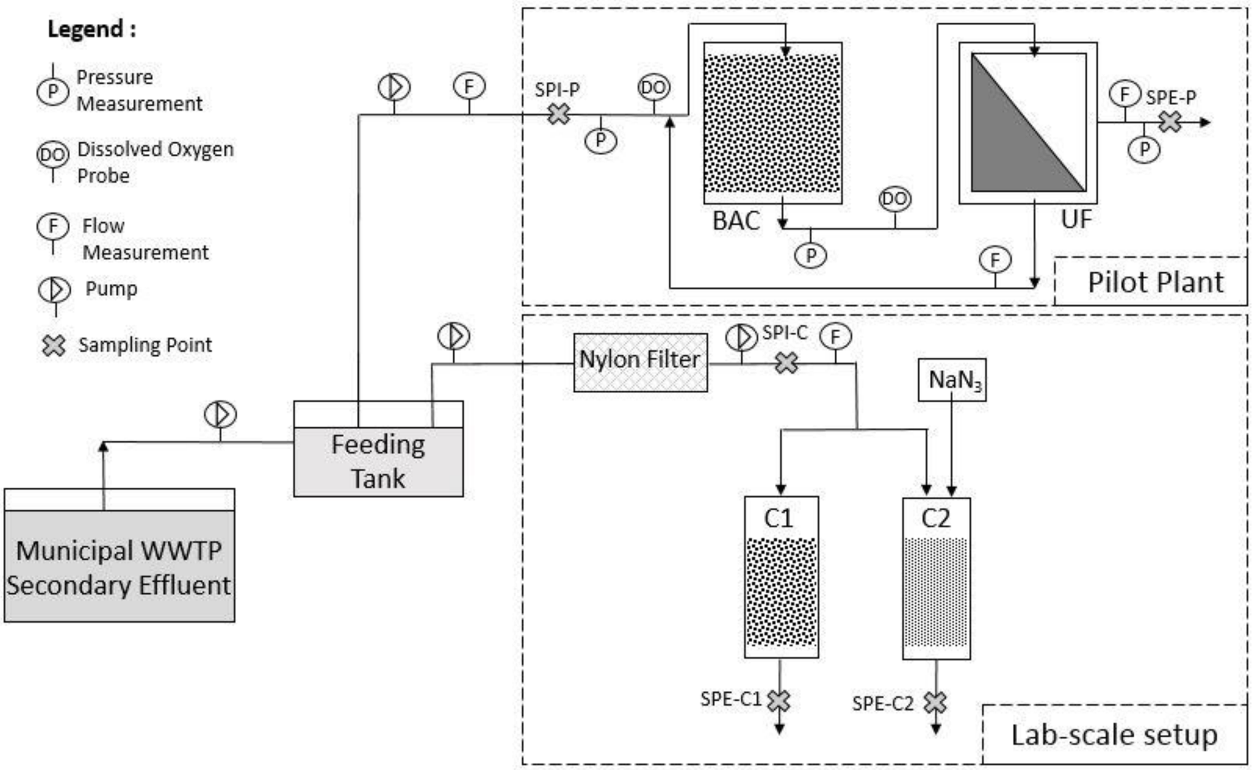


Figure 3 : Scheme of the BAC-UF pilot plant and the lab-scale setup. SPI-P: Sampling Point Influent-Pilot; SPE-P: Sampling Point Effluent-Pilot; SPI-C: Sampling Point Influent Columns; SPE-C1: Sampling Point Effluent Column 1; SPE-C2: Sampling Point Effluent Column 2; C1: Column 1 = Biologically active column; C2: Column 2 = Biologically inhibited column.

Figure 4 : Picture of the BAC-UF pilot plant

The BAC outlet fed the ultrafiltration (UF) tank. The ultrafiltration membrane were placed after the BAC in order to minimize the amount of BAC particles that leached into the finished water, and at the same time to avoid microbial breakthrough. The UF operating conditions are shown in Table 4. The UF tank water, known as concentrate, was recirculated on top of the BAC filter with a flow rate of 60 m^3/day (Figure 3). Continuous oxygenation of the BAC unit through recycling of the concentrate was provided while the UF membrane was operated in a 10/10 seconds mode with scouring coarse bubbles. The pilot plant was equipped with pressure and oxygen probes, as well as flow meters arranged in several spots (Figure 3) to monitor and control the biological performance of the BAC filter bed and ensure the standard functioning of the entire system.

Table 4 : UF operating conditions

UF total surface	220 m²
Nominal pore size	0.04 micron
MWCO*	2000 kDa
Filtration	5 minutes @ 3000 l/h
Backwash	30 sec @ 6000 l/h
Relaxation	10 sec
Flux	13 l/m^2/h

* MWCO: Molecular Weight Cut-Off

Lab-scale set-up

The lab-scale setup consisted of 2 transparent PVC columns (L=42 cm, D=5.5 cm) filled with the same GAC used in the pilot plant. Column C1 was kept biologically active, and both adsorption and biodegradation occurred. Column C2 was biologically inactivated by continuously adding sodium azide (NaN_3) to a final concentration of 250 mg/L, with the goal of inhibiting any biological activity [60]; thus limiting the PhACs removal mechanisms to only adsorption. NaN_3 was applied from day zero until the last day of operation. The columns were operated from top to bottom at room temperature in the dark (to prevent algae growth and PhACs photolysis). The influent flow was set to achieve an EBCT value of 50 minutes, the same as that in the BAC pilot plant. No automatic backwashing operation of the columns was performed. To prevent clogging phenomena, the secondary effluent was filtered through a 200 µm nylon filter prior to column filtration. After the 200 µm nylon filter, the wastewater was directly pumped through the columns by a peristaltic pump (Watson Marlow, The Netherlands). Then, in order to reduce pressure build up, the columns were manually backwashed monthly. The backwash procedure was applied with water and air simultaneously, with a duration of thirty seconds. This is the time necessary to reach the overflow opening. This lab-scale setup was operated for four months.

Biological activity

With the objective of monitoring the biological activity of the biomass attached to the GAC particles and inside the BAC filter bed, the following measurements were carried out.

Biomass quantification

After 5,750 BV (five months) of operation of the BAC-UF pilot plant, the biomass attached to the GAC particles was quantified by an adenosine triphosphate (ATP) measurement. To conduct these measurements, GAC samples were treated according to the protocol described by Velten et al. [100]. In short, the GAC particles were rinsed three times in phosphate buffer. Then, 200 mg (wet weight) of sample was transferred to an Eppendorf tube together with 100 mL sterile phosphate buffer and 300 mL BacTiterGlo TM (Promega Corporation, Madison, WI, USA), and the resulting luminescence was measured as relative light units (RLU). The results were converted to ATP concentrations using a calibration curve.

Respirometric assays

Together with biomass quantification, the same GAC samples taken after 5,750 BV for ATP measurements were also used in a series of respirometric batch experiments aiming at determining biomass activity. In this set of experiments, the specific heterotrophic activity (SHA), which is the maximum organic matter uptake rate per gram of biomass (g $COD*g^{-1}$ $SS*d^{-1}$), and specific nitrifying activity (SNA), which is the maximum ammonia uptake per gram of biomass (g $NH_4^{+}*g^{-1}$ $SS*d^{-1}$), were determined by means of the following respirometric method : i) the biomass was harvested from the GAC samples; ii) 1 L glass bottles containing 10 mL of biomass were saturated with oxygen; iii) aeration was interrupted; iv) a non-limiting concentration of substrate was added (200 mg $COD*L^{-1}$ and 20 mg $NH_4^{+}*L^{-1}$); v) the decrease in the DO concentration was monitored and vi) the COD and NH_4^{+} concentrations after 1, 3 and 6 hours of reaction were measured [60].

Textural properties

To gain insights into the status of the GAC particles throughout the operational period of the pilot plant, the porosity of the particles inside the filter was measured. The specific surface area (calculated with the Brunauer, Emmet and Teller method, i.e., the BET surface), micropore area and volume were determined on the basis of the adsorption isotherms of nitrogen [101]. These measurements were realized at Quantachrome GmbH & Co. KG laboratory in Odelzhausen (Germany). First, the samples were pretreated at 80°C for 3 hours under vacuum. Subsequent analysis was performed on a Quantachrome Quadrasorb with nitrogen at 77 K. The micropore area and micropore volume were calculated with the “t-Plot-method”.

Sulfate based-AOPs

This paragraph illustrates the equipment used in order to evaluate the advanced oxidation processes involving the application of UV-C radiation as PDS and PMS activator. Since the lab-scale apparatus and the pilot-plant system are based on the same principle, but sensibly differ in terms of inner mechanisms (UV-C light emission, distance between water and UV lamp, mode of operation), a clear distinction has been proposed as follows.

Lab-scale set-up : collimated beam experiments

Experiments were carried out using quasi-collimated beam UV apparatus equipped with a 10W low pressure Hg UV lamp (Ster-L-Ray Germicidal Lamp, model G12T6L 15114, Atlantic Ultraviolet Corporation, USA) with monochromatic emission at λ_{max} = 254 nm. The UV fluence (mJ cm^{-2}) used in this study was further calculated following the protocol established by Bolton and Linden (2003) [102]. Briefly, the UV fluence is calculated as the product of fluence rate (irradiance) and exposure time. The irradiance is usually measured with a radiometer, which consists of a very sensitive electronic ammeter to which is connected a UV sensor head, which produces a current proportional to the incident irradiance. The radiometer usually reads directly in units of mW/cm^2, W/m^2 or W/cm^2. The irradiance of the low pressure UV lamp used in this work is represented in Figure 5. The UV irradiance at the center of the UV beam at the surface of the reactor level was measured by a radiometer (Model IL 1400A with an SED240 Detector, International Light Inc.), which was calibrated at 254 nm. The radiometer detector only provides a measure of the irradiance incident on the water at the center of the beam. Several corrections are required to obtain the average irradiance in the water. This latter value is most important, since this provides an estimate of the average fluence rate to which each microorganism is exposed and is the basis on which the delivered fluence (UV dose) to a sample can be calculated. The corrections which is necessary to apply to obtain the average irradiance in the water, are the following : reflection factor, petri Factor, water factor and the divergence factor. Thus for low pressure UV lamp the formula too be applied to calculate the average irradiance E_{avg} (W/m^2) in the water is given by :

Eq. (2) $E_{avg} = E_0$ X Petri Factor X Reflection Factor X Water Factor X Divergence Factor.

Where E_0 = radiometer reading at the center of the glass reactor and at a vertical position so that the calibration plane of the detector head is at the same level as the top of the solution. The average UV fluence (e.i. UV dose) (mJ/cm^2) is then given by the product of E_{avg} and the exposure time (sec). Fluences were applied to 200 mL of solution in a 10 cm of diameter glass reactor, which coincided in the middle of the circular opening of the collimated tube (11 cm diameter). Actual spreadsheets to calculate the UV dose are available from the Web Site of the International Ultraviolet Association (www.iuva.org). The further data needed to calculate the UV dose are the surface of the solution and its height. The surface of the solution was about 78.5 cm² and the height of the solution column was 2.55 cm. Experiments were carried out under constant stirring and at 21ºC, in a total time of 30 min.

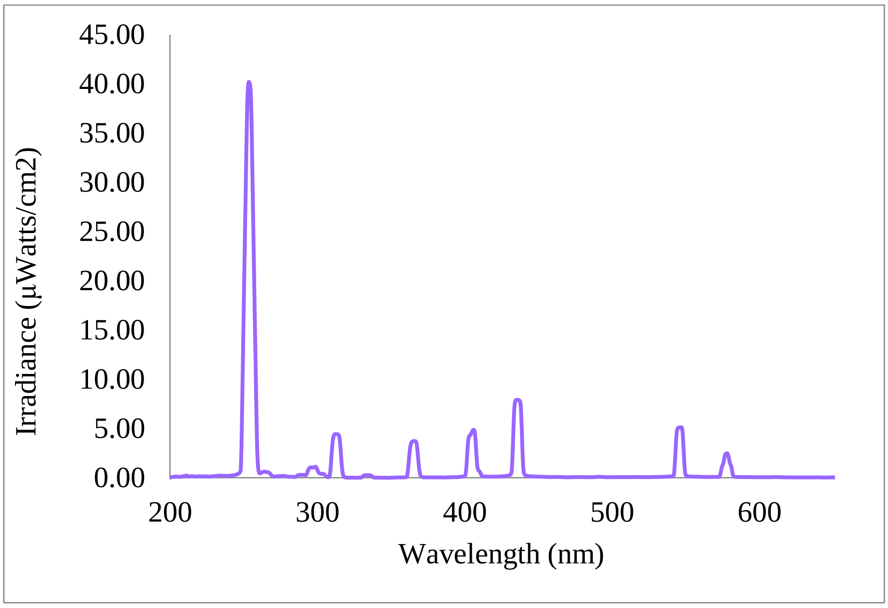


Figure 5 : Spectrum of low pressure UV lamp of the collimated beam device

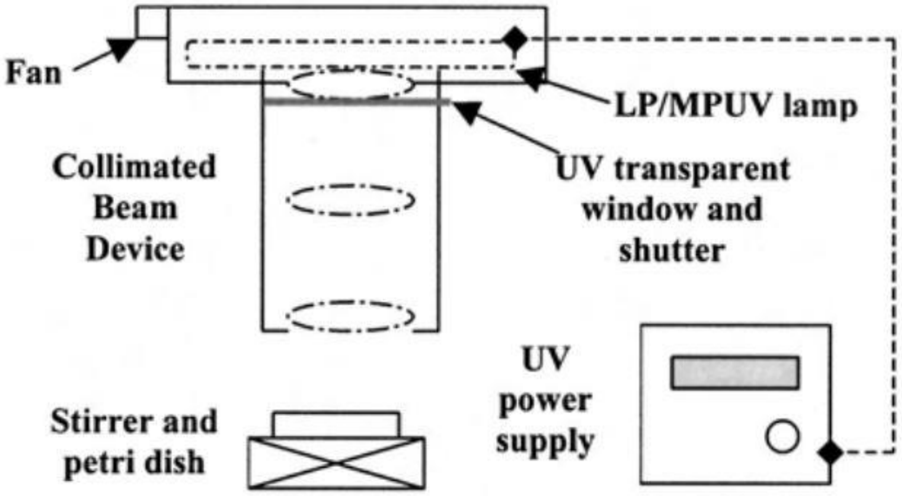


Figure 6 : Scheme of the collimated beam device for UV experiments. (Adapted from Bolton and Linden, (2015))

Figure 7 : Picture of the collimated beam device for UV experiments

Pilot plant : UV-C reactor

The pilot-scale installation consisted of a flow-through chamber high-grade stainless steel reactor containing high-output amalgam lamp (45 W), with a maximum emission peak at 253.7 nm, besides minor emission in the UV-B, UV-A and visible range totaling about 10% of the total radiant power. UV-C reactor was purchased by ProMinent for research purposes . The reactor was cylindrical with 45.7 L of inner volume. UV-C lamp is placed in quartz tube distributed at the section of the cylinder and taking up all its length. The tight positioning of the lamp enabled the treatment of water with low UV transmittance. The reactor was equipped with a UV-radiometer at the inner wall measuring the number of Watts incident on each square meter of water to be treated (W/m^2); namely the irradiance. With clean pure water, the average incident light flux inside the reactor was provided by manufacturer to be 45 W/m^2. A counter check of this irradiance value has been done operating the lamp with pure water in a closed loop. When the reactor was fed with secondary effluent from WWTP, the resulting irradiance value was 17 W/m^2; suggesting a significant reduction of the transmittance value; e.i. higher absorbance. Although the reactor is able to treat a maximum water flow of 2 m^3/h, lower flow rate was used during the experiments. Both UV irradiance and wastewater flow rate need to be paid attention to because of their relevance in AOPs. In fact, the degradation by photolysis and radical oxidation (during UV/PDS and UV/PMS processes) is a result of the UV-dose applied to the wastewater to be treated. The UV-dose to the wastewater in turn is a result of the flow through the reactor, the installed UV-power and the transmitted UV-dose, which depends on the UV-transmittance of the wastewater and the light blocking by particles. The pilot system was fed with secondary effluent from the nearest WWTP of Quart (Girona, Spain). A brief description of the WWTP will be presented in the following section (5.1).

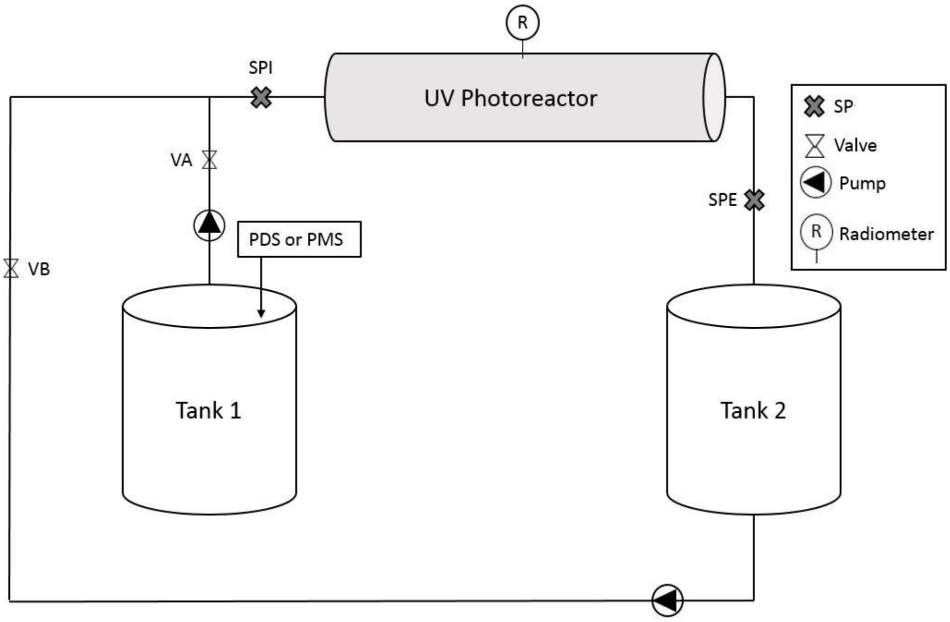


Figure 8 : Scheme of the UV reactor pilot plant. SPI : Sampling Point Influent; SPE : Sampling Point Effluent

Figure 9 : Picture of the UV reactor pilot plant

Cost estimation

An evaluation of the operational costs of the studied technologies has been carried out. The outcomes of this evaluation were then compared with GAC filtration and ozonation, considered as state-of-the-art technologies for advanced wastewater treatment.

Energy audit of the pilot plants

In order to assess the operating cost of the studied technologies, an inventory of all pumps and engine components used in the pilot plants (both the BAC-UF and the UV reactor) was made. Power consumption of all consumers (blowers, pumps, compressors, lamps) was measured with a Kyoritsu Power Analyser 6310 power logger. The energy logging was performed during continuous and automatic operation for 1 hour time window for each running device. These values are directly used to quantify the power consumption of the technologies described in the previous sections. The electricity costs for the Belgian energy grid is used to model the total cost, i.e. 0.11 euro/kWh. There is no difference in day and night tariff. With regard to the radiation needed to activate PDS and PMS, the energy consumption of the low pressure UV lamp is obtained by multiplying the nominal consumption and the irradiation time.

Consumables cost

The cost of the GAC media is based on the experimentally derived breakthrough of the BAC-UF pilot plant. This means that a GAC life span to ensure 80% average PhACs removal was considered. After this period, a replacement of this filtering media has been considered and included in the cost calculation. Different market prices for GAC based on coconut shell were observed in literature , ranging from 0.3 €/kg to 7.9 €/kg [103]. The GAC used in this work were purchased by DESOTEC (www.desotec.com) with cost of 1.24 €/kg. This was the price used for cost estimation. Regarding UV/PDS and UV/PMS systems, the supply of both PDS and PMS is considered from large scale applications. PMS is supplied in form of Oxone (98% purity) with a cost of 2,000 €/ton, which corresponds to 0.64 €/mol. On the other hand, the purchase cost for PDS was 1,100 €/ton, (99% purity). PDS is supplied in form of $Na_2S_2O_8$ resulting in 0.26 €/mol. Final oxidant cost was estimated considering that both oxidation processes require 0.4 moles for each m^3 of WWTP secondary effluent to be treated.

Life Cycle Assessment

Functional unit

The functional unit selected to quantify the performance of the proposed advanced technologies is the treatment of 1m³ of (biologically pre-treated) urban wastewater with an effective average PhACs removal of 80%; with a life-span of each technology of 20 years of operation. The life cycle inventory (LCI) for each technology under study was then normalized per functional unit.

This actual functional unit considers the direct consumption related to the operation of these technologies. However, at the same time, it also includes every material, chemical and equipment involved in the daily operation, for which either a replacement or an adjustment may be required during the 20 years of operation. The indirect consumption associated to these factors includes the activated carbon, pumps, membranes and UV lamps utilized along the 20 years. For each of the above mentioned sub-unit, the individual consumption was associated to 1m³ of wastewater to be treated. With specific regard, the following assumptions were taken into consideration during the calculation :

- spent GAC particles need to be either regenerated or replaced with fresh material after 7 months of operation,
- pumps need to be changed after 15 years of operation,
- maintenance cleaning of the UF membrane is performed every 6 months, and they need to be replaced after 10 years of operation, and
- UV lamps need to be changed after 12.000 hours of operation.

Assumptions and limitations

Due to the lack of available inventory data in the chosen database (Ecoinvent), specific assumptions and limitations could not be avoided, and are listed as follows:

- With regard to GAC reactivation, lacking similar inventory data, the impact calculated by Munoz et al. (2006) has been used [91].
- With regard to landfilling of spent GAC, no data were available concerning spent GAC used in wastewater treatment operation. The closest process included in Ecoinvent was the disposal of spent GAC containing mercury. No critical aspect for using these data, as substitute, was encountered and therefore was included in the study.
- Due to the lack of inventory data concerning the material composing the UF membrane, polyethylene was chosen as substitute material as it was also suggested by Corominas et al. (2013) [87].

- Concerning the fabrication of the blower used during the UF process, this device has been considered as an engine/motor, according to the information reported by Morera et al. (2016) [86].
- Due to the scarce contribution of the processes for membrane and associated equipment production, the end-of-life of the entire UF system has not been taken into account in the study.
- With regard to UV lamp production, inventory data from Köhler et al. (2012) [96] have been selected due to the absence of such information in the database.
- The end-of-life for the UV lamp was considered equivalent to the end-of-life of fluorescent lamps described in Ecoinvent database.
- Finally, due to the lack of any information regarding the production procedure of peroxymonosulfate in Ecoinvent database, a new production procedure has been created by combining the three principal substances (sulfuric acid, hydrogen peroxide and potassium hydroxide) used to produce the peroxymonosulfate.

System boundaries

The system boundaries define which unit process (the smallest elements for which input and output data are quantified in the LCI) are included in the LCA. Energy and raw materials requirements, materials disposal or recycling are included within system boundaries.

Figure 10 represents the 2 alternative options (with GAC regeneration and without GAC regeneration) considered for the LCI of the BAC-UF pilot plant. In detail, the following factors have been included within the systems boundaries: electricity, GAC, GAC transport, all machinery production and transport to the pilot-plant, membrane production and transport, NaClO and citric acid used during the cleaning procedure of the membrane, GAC transport to the landfill site or GAC reactivation.

Figure 11 shows the system boundaries of the UV/PDS and UV/PMS processes. With this regard, the acknowledged elements included within the system were: electricity, UV lamp production and transport, end-of-life treatment of the UV lamp, pumps and all electrical devices fabrication together with their transport to the pilot-plant site, and the consumption of chemical substances used as oxidizing agents as well as their transport.

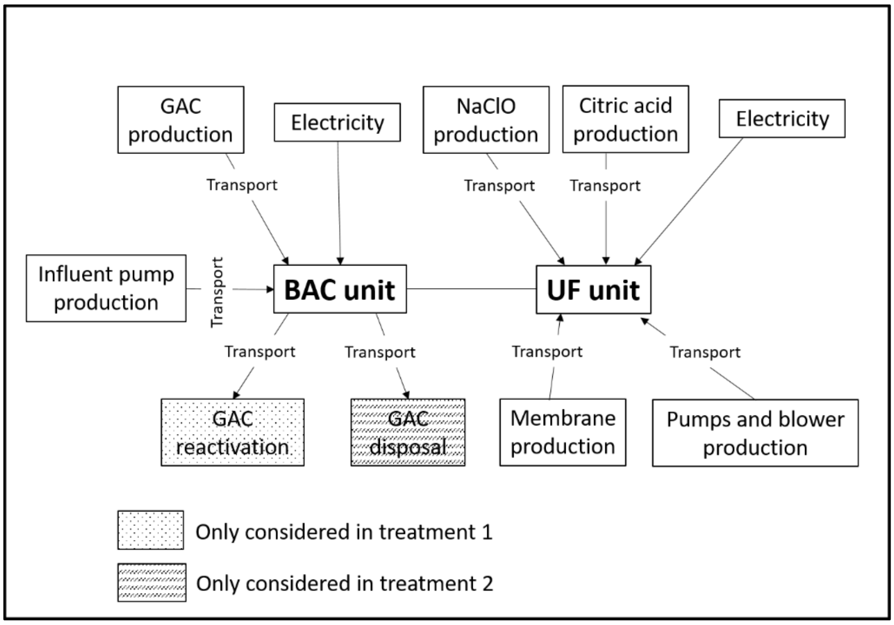


Figure 10 : System boundaries for the BAC-UF process

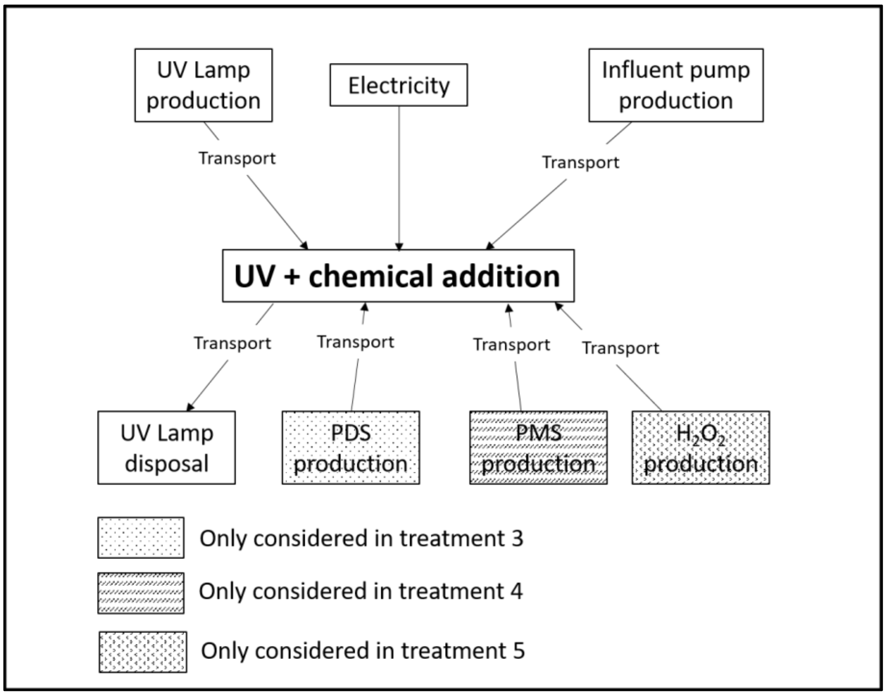


Figure 11 : System boundaries for the AOPs evaluated in this work: UV/PDS, UV/PMS

Life cycle inventory

Life cycle inventory (LCI) analysis is the process of quantifying energy and raw material requirements, atmospheric and waterborne emissions, as well as solid wastes released during the entire life cycle of a product, process, or activity. The LCI calculated in order to assess the impact of each technology are summarized in Table 5. Table includes data referred to every technical option evaluated in this part of the study, and all data are referred to the functional unit expressed in section 3.7.1. In this calculation, pumps, the blower and UV lamp have been considered as single units. This is due to previous considerations concerning their production and transportation already included in the dataset associated to these units.

Table 5 : Life cycle inventory

Type of process	**Process**	**Unidad**	**BAC-UF_no regeneration**	**BAC-UF_ regeneration**	**UV/PDS**	**UV/PMS**	**UV/H_2O_2**
Energy	Electricity consumption	Kwh/m^3	$5,00 \cdot 10^{-2}$ (BAC)	$5,00 \cdot 10^{-2}$ (BAC)	$6,90 \cdot 10^{-1}$	$6,40 \cdot 10^{-1}$	$6,40 \cdot 10^{-1}$
			$6,60 \cdot 10^{-1}$ (UF)	$6,60 \cdot 10^{-1}$ (UF)			
Reagents and transport	NaClO	Kg/m^3	$5,56 \cdot 10^{-4}$	$5,56 \cdot 10^{-4}$			
	Transport NaClO	Tkm/ m^3	$1,67 \cdot 10^{-5}$	$1,67 \cdot 10^{-5}$			
	Cítric acid	Kg/m^3	$2,77 \cdot 10^{-3}$	$2,77 \cdot 10^{-3}$			
	Transport citric ácid	Tkm/m^3	$8,31 \cdot 10^{-5}$	$8,31 \cdot 10^{-5}$			
	PDS	Kg/m^3			$1,23 \cdot 10^{-1}$		
	Transport PDS	Tkm/m^3			$1,23 \cdot 10^{-2}$		
	PMS	Kg/m^3				$1,08 \cdot 10^{-1}$	
	Transport PMS	Kg/m^3				$1,08 \cdot 10^{-2}$	
	H2O2	Kg/m^3					$1,23 \cdot 10^{-1}$
	Transport H2O2	Tkm/m^3					$1,23 \cdot 10^{-2}$
Electrical devices and consumables	Influent pump	p/m^3	$3,09 \cdot 10^{-6}$	$3,09 \cdot 10^{-6}$	$2,14 \cdot 10^{-5}$	$2,14 \cdot 10^{-5}$	$2,14 \cdot 10^{-5}$
	Recirculation pump	p/m^3	$3,09 \cdot 10^{-6}$	$3,09 \cdot 10^{-6}$			
	Filtration pump	p/m^3	$3,09 \cdot 10^{-6}$	$3,09 \cdot 10^{-6}$			
	Blower	p/m^3	$3,09 \cdot 10^{-6}$	$3,09 \cdot 10^{-6}$			
	Membrane UF	Kg/m^3	$5,09 \cdot 10^{-4}$	$5,09 \cdot 10^{-4}$			
	Transport Membrane	Tkm/m^3	$5,09 \cdot 10^{-5}$	$5,09 \cdot 10^{-5}$			
	UV lamp	p/m^3			$2,35 \cdot 10^{-4}$	$2,35 \cdot 10^{-4}$	$2,35 \cdot 10^{-4}$
	Transport UV lamp	Tkm/m^3			$4,54 \cdot 10^{-4}$	$4,54 \cdot 10^{-4}$	$4,54 \cdot 10^{-4}$
	Activated carbon	Kg/m^3	$7,94 \cdot 10^{-2}$	$1,03 \cdot 10^{-2}$			
	Transport activated carbon	Tkm/m^3	$7,94 \cdot 10^{-3}$	$1,03 \cdot 10^{-3}$			
Disposal and regeneration of GAC	Activated carbón disposal	Kg/m^3	$7,94 \cdot 10^{-2}$				
	Transport to landdfill	Tkm/m^3	$7,94 \cdot 10^{-3}$				
	Regeneration	Kg/m^3		$7,71 \cdot 10^{-2}$			
	Transport to regeneration	Tkm/m^3		$7,71 \cdot 10^{-3}$			
	Disposal of UV lamp	Kg/m^3			$1,51 \cdot 10^{-2}$	$1,51 \cdot 10^{-2}$	$1,51 \cdot 10\text{-}^{2}$
	Transport for UV lamp disposal	Tkm/m^3			$1,51 \cdot 10^{-3}$	$1,51 \cdot 10^{-3}$	$1,51 \cdot 10^{-3}$

Life cycle impact assessment

The life cycle impact assessment (LCIA) is one of the most important stages in the LCA, since in this stage the collected inventory data are associated with specific environmental impacts/damages and also these impacts/damages are analyzed and assessed. According to ISO 14040:2006 and ISO 14044:2006, LCIA consists of the following (a) mandatory elements: (i) selection of impact categories, category indicators and characterization models; (ii) classification, i.e. assigning inventory data to selected impact categories; and (iii) characterization, i.e. modelling the inventory data within impact categories; and (b) optional elements: (iv) normalization, i.e. calculate the magnitude of category indicator results relatively to reference information; (v) grouping, i.e. impact categories sorting/ranking; (vi) weighting, i.e. converting/aggregating indicator results across impact categories; and (vii) data quality analysis, i.e. better understanding the reliability of the collection of indicator results (e.g. sensitivity analysis) (ISO, 2006a; ISO, 2006b). Here, all mandatory elements were considered, while regarding the optional elements, only normalization and grouping have been taken into account. Moreover, results can be expressed at: (a) midpoint level (problem oriented approach), where environmental impacts are examined earlier in the cause-effect chain and are translated into environmental themes, such as climate change and human toxicity and (b) endpoint level (damage-oriented approach), where impacts are examined at the end of the cause-effect chain, after midpoint is reached, thus translating environmental impacts into issues of concern, such as damage to human health and to ecosystem quality [104]. Due to data gaps and assumptions stacking up along the cause-effect chain, the endpoint approach is associated with higher levels of statistical uncertainty, but is easier to comprehend by policy- and decision-makers [105]. Therefore, in order to obtain a comprehensive overview and in-depth understanding results were analyzed both at mid- and end-point level using ReCiPe impact assessment method. ReCiPe comprises 18 midpoint impact categories, i.e. climate change (CC), ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), human toxicity (HT), photochemical oxidant formation (POF), particulate matter formation (PMF), terrestrial ecotoxicity (TET), freshwater ecotoxicity (FET), marine ecotoxicity (MET), ionising radiation (IR), agricultural land occupation (ALO), urban land occupation (ULO), natural land transformation (NLT),water depletion (WD), mineral resource depletion (MRD), fossil fuel depletion (FD). At the endpoint level, most of these midpoint impact categories are further converted and aggregated into three endpoint categories, i.e. damage to human health (HH), damage to ecosystem diversity (ED) and damage to resource availability (RA) [104]. The hierarchist perspective, which is a consensus model based on the most common policy principles, with regard to time frame and other issues, was used [104,105]. ReCiPe is a robust multi-issue impact assessment method and therefore it can provide a more holistic overview of the environmental sustainability of the studied advanced wastewater treatments. First, ReCiPe characterization model (midpoint-oriented indicators) is used to calculate the contribution of each parameter to each of the 18 midpoint impact categories. Starting from these 18 categories we selected 5 of them which resulted to be the more affected, within the current work, among all of them. These chosen categories are climate change, ozone depletion, terrestrial acidification, human toxicity and fossil depletion.

With regard to the present work, and the results described in the following sections, it is important to notice that, with very few exceptions, LCA studies do not consider aspects like water quality standards and treatability in the definition of the functional unit [106]. Moreover, the literature on life cycle environmental impacts of advanced wastewater treatment technologies is in general scarce, and as far as we know there are no studies that considered specifically the impact of the same technology proposed in the current work. The existing studies also differ greatly in terms of study goals, system boundaries, functional units, assumptions and impact assessment methodologies. Therefore, when this happen, a meaningful comparison among them is difficult if impossible in some cases [98]. Nonetheless, an attempt is made to benchmark the findings of the present study with some others.

Results and Discussion

Chapter 1 : Application of BAC-UF technology to remove PhACs

Some of the contents of this chapter have been re-drafted from : L. Sbardella, J. Comas, A. Fenu, I. Rodriguez-Roda, M. Weemaes, Advanced biological activated carbon filter for removing pharmaceutically active compounds from treated wastewater, Sci. Total Environ. 636 (2018). doi:10.1016/j.scitotenv.2018.04.214.

This section presents the results corresponding to the long-term monitoring of the biological activity assessment (4.2) and removal of PhACs (4.3). Since the understanding of the respective roles of adsorption and biodegradation is key for the design of the BAC filtration units, the distinction between these two mechanisms is addressed in section 4.4.

1.1 Experimental plan

The BAC-UF pilot plant was operated continuously for one year, covering the start-up, steady operation, and GAC breakthrough, thereby allowing for a well-developed active biofilm. During this period, the experimental plan consisted of (i) measuring the concentrations of PhACs in the influent and effluent of the BAC-UF pilot plant to calculate the removal efficiencies after different time intervals, (ii) assessing the biological activity of the biomass attached to GAC particles and inside the BAC filter bed (respirometric assay and ATP measure), and (iii) evaluating the textural properties of the GAC particles as indicators of their adsorption capacity. Table 5 summarizes the primary studied parameters with the related sampling strategies. The BAC-UF pilot plant was equipped with two sampling machines from which 24 h composite samples were withdrawn during each sampling campaign. During the sampling campaigns, both the EBCT and the hydraulic retention times were considered. These two samplers were positioned as depicted in Figure 3. The first machine sampled the influent (SPI-P: Figure 3), while the second machine sampled the effluent from the UF tank (SPE-P: Figure 3). Additionally, in the lab-scale setup, grab samples were taken at different time intervals during each sampling event, and composite samples were manually prepared. From both the pilot plant and the columns, water samples were taken either monthly (PhACs measurement) or twice per week (conventional pollutant), and all underwent the same treatment. Briefly, amber glass bottles pre-rinsed with methanol and MilliQ water were used to take samples from both installations. The samples were pre-filtered with 0.45 µm filters, and a fraction of the volume was used for conventional pollutant analysis, while the remaining volume was stored at -25°C until the solid phase extraction (SPE) procedure for the analysis of PhACs was performed.

Table 6 : Experimental plan

	BAC-UF pilot plant		Lab-scale			
	Sampling point	Sample type	Sampling point	Sample type	Frequency	Method
PhACs	SPI-P, SPE-P (Figure1)†	24h Composite	SPI-C, SPE-C1, SPE-C2 (Figure1)†	24h manually composed	Monthly	[107]
TOC, COD, NH_4^+, NH^{3-}					Twice per month	[99]
ATP	BAC filter bed (h=1m)*	Grab	[-]		Every 15 days	[100]
Respirometry			[-]			[60]
Micropore			[-]		Every 3 months	[101]

* Height measured from the bottom of the filter. † The position of the sampling points is shown in Figure 3.

1.2 BAC-UF pilot plant: biological activity assessment

A screening of the removal of conventional pollutants was performed throughout the experimental cycle to monitor the performances of the pilot plant. The total organic carbon (TOC) removal of 11.9% has to be mostly attributed to GAC adsorption (Table 6). However this mean value is lower than typical TOC removal values obtained with GAC filters applied as tertiary treatment. The low removal range may depend on the specific characteristics of the residual TOC. Li et al. [108] found that when the ratio between the biodegradable fraction of TOC (BTOC) and TOC was below certain values (0.2-0.3), only 14% TOC removal was achieved by BAC filtration of WWTP secondary effluent. On the other hand, although only partially, this could also be related to the carbon particle size. GAC with bigger particle size, as the ones used in the current work (Table S2), would exhibit more pore blockage and thus lower organic matter removal [109]. Accordingly, when GAC particles with features similar to the ones used in the current work were implemented in BAC filters, the mean TOC removal ranged between 11.6 and 15.7% [110,111]. The consumption of dissolved oxygen (DO) together with the nitrification and removal of COD that took place throughout the BAC filter (Table 6) suggested the presence of biological activity on the GAC particles in the filter bed. Furthermore, ATP measurements, which have been proven to be a suitable parameter for the quantification of active biomass in GAC filters [112], were performed to confirm these results (Table 7). The amount of ATP in the analyzed samples is between 6E-04 and 10E-04 [g ATP/g GAC]. These values are in line with the ATP concentrations measured in 30 different GAC filters at nine treatment plants with biological activity in the Netherlands [112]. Additional evidence of the biological activity of the biomass attached to the GAC particles was provided by the heterotrophic (0.23 g $COD^{*}g^{-1}SS^{*}d^{-1}$) and nitrifying (0.095 g $NH_4^{+*}g^{-1}SS^{*}d^{-1}$) activity measurements. These values provide further information on the activity of the microorganisms developed inside the BAC filter bed [60].

Table 7 : Pollutants and parameters measured to monitor the biological activity

	Pilot plant BAC-UF	Lab-scale Biotic (C1)	Lab-scale Abiotic (C2)
	Removal * (0-13,800 BV) (%)		
TOC	11.9 ± 5.2	34.7 ± 9.1	26.2 ± 7.0
COD	37.9 ± 5.9	40 ± 5	13 ± 1
NH_4^+	86.6 ± 6.0	66 ± 13	20 ± 7
	Formation * (0-13,800 BV) (%)		
NO_3^-	47.4 ± 15.7	17 ± 10	(-)
	Consumption * (0-13,800 BV) (%)		
DO	23.5 ± 4.8	n.a.	n.a.
ATP # (g ATP/ g GAC)	7.64E-04 ± 1.00E-04		
Heterotrophic activity # (g COD*g^{-1} SS*d^{-1})	0.229 ± 0.081		
Nitrifying activity # (g NH_4^+*g^{-1} SS*d^{-1})	0.095 ± 0.024		

* Error represent standard deviation values (n=20). # Mean values calculated in the BV interval (5,750-6,900 BV), error represent standard deviation values (n=3). n.a. not analyzed. (-): No formation of nitrate has been observed in C2.

1.3 Long-term performance of BAC-UF pilot plant: PhACs removal

In the following section, the long-term performance of the BAC-UF pilot plant is reported in terms of the removal of PhACs. Two distinct phases (phase 1, P1, and phase 2, P2) can be clearly distinguished by the two different PhACs removal efficiencies during the operational period of the pilot plant (Figure

12). The P1 phase spanned the first eight months of operation from January 2016 to September 2016 and corresponded to 9,200 (BV) of treated wastewater. The second phase started in October 2016 and ended in January 2017. During this cycle, 4,600 additional BV were treated by the BAC-UF pilot plant. The whole experimental period resulted in a final value of 13,800 treated BV, after one year of operation. During P1, an average removal of 82% was achieved, while this value dropped consistently to an average of 38% during P2. For the duration of P1, markedly lower concentrations of antibiotics, beta-blockers and psychiatric drugs were observed in the effluent. In fact, the compounds belonging to these therapeutic groups were very well removed, reaching average removal values of 78, 89 and 83%, respectively (Figure 4.1). Additionally, for the three remaining compounds representative of the other therapeutic groups, the mean removal throughout P1 was also high (79% on average). The reported values of the micropore volume, area and BET surface of the carbon particles measured during this first experimental cycle (Table 7) were close to the values of the fresh material. Hence, the GAC particles were characterized by a high adsorption capacity, which may contribute to the high abatement level. A total of 44 pilot and full-scale studies with GAC were reviewed by Benstoem et al. [42], who reported that an average PhACs removal of 80% was reached for BV values in the range of 800-20,000; however, for most studies, such high removals occurred at BV values less than 10,000. On the other hand, in the GAC sample taken after 11 months of operation (Table 7), the GAC properties had decayed. This phenomenon seems in line with the decay of the adsorption performances of the BAC-UF pilot plant during P2, resembling a breakthrough curve. The breakthrough of PhACs in BAC and GAC filters is regulated by several factors (i.e., the adsorbability of the substance itself, the background matrix, the adsorbent, the temperature, and the filtration parameters), which differ for each compound [113,114]. Therefore, each compound may display a different breakthrough curve. Nevertheless, P2 was characterized by an overall significant drop in the removal efficiency.

Table 8 : Textural properties of the GAC particles

	Month 0	Month 4	Month 7	Month 11
	0 BV	4,600 BV	8,050 BV	12,650 BV
BET-surface [m²/g]	1,155	1,123	1,182	959
Micropore area [m²/g]	1,105	1,058	1,148	925
Micropore volume [cm³/g]	0.439	0.419	0.463	0.371

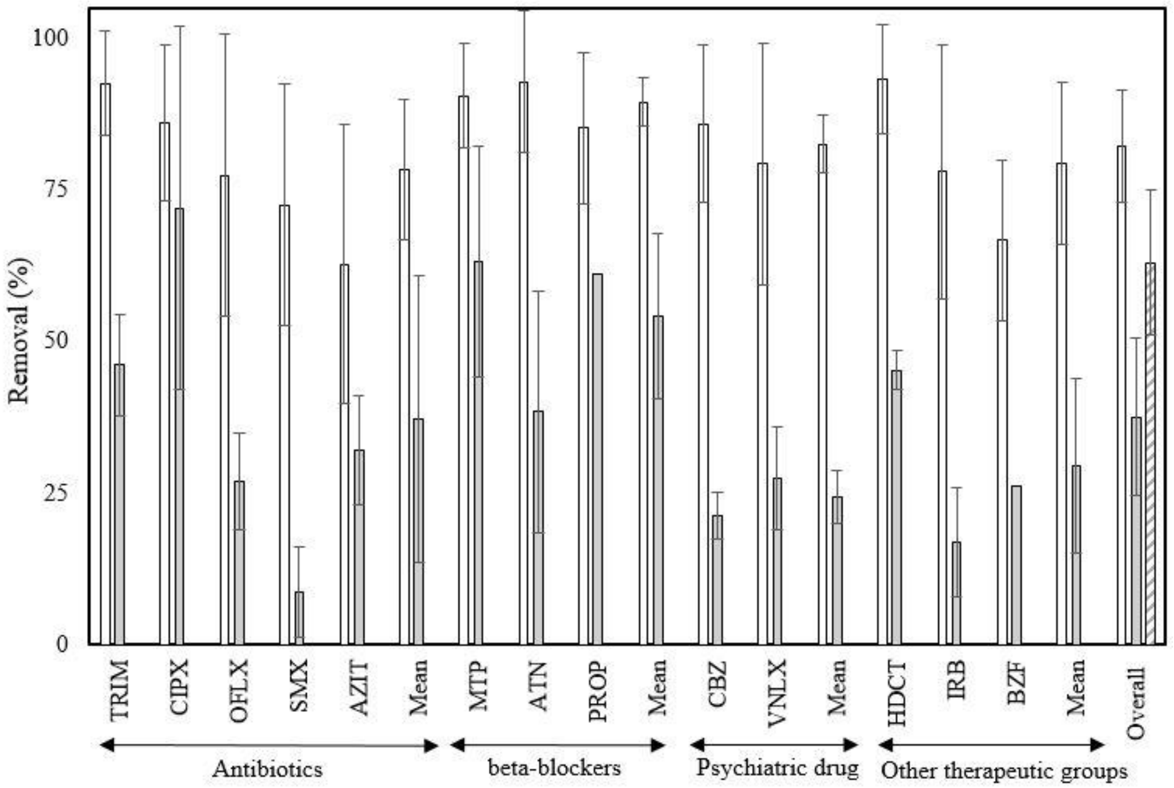


Figure 12 : BAC-UF pilot plant mean removals obtained during the first phase: P1 ☐ (0-9,200 BV), second phase: P2 ■ (9,200-13,800 BV) and one year ▨ (0-13,800 BV). Error bars represent standard deviation values calculated for P1 (n=8), P2 (n=4) and for the overall removal (n=12).

Table 8 summarizes the studies that are considered state-of-the-art references, together with the related operational conditions applied. These references are compared with our results. For the removal of compounds not previously studied with BAC filtration, our results are compared with removals obtained by the pilot and full-scale GAC filtration units.

Table 9 : Review of studies involving removal of PhACs with BAC filters

	Water type	Pre-treatment prior BAC	EBCT (min)	Scale [**]	PhACs in common with the present study	PhACs [*]	Long-term[†]	BV
This Study	S.E.	[-]	50	Pilot		[31 - 938] ng/L	YES	13,800
[17]	S.E.	[-]	10	Pilot	CBZ, TRIM, BZF, ERY,	NR	NO	1,523
[16]	Synthetic S.E.	[-]	4608	Lab	CBZ, TRIM,	[1 - 40] µg/L Spiked	NO	13
[13]	Treated S.E.	Pre-ozonation + Coagulation/Flocculation + Dissolved air flotation-sand filtration	60	Lab. (Batch exp.)	MTP, ATN, VNLX, HDCT, ERY, SMX	[46 – 1,256] ng/L	NO	35,000
[15]	Treated S.E.	Ultrafiltration + O_3/H_2O_2	30	Pilot	CBZ, ATN, SMX	[13 – 1,267] ng/L	NO	30,136
[14]	Treated S.E.	Sand filtration + Ozonation	9; 18; 45	Full	MTP, ATN, CBZ, SMX, HDCT, ERY, VNLX, TRIM	NR	NO	13,000; 68,000; 95,000
[34]	Treated S.E.	Pre-ozonation + Coagulation/Flocculation + Dissolved air flotation-sand filtration	30; 60; 90; 120	Pilot	MTP, ATN, CBZ, SMX, HDCT, ERY, VNLX, TRIM	[10 - 1,800] ng/L	NO	1,440
[12]	Surface water	Coagulation and clarification Addition of nutrients	10; 18	Lab	ATN, CBZ, SMX, ERY,	± 1 µg/L Spiked	NO	17,181
[11]	RO brine	[-]	45	Lab	ATN, CBZ, SMX	[20 - 628] ng/L	NO	7,532

S.E.: secondary effluent; RO: reverse osmosis; NR not reported. [*] Range of PhACs initial concentrations. [**]Range of influent flow defining the scale: Lab (0.001-1 m^3/d); Pilot (1-100 m^3/d); Full (>100 m^3/d). [†] Continuous monitoring at long-term, i.e. for a period longer than 8 months.

Antibiotics

The removal of trimethoprim, a bacteriostatic agent commonly found in secondary effluents of WWTPs, was over 90%. This antibiotic had the highest removal efficiency calculated in this study. Nonetheless, the compound is hydrophilic (log K_{ow} is 0.91). Additionally, at pH 7, this molecule is almost completely neutral. These features should suggest a low affinity for GAC adsorption, but in spite of that, this compound showed good adsorption onto GAC [115,116]. Therefore, when BAC filters were applied as advanced treatments to remove PhACs from synthetic wastewater, and in drinking water treatment plants (DWTPs), 95% of trimethoprim was removed [58,60,117]. Notably, a BAC filter operated with an EBCT of 10 minutes was able to reach only 55% trimethoprim removal [118], thus suggesting that the EBCT is crucial for the removal of certain PhACs with BAC filtration. The fluoroquinolone antibiotics ciprofloxacin and ofloxacin displayed 86% and 77% removal during the first 9,200 BV. Ciprofloxacin is relatively hydrophilic (log K_{ow}<1.7); thus, it should not be highly adsorbed onto GAC. The BAC filter bed is continuously loaded with effluent organic matter that supports biofilm growth, and the biofilm is usually negatively charged. In contrast, ciprofloxacin has a positive charge at pH values of approximately 7. Therefore, the electrostatic interactions taking place between the molecules and the biofilm surface significantly enhanced the removal of this compound in the BAC-UF pilot plant. In all likelihood, the 86% removal should be attributed to the cooperation of adsorption with other mechanisms. The structure of ofloxacin includes halogens (Cl or F), ketone functions and aromatic rings, which are known to enhance adsorption on activated carbon[119]. Similar results were reported by Mailler et al. [120], although these authors applied a filter filled with micro-GAC and powdered activated carbon (PAC)at pilot scale. However, there is a lack of studies on the BAC removal of these two fluoroquinolone antibiotics. Therefore, these results supply useful information on this topic.

Sulfamethoxazole and azithromycin were the compounds with the lowest adsorbability during P1. This trend also continued during P2. The average removal calculated throughout the experimental period was 51% for both antibiotics, while during P1, the removals were 73% and 63% for sulfamethoxazole and azithromycin, respectively. Although their distinct pKa and log D values (pka=1.6 and 8.75; log D=0.89 and 4.02 for sulfamethoxazole and azithromycin respectively) would suggest different behaviors, they exhibited similar removals. Azithromycin belongs to the macrolide group of antibiotics. Macrolides are characterized by relatively high log D values and by a positive charge state at pH 7 [9]. According to these features, a good adsorption capacity is expected. However, azithromycin exhibited only moderate removal (63%) during the first 9,200 BV of operation. Macrolides exhibited 80-95% removal in DWTPs that utilized PAC with a contact time of 4 h in river water with an initial DOC concentration of 3.5 mg/L [121]. Nevertheless, no studies with GAC and/or BAC were found with regard to azithromycin removal from WWTP effluents. In addition, since this antibiotic is one of the few PhACs included in the watch list of substances for European Union-wide monitoring (Decision 2015/495/EU of 20 March 2015 [17]), the current work provides relevant information concerning applicable tertiary treatment for the abatement of this watch-list-substance. In contrast, the low removal of sulfamethoxazole is clearly ascribable to its negative charge at pH =7-8, which causes electrostatic repulsion with the negatively charged activated carbon surface. Moreover, due to the low log D value of 0.89, sulfamethoxazole prefers to remain in the water phase instead of being adsorbed. In other BAC filtration studies, this sulfonamide antibiotic was highly removed (90%) [122]. However, two main features differentiate the current work from the reported studies with higher sulfamethoxazole removals: the quality of the source water feeding the BAC, as well as the number of BV. With regard to the number of BV, no information is available in those studies. On the other hand, the pretreatment applied before feeding the BAC may explain the better performance obtained for sulfamethoxazole removal. In fact increasing the pretreatment before BAC results in lower concentrations of both dissolved organic matter (DOM) and particulate organic matter (POM). Less DOM entails less competition with PhACs, while less POM results in less pore blockage with consequential easier access for organic MPs [123]. In keeping with these statements, only 12% sulfamethoxazole removal was obtained when the BAC filters were fed with reverse osmosis brine [57], even though this concentrated water was pretreated with an advanced oxidation process (Table 8). The highest removal efficiency found in other biofiltration studies for sulfamethoxazole was 60% [124]. However, this 60% removal was achieved after 2,160 BV passed throughout the filter, and with filter operations resulting in an EBCT of 33 hours, which is forty times higher than the EBCT used in the current work.

Beta-blockers

The three beta-blockers, metoprolol, atenolol and propanolol, were highly removed during the 9,200 BV phase, with mean values of 90, 93 and 83%, respectively. The specific adsorption capacity on GAC for metoprolol and atenolol suggested that these compounds have high affinities for this porous material [115]. Furthermore, the positive charge of these compounds at the pH of the wastewater enhanced their electrostatic attraction to the GAC surface as well as to the organic matter adsorbed onto it. Hence, although they are resistant to biodegradation, high removals can be achieved due to their tendency to be adsorbed onto GAC. Therefore, in studies conducted with BAC filters, removal efficiencies similar to the values achieved by the BAC-UF pilot plant in the current study were obtained [58,60]. Considerably lower removals were obtained when filtering materials other than GAC were applied in sequential biofiltration of wastewater [124], and when 10mg/L PAC were added [125]. No studies on the interaction of propanolol and BAC filters, have been found.

Psychiatric drug

The psychiatric drug carbamazepine was highly removed during the 9,200 BV phase, with an average value of 86%, whereas venlafaxine displayed 79% removal. The positive charge of these compounds at the pH of the wastewater enhanced the electrostatic attraction to the GAC surface and the organic matter adsorbed onto it. Hence, although they are resistant to biodegradation, due to their tendency to be adsorbed onto GAC, high removal efficiencies were also obtained when applying BAC filters at the laboratory scale [60]. However, to achieve higher removal values (90–95%) with BAC filtration, energy and cost-intensive pretreatments would be required [117]. For these two compounds, no removal was observed during a 639-day study with biologically activated anthracite and sand filters operating as a stand-alone tertiary treatment [124].

Other therapeutic groups

The diuretic drug hydrochlorothiazide was one of the compounds that were removed to a great extent, showing 93% mean removal during the first phase. Hydrochlorothiazide is hydrophilic and almost neutral at pH 7; hence, according, to these features it should not be removed very well via AC adsorption. Thus, when PAC was applied in a lab-scale filter bed to remove PhACs from the secondary effluent, a 20% breakthrough for hydrochlorothiazide was reached after 10 hours of operation [126]. Hydrochlorothiazide has been reported to be resistant to biodegradation in both sand and anthracite filters [45,127], while up to 70% of it was removed in batch experiments with BAC [53]. These differences may suggest that this compound exhibits a major affinity for the biomass the develops on GAC rather than other support material. This high affinity may explain the 93% removal, which has never been reported before in previous studies on the biofiltration of secondary effluent. The antihypertensive drug irbesartan was steadily removed throughout P1 yielding an average value of 79%. Irbesartan is negatively charged, and therefore, no electrostatic attraction with the GAC surface should occur. In this regard, the charge of PhACs is more relevant to the adsorption process than the hydrophobic interactions. However, hydrophobic interactions are expected to be more significant for negatively charged solutes than for neutral or positively charged solutes [119]. Thus, due to the high hydrophobicity of irbesartan (log K_{ow}=5.31), interactions with the GAC surface and adsorption mechanisms are promoted. Similar achievements were obtained with two GAC pilot-scale columns in series applied to treat secondary effluents [115].The authors that performed this study observed a breakthrough for irbesartan that was earlier than the value reported in the present study. In our case, an approximately 20% breakthrough is reached after 9,200 BV, while in the mentioned study, a 90% breakthrough is reached after 5,000 BV of treated wastewater. One explanation of the dissimilarity between the results presented above and other similar studies with activated carbon is the biomass presence and activity characterizing the BAC system. The discrepancy between the values obtained in the current work and those predicted based on both substance-related properties and lab-scale studies highlight two aspects that should be taken into account. First, for some compounds, the physical-chemical properties are not perfectly suited to explain the behavior during the AC processes. Second, applying technology in real conditions entails some aspects that do not occur in more controlled environments. One compound with physical-chemical properties that correctly predict the adsorptive behavior is the cholesterol-lowering drug bezafibrate. For this compound, a 67% concentration reduction was achieved. This molecule is negatively charged and also has a log D value of -0.11, thus making it highly hydrophilic. These properties may explain the reason why bezafibrate was the compound with the lowest removal value. However, the removal obtained in the current work (67%) is higher than the results achieved with a large scale micro GAC fluidized bed operating as a tertiary treatment, in which this compound was moderately removed (bezafibrate=53-55%) [128]. Similar behavior was also observed in a BAC filter followed by a UF step in preliminary short-term studies, where 52% of bezafibrate was removed [118].

1.4 Contributions of adsorption and biodegradation processes

In this section, the contributions of adsorption and biodegradation processes for the removal of PhACs in the BAC filter are addressed. Firstly, the biofilm contribution has been examined in the lab-scale set-up. Secondly, the results obtained at lab-scale have been used to investigate the added value of biofilm presence in the pilot plant.

Lab-scale column set-up

This comparison has been done by comparing two lab-scale systems, one biotic (with biologically active biomass, C1) and the one abiotic (C2). The difference between the removal efficiencies of the two systems (C1 and C2) can be used as a measure of the contribution of the biomass to the overall abatement of the PhACs. In the functioning of the biotic column (C1), we were able to identify two distinct phases with regard to biomass establishment inside the column and its role in the removal of PhACs. The first phase (from day 1 to day 40) was before the colonization occurred, while the second phase (days 40 to 120) was after biomass colonized the filter bed. In terms of bed volumes, the first phase was from 0 to 1,440 BV, while the second one covered the last eighty days of operation, resulting in a total of 4,320 BV. In the biotic column C1, the removal for some compounds were higher in the second phase than before colonization (Table 9). This lag was due to the time required for the biofilm to grow and establish a well-developed structure. Since the study was started with fresh GAC particles, it took almost two months of operation for the biofilm to actively begin participating in the removal process. A similar lag-phase lasting 60 days was observed by Maeng et al. [129]. Furthermore, when studying the functional diversity of the microbial community in BAC filters, Xiang et al. [130] noticed that a relatively stable steady state was reached by day 40.

Table 10 : Removal values obtained in the lab-scale study

Compound	Biotic Column: C1 Removal Before Colonization *	 Removal After Colonization **	Abiotic Column: C2 Removal	Removal Improvement due to Biofilm	Removal Mechanism
Metoprolol	>99	>99	>99	n.a.	(a) Only Adsorption
Atenolol	>99	>99	>99	n.a.	
Trimethoprim	>99	>99	>99	n.a.	
Propanolol	>99	>99	>99	n.a.	
Hydrochlorothiazide	95 ± 2	98 ± 2	94 ± 3	4	(b) Mostly Adsorption + Biodegradation
Venlafaxine	79 ± 0	83 ± 0	78 ± 0	7	
Carbamazepine	87 ± 3	94 ± 2	87 ± 3	7	
Irbesartan	75 ± 3	85 ± 3	73 ± 3	14	
Ciprofloxacin	63 ± 5	75 ± 4	59 ± 4	22	(c) Adsorption + Biodegradation
Bezafibrate	47 ± 0	64 ± 0	44 ± 0	32	
Ofloxacin	65 ± 6	80 ± 5	60 ± 6	25	
Azithromycin	43 ± 6	63 ± 6	40 ± 5	36	
Sulfamethoxazole	56 ± 1	75 ±1	53 ± 0	30	

* n=3
** n=4

By analyzing the removal mechanisms, we found three different classes of behavior: (a) compounds with very high removal due to only adsorption onto GAC, (b) compounds with very high removal mostly due to adsorption onto GAC with a slight contribution by the biofilm and (c) compounds with high removal due to adsorption with a very significant contribution by the biofilm.

(a) Very high removal due to only adsorption

This group comprises the PhACs for which the concentrations decreased below their quantification limits (LOQ and LOD are reported in Table 10) in both C1 and C2. Metoprolol, atenolol, trimethoprim and propranolol were indeed completely removed in every sampling event. Since there was no biological activity in C2 and since photolysis was prevented (the columns were covered with aluminum foil), evaporation can be considered negligible [15], and biosorption was shown to be insignificant [127]; thus, adsorption onto GAC is the only process in charge of the abatement of PhACs. With regard to C1, although biodegradation can occur, the extent to which it occurs could not be detected due to the predominant role of adsorption. As a confirmation of their affinity for GAC, these four PhACs reported high removal efficiencies (>75%) in several GAC pilot plant studies [115,131,132], but those efficiencies were still lower than the removal efficiencies obtained in the present study.

(b) Very high removal mostly due to adsorption

The removal of hydrochlorothiazide, venlafaxine, carbamazepine and irbesartan increased slightly with the transition from pre- and post-colonization, and these compounds were highly removed (>83%) by the biologically active filter. For this group, a small difference between C1 and C2 was found. This difference may suggest that the biomass contributed to the overall removal. After the biofilm developed after 40 days, the total removal was improved by 4% for hydrochlorothiazide, 7% for venlafaxine and carbamazepine, and 14% for irbesartan. Biodegradation alone, when operating as the sole removal process, is not efficient in abating the two psychiatric drugs encountered in the current work [12]. These compounds have been reported as recalcitrant to biodegradation in several biofiltration studies [133]. No studies were found regarding the biodegradation of hydrochlorothiazide or irbesartan in biologically active filters, but the diuretic and antihypertensive drugs were found to be unaffected by either full-scale MBR treatment [134], or by conventional activated sludge systems [135]. In the current work, although these compounds were adequately removed by the BAC column, we observed a small difference between the two different columns. Consequently, adsorption has to be considered as the main mechanism involved.

(c) High removal due to adsorption and biodegradation

The remaining five PhACs were positively affected by the growth and development of biomass inside C1. The altered conditions inside column C1 contributed to an increase in the removal efficiency. The removals in C1 were higher than the removals achieved in C2. The effect of biological activity on the overall removal resulted in a 36% improvement for the most affected PhACs (azithromycin) and a 22% improvement for the least affected compound (ciprofloxacin). The improvements for ofloxacin, sulfamethoxazole and bezafibrate produced by the biofilm contribution to the overall removal were 25, 30 and 32%, respectively. To the best of our knowledge, there is a lack of information on the role played by biodegradation in biofilters for all these substances, but sulfamethoxazole showed a recalcitrant behavior with respect to biodegradation in several biofiltration studies [133]. Nevertheless, Table 9 indicates that the 30% improvement in sulfamethoxazole removal was the result of the removal increasing from 53% in C2 to 75% in C1. Ciprofloxacin, ofloxacin and azithromycin have been reported to be poorly biodegradable during conventional wastewater treatment [12,136]. However, the conditions present inside a BAC filter –operating as an attached growth reactor- can be significantly different from a conventional activated sludge reactor; thus, different removal efficiencies can be achieved [21]. Unlike most of the studied PhACs, the 32% improvement obtained for bezafibrate may be explained by its relatively high biodegradability [137].

As supported by the findings related to group (c), the use of GAC as filtering material may result in higher biological activity compared to the less porous support for biomass growth. Globally, for nine out of the thirteen compounds studied in the lab-scale setup, it was possible to identify the added value of having biomass throughout the biofilter, i.e., the role of biodegradation.

Table 11 : PhACs influent concentration with their Limit of Detection and Quantification

Compound	Influent Concentration (ng/L)*	LOD (ng/L)	LOQ (ng/L)
Antibiotics :			
sulfamethoxazole	120 ± 97	5.5	18.0
azithromycin	480 ± 73	0.4	1.2
ofloxacin	340 ± 81	0.6	1.8
trimethoprim	120 ± 8	2.4	8.1
ciprofloxacin	173 ± 55	7.0	23.0
beta-blockers :			
metoprolol	163 ± 6	8.7	28.0
atenolol	152 ± 85	3.9	12.9
propanolol	243 ± 29	3.5	13.3
Psychiatric drugs :			
carbamazepine	181 ± 81	2.4	8.0
venlafaxine	173 ± 73	0.6	2.1
Other therapeutic groups :			
hydrochlorothiazide	320 ± 74	1.0	2.6
irbesartan	503 ± 96	1.2	3.9
bezafibrate	217 ± 61	1.0	3.3

* Mean concentrations. Number of measurements n=10.

BAC-UF Pilot plant

The lab-scale BAC filtration experiments revealed the role played by biodegradation in the overall PhACs removal process. Although this contribution is different for each compound, this work help to provide a further explanation of the processes taking place in the long-term study carried out with the pilot-scale BAC-UF. In this regard, note that during the second phase of the pilot plant operation (P2, after the fall related to surpassing 9,200 BV), and more precisely after the drop observed from day 240 onwards, two different trends in terms of the removal of PhACs were identified. For the first group of compounds (group a), the removal efficiency continued to decrease throughout the remaining time. This group included the substances for which physical adsorption onto GAC particles was the main removal mechanism. This decreasing trend is confirmed by the GAC sample analyzed for textural property measurements during P2 (Table 7, Month 11). The results reveal decreases in all the parameters used to represent the adsorption capacity (micropore volume and BET surface). These results reflect the saturation of the GAC particles and, therefore, explain the removal efficiency drop that was observed for the compounds belonging to group (a). In group (a), since there are no further mechanisms involved in the removal, beyond adsorption, an increase in the saturation level results in a decrease in the removal capacity. Metoprolol was selected as a representative of this group (Figure 13.a). On the other hand, the second observed trend was exhibited by compounds that displayed an additional removal capacity after the fall related to 9,200 BV. The extra removal capacities shown by some compounds may be the result of biodegradation phenomena taking place within the BAC filter. This trend was associated with compounds whose removals were positively affected by biofilm development inside the biotic column during the lab-scale experiments (group c). Azithromycin was chosen as a representative compound and is depicted in Figure 3.b. From the trend of azithromycin, we can see that the removal efficiency decreased between 9,200 and 11,500 BV, but then remained stable from 11,500 BV until the end of the monitoring period. Since this compound was characterized by a positive biofilm contribution in the lab-scale column experiment (Table 9), we hypothesize that biodegradation is the mechanism that allows for the additional abatement of PhACs when GAC filter beds reach high BV values; i.e., at long operating times.

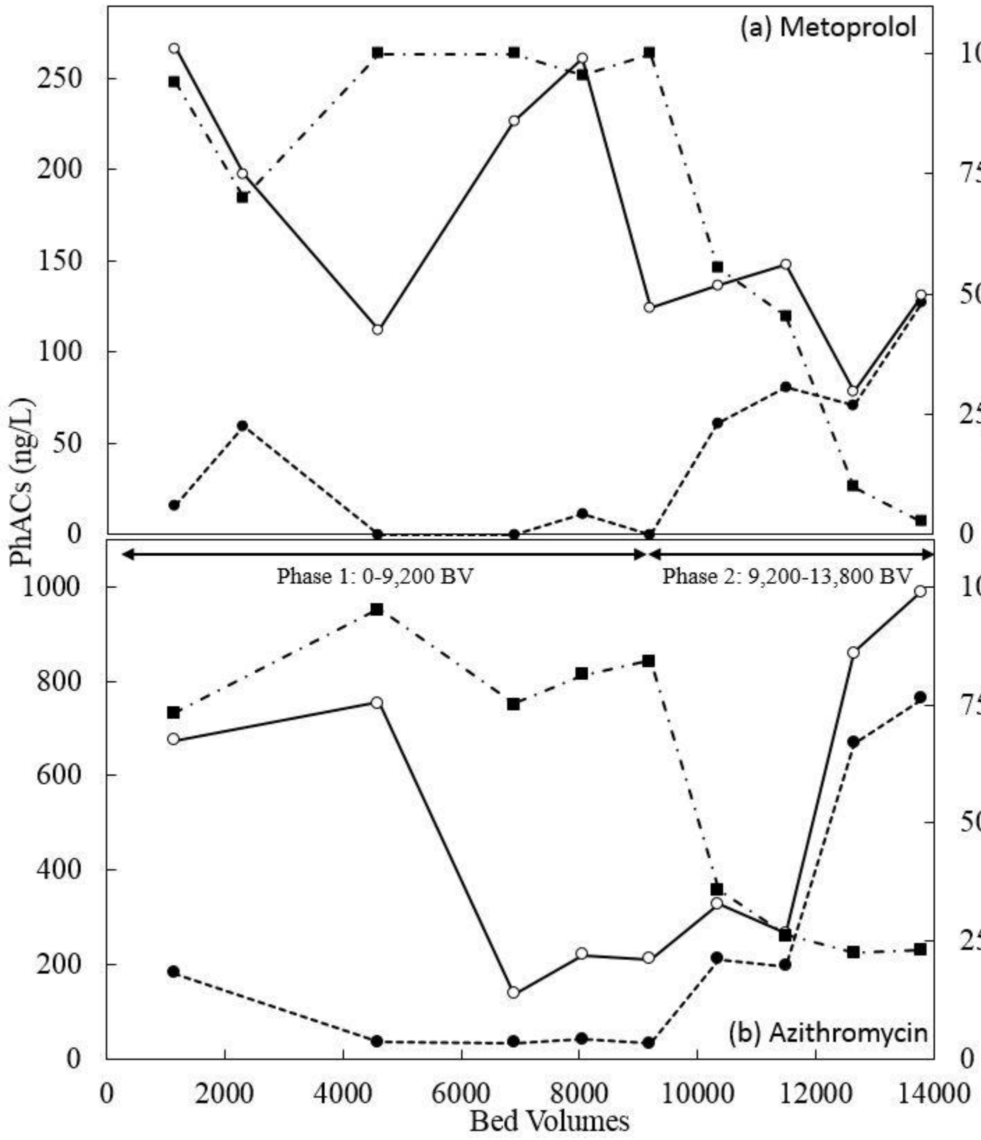


Figure 13 : Influent (—○—), effluent (—●—) and removal (—■—) of metoprolol (a) and azithromycin (b) in the BAC-UF pilot plant. The arrows indicate the length of phase 1 (P1) and phase 2 (P2).

As long as GAC particles maintained their adsorption capacities, lower influent concentrations should result in either higher or constant removal by adsorption onto GAC. However, when the carbon particles became saturated, the removal efficiencies over a given time span decreased, despite the stable influent concentrations (Figure 13.b). However, after the drop (beginning of Phase 2 : 9,200 – 13,800 BV), the removal efficiency was stabilized at value of approximately 25%. This stabilization is likely attributable to biodegradation processes. Nevertheless, the stabilization of the removal of azithromycin after 11,500 BV, which is considered to be due to biological degradation, is based only on three measurements. The presence of biomass partially compensates for the diminished GAC adsorption capacity.

Chapter 2 : Application of UV/PDS and UV/PMS technologies to remove PhACs

Some of the contents of this chapter have been re-drafted from : L. Sbardella, I. Velo Gala, J. Comas, I. Rodriguez-Roda, A. Fenu, W. Gernjak, Impact of wastewater matrix on degradation of PhACs during UV sulfate-based oxidation processes, (Accepted to Journal of Hazardous Material).

In this chapter two innovative AOPs for PhACs removal from WWTP secondary effluent have been investigated. The UV-C radiation has been used to activated the PDS or the PMS. The first level of UV/PDS and UV/PMS processes analysis has been conducted at lab-scale using a collimated beam device. The second step of the evaluation consisted in the validation of the results at pilot-scale.

2.1 Experimental plan

In order to investigate the effects of oxidant concentration, UV fluence effluent, and wastewater characteristics as the organic matter (EfOM), pH and mineral composition (HCO_3^-, Cl^-, NO_3^-) several experimental conditions have been applied. If not stated otherwise, experiments were conducted in wastewater effluent (see characteristics in Table 11) collected at the WWTP of Quart (Girona, Spain). This plant serves a population of 10,000 person equivalent and the treatment line consists of a preliminary screening coupled with grit removal, an aeration basin for carbon and nitrogen removal, followed by a secondary clarifier. In order to perform experiments without EfOM, synthetic mineral water (SMW) was produces with Milli-Q water spiked with a mixture of inorganic anions (Table 11). A mixture of all PhACs was prepared in Milli-Q water and spiked at the beginning of each experiments in order to reach 10 µg/L for each compound. Aliquots of PDS and PMS were added directly from stock solution before UV exposure with an initial concentration in the range 0.1 mM – 0.8 mM, according to the different experimental conditions (Table 11). At given UV fluence (e.i. time intervals), 10 mL of irradiated solution was sampled and mixed with sodium sulphite (1.60×10^{-5} M) to quench the reaction. In order to validate the effects, of the studied parameters on PhACs degradation in wastewater effluent by UV/PDS and UV/PMS, a statistical procedure has been implemented. The used procedure is a one sample T-test. This test was implemented in order to compare the K_{obs} values obtained during each experiments, aiming at determining whether the changed conditions resulted in higher or lower values of the calculated degradation rate constants. More information on the T-test approach and the related results are available in Table A1.

Additional details on the PhACs degradation experiments are described in Table 11.

Table 12 : WWTP secondary effluent characteristics and experimental plan

N°	Matrix	PDS	PMS	pH	Cl^- mM	NO_3^- mM	HCO_3^- mM	EfOM mg/L	$H_2PO_4^-$ mM	SO_4^- mM
1	Milli-Q	0.4 mM		8.2	0	0	0	0	0	0
2	Milli-Q		0.4 mM	8.2	0	0	0	0	0	0
3	WW	0.4 mM		8.2	9	1	3	18	0.075	0.21
4	WW		0.4 mM	8.2	9	1	3	18	0.075	0.21
5	WW	0	0	8.2	9	1	3	18	0.075	0.21
6	WW	0.1 mM		8.2	9	1	3	18	0.075	0.21
7	WW	0.2 mM		8.2	9	1	3	18	0.075	0.21
8	WW	0.4 mM		8.2	9	1	3	18	0.075	0.21
9	WW	0.8 mM		8.2	9	1	3	18	0.075	0.21
10	WW		0.1 mM	8.2	9	1	3	18	0.075	0.21
11	WW		0.2 mM	8.2	9	1	3	18	0.075	0.21
12	WW		0.4 mM	8.2	9	1	3	18	0.075	0.21
13	WW		0.8 mM	8.2	9	1	3	18	0.075	0.21
14	WW	0.4 mM		6	9	1	3	18	0.075	0.21
15	WW		0.4 mM	6	9	1	3	18	0.075	0.21
16	WW	0.4 mM		8.2	27	1	3	18	0.075	0.21
17	WW		0.4 mM	8.2	27	1	3	18	0.075	0.21
18	WW	0.4 mM		8.2	9	10	3	18	0.075	0.21
19	WW		0.4 mM	8.2	9	10	3	18	0.075	0.21
20	WW	0.4 mM		8.2	9	1	6	18	0.075	0.21
21	WW		0.4 mM	8.2	9	1	6	18	0.075	0.21
22	SMW	0.4 mM		8.2	9	1	3	0	0.075	0.21
23	SMW		0.4 mM	8.2	9	1	3	0	0.075	0.21

2.2 PhACs removal in distilled water

PDS performed better than PMS for all the studied compounds, except for CPFX which reached 70% removal after 2 minutes (92 mJ/cm²) of reaction in both cases (Figure 14). In the UV/PDS system removals calculated after 92 mJ/cm² of UV fluence ranged between 40% (DZP and NDL) up to values greater than 80% for SMX, ATNL and OFXC; with an average value of 67%. The UV/PMS was characterized by lower values of PhACs removals, with an average value of 44% (Figure 14). Nonetheless, after 5 minutes (UV fluence = 231 mJ/cm²) of reaction, both processes were able to almost completely degrade the target compounds. In fact, the concentration of all PhAC decreased below the limit of quantification in the UV/PDS, while the average removal reached 86% in the UV/PMS AOP (Table A2). PhACs degradation in the two UV-based AOPs followed the pseudo-first order kinetic pattern:

$$ln\left(\frac{[PhAC]}{[PhAC]_0}\right) \;=\; -K_{obs} * I$$

Where K_{obs} is the fluence-base degradation rate constant (cm^2/J), I is the UV fluence (J/cm^2), $[PhAC]_0$ and [PhAC] are the initial and final PhAC concentrations, respectively. According to the removal values, the fluence-based degradation rates calculated for the UV/PDS process were higher than the rates calculated in the UV/PMS experiment.

The general trend of greater removal by UV/PDS than by UV/PMS, is consistent with several studies where UV-activated PDS or PMS were applied to degrade PhACs [138,139]. In Milli-Q water, where no other constituents are present, the efficiency of a UV/oxidant process depends on two basic factors: (1) efficiency of activation of the oxidant by UV radiation and (2) second-order rate constant of a pollutant and its degradation products with the reactive radicals. When irradiated with UV the peroxide bond (O-O bond energy) cleaves homolytically and produces reactive radicals, which subsequently react with pollutant molecules at or close to diffusion controlled rate. Regarding the PDS, the bond dissociation energy and bond length of $[O_3SO\text{-}OSO_3]^{2-}$ were respectively determined to be 140 kJ mol^{-1} and 1.497 Å (Table S4). In comparison to PDS, PMS has a shorter bond length (1.46 Å), which translates to a higher bond dissociation energy (377 kJ mol^{-1}). In other words, PMS requires more energy to produce radicals in the homolytic cleavage of the peroxide bond [140]. Based on these properties, the easier activation of oxidants by UV radiation follows the order: $S_2O_8^{2-} > HSO_5^-$, suggesting a higher efficiency of $UV/S_2O_8{}^{2-}$ than UV/HSO_5^-. Better removals and faster kinetics for PDS were also reported in previous studies with organic MPs [141,142].

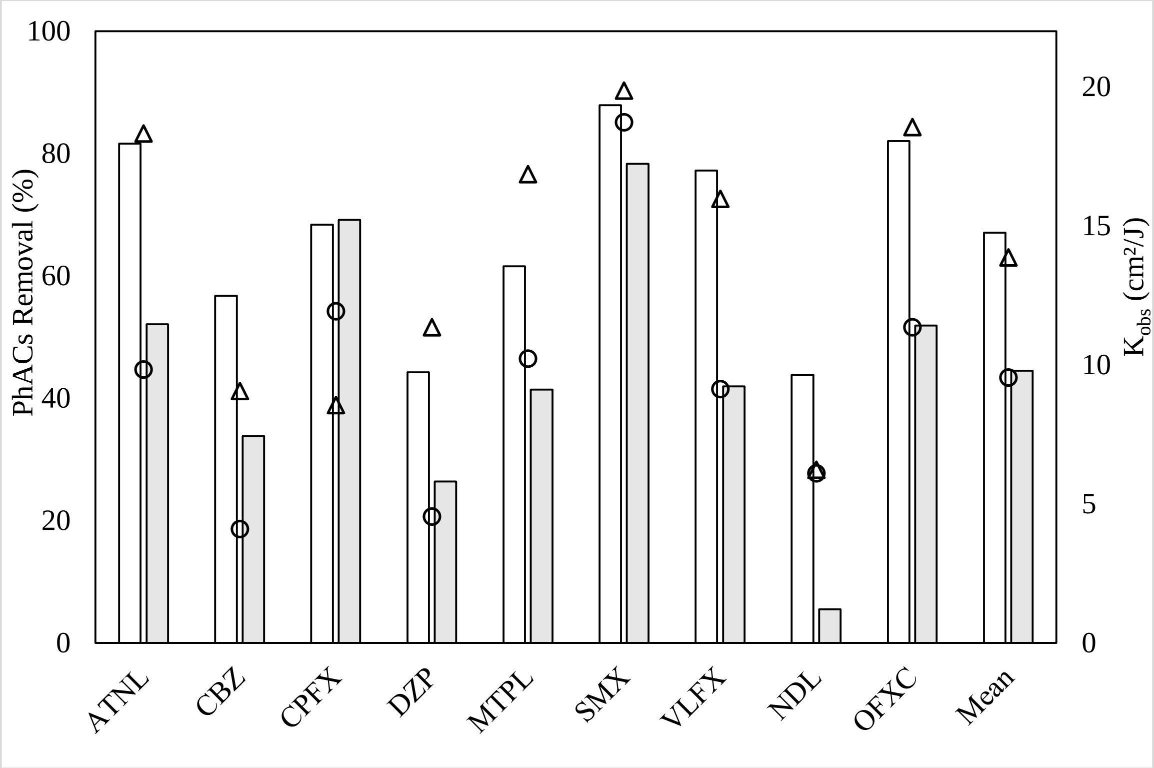


Figure 14 : Removal (PDS: ☐ ; PMS: ▨) and fluence-based rate constants (PDS Δ ; PMS ○) of PhACs in Milli-Q water during UV/PDS and UV/PMS processes (Fluence= 92.5 mJ/cm² (2 min); Oxidant concentration= 0.4 mM; [PhACs]0 = 1 µg/L each; pH = 8.2).

2.3 PhACs removal in WWTP secondary effluent

When experiments were carried out in WWTP effluent rather than Milli-Q, the average PhACs removal calculated at fluence value 92 mJ/cm² was reduced from 67% to 34% and from 44% to 37% for UV/PDS and UV/PMS processes, respectively. These reductions indicate the strong scavenging effect of the water matrix on both oxidant systems, and therefore on both radicals involved in the reactions. The higher degradation observed in the UV/PMS system (with respect to PDS) may be the results of the cooperation of the two main radical species acting during the oxidation processes. Similarly, previous studies showed that the simultaneous presence of both $SO_4^{\bullet -}$ and $OH^{\bullet}$, allowed for better performances for PhACs removal from wastewater effluents, thus resulting in higher degradation efficiencies with PMS rather than PDS [82,143]. As depicted in Figure 15, the two systems showed similar removals for 4 compounds (CBZ, CPFX, OFXC and NDL). UV/PMS performed better for 4 compounds (DZP, MTPL, VLFX and SMX), while UV/PDS only achieved greater degradation efficiencies for ATNL. Overall, the average K_{obs} value for UV/PMS was greater than for UV/PDS. The three studied antibiotics, CPFX (97% and 93%), SMX (96% and 69%) and OFXC (98% and 99%) showed the highest removal efficiencies during both processes. Previous studies pointed out that antibiotics degradation through UV processes was also associated to a significant decline of antibiotic activity of the final effluent [81]. An increase in the UV fluence resulted in increasing of degradation efficiencies (Figure 16). In fact, after 851 mJ/cm² (30 minutes) of UV fluence the mean removals obtained by the two AOPs were 62% and 72% for UV/PDS and UV/PMS. This is an expected behavior when AOPs are applied to water with low levels of impurities, e.i. previously treated. The results obtained in the current work demonstrates that even with a complex wastewater matrix, more UV fluence is able to enhance the oxidation process, achieving greater PhACs degradations. Nevertheless, at the highest UV fluence applied in this study (851 mJ/cm²), the degradation remained moderate (25% < removal < 70%) for 4 and 5 compounds during UV/PMS and UV/PDS processes, respectively.

Oxidant concentration can also influence PhACs degradation. We therefore tested four different molar concentration of PDS and PMS (0.1, 0.2, 0.4 and 0.8 mM) with the aim of evaluating their response under UV radiation in WWTP effluent wastewater. Increasing oxidant concentration resulted in two main different behavior: some compound showed faster kinetics with higher oxidant concentration, while some other were not affected; e.i. the degradation rates did not change. In UV/PDS system, 5 compounds (SMX, MTPL, CPX, NDL, CBZ) were positively affected by higher oxidant concentrations, while with PMS, only 3 compounds (SMX, CPX, OFXC) were characterized by faster kinetics when higher amounts of oxidant were applied (Table A2). Similarly, with increasing oxidant concentrations, a more marked removal increase has been observed by UV/PDS rather than UV/PMS (Figure 17). This difference can be explained considering the main radical species acting in these two systems. Sulfate radicals are more selective than hydroxyl radicals, hence less prone to be scavenged by the main wastewater components. At lower oxidant doses, there is higher competition for sulfate radicals between PhACs and electron rich moieties of effluent organic matter (EfOM). With an increase of the selective oxidant doses higher than the initial consumption by the moieties of EfOM, the residual concentration of PhACs can decrease more significantly. Therefore with higher PDS concentrations, more $SO_4^{\bullet -}$ will be available in solution to oxidize PhACs. Recent studies reported that in hydroxyl radical-based AOP, due to its high non-selectivity, the scavenging effect increases proportionally to the increase of the hydroxyl radical concentration [80]. Consequently, higher $OH^{\bullet}$ may not result in faster PhACs degradation rates. Therefore, in UV/PDS, using higher oxidant concentrations may be a reasonable strategy to enhance PhACs degradation, while it may have minor effects in UV/PMS.

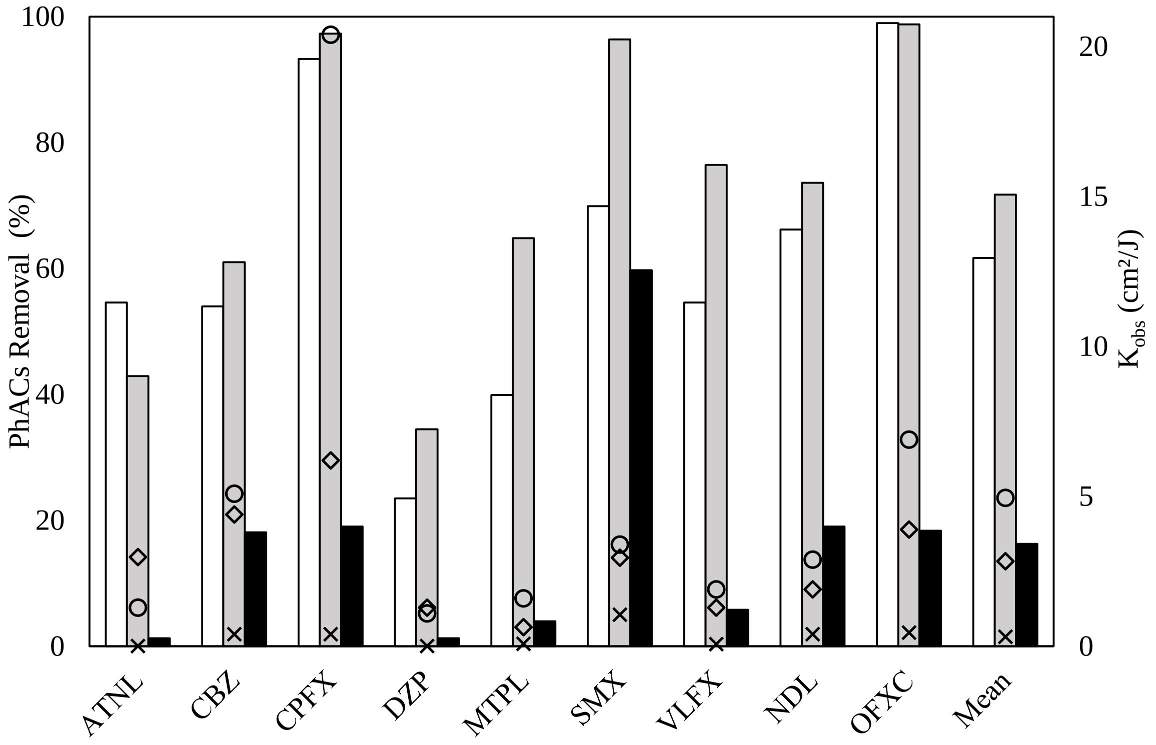


Figure 15 : Removal (PDS: □ PMS: ▨ UV only: ■) and fluence-based rate constants (PDS : ◊; PMS : ○; UV only: X) of PhACs in wastewater effluent during UV/PDS and UV/PMS processes (Fluence= 851 mJ/cm² (30 min); Oxidant concentration= 0.4 mM; [PhAC]0 = 1 µg/L; pH = 8.2)

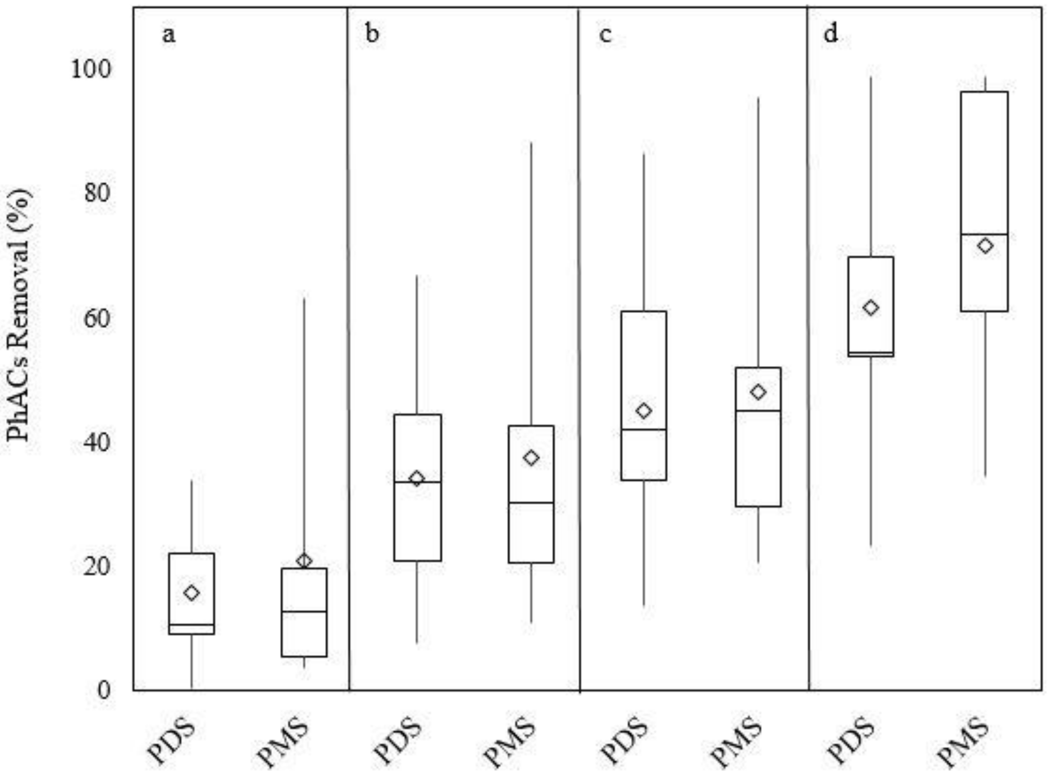


Figure 16 : PhACs removal in wastewater effluent obtained during UV/PDS and UV/PMS processes, calculated at (a): 56.8 mJ/cm² (2 min), (b): 141.9 mJ/cm² (5 min), (c): 283.8 mJ/cm² (10 min) and (d): 851.4 mJ/cm² (30 min) of UV fluence (Oxidant concentration = 0.4 mM; [PhAC]$_0$ = 1 µg/L; pH = 8.2; n° of PhACs = 9).

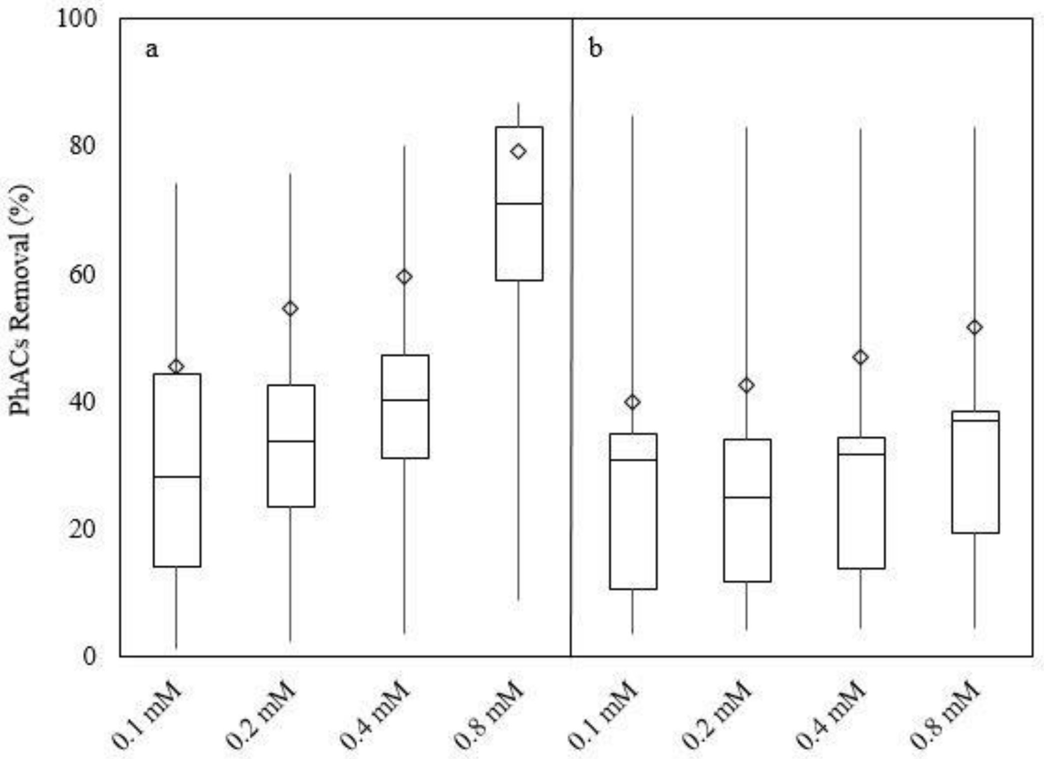


Figure 17 : PhACs removal in wastewater effluent obtained during UV/PDS (a) and UV/PMS (b) processes; application of increasing oxidant concentration (Fluence = 851.4 mJ/cm² (30 min); $[PhAC]_0$ = 1 µg/L; pH = 8.2; n) of PhACs = 9).

Influencing factors

WWTP effluents are characterized by several components which may have an impact on UV/PDS and UV/PMS processes. The most impacting components are pH, the inorganic fraction and effluent organic matter. With the aim of elucidating how these factors contribute to influencing these two sulfate-based AOPs, the main parameters of wastewater effluents were investigated in the following sections (Experiments 14 – 23: Table 11).

Effect of pH

Solution pH is another key experimental parameter which can greatly influence the performance of the oxidation processes by altering the radical’s speciation and concentration in the reaction solution (Reaction (1) – (2); Table 12). Experiment were performed with the natural pH of the secondary effluent wastewater (pH 8.2) and at pH = 6 (Experiments 14 and 15: Table 11). The main experimental evidence is that lowering the pH has a negative effect on the reaction for both oxidant species evaluated in this study. The positive effect of operating at slightly basic pH rather than more acidic pH can be deducted by the removal values (Figure 18) obtained by applying either PDS or PMS. Although the extent of the pH effect was different for each compound, during the experiments performed at higher pH, the mean K_{obs} values increased by 25% and 15%, for UV/PDS and UV/PMS, respectively (Figure 23). The application of 0.4 mM PDS or PMS at pH 8.2, compared to pH 6, resulted in greater removal values for all the investigated compounds (Figure 18). The better performances obtained at pH = 8.2 were also proved to be statistically significant (Table A1). Changes in pH values contribute to PhACs ionization in accordance with their pKa values. In respect to this, it is worth mentioning that the more significant improvements (Figure 18) were obtained for those PhACs with pKa values of between 9.28 and 10.09 (OFXC, ATNL, MTPL, NDL, VLFX and CPFX; Table S2). The amino groups of these compounds at pH = 6 were partially or completely protonated [145]. With pH decreasing from 8.2 to 6, the increasing degree of protonation, might hinder the electrophilic attack by reactive radicals, especially $SO_4^{\bullet-}$. Previous studies showed that the protonated forms of PhACs had lower reactivity than that of deprotonated forms [146]. According to reaction (1) (Table 12), $SO_4^{\bullet-}$ undergo to transformation reactions generating extra $OH^{\bullet}$. These newly formed hydroxyl radicals can positively contribute to PhACs degradation. This is because they can foster the decomposition of persulfate, yielding higher sulfate radical concentration in the reaction volume (Reaction (3); Table 12), while at the same time, they can contribute to the reaction themselves, increasing the degradation rate. Finally, since $OH^{\bullet}$ are less selective than $SO_4^{\bullet-}$, they can have faster reaction with the dissolved organic matter (Reaction (5) and (6); Table 12), resulting in a lower competition between EfOM and PhACs for sulfate radical [79], and therefore higher $SO_4^{\bullet-}$ concentration. Nevertheless, reaction (1) (Table 12) became predominant at pH > 11, which means there is still the coexistence of $OH^{\bullet}$ with $SO_4^{\bullet-}$ at the unaltered wastewater pH [147]. Furthermore, hydroxyl radicals can react with sulfate radicals forming HSO_5^- for which a sharp increase in the molar adsorption coefficient was observed, increasing the pH from 6 to 9 [147]. The consequence of this increase was a greater photolysis rate. The resulting enhanced decomposition of PMS into $SO_4^{\bullet-}$ and $OH^{\bullet}$ would then be a positive contribution for the enhanced degradation of PhACs at higher pH. This is visible during the UV/PMS process, where an increase in the pH value yielded a greater average degradation efficiency than UV/PDS (Figure 18). It is worth mentioning that since the pH of municipal wastewater after biological treatment typically falls in the range 7-8, no pH adjustment may be needed for UV/PDS and UV/PMS application.

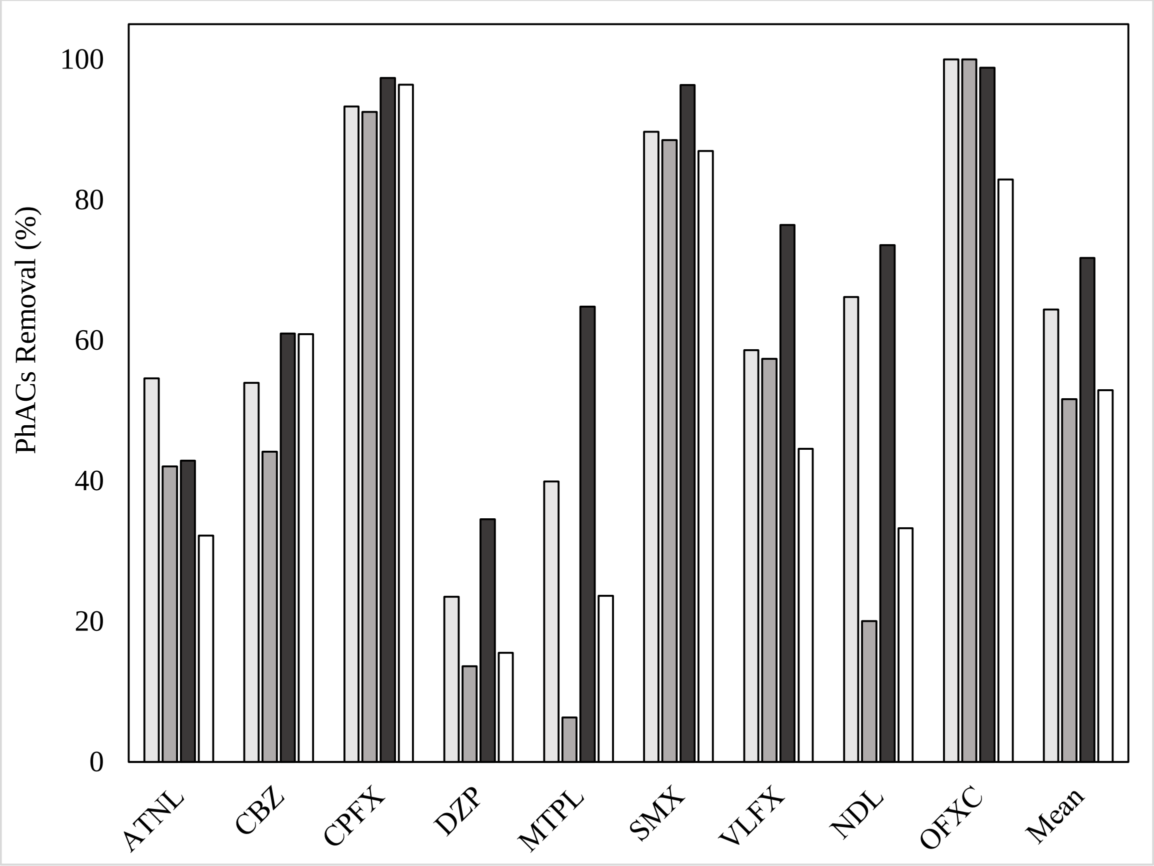


Figure 18 : Removal of PhACs in wastewater effluent during UV/PDS at pH8.2 ☐ and pH6 ▨ , and during UV/PMS at pH8.2 ■ and pH6 ☐ . (Fluence= 851.4 mJ/cm² (30 min); Oxidant concentration= 0.4 mM; [PhAC]₀ = 1 µg/L).

Chloride

Chloride anion is present in several water matrices. Cl^- can be found in WWTP effluents at varying concentrations, depending on the salinity level of raw influent wastewater. Chloride anion can influence the oxidation processes, and its impact on PhACs removal has therefore been evaluated in the following section.

During experiment 16 and 17 (Table 11), we observed that at 851 mJ/cm² of UV fluence, chloride concentrations three times the background value do not result in significant change to the mean removal values (Figure 19). In fact, although Cl^- concentration were tripled, the average levels of PhACs removal stayed in the range of 60% and 70% for PDS and PMS, respectively. Increasing chloride anions concentration in the reaction media does not create significant changes (< 5%) in the removal efficiencies during the UV/PDS process, except for CBZ (17% greater removal) and CPFX (14% lower removal). Although average removals did not change, a higher Cl^- concentration caused slower kinetics for 4 PhACs (ATNL, CBZ, CPFX, SMX and NDL), albeit only between 7% and 10% (Table A2). According to these results, the average K_{obs} decreased from 2.8 cm²/J to 2.2 cm²/J (Figure 23). A similar trend was found for the UV/PMS system, where increased chloride concentration did not affect the average removal (72% and 71% with Cl^- = 9 mM and Cl^- = 27 mM, respectively). Slower kinetics for 4 PhACs have been observed in this system. The inappreciable effect of Cl^- may be explained through two main reasons. The forward reaction of chloride anion with sulfate radical to obtain anion sulfate and $Cl^{\bullet}$ has a similar rate constant for the reversed reaction (Reaction 12; Table 12). This fact may push the reaction backward, hence the sulfate radical concentration was almost no affected [148]. Secondly, $Cl^{\bullet}$ reacts with Cl^- in order to generate $Cl_2^{\bullet}$-. This newly formed radical is less reactive with organic matter and has a longer half-life time (microseconds) than $OH^{\bullet}$, $SO_4^{\bullet -}$ and $Cl^{\bullet}$ [149]. Therefore at longer reaction times, $Cl_2^{\bullet -}$ is the predominant radical. The contribution of reactive chlorine species to the degradation of PhACs have been studied recently [149,150]. In the case of trimethoprim, for example, the contribution of $Cl_2^{\bullet -}$ was proven to be greater than hydroxyl radical [7]. However, these reactions are complex, poorly understood and there is a lack of knowledge about degradation rate constant of reactive chlorine species with PhACs [151]. This radical can show activity towards the PhACs investigated in this study. However, the observed slower kinetics with 27mM of Cl^- can be attributed to the smaller redox potential (E_0 = 2.0-2.126 V) than that of $SO_4^{\bullet -}$. The overall effect was in fact minimal as has been reported by other authors [152]. At the same time, in the UV/PMS system, hydroxyl radical reacts faster with chloride anion forming $HOCl^{\bullet -}$ (Reaction (9); Table 12). $HOCl^{\bullet -}$, dissociates into $OH^{\bullet}$ and Cl^- faster than its formation (Reaction (10)). Therefore reaction (9) (Table 12) (e.i. chloride scavenging capacity toward $OH^{\bullet}$) can be considered negligible. Von Gunten (2003) also observed that this reaction was almost negligible for Cl^- lower than 100 mM [35]. At acidic pHs, $HOCl^{\bullet -}$ rapidly transformed into $Cl^{\bullet}$ and H_2O, according to reaction (11) which is faster than reaction (10) (Table 12). Taking the above consideration into account, at pH = 6, $Cl^{\bullet}$ concentration should be higher than $OH^{\bullet}$ concentration, causing a reduction in the oxidation efficiency. These chain reactions ((9) – (11); Table 12), might help to better explain the performance obtained at higher pH in the previous section. From a practical point of view, the obtained results indicate how UV/PDS and UV/PMS may be considered feasible technologies for removing PhACs in brackish WWTPs effluents.

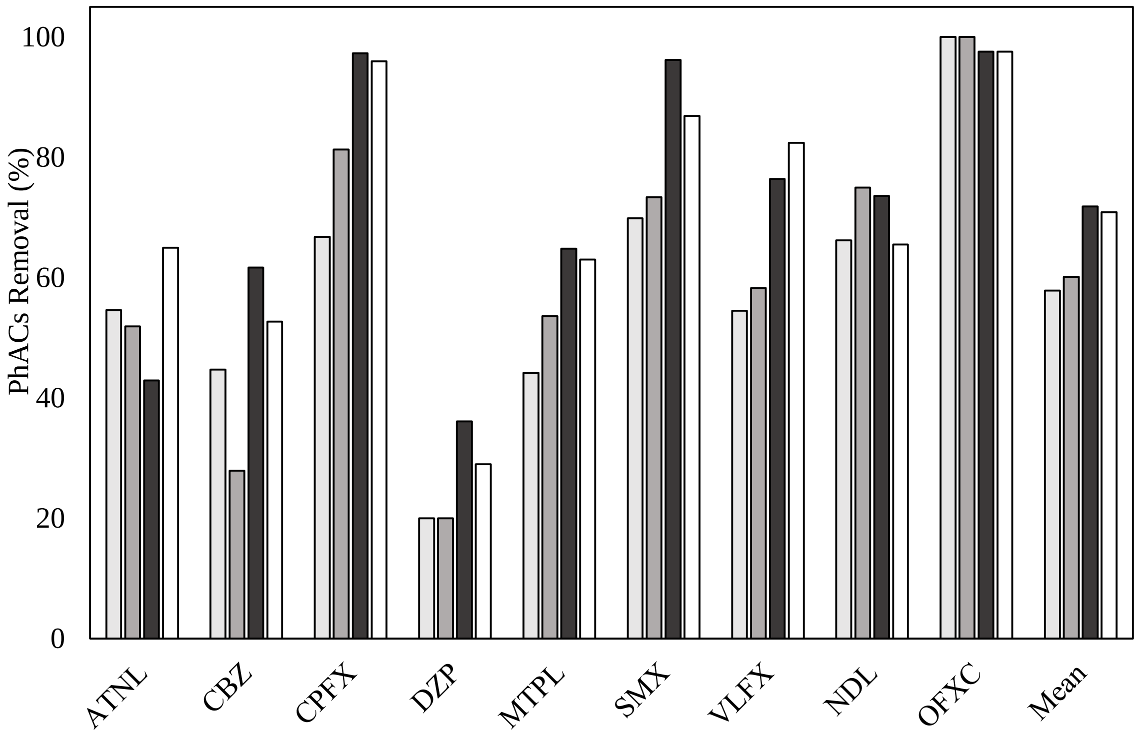


Figure 19 : Removal of PhACs in wastewater effluent during UV/PDS with Cl^-= 9mM ☐ and Cl^-= 27mM ▨, and during UV/PMS with Cl^-= 9mM ■ and Cl^-= 27mM ☐. (Fluence= 851.4 mJ/cm² (30 min); Oxidant concentration= 0.4 mM; $[PhAC]_0$ = 1 µg/L).

Nitrate

The influence of nitrate on the two AOPs was evaluated (Experiments 18 and 19: Table 11). Adding NO_3^- into the UV-based systems improved the kinetics, whereas did not affect degradation efficiencies. The improvement was more evident in UV/PMS, where the average degradation rate increased from 4.9 cm²/J to 7.7 cm²/J, when the NO_3^- concentration increased from 1 mM to 10 mM (Figure 23). However, average removal during experiments with 1 mM and 10 mM did not change, being indeed 72% and 73%, respectively (Figure 20). The most significant improvement due to the higher concentration of nitrate has been noticed for ATNL, whose degradation rate increased by 42% (Figure 4.9). In the case of UV/PDS, the average K_{obs} value (3.1 cm²/J) did not change (Figure 23). This evidence is the direct consequence of the heterogeneous behavior showed by each compound. For example, NDL was negatively affected (29% higher removal) while CPFX showed a positive impact (27% lower removal) (Figure 20). This may be due to a balance where $SO_4^{\bullet-}$ is removed, while $NO_3^{\bullet}$ is formed (Reaction (15); Table 12). The reaction responsible for the formation of $NO_3^{\bullet}$ is relatively slow (K = 2.1 x 10^6), but since nitrate is present in high concentration (10 mM), this reaction cannot be neglected. Sulfate and nitrate radical have almost the same redox potential value (2.466 V and 2.437 V, respectively for $NO_3^{\bullet}$ and $SO_4^{\bullet-}$), the end result being that the degradation efficiency does not change.

At the same time, we should have $OH^{\bullet}$ formation through reaction (16) (Table 12) by the NO_3^- photolysis . In fact both the hydroxyl and nitrite radicals can participate in the oxidation of PhACs. However, in the UV/PDS system, since there is high concentration of $SO_4^{\bullet -}$, according to reaction (17) (Table 12) these radicals can scavenge the newly formed $OH^{\bullet}$. As a consequence, the added value of the produced $OH^{\bullet}$ cannot be appreciated. On the other hand, in the UV/PMS system, due to the lower concentration of $SO_4^{\bullet -}$, reaction (17) (Table 12) is less likely to happen. Additionally, the $SO_4^{\bullet -}$ reaction with nitrate anion (15) is faster than hydroxyl radical (Reaction (18) ; Table 12), which means the latter is less likely to happen. Consequently, higher NO_3^- concentration results in higher $OH^{\bullet}$ concentration, which provides for faster degradation rates.

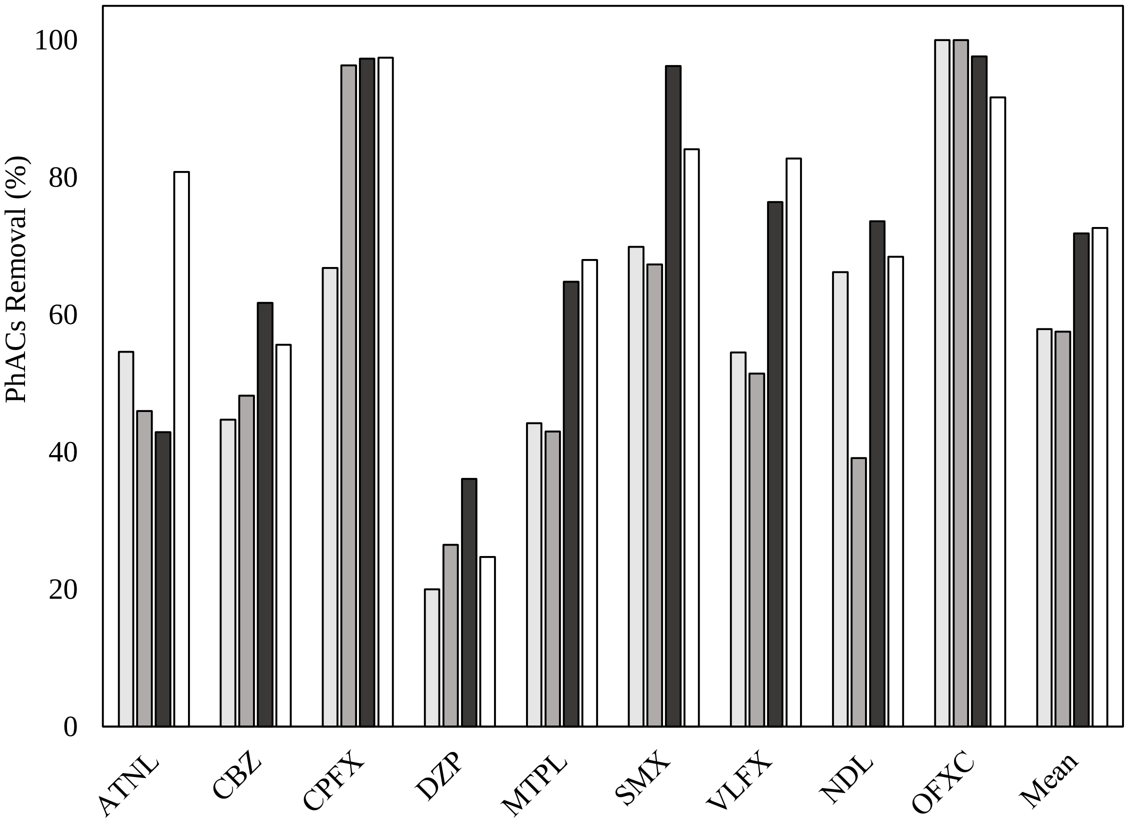


Figure 20 : Removal of PhACs in wastewater effluent during UV/PDS with NO_3^-= 1mM □ and NO_3^-= 10mM ▨ , and during UV/PMS with NO_3^- = 1mM ■ and NO_3^-= 10mM □ (Fluence= 851.4 mJ/cm² (30 min); Oxidant concentration= 0.4 mM; $[PhAC]_0$ = 1 µg/L).

Bicarbonate

Bicarbonate is one of the most commonly found anions in water. Because of this ubiquity in water, its effects on UV/PDS and UV/PMS have been investigated (Experiments 20 and 21: Table 5.1). When bicarbonate concentration was doubled, average removals increased from 34% to 81% and from 37% to

66% by UV/PDS and UV/PMS, respectively (Figure 21). CBZ was the only compound not affected by higher bicarbonate concentration during the UV/PMS process. In the UV/ $S_2O_8^{2-}$ system the mean K_{obs} value increased from 2.84 cm²/J 16.1 cm²/J to, for experiments with 6 mM and 3 mM of bicarbonate, whereas passed from 4.9 cm²/J to 15.4 cm²/J in the UV/HSO_5^- process (Figure 23). These findings can mostly be ascribed to generation of the carbonate radical $CO_3^{\bullet-}$. $CO_3^{\bullet-}$ can be generated via the reaction of $OH^{\bullet}$ and $SO_4^{\bullet-}$ with HCO_3^- (Reactions. (19) and (20)). Zhang et al [153] found that although the rate constants of the target antibiotics with CO_3^- were lower than those with OH, the higher selectivity of carbonate radical rendered it less susceptible to scavenging effects by the solution matrix. In a kinetic modelling, they proved that the $CO_3^{\bullet-}$ concentration was 3-4 orders of magnitude higher than that of $OH^{\bullet}$ in different matrices. Furthermore, the presence of bicarbonate anions was shown to be able to activate both PDS and PMS [73,154]. The slightly better performance of UV/PDS system could be due to the slightly faster formation of $CO_3^{\bullet-}$ by $SO_4^{\bullet-}$ than $OH^{\bullet}$ (Neta et al., 1988).

The better performances obtained with higher concentration of bicarbonate are in line with the results obtained with higher values of alkalinity. This may be due to the fact that there is 50% of bicarbonate and 50% of CO_2 at pH = 6, while at pH 8.2 bicarbonate is the only specie with regard to the carbonate equilibrium.

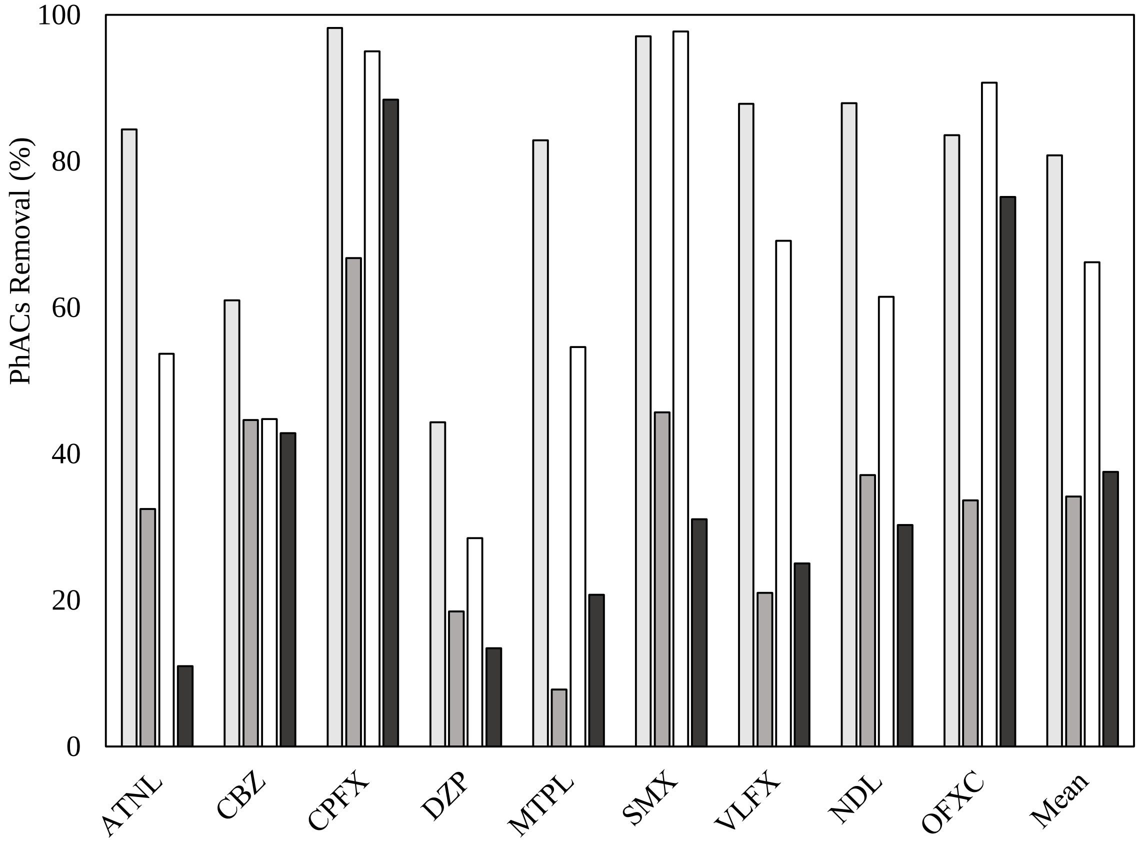


Figure 21 : Removal of PhACs in wastewater effluent during UV/PDS with HCO_3^-= 3mM ▨ and HCO_3^-= 6mM ☐, and during UV/PMS with HCO_3^-= 3mM ■ and HCO_3^-= 6mM ☐. (Fluence= 142 mJ/cm² (5 min); Oxidant concentration= 0.4 mM; $[PhAC]_0$ = 1 µg/L).

Effluent organic matter

EfOM has been highlighted as the main factor contributing to radical scavenging [144]. Considering this, we studied the effect of EfOM on PhACs degradation during UV/PDS and UV/PMS (Experiment 21 and 22: Table 5.1). In absence of EfOM, both systems achieved high average removals and fast degradation rates (98% and 6.8 cm^2/J and 86% and 7.8 m^2/J for UV/PDS and UV/PMS respectively) (Table A2). The oxidation capacity of both UV/PDS and UV/PMS were significantly depleted when EfOM was in solution. In the UV/PDS system, mean removal decreased by 47%, whereas for UV/PMS the loss accounted for 30% of removal (Figure 22). This is in line with previous studies showing that, depending on the water matrix, EfOM can contribute up to 95% of total scavenging capacity [155]. Accordingly, the variation in the K_{obs} values followed a similar trend. The average K_{obs} values declined by 60% for UV/PDS and 43% for UV/PMS. Without EfOM, the $SO_4^{\bullet -}$ based system achieved removal efficiencies (Figure 23) that were either higher than or equal to the $OH^{\bullet}$-$SO_4^{\bullet -}$based system for all PhACs, except SMX. At the same time, faster kinetics for 7 PhACs out of 9 were obtained in the UV/PDS process rather than UV/PMS (Table A2). However, the scenario with EfOM, was characterized by an opposite trend. In fact, UV/PMS achieved faster kinetics and higher removals for all PhACs, except for NDL and ATNL. Both UV/PDS and UV/PMS processes are in fact compound-specific and are characterized by heterogeneous behaviors when the target is a group of mixed contaminants with different physic-chemical properties rather than a single particular molecule. The above described trends verified during the UV/PDS and UV/PMS processes in presence and absence of EfOM, were corroborated at statistical level (Table A1). In both oxidation systems, EfOM can scavenge $SO_4^{\bullet -}$, $OH^{\bullet}$, and also all the other secondary radicals formed by the reaction of sulfate radical with the principal wastewater components [144]. Moreover, since EfOM comprises a mixture of light absorptive substances (such as humic and fatty acids), the latter could compete with PhACs, PDS and PMS for the incident light. This light filtering effect would affect the UV direct photolysis of PhACs and at the same time reduce the formation of $SO_4^{\bullet -}$ and $OH^{\bullet}$ [156]. Although organic matter has lower reactivity with $SO_4^{\bullet -}$ (reactions (6) and (8)) compared to $OH^{\bullet}$ (reactions (5) and (7)), if $OH^{\bullet}$ is not available, then sulfate radicals are consumed and the degradation efficiency decreases. However, when both hydroxyl and sulfate radicals are in solution at the same time, EfOM reacts faster with $OH^{\bullet}$ which are then highly scavenged. Since EfOM is oxidized by $OH^{\bullet}$, we speculate that the other radical species could be less consumed by this major wastewater component. As a consequence, in this scenario more sulfate radicals would be available for PhACs oxidation. Therefore, further research is needed to verify whether the co-presence of the two main radical species characterizing the UV/PMS system may be the explanation for the better efficiencies achieved by this system when EfOM is the main scavenging contributor.

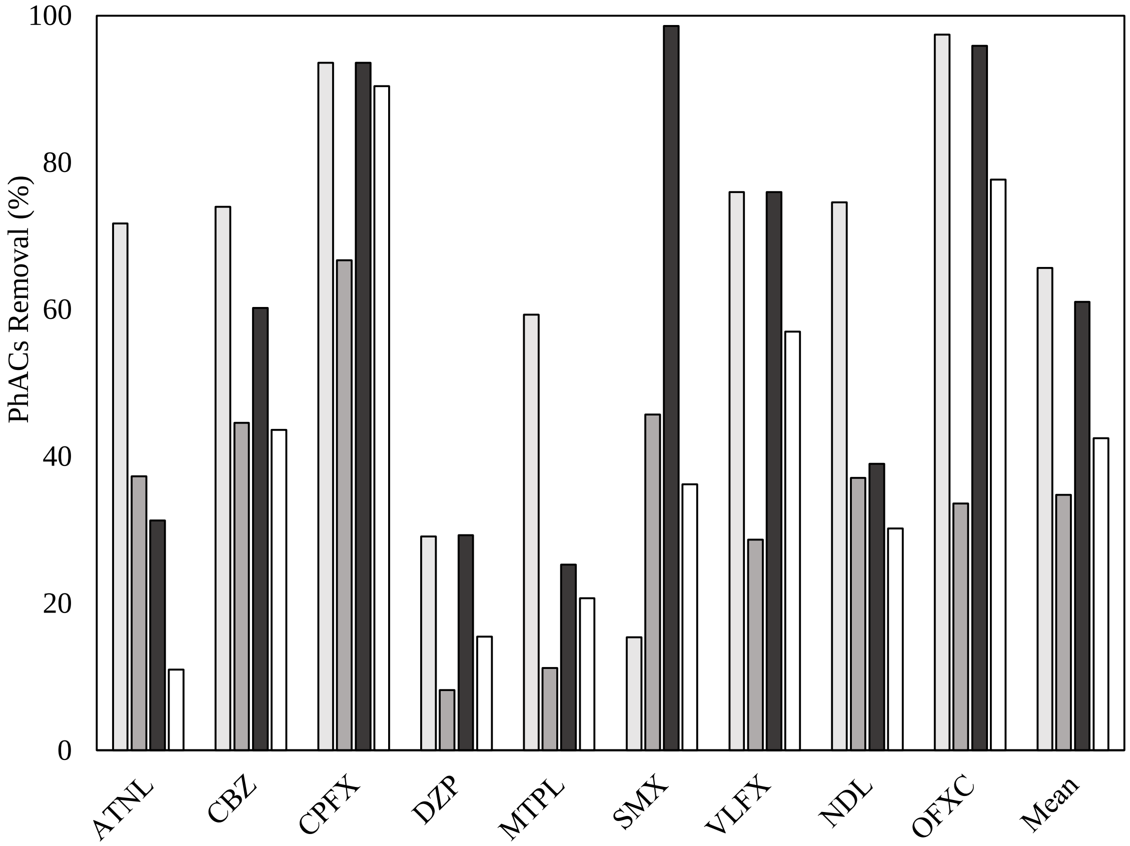


Figure 22 : Removal values obtained during the UV/PDS and UV/PMS process. UV/PDS without EfOM ▒ , UV/PDS with EfOM ▨, UV/PMS without EfOM ■ and UV/PMS with EfOM □ . (Fluence = 283.8 mJ/cm² (10 min); oxidant concentration = 0.4mM; [PhAC]₀ = 1 µg/L)

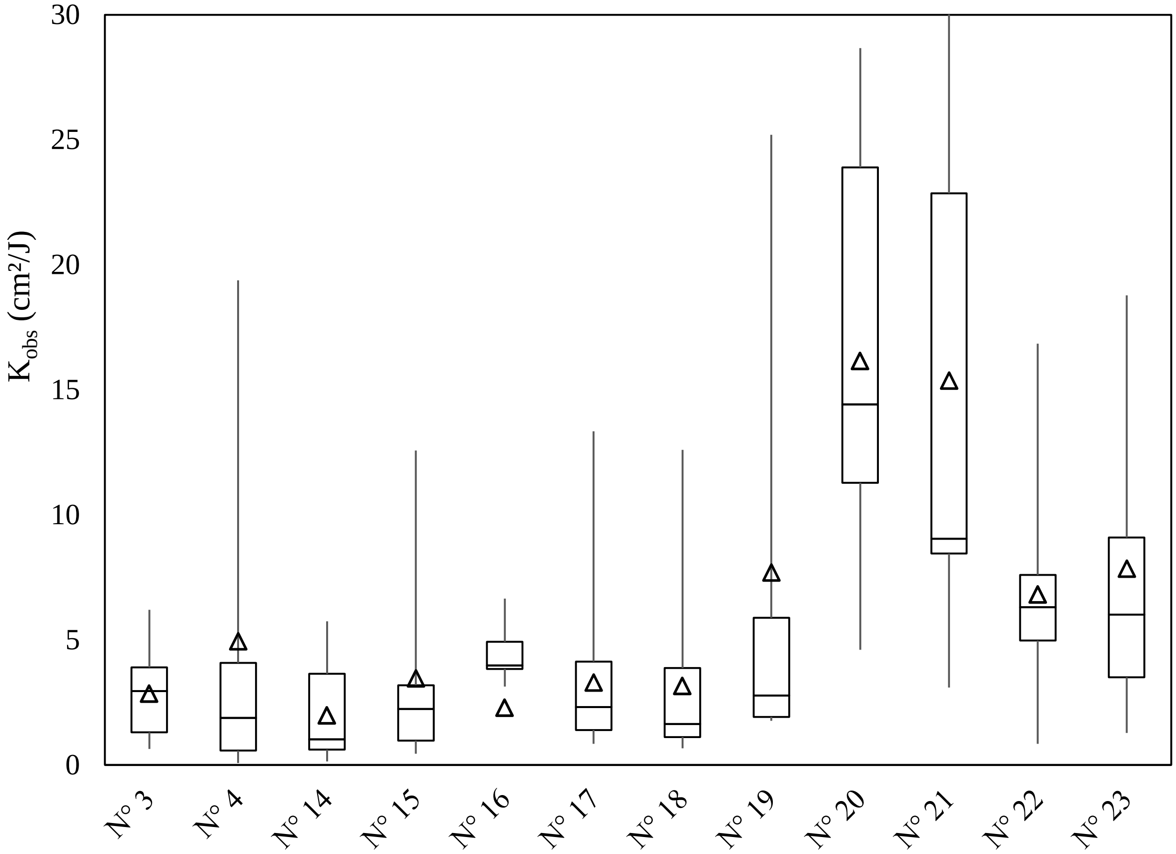


Figure 23 : Fluence-based degradation rate constants (min, 1st, median, 3rd, max and average values) calculated for each tested experimental condition (N° refers to Table 4.2.1) during UV/PDS and UV/PMS. (Oxidant concentration = 0.4 mM; [PhAC]0 = 1 µg/L; n° of PhACs = 9)

Transformation products

Although UV/PDS and UV/PMS technologies have proved to be effective treatments for PhACs removal from WWTP secondary effluents, further considerations need to be taken into account. In most AOPs studies, mineralization was found to be low compared to the degradation/removal of a specific pharmaceutical; a fact that clearly implies that a considerable organic load remains attributed to the presence of persistent oxidation products. The transformation of PhACs and their products formation by $OH^{\bullet}$-based AOPs have been documented previously [157,158]. These studies show hydroxylation and ring-opening are the major reaction pathways. Nevertheless, very few studies have investigated the transformation of PhACs by $SO_4^{\bullet-}$ based AOPs. The different reactivity between $OH^{\bullet}$ and $SO_4^{\bullet-}$ in the formation and the yield of different products have been demonstrated in the transformation of diclofenac, sulfamethoxazole and propanolol [139,143,159]. Lu et al. (2017) reported that mineralization of DCF was limited (32% TOC removal) even after 180 min of UV/PDS treatment [159]. Mahdi Ahmed et al. (2012) observed that DCF and SMX degradation upon $SO_4^{\bullet-}$ oxidation generated, respectively, eight and six fully separated transformation products [143]. Similarly, Guo et al. (2017) reported the formation of nine transformation products derived from the degradation of the antibiotic norfloxacin, after the application of the UV/PDS process [160]. Moreover, different transformation pathways lead to different transformation products, which are then associated to different degree of toxicity [157]. With this regard, if a substance is not completely eliminated, a number of transformation products can eventually reach the environment with the potential of adversely affecting aquatic and terrestrial rendering, thus toxicity measurements as an indispensable task [161]. In addition to that, applying AOPs as tertiary treatment for wastewater, implies several interactions of matrix components with radicals. These interactions generate oxidation by-products with potential negative effects [35]. With this respect, it is noted that chloride and nitrate radicals resulted in the chlorinated by-products [162] and nitrated by-products [163], which might pose potential risk on environment and human health. On the other hand, the formation of bromate (BrO_3^-) is suppressed in $SO_4^{\bullet-}$-based treatment by organic matter, then is not to be expected in a hypothetical application of UV/PDS and UV/PMS during oxidative wastewater treatment [66]. Hence, in future studies dealing with complex water and wastewater matrices, this point needs to be emphasized.

However, transformation products and ecotoxicity assessment of the treated samples by AOPs is beyond the scope of this thesis. Nevertheless, future research should address these issues in order to produce complementary information with regard to which technologies produce a better effluent, also according toxicity standards.

Table 13 : Reactions of the radical species considered relevant in the current work.

N°	**Reaction**	**Rate Constant**	**Reference**
(1)	$SO_4^{\bullet -} + OH^- \rightarrow OH^\bullet + SO_4^{2-}$	7.0 x 10^7 $M^{-1}s^{-1}$	[164]
(2a)	$OH^\bullet + OH^- \rightarrow O^{\bullet -} + H_2O$	1.2 x 10^{10} $M^{-1}s^{-1}$	[165]
(2b)	$O^{\bullet -} + H_2O \rightarrow OH^\bullet + OH^-$	1.7 x 10^6 $M^{-1}s^{-1}$	[165]
(3)	$OH^\bullet + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO4^{\bullet -} + ½ O_2 + H^+$	1.4 x 10^7 $M^{-1}s^{-1}$	[166]
(4)	$SO_4^{\bullet -} + H_2O \rightarrow H^+ + OH^\bullet + SO_4^{2-}$	2 x 10^{-3} $M^{-1}s^{-1}$	[167]
(5)	Suwannee River NOM + $OH^\bullet \rightarrow$ Products + OH^-	3.3 x 10^8 $M^{-1}s^{-1}$	[168]
(6)	Suwannee River NOM + $SO_4^{\bullet -} \rightarrow$ Products + SO_4^{2-}	4.6 x 10^6 $M^{-1}s^{-1}$	[168]
(7)	$Cl^- + OH^\bullet \rightarrow HOCl^{\bullet -}$	4.3 x 10^9 $M^{-1}s^{-1}$	[169]
(8)	$HOCl^{\bullet -} \rightarrow OH^\bullet + Cl^-$	6.1 x 10^9 $M^{-1}s^{-1}$	[169]
(9)	$HOCl^{\bullet -} + H+ \rightarrow Cl^\bullet + H_2O$	2.1 x 10^{10} $M^{-1}s^{-1}$	[169]
(10)	$Cl^- + SO_4^{\bullet -} \rightarrow Cl^\bullet + SO_4^{2-}$	3.0 x 10^8 $M^{-1}s^{-1}$	[170]
(11)	$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet -}$	7.8 x 10^9 $M^{-1}s^{-1}$	[171]
(12)	$SO_4^{\bullet -} + SO_4^{\bullet -} \rightarrow S_2O_8^{2-}$	7.0 x 10^8 $M^{-1}s^{-1}$	[170]
(13)	$SO_4^{\bullet -} + NO_3^- \rightarrow NO_3^\bullet + SO_4^{2-}$	2.1 x 10^6 $M^{-1}s^{-1}$	[172]
(14a)	$NO_3^- + H_2O + h\nu \rightarrow NO_2^\bullet + O^{\bullet -}$	$\Phi = 0.028 – 0.053$	[173]
(14b)	$O^{\bullet -} + H_2O + h\nu \rightarrow OH^- + OH^\bullet$	1.7 x 10^6 $M^{-1}s^{-1}$	[165]
(15)	$SO_4^{\bullet -} + OH^\bullet \rightarrow HSO_5^-$	1.0 x 10^{10} $M^{-1}s^{-1}$	[174]
(16)	$OH^\bullet + NO_3^- \rightarrow$ products	< 1.0 x 10^5 $M^{-1}s^{-1}$	[175]
(17)	$HO^\bullet + HCO_3^- \rightarrow CO_3^{\bullet -} + H_2O$	8.5 x 10^6 $M^{-1}s^{-1}$	[165]
(18)	$SO_4^{\bullet -} + HCO_3^- \rightarrow CO_3^{\bullet -} + H^+ + SO_4^{2-}$	2.8 x 10^6 $M^{-1}s^{-1}$	[176]

2.5 PhACs removal : validation at pilot-scale

Aiming at evaluating these sulfate based-AOPs and their application as tertiary treatment to remove PhACs from WWTP effluents, a scale up study of these two technologies has been conducted. As mentioned previously in Chapter 3, the scale up process consisted in applying UV/PDS and UV/PMS at pilot-scale. The evaluation has been done in terms of removal efficiencies, fluence-based degradation rate constants and electrical energy per order (E_{EO}).

2.5.1 Experimental plan

Feed water (WWTP secondary effluent) was stocked into a 200 L plastic tank (influent tank). The lamp was switched on 30 minutes before each experimental session in order to reach the optimal temperature inside the reactor. During UV/PDS and UV/PMS experiments, the radical precursors (PDS or PMS), were added into the influent at a molar concentration of 0.4 mM. An additional experiment has been conducted doubling PDS initial concentration (0.8 mM). Then, an homogeneous distribution of the oxidant was maintained by an internal recirculation pump which also provided wastewater mixing to ensure homogeneous conditions of influent water. After oxidant dosage and mixing, wastewater was pumped into the UV reactor. The pilot-plant was operated with a flow rate value of 0.36m³/h. The pilot plant was constantly operated with a minimum of 5 reactor volume to reach stable operating conditions, and after this time, initial and final samples were manually collected from right before and after the reactor. Several samples (influent and effluent) were collected for each treatment, at different time. These samples eventually were mixed together aiming at obtaining a "manually composite sample". Manually composite samples were chosen in order to overcome possible fluctuations in terms of influent wastewater characteristics, lamp operations, environmental factors. The samples were immediately divided in two fractions: one was quenched with sodium sulphite (1.60×10^{-5} M), while the second one was directly used for the measurement of (i) UV 254 nm absorbance and (ii) conventional wastewater parameter (TOC, NH_4^+, NO_3^-, NO_2^-, HCO_3^-, pH). The quenched fraction was then treated according to procedure reported above (3.2.1) for PhACs analysis. After the advanced oxidation process, the tertiary treated wastewater was collected into a second 200 L plastic tank (see Figure 8; Tank 2).

Short term experiments were conducted for the determination of removal and removal kinetics for UV alone, UV/PDS and UV/PMS process at pilot-scale. These experiments consisted of a series of oxidation cycles, one cycle after the other. Operating conditions do not change during the different cycles. Since PDS or PMS were added only at the beginning (e.i. first cycle), this procedure simulates consecutive passages of UV irradiation. Increasing the passages, results in increasing the irradiation time and therefore the applied UV-dose. Due to the above described procedure, PhACs degradation at different

UV-dose can be calculated. Hence, fitting concentration values measured at different UV-doses into the pseudo-first order model, fluence-based degradation rate constants in pilot experiments (K_{obs}-Pilot) can be calculated. The calculated UV-dose, taking into account 17 W/m² of irradiance and 0.36 m³/h of flow rate, corresponding to a contact time of 45.7 seconds, resulted in 83 mJ/cm². Each cycle account for 83 mJ/cm² of UV delivered to wastewater. The passage from one cycle to the following one was done as follows: (i) once Tank 1 was empty, (ii) valve A (see VA in Figure 8) was closed, (iii) valve B (VB : Figure 8) was opened, and (iv) Tank 2 become the influent tank while Tank 1 served as effluent/discharge tank. This procedure has been repeated for 5 cycles, thus the highest UV-dose applied was 415 mJ/cm².

2.5.2 Determination of degradation efficiencies and removal kinetics

Firstly, the effect of UV-C irradiation alone, with different contact times (e.i. UV fluence values) has been assessed. Figure 24 shows the positive effect of longer UV-C radiation in PhACs removal. This was also confirmed by the reduction of light absorbance at 254 nm (Figure A1). During photolysis experiments, the average PhACs removal improved from 12% to 32%, increasing UV fluence from 83 mJ/cm² to 416 mJ/cm² respectively. However, photolysis alone was not able to degrade PhACs to a significant extent from WWTP secondary effluent (Figures 5.11 and 5.12). Similar results have been reported by several studies [82,177,178], where the addition of an oxidizing agent has been proposed as an effective way to overcome this limitation. The addition of 0.4 mM of PDS or PMS, at the lowest UV fluence value (83 mJ/cm²), tripled the average removal obtained with UV alone, reaching 35% and 36% respectively for UV/PDS and UV/PMS. Similarly to the case of UV alone, higher UV fluences allow to reach higher removals. In fact as it can be seen from Figure 24, applying 416 mJ/cm² instead of 83 mJ/cm², resulted in increasing average removal from 35% and 36% to 84% and 85%, respectively for UV/PDS and UV/PMS. Figure 25 allows to compare the two processes in terms of removal. UV/PDS reached greater removals for CBZ and CPFX, while the opposite trend was observed for ATNL and DZP. No significant differences (<5%) were observed for the remaining 5 PhACs. Increasing PDS concentration, did not result in better performances of UV/PDS process. In fact PhACs elimination at 416 mJ/cm² with 0.8 mM PDS was lower than the elimination obtained with 0.4 mM of PDS or PMS. This behavior has already been observed and it is known as self-scavenging mechanism. According to this mechanism, sulfate radical can react with themselves forming $S_2O_8^{2-}$ according to reaction (14) and (15). Therefore increasing amount of PDS may obstacle the reaction resulting in lower degradation of some PhACs. The only exceptions were CBZ and CPFX, for which UV/PDS-0.8mM resulted in greater removals than UV/PMS-0.4mM. This may be explained with the greater affinity of these two compounds with $SO_4^{\bullet-}$ rather than $OH^{\bullet}$.

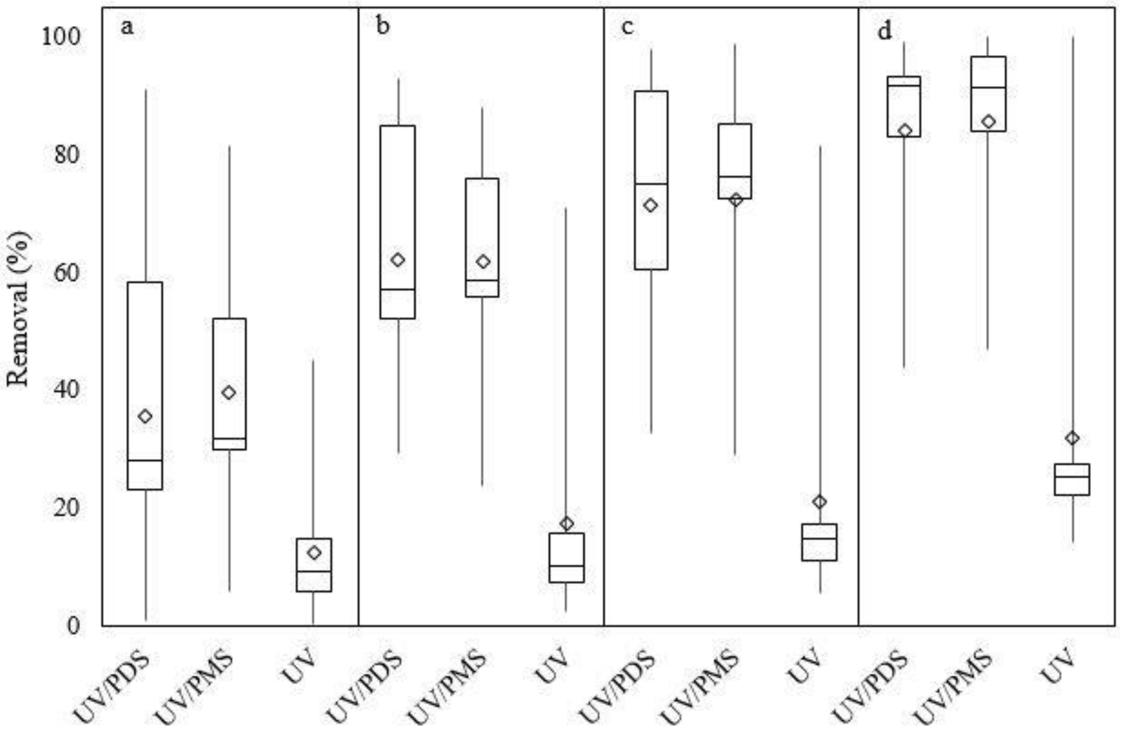


Figure 24 : PhACs removal in wastewater effluent obtained during UV/PDS, UV/PMS and UV processes, calculated at (a): 83 mJ/cm² (0.82 min), (b): 166 mJ/cm² (1.63 min), (c): 249 mJ/cm² (2.45 min) and (d): 416 mJ/cm² (4.08 min) of UV fluence (Oxidant concentration = 0.4 mM; [PhAC]$_0$ = 1 µg/L; pH = 8.2; n° of PhACs = 9).

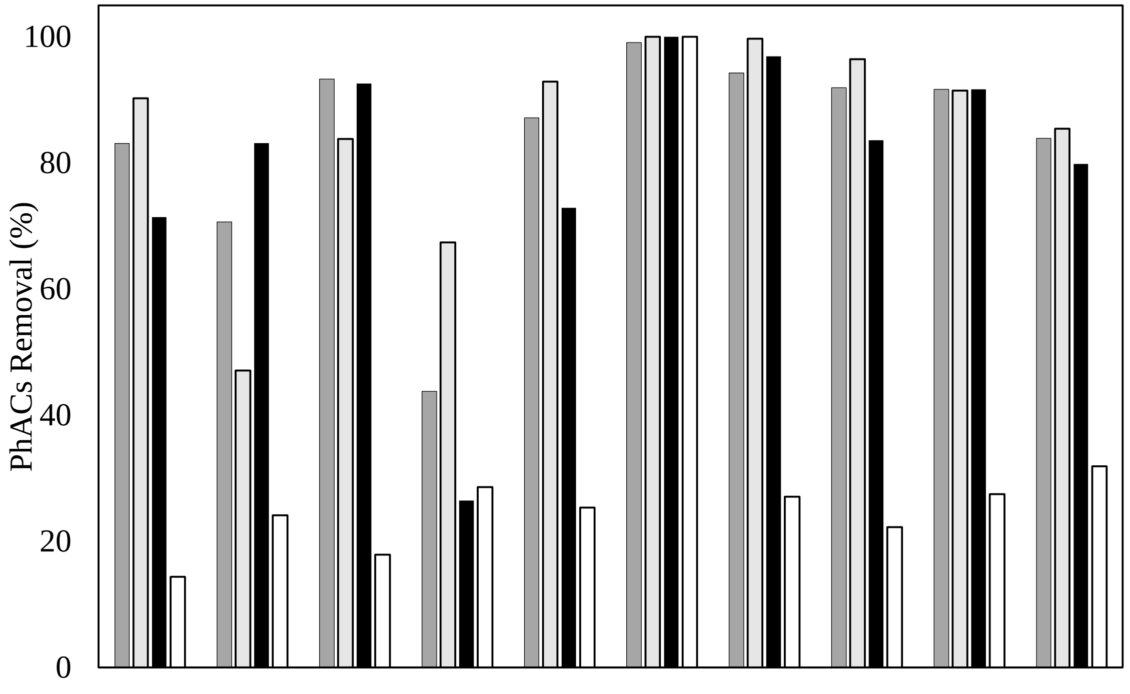


Figure 25: Removal (UV/PDS-0.4mM: ▩ UV/PM-0.4mMS: □ UV/PDS-0.8mM: ■ UV only: □) of PhACs in WWTP effluent (Fluence= 416 mJ/cm² (4.08 min); [PhAC]$_0$ = 50 µg/L; pH = 8.2).

These findings are in general agreement with the latest studies where UV/PDS and UV/PMS have been evaluated at pilot scale [80,82]. However it is interesting to point out some differences between the current work and above mentioned ones. In order to carry out this comparison, metoprolol (MTPL) was chosen as model compound. In the present work, MTPL removal after 416 mJ/cm² of UV fluence, followed the order: UV/PMS (93%) > UV/PDS (87%) > UV (25%). Rodriguez-Chueca et al. (2018) [82] found the same trend, but with significantly lower values: UV/PMS (38%) > UV/PDS (10%) > UV (0%), while Nihemaiti et al. (2018), reported 49% MTPL elimination at 1,200 mJ/cm² with 0.6 mM PDS [80]. There are very few studies assessing the degradation of PhACs from WWTP secondary effluent, during pilot-scale UV/PDS and UV/PMS processes. Nevertheless, as in the case of MTPL, the published results are characterized by a significant variability which may be the results of (a) wastewater properties, (b) AOPs pretreatment, (c) type of low pressure lamp, (d) number of lamps (e.i. total installed power) and (e) initial PhACs concentration. These facts clearly highlight the importance to validate these treatments at pilot-scale, taking into account all these process variabilities. The chosen model compound (MTPL) may be useful also to compare UV/PDS and UV/PMS performances with their state-of-the-art reference technology; UV/H_2O_2. Rodriguez-Chueca et al. (2018) [82] found that the greatest MTPL removal (60%) was obtained when H_2O_2 was used as main oxidizing agent instead of PDS or PMS. Coherently, in a recent publication by Miklos et al. (2018) [178], the application of UV/H_2O_2 at pilot-scale allowed for an average MTPL removal ranging between 40% and 60% at 600 mJ/cm². With this regard, it is worth mentioning that MTPL removals obtained during UV/H_2O_2 process by these above mentioned authors, were lower than what we found during our study. However, due to the process variability mentioned before, and the lack of exhaustive information about the application of UV/PDS and UV/PMS at pilot-scale with real WWTP secondary effluent, more studies are needed in order to assess whether these sulfate based-AOPs can be considered feasible alternatives to hydroxyl radical based-AOPs. In this context, aiming at gathering more evidences about UV/PDS and UV/PMS, it is also important to investigate PhACs removal kinetics rather than just removal percentages. The value of the fluence-based degradation constants (K_{obs}) are in general agreement with the removal values calculated at 416 mJ/cm² (Figure 26). In fact UV/PDS performed better only for CBZ, CPFX and OFXC, whereas UV/PMS process was characterized by faster kinetics for all the remaining compounds. As it was the case for the removal efficiencies, doubling the molar concentration of PDS had a positive impact only on CBZ and CPFX. This fact may suggest a greater affinity of these two PhACs with $SO_4^{\bullet-}$ than $OH^{\bullet}$. However, the mean values do not differ in a significant extent being indeed 8.7 cm²/J, 8.8 cm²/J and 8.2 cm²/J, respectively for UV/PDS-0.4mM, UV/PMS-0.4mM and UV/PDS-0.8mM. These K_{obs} values also confirmed the little role played by photolysis alone. Photodegradation alone was indeed the slower process having a K_{obs} value (1.4 cm³/J) almost 8 times lower than the other studied processes. In order to gain few insights more regarding the role of direct photolysis, the ratio between K_{obs}-$_{UV}$ and K_{obs}-$_{AOP}$ has been calculated (Figure 27). Ratio value greater than 0.8 indicates that the degradation was mainly attributed to direct photolysis. Ratio between 0.5 and 0.8 indicates that both processes contribute to the elimination, while ratio lower than 0.5 suggest that radical oxidation was the predominant process for PhACs removal. During the UV/PDS process, the $K_{obs\text{-}UV}/K_{obs\text{-}AOP}$ was calculated to be 0.5 and 0.6 only for DZP and SMX respectively; while for all the remaining compounds was lower than 0.5. On the other hand, in UV/PMS system, the $K_{obs\text{-}UV}/K_{obs\text{-}AOP}$ ratio was lower than 0.5 for all PhACs. However, the average ratio value for both processes was 0.2, hence direct photolysis only had a minor role in PhACs degradation; confirming what has been reported previously in this section. Even though the photolysis of one mole of PDS produces two moles of $SO_4^{\bullet-}$, it has been already reported that during UV/PDS process, hydroxyl radicals can be formed through reaction (1) and take part to the oxidation of contaminants. On the other hand, one mole of PMS generates one mole of $SO_4^{\bullet-}$ and one mole of $OH^{\bullet}$. Therefore in both systems these two radicals participate to the transformation of PhACs, thus improving direct photo-degradation which cannot be considered as a viable treatment to remove PhACs from WWTP secondary effluent.

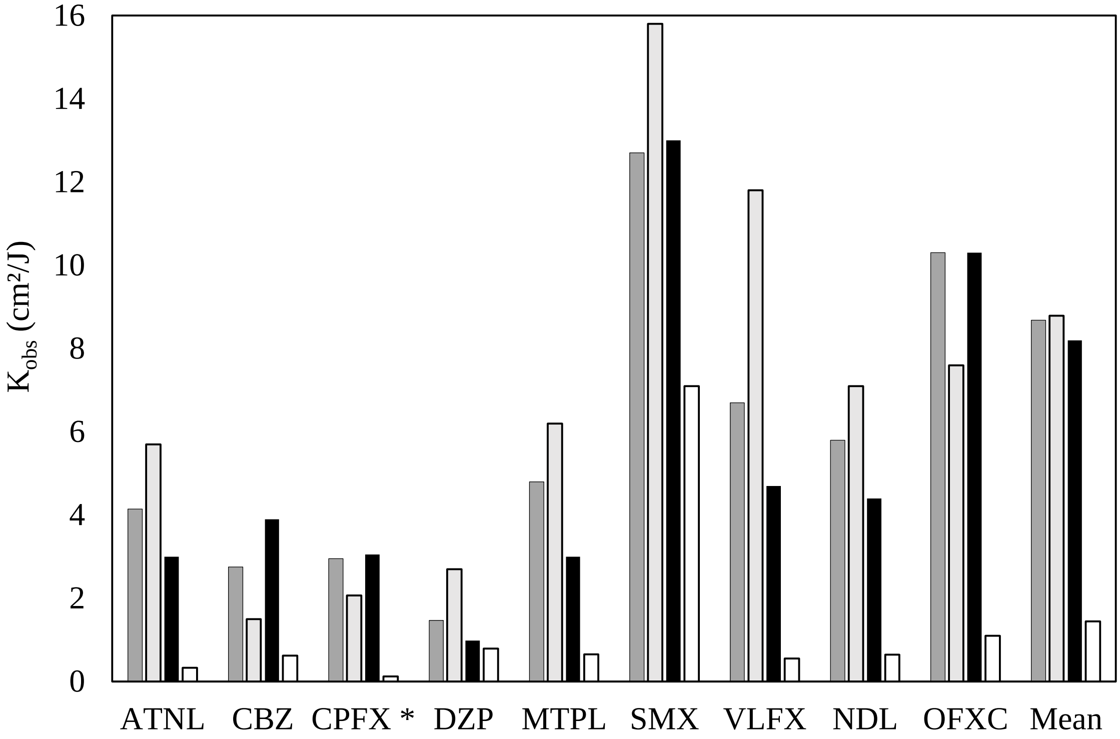


Figure 26 : Fluence-based degradation rate constant of PhACs for UV/PDS-0.4mM: ▨ UV/PMS-0.4mM: □ UV/PDS-0.8mM: ■ UV only: □ ($[PhAC]_0$ = 10 µg/L; pH = 8.2).

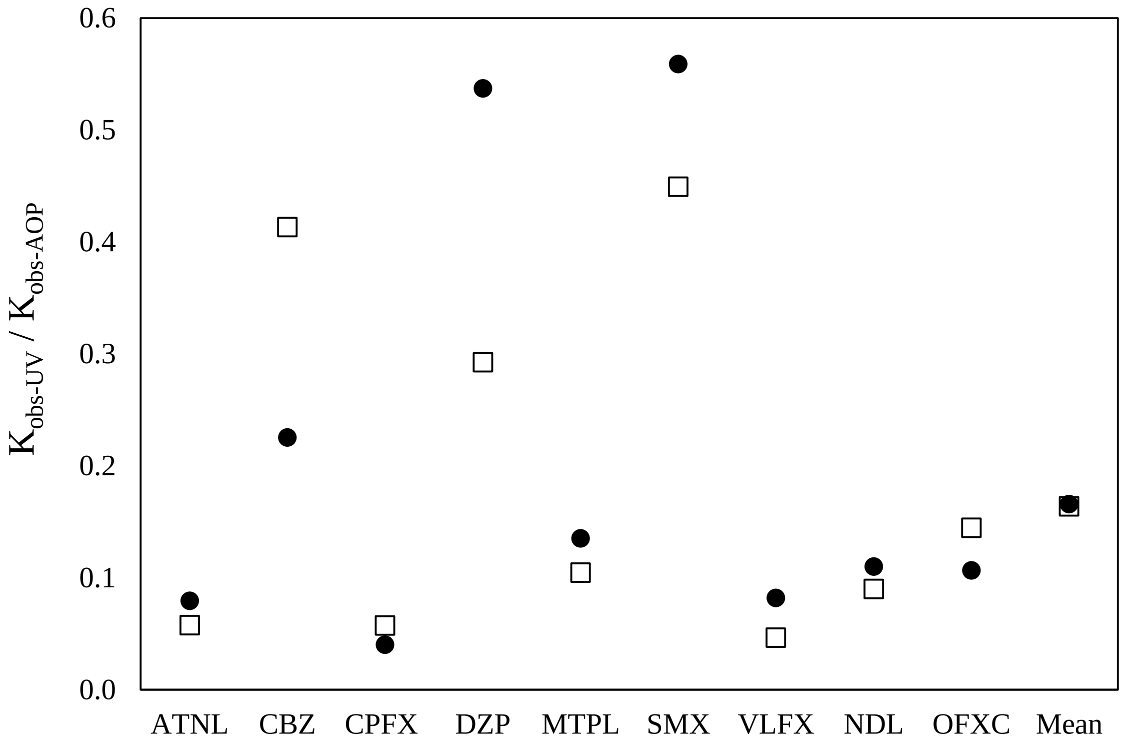


Figure 27 : Ratio between fluence based degradation rate constant obtained during UV alone experiments (Kobs-UV) and UV/oxidant experiments (Kobs-AOP); respectively for UV/PDS ● and UV/PMS □

2.5.3 Treatment energy estimation

Evaluating a new technology at pilot-scale for real application implies to take into account also additional parameters rather than just removal efficiencies and degradation rate constants. Along with the pilot-scale investigation goes the analysis of the energetic consumption required by the studied technologies. With the aim of including this extra information into the overall assessment of the studied systems, degradation of each PhAC has been plotted versus the energy input (kWh/m³) needed to obtain a certain removal. The efficiency of both UV/PDS and UV/PMS increased linearly with increasing value of kWh per m³ of treated wastewater (Figure 28). On the other hand, in the case of UV alone, more energy resulted in little removal improvement. For all the studied PhACs, UV/PMS proved to be more efficient than UV/PDS, since at equal energy inputs corresponded higher removal. Nevertheless, in the range 0.5 – 0.7 kWh/m³ both processes were able to reach high removal efficiencies (> 70%). The results obtained operating the UV/PDS system with 0.8 mM of PDS instead of 0.4 mM provide useful evidences with regard a future application of this advanced oxidation process. It is indeed important to point out that oxidant dosages higher than the optimum value may results in two relevant drawbacks. Firstly, more oxidant can reduce the degradation capacity due to the self-scavenging-mechanism described above, and secondly, as a direct consequence of that, more energy would be required by the system in order to achieve the same removal standards. These evidences suggest the importance of further investigations for optimizing the amount of oxidant applied during these sulfate based-AOPs. With this respect, it is also worth mentioning that the molar ratio between oxidant and contaminant has been observed to be process- and contaminant-specific. Hence, case-specific studies are needed in order to optimize these treatments with regard to specific class of contaminants and wastewater characteristics.

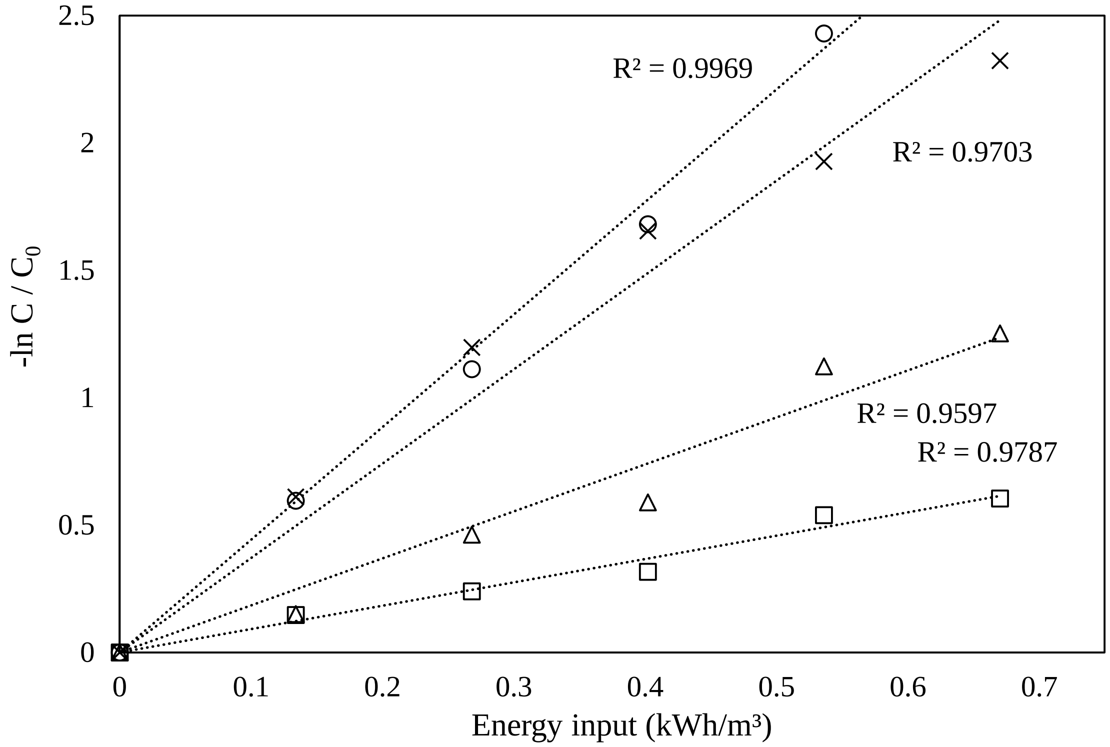


Figure 28 : Average PhACs removal versus the energy input. UV/PDS-0.4mM X, UV/PMS-0.4mM ○, UV/PDS-0.8mM △, UV alone □. ([PhAC]0 = 10 µg/L; pH = 8.2).

To enable comparison of UV/PDS and UV/PMS efficiency with other AOPs and alternative treatment processes, Bolton and coworkers developed figures of merit for the comparison of advanced oxidation processes [61,102]. These are based on electrical energy consumption which often represents a major fraction of the AOP operating cost. For low contaminant concentrations (typically < 100 mg/L), the degradation of organic contaminants by AOPs follows a pseudo-first kinetic. Thus, the oxidant or energy consumption changes proportionally to the volume to be treated and the treatment goals (i.e. order of magnitude of reduction per unit volume). Hence this parameter is defined as E_{EO} (electrical energy per order):

"*Electrical energy per order is the electrical energy expressed in kWh required to degrade a contaminant C by one order of magnitude in 1 m³ of contaminated water*" (Bolton et al., 1995) [179].

In continuous mode reactions can be calculated from Eq. :

Eq. (2)
$$E_{EO} = \frac{P}{F * \log\left(\frac{Ci}{C_f}\right)}$$

where P is the rated power (kW) of the AOP system, F is the flow rate, C_i and C_f are the initial and the final pollutant concentration. Above in the text we reported the higher energy efficiency, in terms of kWh/m^3, for UV/PMS than UV/PDS. It is interesting to notice that, including the degradation capacity (log C_i/C_f) into the energy assessment, the gap between these two techniques decreases. In fact the E_{EO} calculated for UV/PDS and UV/PMS is 0.9 kWh/m^3/order and 0.8 kWh/m^3/order, respectively (Table 13). Moreover, as expected the need of kWh to remove PhACs decreases during UV/PDS and UV/PMS processes, regarding to the need in the UV alone (5.3 kWh/m^3) treatment. Table 13 also provides information regarding the variability of these studied AOPs. In fact, reflecting the findings of the degradation assays, the performances of these two systems, in this section expressed in terms of kWh/m^3/order, may differ from each target compound to be degraded. The case of DZP and CPFX provides a clear example of this specificity. Miklos et al. (2018) [61] critically reviewed E_{EO} obtained during several advanced oxidation processes for water and wastewater treatment. With regard to UV/PDS they reported a median value of 0.67 kWh/m^3/order, slightly lower than our findings. This may be due to the fact that the studies included in the review comprise also application with pure or drinking water which are more energy efficient compared to application with wastewater. Moreover, this review also highlights two important considerations to be taken into account for the evaluation of these AOPs: (i) higher energy efficiencies for sulfate radical based AOPs than conventional UV/H_2O_2, and (ii) UV/PDS and UV/PMS belong to the group with median E_{EO} values < 1 kWh/m^3, thus representing a realistic range for full scale application. However, a reliable comparison of different AOPs should be done with the same water matrix, considering a wide range of target contaminants, using the same oxidant dose, operating the same reactor under the same optimized operating conditions, and possibly at pilot or full-scale.

Table 14 : Electrical energy per order, calculated for each PhACs

	E_{EO} (kWh/m³/order)			
	PDS 0.4 mM	PMS 0.4 mM	PDS 0.8 mM	UV only
ATNL	0.9	0.7	1.3	11.4
CBZ	1.4	2.5	1.0	6.1
CPFX	0.1	0.2	0.1	3.2
DZP	2.6	1.4	3.9	4.8
MTPL	0.8	0.6	1.3	5.8
SMX	0.3	0.2	0.3	0.5
VLFX	0.6	0.3	0.8	6.9
NDL	0.7	0.5	0.9	5.9
OFXC	0.4	0.5	0.4	3.4
Mean	**0.9**	**0.8**	**1.1**	**5.3**

Chapter 3 : Comprehensive evaluation of advanced treatment technologies for PhACs removal

Some of the contents of this chapter have been re-drafted from : L. Sbardella, I. Velo Gala, J. Comas, , I. Rodriguez-Roda, W. Gernjak, Holistic evaluation of PhACs degradation during UV sulfate-based oxidation processes as advanced wastewater treatment. (Submitted to Journal of Cleaner Production)

In this chapter the overall performance of the studied advanced wastewater technologies (BAC-UF, UV/PDS and UV/PMS) have been comprehensively assessed considering technical, energetic, economic and environmental criteria. These outcomes have been then compared with state-of-the-art technologies.

3.1 Methodology

As discussed in the previous chapters, the MPs removal efficiencies from wastewater differ considerably with respect to the different target substances, the applied treatment techniques and operating conditions of each technology. For example, higher ozone dosage or higher EBCT during GAC filtration, will lead to a higher removal efficiency for most pollutants. To accurately design a post treatment for MPs removal and to properly estimate the costs and the environmental impacts, a common criterion should be proposed and taken into consideration. For application purposes, an specific value for the average removal efficiency can be chosen as common benchmark to evaluate d technologies. This average removal should be obtained considering the entire set of different MPs selected as target compounds. With the goal of estimating the cost, for example, in Switzerland five substances have been chosen for which a minimum removal of 80% should be achieved: Diclofenac (painkiller), Carbamazepine (anticonvulsant), Sulfamethoxazole (antibiotic), Benzotriazole (corrosion inhibitor), and Mecoprop (herbicide).

In order to examine the performance of the advanced treatment technologies studied in the current work, between them, and with respect to other technological alternatives (O_3, GAC, PAC), it is important to adopt a common functional unit. Moreover, this common unit also allows the author to compare the costs (6.4) and the environmental impacts (6.5) involved in each technology. In this framework, data on investment and operational costs have been established/calculated with fixed operating conditions. These are the conditions which allow to reach an average MPs (in our case study, of PhACs) removal equal to 80%.

In the following sections, a comparison of removal efficiencies (6.2), energy consumption (6.3), operational cots (6.4) and environmental sustainability (6.5) will be presented.

3.2 Assessment of removal efficiencies

When the main task is to compare different technologies in terms of removal efficiencies, it is important to define which are the boundaries within which this “treatment goal” has been achieved. In the context of our study, we showed how BAC-UF filtration, UV/PDS and UV/PMS are able to reach 80% average PhACs removal under specific operating conditions. These operating conditions are essential information for a reliable evaluation of the proposed advanced treatment, as well as for their direct comparison with alternative options. Table 14, Table 15, Table 3.3 and Table 3.4 summarize the most relevant settings for the three main technologies assessed in this thesis.

Table 15 : UV/PDS operating conditions

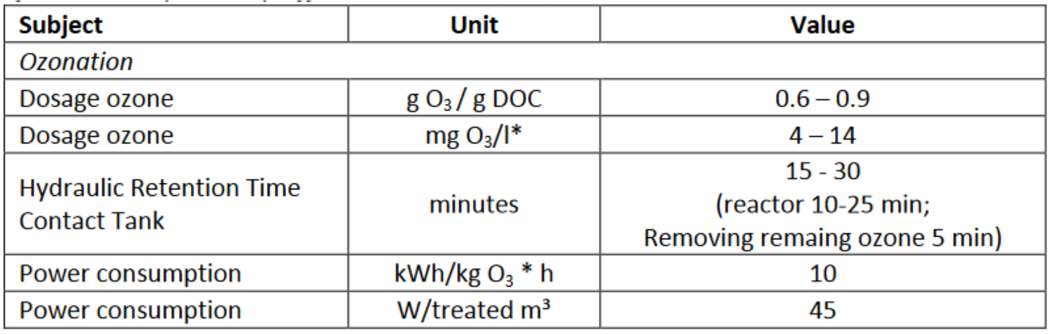
Subject	Unit	Value
UV/PDS		
Dosage PDS	g PDS / g DOC	6
Dosage PDS	mg/L	108
Hydraulic Retention Time Contact Tank	minutes	3.6
Power consumption	kWh/m³	0.59

Table 16 : UV/PMS operating conditions

Subject	Unit	Value
UV/PMS		
Dosage PMS	g PDS / g DOC	6
Dosage PMS	mg/L	108
Hydraulic Retention Time Contact Tank	minutes	3.3
Power consumption	kWh/m³	0.54

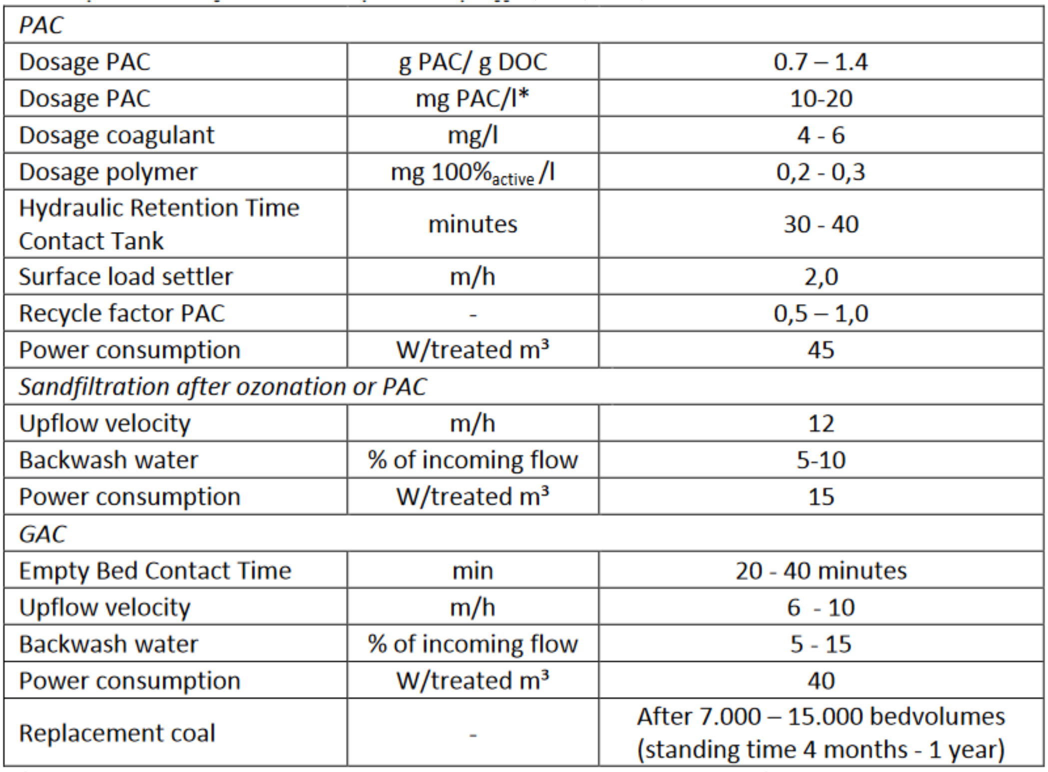
In a recent Swiss research, the removal of several classes of MPs has been extensively researched for different techniques such as ozonation, GAC and PAC on a large pilot scale (> 200 m³/h) or full-scale. Acknowledged design data are displayed in the tables below (Table 16 and 6.2.4).

Table 17 : Common design criteria for removal of MPs from municipal WWTP effluent with ozonation (Adapted from Mulder et al. (2015) [46]).



Subject	Unit	Value
Ozonation		
Dosage ozone	g O_3 / g DOC	0.6 – 0.9
Dosage ozone	mg O_3/l*	4 – 14
Hydraulic Retention Time Contact Tank	minutes	15 - 30 (reactor 10-25 min; Removing remaing ozone 5 min)
Power consumption	kWh/kg O_3 * h	10
Power consumption	W/treated m^3	45

Table 18 : Common design criteria for removal of MPs from municipal WWTP effluent with GAC filtration (Adapted from Mulder et al. (2015) [46]).

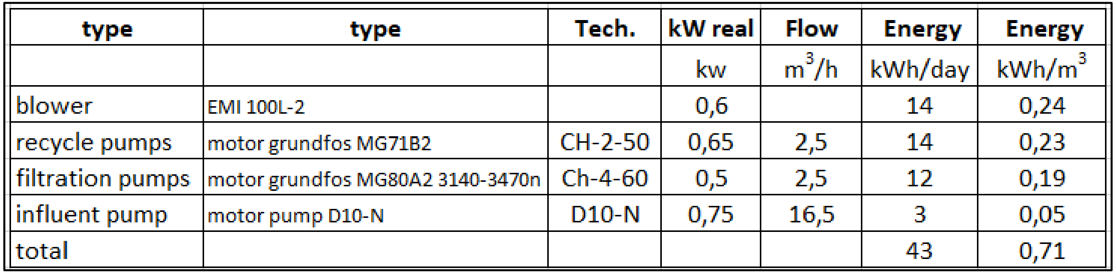


PAC		
Dosage PAC	g PAC/ g DOC	0.7 – 1.4
Dosage PAC	mg PAC/l*	10-20
Dosage coagulant	mg/l	4 - 6
Dosage polymer	mg $100\%_{active}$ /l	0,2 - 0,3
Hydraulic Retention Time Contact Tank	minutes	30 - 40
Surface load settler	m/h	2,0
Recycle factor PAC	-	0,5 – 1,0
Power consumption	W/treated m^3	45
Sandfiltration after ozonation or PAC		
Upflow velocity	m/h	12
Backwash water	% of incoming flow	5-10
Power consumption	W/treated m^3	15
GAC		
Empty Bed Contact Time	min	20 - 40 minutes
Upflow velocity	m/h	6 - 10
Backwash water	% of incoming flow	5 - 15
Power consumption	W/treated m^3	40
Replacement coal	-	After 7.000 – 15.000 bedvolumes (standing time 4 months - 1 year)

3.3 Assessment and comparison of energy consumption

The operational cost of the pilot plants have been calculated and discussed in this section. As stated in the previous section, the consumptions (kWh/m³) are calculated for fixed operating conditions (Table 14 and 6.2.2) which allow for 80% average PhACs removal. Table 18 reports the results of the energy audit applied to the BAC-UF pilot plant. A first look at the data immediately indicates that recycling pumps and coarse aeration blowers are the most consuming energy devices. The total energy consumption amounts to 0.71 kWh/m^3. This energy consumption closely resembles the energy consumption of a full scale MBR system, i.e. 0.63 kWh/m^3 permeate (Fenu et al., 2010). It is thus useful to notice that both coarse aeration blower and filtration pumps are devices typically implemented in pure filtration processes, while they have never been incorporated in a BAC filter. In other words, more than the 50% of the energy consumption reported for the BAC-UF pilot plant does not refer to operational settings to provide higher contact time between the secondary effluent and the filtering material. That is to say that half of the energy consumed in this system is not spent aiming at optimizing the functioning of the GAC-based filtration unit, but for the UF unit. Whilst the above, the aim of the UF membrane placed immediately after the BAC filter was to: (i) increase the amount of biomass throughout the filter bed by avoiding the wash out of suspended solids, nutrients and organic carbon, (ii) produce high-quality tertiary effluent due to the capacity of UF to retain viruses, bacteria and fine particles, and finally (iii) to contribute, although only partially, to MPs removal. However, since UF operation accounted for 50% of the total energy consumption, their implementation as tertiary treatment should be considered only when an ultrafiltration step exert a clear advantage. To the best of our knowledge, no studies examining the energy consumption of BAC applied as tertiary treatment for MPs removal are available. Because of that, a comparison can only be done with GAC filtration unit operated as post treatment in WWTPs. From the few studies assessing this feature, we can observe that GAC energy consumption is significantly lower than the value obtained in the current work, being in fact in the range of 0.05 - 0.10 kWh/m^3 [46,47]. However, studies assessing GAC filtration energy consumption are based on data gathered from full-scale application, hence a direct comparison with an experimental pilot-scale installation may be not completely reliable [180].

Table 19 : Data collected during the energy audit of the BAC-UF pilot



type	type	Tech.	kW real	Flow	Energy	Energy
			kw	m^3/h	kWh/day	kWh/m^3
blower	EMI 100L-2		0,6		14	0,24
recycle pumps	motor grundfos MG71B2	CH-2-50	0,65	2,5	14	0,23
filtration pumps	motor grundfos MG80A2 3140-3470n	Ch-4-60	0,5	2,5	12	0,19
influent pump	motor pump D10-N	D10-N	0,75	16,5	3	0,05
total					43	0,71

The same audit methodology has been applied to the UV reactor utilized during UV/PDS and UV/PMS processes. The first aspect to be considered is that less devices are connected. The pilot installation related to the AOP technology basically consisted of a UV photoreactor and of an influent pump feeding the system; thus being a simpler process, with less electromechanical devices. As it was the case of the BAC-UF, the UV/PDS and UV/PMS energy consumption has been assessed with specific operational settings necessary to reach 80% average PhACs removal. This choice has been done aiming at producing energy consumption outputs (kWh/m³) comparable for the different tested technologies. At the same time, this methodology can be also used to compare our findings with the published literature. In this scenario, the specific energy consumption of the UV/PMS and UV/PDS processes was measured to be 0.54 kWh/m³ and 0.59 kWh/m³, respectively. By comparing these values (referred to 80 % average PhACs removal) with Table 13 (referred to 90% average PhACs removal), it can be seen how the removal target directly affects the energy needed by each specific treatment. The ozone treatment, as most of the AOPs, is more energy intensive than GAC systems. Ozone production is the most relevant figure in the overall energy demand. At the same time, wastewater characteristics also contribute to the energy consumption. In fact, more DOC, results in more O_3 needed, thus in higher energy demand for O_3 production. An extensive report gathering large scale experiences, where the ozone dose has been optimized down to 0.4-0.7 $gO_3/gDOC$, was considered as main reference to compare different results. In this report, the energy consumption was reported to be in the range of 0.2-0.4 kWh/m³ [47]. Due to the great variability characterizing these techniques, different results can be easily found in literature. For example Katsoyiannis et al., (2011) compared the efficiency and the energy demand of O_3 and UV/H_2O_2 for MPs transformation [181]. These authors showed how ozonation may offer better performances than UV/H_2O_2, with energy consumption values (kWh/m³) up to two order of magnitude lower for ozonation. On the other hand, the same paper shows that energy consumption can also be compound-specific, with some compound requiring less energy with UV/H_2O_2 than O_3, when 90% removal was the treatment target. It is important to point out that there is a great variability with respect to energy consumption values reported in literature. In fact it has been already established how these advanced treatment for MPs removal are case-specific, this specificity implies the difficulty to draw general conclusions and “out-of-doubt” recommendations for real case applications.

This examination of energy consumption data allows to conclude that the lowest energy consumption would result for the GAC technology; being indeed the latter mainly based on sorption properties and driven by gravity, few electrical devices need to be operated. Nevertheless, it has to be remarked that in the above described calculations, energy cost for GAC production and regeneration are not included [131,180]. This may be a relevant voice in the whole energy calculation since GAC need to be replaced after 6 to 8 months in order to ensure a certain removal level. Differently, AOPs, if operated according to precise design criteria, can constantly reach the established removal target (in the case of this study: 80% average PhACs removal).

3.4 Assessment and comparison of operational costs

In this section, according to the findings reported above (6.3), energy consumption data have been translated into cost values. In this way, all cost components can be uniformly compared and limitations derived from considering only the energy demand can be overcome.

Figure 29 shows a direct comparison of operational costs for the proposed technologies (BAC-UF, UV/PDS, UV/PMS and UV alone) and allow to examine them together with state of the art technologies already implemented at full scale for MPs removal from secondary effluents of municipal WWTP, namely GAC and O_3. The BAC-UF is evidently more expensive than its most similar technological alternative (GAC), whereas this gap increases even more in the case of direct comparison with ozonation. The calculated cost for the BAC-UF advanced treatment was estimated to be 0.18 €/m³. It is interesting to highlight the similar contribution of activated carbon replacement and energy demand on the overall cost. In this context it may be key to assess the best alternatives for GAC breakthrough, i.e. performing an extensive evaluation on replacement and regeneration. The different scale of the study (pilot for BAC-UF vs full-scale for GAC) can only partially explain the competitive disadvantage. In fact, the BAC-UF system is characterized by three major costs related problems:

- The presence of the UF. An additional ultrafiltration step, after the BAC process, may have an added value as it has been mentioned previously (section 6.3). Unfortunately, since this possible advantage caused by the membrane unit has not been highlighted in this study, the raised cost (both OPEX and CAPEX) would not be justifiable.
- The cost variability for the granular activated carbon affects both the operational (due to GAC replacement) and investment cost.
- The choice between GAC regeneration and GAC replacement.

With respect to the ultrafiltration, since the benefits of having such treatment after the BAC filtration have not been proved, a different configuration may be suggested. Following the multi-barrier criteria applied in wastewater reclamation treatment plants for potable reuse,, an UF step before BAC/GAC filters may result in improved performances of the filter due to the smaller load of suspended solids and fine particles, thus removing obstacles to MPs removals. Margot et al. (2013) investigated two PAC full-scale installation, one followed by sand filtration (PAC-SF) and the second one followed by UF (PAC-UF) [38]. These authors observed that PAC-UF showed an operating cost (0.404 €/m³) seven fold higher than PAC-SF (0.054 €/m³) and ten times higher than ozonation (0.043 €/m³). Furthermore, this study also showed how adsorption processes (PAC, GAC, BAC) gain significant advantages over ozonation when investment costs are considered. For example, PAC-SF presented a total cost of 0.16

€/m³ very similar to ozonation (0.18 €/m³) [38]. We may conclude that adsorption processes based on activated carbon proved to be technically feasible at large scale in municipal WWTP.

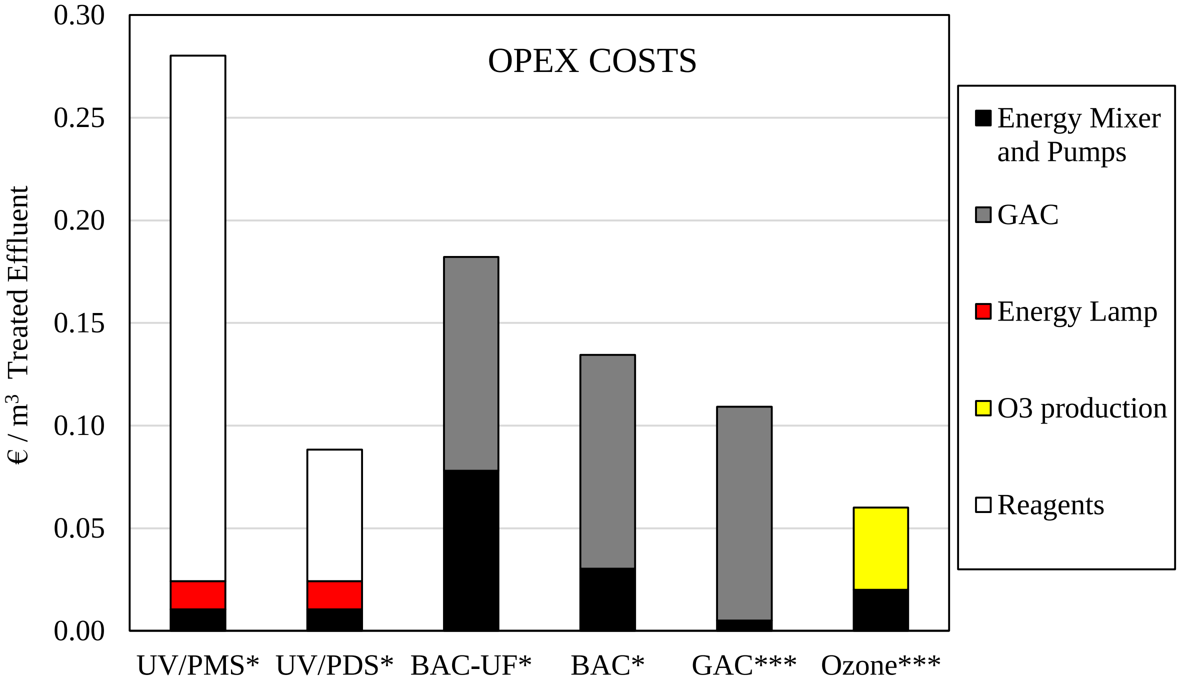


Figure 29 : Operational cost (€/m³ of treated wastewater) for different technologies. Costs are calculated for specific operating conditions selected in order to reach and maintain 80% average PhACs removal from WWTP effluent. (*) = Data experimentally derived in this research study. (***) = Literature data.

The operating cost of the applying UV/PDS, UV/PMS or UV for PhACs removal from WWTP secondary effluent is determined primarily by :

- The energy demand of the UV device,
- The PDS and PMS demand and,
- The replacement frequency of critical, high-cost components.

The first two of these are deeply influenced by wastewater characteristics, photodegradability of target compounds and radicals ($SO_4^{\bullet-}$ and $OH^{\bullet}$) capacity to degrade target MPs. The first two columns of Figure 29 reflect only partially the E_{EO} results reported above (Table 13). In fact it can be seen that the first section (red box) of these two columns, it is related to the energy demand and then it is almost the same of both processes, as it was the case for the E_{EO} value. Nonetheless, the scenario completely changes when nominal prices of oxidant reagents are considered and included in the general cost calculation. The overall operational cost of UV/PDS and UV/PMS, based on 80% average PhACs removal was 0.14 €/m³ and 0.32 €/m³, respectively. The UV-C radiation alone exerts very limited efficiency in removing the target pollutants. Since direct photolysis was not able to achieve removal values close to 80%, this process has not been taken into consideration for the cost analysis. The UV/PMS appears to be more expensive than the UV/PDS, as the reagent is 4 times more expensive. Being PDS a cheaper reagent, allowing for very similar removal efficiencies to UV/PMS, the latter is a far less attractive technology. Comparing our findings with the cost of alternative advanced treatment for MPs removal might help to elucidate whether the proposed processes can be considered promising techniques or not. Very few economic assessment regarding sulfate based AOPs at pilot and/or full scale level are available in literature. Therefore a direct comparison with UV/H_2O_2 may be useful. Keeping the above consideration in mind, it is worth mentioning that Cedat and co-workers (2016) [182] designed a full scale UV/H_2O_2 process to treat secondary effluent of a small WWTPs (2,000 < PE < 10,000). The total calculated operating cost (allowing at least 80% of estrogenic activity removal) of this treatment ranged between 0.151 €/m³ and 0.203 €/m³. A further example was given by De la Cruz et al. (2013), studying UV/H_2O_2 applicability to wastewater to remove 95% of 22 emerging MPs. The authors concluded that the operating cost to reach that treatment goal was 0.13 €/m³. Similarly James et al. (2014) evaluated the cost for microfiltration of secondary effluent followed by UV/H_2O_2 [183] for MPs removal. They reported a total operating cost of 0.42 €/m³ for this MF-AOP configuration associated to >75% removal of metaldehyde; the compound with the lowest removal efficiency among the set of studied MPs. The choice of this recalcitrant substance as model compound to be used for OPEX calculation, it is indeed a remark of the strong dependency of the treatment cost on (a) treatment goals, (b) compounds affinity with radical species involved in the reaction [181], and (c) wastewater characteristics (mostly, transmittance) [183]. The same authors also showed how, adding an additional treatment before the AOP, would result in lower total operating cost. The lower costs were the consequence of increased wastewater quality, i.e. higher transmittance values. This evidence suggested the greater weight of factor (c) among the other factors listed above. Considering the above reported cost figures, it is then evident that UV/PDS process examined in our work may represent a feasible option in terms of both removal capacity and costs. In addition to that, the potential of UV/PDS appears evident from Figure 29 by comparing its cost with GAC filtration systems. UV/PDS operational costs are slightly higher than GAC, but the oxidation process possesses several advantages if compared to GAC filtration units:

1. there is no associated sludge production, transport and disposal,
2. there is no breakthrough of the process which can indeed run continuously, ensuring stable performances, and,
3. the process is not fully explored yet, meaning that there are several aspects for which optimization is possible.

With regard to optimization, since oxidant is the major operating cost of the treatment, it is of high importance to give priority to low PDS concentrations rather than low UV fluence. Besides the great potential for this sulfate based-AOP, ozonation remains a cheaper alternative. However, UV/PDS is at an early stage development as advanced wastewater technology, while ozonation has been already optimized for full-scale implementation.

3.5 Assessment and comparison of environmental sustainability

In order to consider the environmental performance of the studied technologies, life cycle assessment (LCA) methodology, as set in ISO 14040 and 14044 was employed. In this framework, the environmental impacts of each of the proposed technology have been assessed, and then compared among them and with the state of the art. With regard to the BAC-UF technology, several scenarios have been considered.

3.5.1 Impact assessment : BAC-UF pilot plant

With the aim of conducting an exhaustive analysis of this technology, two additional technical alternatives regarding the end-of-life of spent/saturated BAC, were considered. These alternatives were OPTION 1, where 90% GAC regeneration after breakthrough was selected as “refilling procedure”, and OPTION 2, where the filter was refilled with fresh material after every breakthrough event. Moreover, the limits derived by operating an ultrafiltration system with doubtfully advantages in terms of overall performance, have also been taken into account. Due to this concern, two different scenarios have been considered: SCENARIO A, where we assessed the impact of the entire process (BAC-UF) and SCENARIO B, where only the first part of the process (BAC) was acknowledged.

During operation according to OPTION 1A, the most impacting factors followed the order: electricity (48.8%) > GAC reactivation (22.9%) > citric acid consumption (7.5%) > GAC production (10%) > transport (5.1%) (Figure 30). Electricity consumption showed the greatest impact for all the considered categories, except for terrestrial ecotoxicity (TET) which was greatly impacted by the production of citric acid for membrane cleaning. Apart from TET, citric acid had the second biggest impact on marine eutrophication (ME) and water depletion (WD). On the other hand, GAC reactivation was the second process showing the greatest environmental impact for all the studied categories. Finally, GAC production also had a negative effect on the environment; for some categories even higher than GAC reactivation and citric acid consumption. These results are in agreement with previous studies assessing the environmental sustainability of drinking water treatment plant [106]. For example Mery et al. (2014) evaluated three different treatment trains and concluded that for some category such as climate change and fossil depletion GAC and electricity had the most impacting effect [184]. In the context of the BAC-UF process, as it has been discussed during the cost and energy assessment, it is worth describing the environmental sustainability of both technologies assembling this system; namely the BAC filter and the UF. In order to reach this more detailed description, OPTION 1B has also been studied. From Figure 31, it is visible how more than half of the environmental impact related to the BAC-UF process is due to operation of the ultrafiltration device. In fact, with the only exception of terrestrial acidification (TA), the UF process showed a greater contribution on each impact categories than the BAC process. In agreement with these findings, Carré et al. (2017) reported that UF is characterized by significant environmental footprint, being indeed greater than an alternative treatment line composed by UV and sand filtration [93]. Evaluating this process from a more general perspective through the end-point procedure, we observed that the trend obtained during the midpoint evaluation was maintained (Figure 32). The order was indeed as previously reported, with just small changes in the average values: electricity (50.5%) > GAC reactivation (25.2%) > citric acid consumption (8.6%) > GAC production (5.8%) > transport (4.5%). Furthermore, the endpoint analysis confirmed that the contribution was equally distributed among the two processes composing the BAC-UF technology, although the UF had a slightly greater impact (57.2%) than the BAC filter (42.8%).

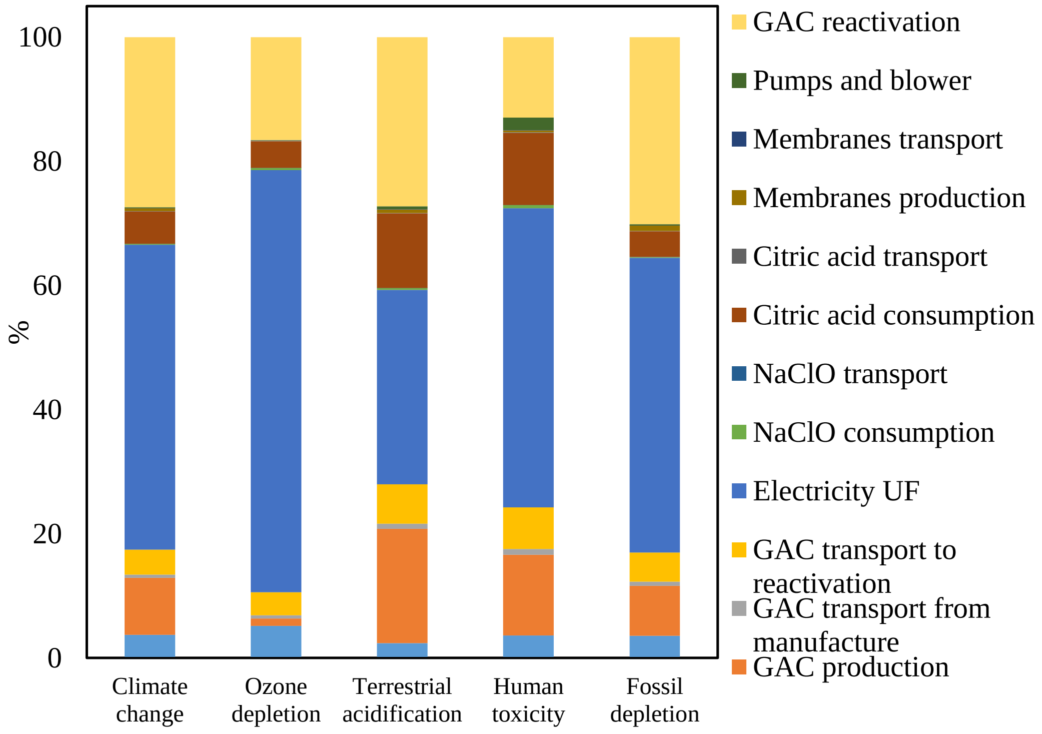


Figure 30 : Midpoint life cycle impact of BAC-UF process (OPTION 2 : with GAC regeneration) for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

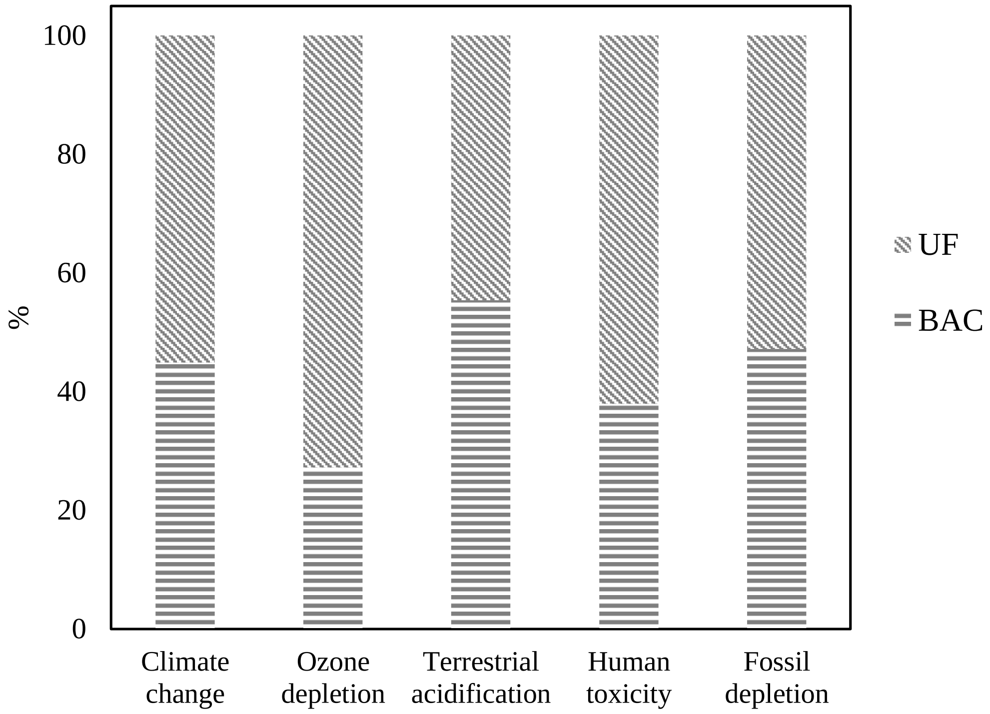


Figure 31 : Midpoint life cycle impact of BAC (OPTION 1 : with GAC regeneration) and UF processes, considered separately, for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

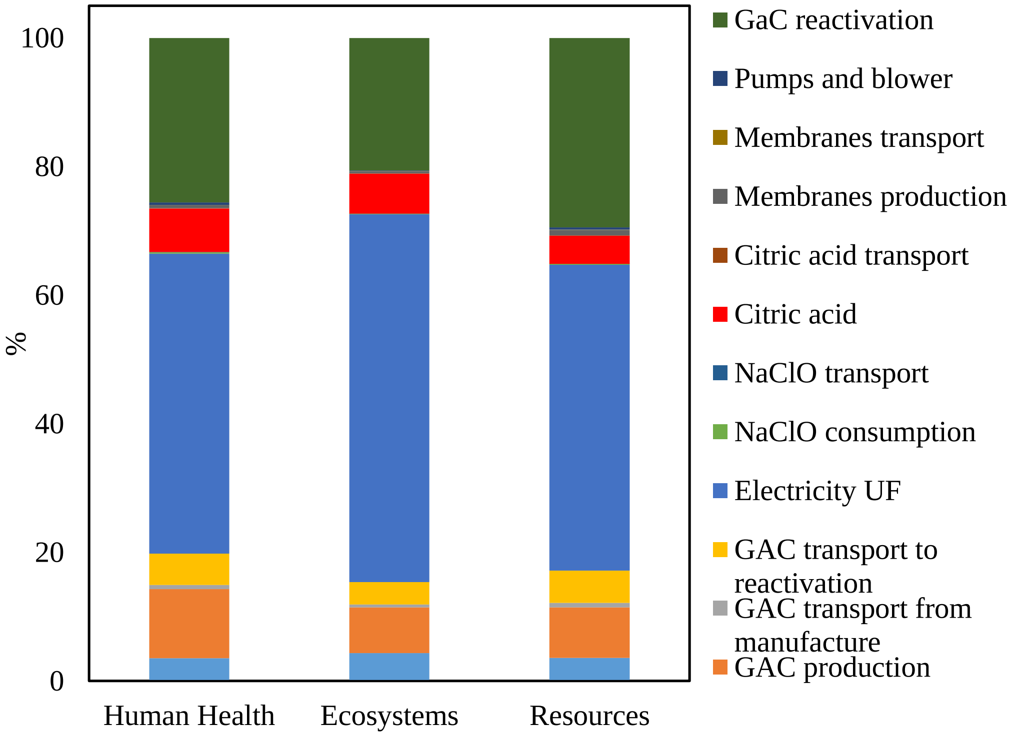


Figure 32 : Endpoint life cycle impact of BAC-UF process (OPTION 2 : with GAC regeneration) for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

Since GAC reactivation accounted for a significant share on the overall environmental assessment analysis, the alternative of using fresh material after every breakthrough event, has also been investigated. In this scenario, the disposal of spent GAC was also included in the LCI. During operation according to OPTION 2A, the major contribution was given by GAC production (46.7%) followed by electricity (36.9%), transport (7%), and citric acid consumption (4.5%) (Figure 33). The relevant negative contribution caused by the routine replacement of spent GAC with fresh material, changes the weights of the two processes; BAC and UF if compared with the outcomes from OPTION 1. With this regard, by separating the impact of these two processes, we obtained the opposite result of the analysis carried out during OPTION 1 operation, which implied GAC regeneration. Figure 34 shows the impact of these two processes. It is evident that BAC has a greater impact than UF, with the exception of ozone depletion. During the end-point analysis, as expected, the findings of the mid-point evaluation have been confirmed. Hence, human health, ecosystems and resources were mostly affected by GAC production, and only secondly impacted by the electricity consumption (Figure 35).

Whilst the above described differentiation between BAC and UF, the environmental sustainability assessment of this technology as a whole, allowed to conclude that the impact on climate change (CG), ozone depletion (OD), terrestrial acidification (TA), human toxicity (HT) and fossil depletion (FD) was calculated to be 0.371 kg CO_2 eq., 6.6 X 10^{-8} kg CFC-11 eq., 1.03 x 10^{-3} kg SO_2 eq., 0.070 kg 1.4 DB eq. and 0.108 kg of oil eq.; respectively. For all these five major categories, the process contributing the most was electricity whose percentage contribution was 49.1%, 67.9%, 31.3%, 48.2% and 47.5%, respectively for CG, OD, TA, HT and FD (Figure 33). As stated before, GAC reactivation was the second largest impacting contributor with specific percentages of 27.4%, 16.6%, 27.2%, 13% and 30.2%, respectively for CG, OD, TA, HT and FD (Figure 33).

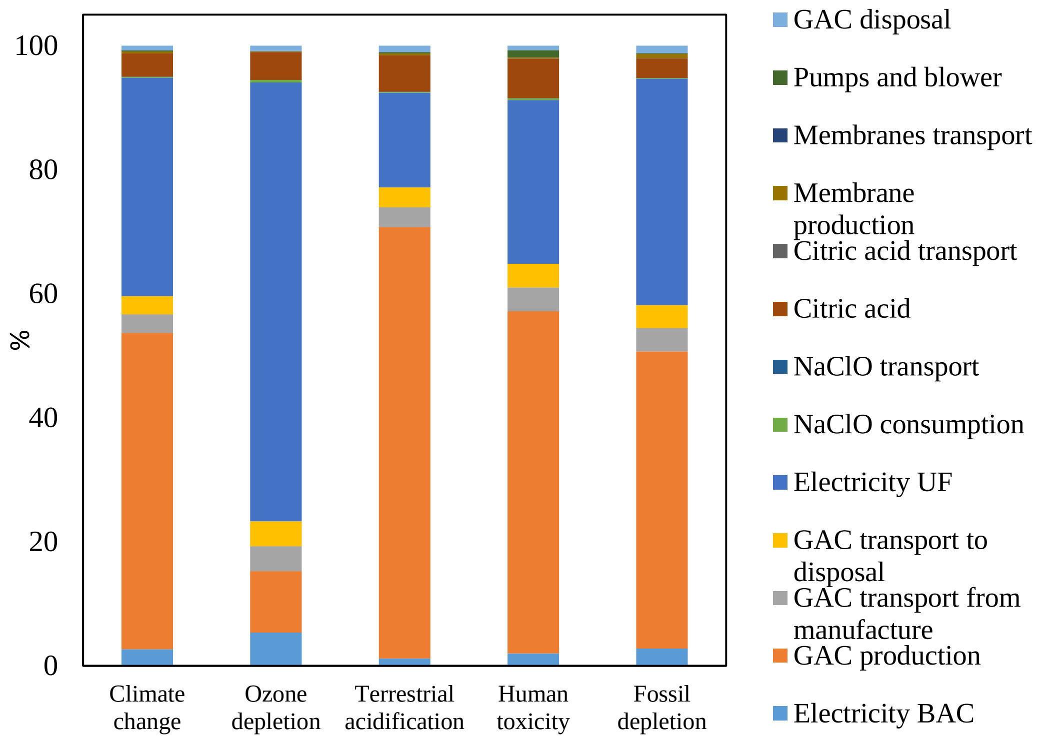


Figure 33 : Midpoint life cycle impact of BAC-UF process (OPTION 2 : without GAC regeneration) for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

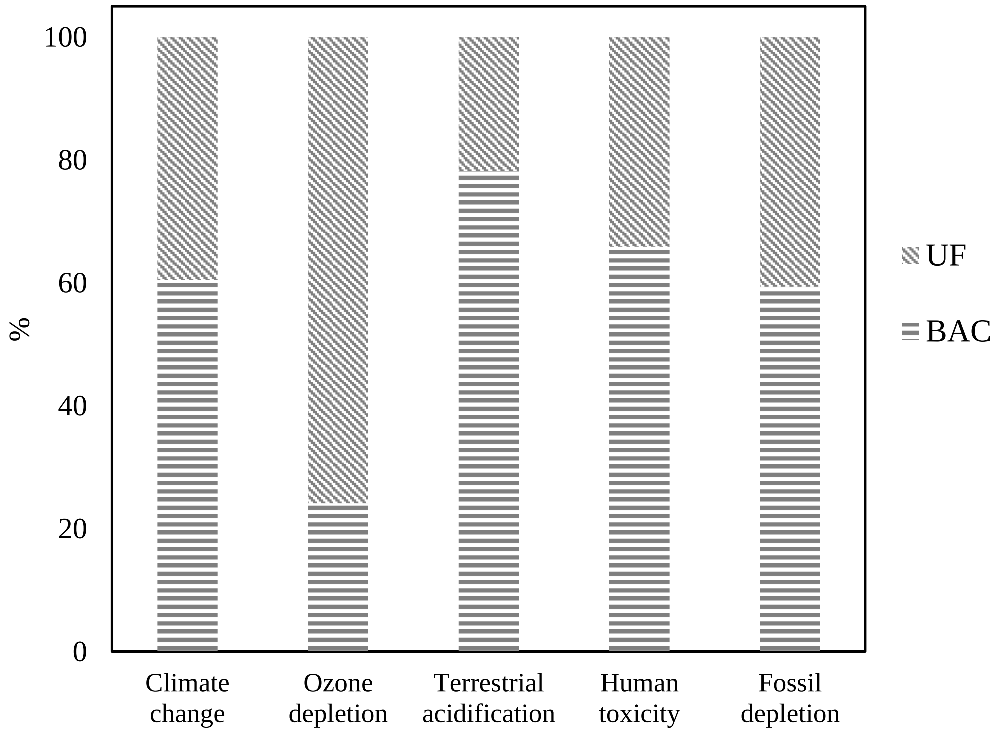


Figure 34 : Midpoint life cycle impact of BAC (OPTION 2 : without GAC regeneration) and UF processes, considered separately, for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

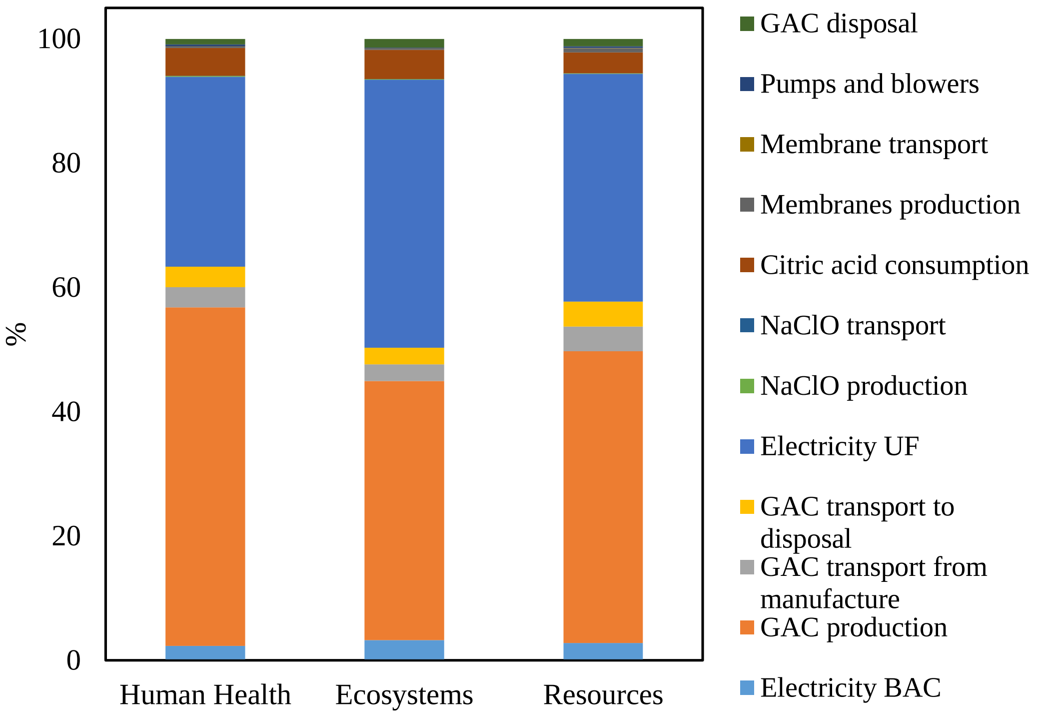


Figure 35 : Endpoint life cycle impact of BAC-UF process (OPTION 2 : without GAC regeneration) for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

3.5.2 Impact assessment : sulfate based AOPs

UV/PDS technology

The application of the UV/PDS technology to remove PhACs from urban wastewater effluent was associated to an environmental impact mainly caused by PDS production (52.9%) (Figure 36). The second factor with the most relevant contribution was electricity consumption (33.4%), followed by the impacts associated to the UV lamp production (7%) and the transport of all chemicals and materials used (4.9%) (Figure 36). PDS production presented the greatest impact on TA, HT and FD, while electricity was the main factor impacting CG. The total climate change impact was quantified as 0.424 kg/CO_2 eq., of which the 45% is due to electricity, and the 40% is caused by the production of the oxidizing agent. The remaining two factors having a non-negligible contribution were the UV-C reactor production (7.4%) and the emissions related to the transportation of the main construction materials and chemical reagents (5.6%). With respect to ozone depletion, the total emission was calculated to be 1.00 x 10^{-7} kg/CFC-11 eq. In this case, the effect provoked by PDS production and electricity was of the same amount; 46.8% and 46.6% respectively. Terrestrial acidification was impacted by 2.08 x 10^{-3} kg/SO_2 eq., of which 69.5% was caused by the production of PDS, while electricity in this case only accounted for the 16.2% of the total amount of kg/SO_2 equivalent. As for CG and OD, smaller contribution was given by UV-C reactor fabrication (7.7%) and transport of materials (5%). The emission of 0.199 kg of

1.4-DB eq. was the impact on human toxicity associated to the UV/PDS process. Also for this category, the major input was given by the chemical production (62.3%) and electricity (17.8%) with proportion similar to the case of TA. Finally, the 0.131 kg of oil equivalent, representative of the fossil depletion were mostly the consequence of PDS production (45.2%) and electricity (41.2%), while only a minor impact resulted from UV-C reactor production (5.8%) and transportation (6.2%). Köhler et al. (2012) demonstrated that H_2O_2 had a greater impact than electricity to remove PhACs from biologically pre-treated hospital wastewater [96]. On the other hand, the great footprint referred to electricity consumption was also observed by de Oliveira Schwaickhardt et al. (2017) during the UV-C irradiation of hospital laundry wastewater [185].

When endpoint evaluation was considered, the findings of the midpoint analysis were confirmed. In fact, considering the three impact categories of HH, ED and RA, PDS production and electricity confirmed their relevance, with 41.3% and 43.7% respectively (Figure 37). Similarly, also UV-C reactor production and transport of materials maintained their percent contribution (7.9% and 5.4% respectively).

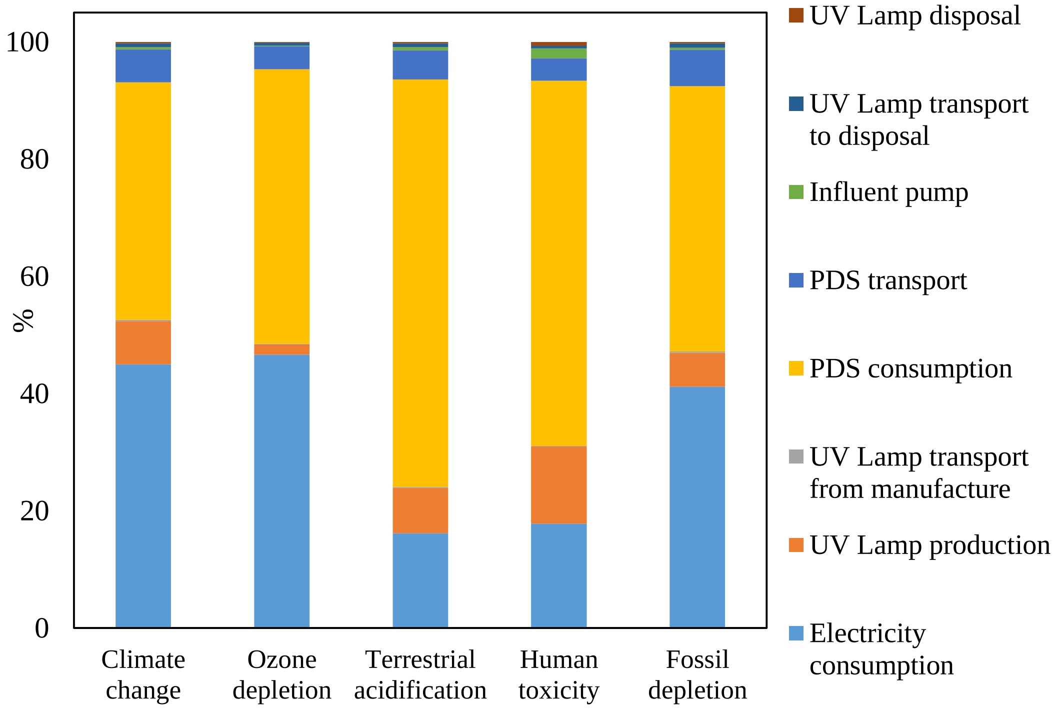


Figure 36 : Midpoint life cycle impact of UV/PDS process for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

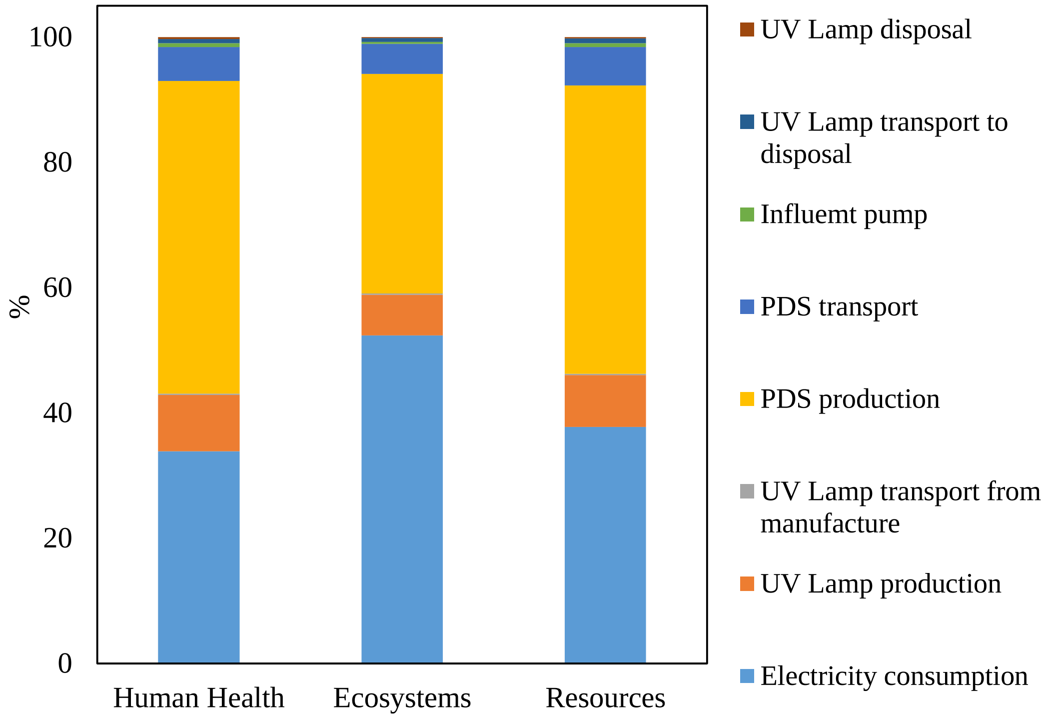


Figure 37 : Endpoint life cycle impact of UV/PDS process for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

UV/PMS technology

The scenario changes drastically when PMS was used as oxidizing agent. From Figure 38 it is indeed visible that PMS production accounted for 85% of the total impact while the second factor, the electricity, only was responsible for the 11.2%. The effect of the other factors is hidden by these two elements. The total environmental impacts regarding the five chosen midpoint categories were 1.569 kg CO_2 eq., 1.63 X 10^{-7} kg CFC-11 eq., 9.49 x 10^{-3} kg SO_2 eq., 0.797 kg 1.4 DB eq. and 0.471 kg of oil eq.; respectively for CG, OD, TA, HT and FD. The respective percentages ascribable to PMS production were 85.01%, 69.7%, 93.7%, 91% and 85.8%, respectively for CG, OD, TA, HT and FD. On the other hand, the difference with UV/PDS process can be observed by the smaller impact of the electricity usage which indeed accounted only for 11.3%, 26.6%, 3.3%, 4.1% and 10.6%, for CG, OD, TA, HT and FD respectively. Hence, the environmental sustainability of this technology was compromised by the chemicals and the processes related to the production of PMS. However, it is important to remind that peroxymonosulfate (purchased as Oxone ®) it is not available in SimaPro, then in order to calculate the impacts associated to it, we considered the fabrication process of this compound and the chemical reagents used during the process itself; namely: (sulfuric acid, hydrogen peroxide and potassium hydroxide). Assessing the environmental impact from a more general perspective, thus considering the endpoint categories: HH, ED and RA, the outcomes of the analysis confirmed the findings obtained with the midpoint assessment. In this scenario, the percentages were almost the same of the midpoint evaluation, e.i. 85.2% and 10.8% respectively for PMS production and electricity (Figure 39).

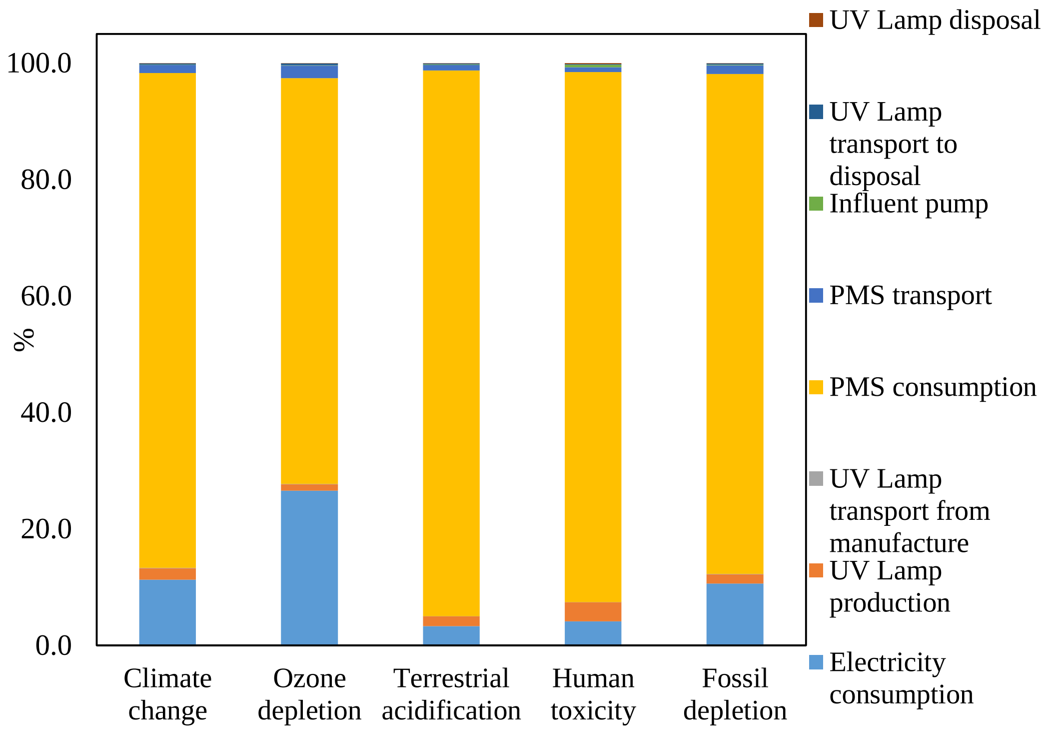


Figure 38 : Midpoint life cycle impact of UV/PMS process for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

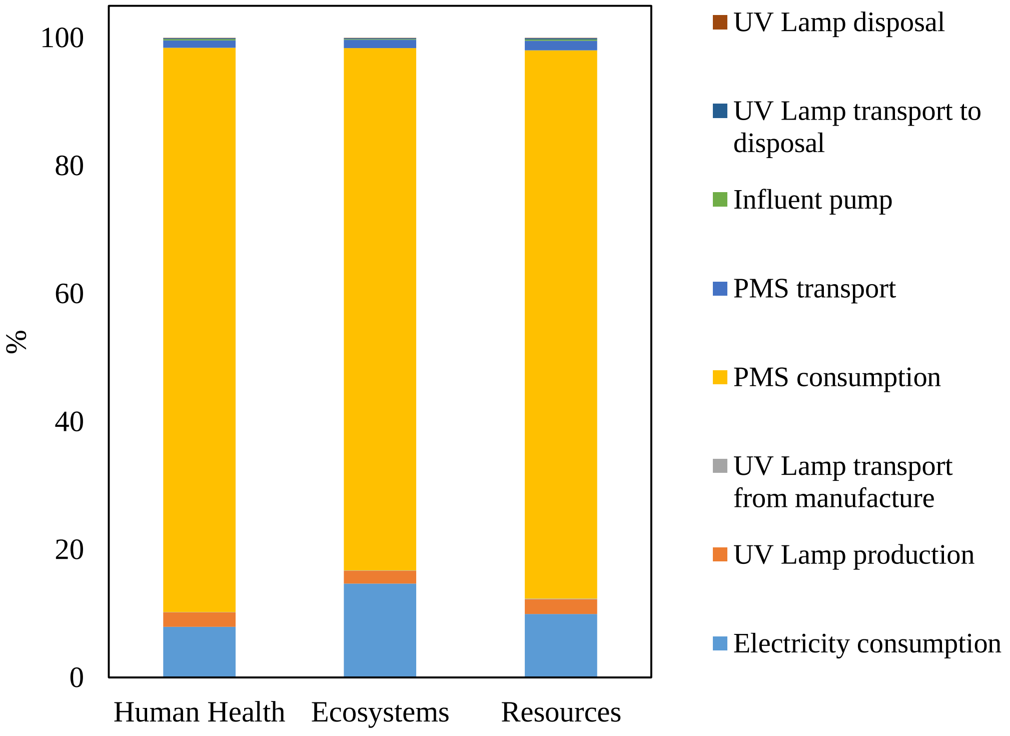


Figure 39 : Endpoint life cycle impact of UV/PMS process for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

Limitations of LCA tool for the assessment of toxicity-related impacts

Environmental impacts assessed with LCA are considered as "potential" impacts rather than actual impacts or risks. This is because the calculated emissions are not specified neither in space nor in time [186]. As a consequence, the results indicate the potential impact of the studied alternatives, from a life cycle perspective. Another limitation refers to leaving out of the assessment one or more critical substances, such as transformation products of oxidative treatments. It can be the case that a parent compound is degraded during the treatment, but a more toxic compound appears; if the latter is not analyzed in the samples or taken into account in the LCA, its impact will be omitted. This is important since previous studies have shown that the degradation products may increase ecotoxicity of wastewater treated with AOPs [187]. Furthermore, the fact that impacts in LCA are obtained as the sum of individual contributions from substances, implies that synergistic and antagonistic effects are not taken into account. These are indeed limitations of LCA as compared to toxicity assays, since the latter reflect the integrated effect of all substances present in water [188,189]. Another critical point is that terrestrial ecotoxicity of PhACs is not included in the evaluation [190]. According to these facts, it has to be observed that LCA addresses only part of the problem of PhACs treatment. Due to that, the evaluation of advanced treatment technologies should be coupled with additional analysis, such as toxicity assessments, in order to shed light to possibly hidden benefits or drawbacks of a specific technological option.

3.5.3 Comparison of environmental sustainability

From a general comparison point of view, in the previous sections, it resulted that for most of the studied criteria, the "use phase" is globally the most impacting, although for some criteria like metal resources exhaustion, the "construction phase" of the pilots is the major contributor, depending on the nature of the materials used. Given the individual environmental sustainability analysis carried out for the three advanced treatment options, a comparative analysis of the environmental footprint associated to each technology has been determined using ReCiPe impact assessment method. Figure 40 shows the comparison between the studied technologies. The main evidence is that BAC-UF process, with regeneration/reactivation of spent GAC particles, had the lowest impact for all the midpoint categories considered (CG, OD, TA, HT and FD). However, if the regeneration is not the chosen option, then UV/PDS gains advantages over BAC-UF. In fact, in this scenario, the technology based on the UV-C activation of PDS had lower emissions of kg CO_2 eq., kg SO_2 eq. and kg of oil eq., compared with BAC-UF process (Figure 40). On the other hand, OD and HT were more impacted from UV/PDS than BAC-UF. It is important to remind that either these two processes have the potential for being optimized in several ways. For example, increasing life-time of BAC and enhancing the role of the UF, could result in more efficient performance of the BAC-UF, whereas decreasing the amount of PDS used during the oxidation process, will have a positive effect on the environmental sustainability of UV/PDS. Nevertheless, under the actual conditions, these two processes were associated, on average, with similar environmental footprints. Tarpani and Azapagic (2018) [98] observed a similar impact for GAC and solar photo fenton for categories such as climate change. Yet, from the overall evaluation, GAC resulted to be more sustainable than the AOP assessed by these authors. This comparison provides further evidences confirming the doubtfully sustainability of UV/PMS process, mostly due to the great impact resulting from PMS production. Nevertheless, Baresel et al. (2015) demonstrated that higher environmental impacts caused by higher quality targets attainable with more advanced treatment processes become less significant when increasing plant size [90]. Accordingly precautions must be taken depending on whether the data come from a pilot-scale study; they could overestimate the impacts [90,191]. Results provided by the single-score-endpoint analysis for the proposed technologies (Figure 41), show that BAC-UF with spent GAC regeneration yielded the lowest environmental footprint of 34.4 mpt per functional unit. This overall footprint was almost equally divided into the three endpoint categories with 13.4 mpt, 12 mpt and 9 mpt respectively for HH, RA and ED. The presented data also allowed to conclude that UV/PDS and BAC-UF without GAC regeneration was characterized by a similar environmental footprint, scoring 45.4 mpt and 48 mpt respectively. With regard to these two technologies, the greatest footprint was registered to be on HH with 19.3 mpt for UV/PDS and 20.4 mpt for BAC-UF (Figure 41). “Human Health” damage is affected by fossil-fuel mining and combustion, which release toxic materials including metals, sulphur, and polycyclic aromatic hydrocarbons to the environment. Fossil-fuel extraction also releases SO_2. Impacts from coal arise from tailpipe emissions after combustion and emissions during blasting at coal mines. The total of 166.4 mpt scored by the UV/PMS suggest that this process is by far the one yielding the highest environmental footprints (Figure 41).

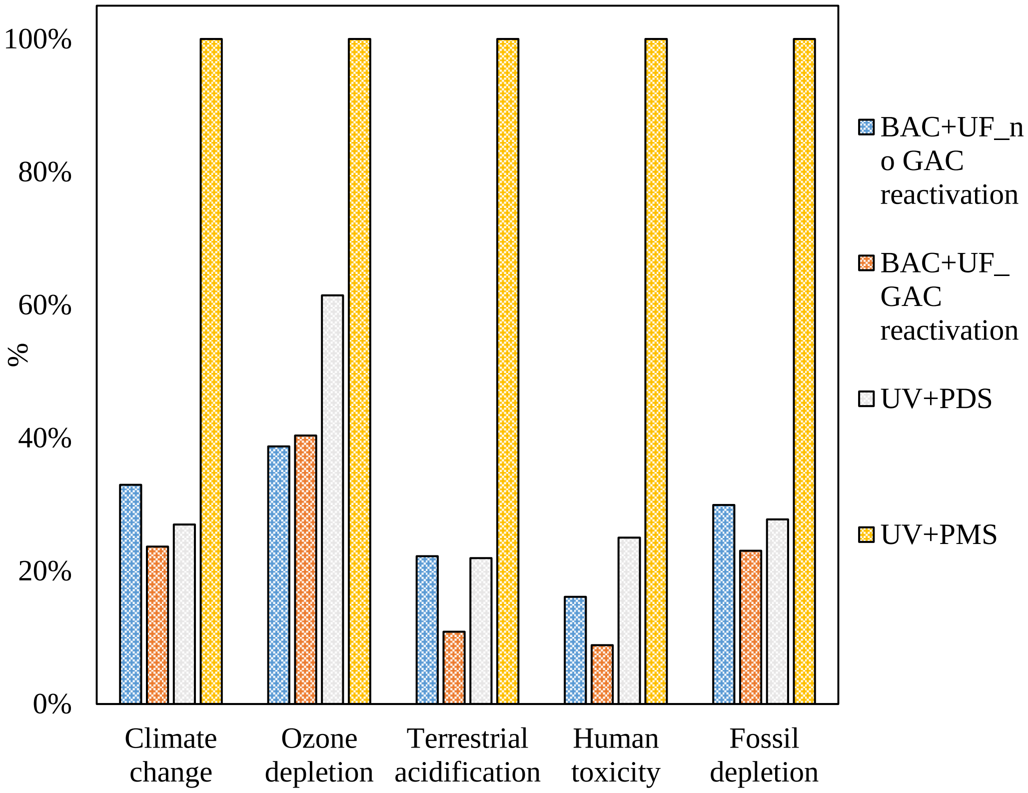


Figure 40 : Midpoint life cycle impact of the advanced treatment technologies for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

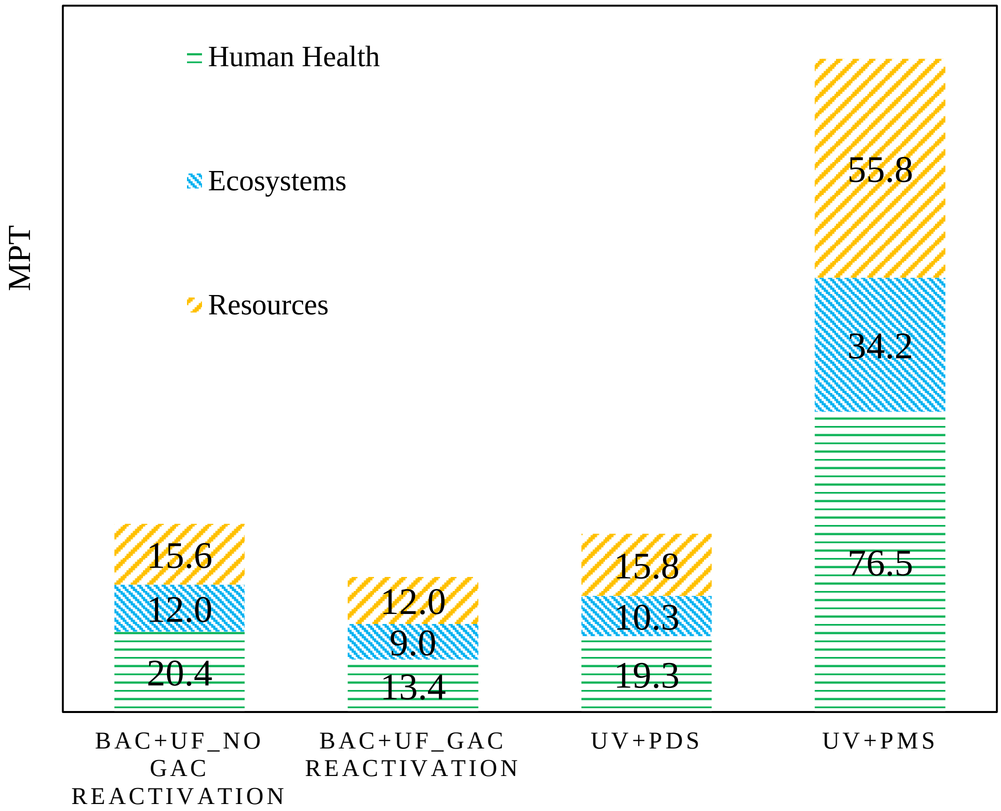


Figure 41 : ReCiPe's normalized endpoint life cycle impact of the advanced treatment technologies for 80% average PhACs removal. All impacts are expressed for 1m³ of treated wastewater.

Conclusions

The present thesis investigated the applicability of alternative advanced treatments for the removal of pharmaceutical active compounds from WWTPs secondary effluent.

The first technology to be studied was a biological activated carbon filter coupled with an ultrafiltration step (BAC-UF). This process was evaluated during one year of operation of a pilot plant treating the secondary effluent of a WWTP containing PhACs at environmentally relevant concentrations. Since this process is mainly based on two removal mechanisms, adsorption and biodegradation, a complementary lab-scale study was performed to shed light on the respective contribution of these two mechanisms (**Chapter 4**).

The second technology to be investigated was a UV-C driven advanced oxidation processes (AOP) based on photolytic decomposition of sulfate-containing oxidants: peroxydisulfate (PDS) and peroxymonosulfate (PMS). A series of lab-scale experiments were previously performed aiming at obtaining removal and kinetic values with real wastewater effluent which is key for the following scale-up procedure. This preliminary investigation was then complemented with a set of experiments designed in order to assess the interference of several factors typical of urban wastewater effluents. The previously obtained results were then corroborated at pilot-scale (**Chapter 5**).

As an industrial research project, the proposed advanced treatments were not only evaluated in terms of removal efficiencies, but also with respect to their energy consumption and the operating cost required for their effective application (with respect to a 80% average PhACs removal). However, to assess the sustainability of a given technology, technical and economic feasibility assessments should also be coupled with environmental considerations. In this context, the life cycle assessment impact for each studied technique has been conducted (**Chapter 6**).

A summary of the main conclusions for each Chapter of the thesis is presented below:

Chapter 4

- The current work shows how a BAC-UF pilot plant can be operated over the long term as a stand-alone tertiary treatment. With regard to PhACs abatement in WWTP effluents, the implementation of this technology allowed for 78, 89, 83 and 79% removal of antibiotics, beta-blockers, psychiatric drugs and a mix of other therapeutic groups, respectively.

- The long-term evaluation highlighted how these high levels of removal are time dependent. The high removal levels were reached and maintained during the first 9,200 bed volumes (BV) of operation. Subsequently, however, the performance of the system diminished due to the saturation of the adsorption capacity. Therefore, actions should be taken to ensure a consistent abatement level.

- Azithromycin, a commonly used antibiotic included in the EU Watch List of emerging contaminants, and five other PhACs (bezafibrate, ofloxacin, irbesartan, propranolol and ciprofloxacin) have been studied for the first time in BAC filtration systems. During BAC filtration of secondary effluent, removals of 63, 67, 77, 79, 83 and 86% were obtained for azithromycin, bezafibrate, ofloxacin, irbesartan, propranolol and ciprofloxacin, respectively.

- Adsorption onto GAC was proven to be the main PhACs removal mechanism in BAC filters. Nevertheless, the biological activity characterizing the BAC filter contributed to reach higher removal efficiencies for five compounds in the BAC filter than in conventional abiotic GAC filters. The removal improvements were 22, 25, 30, 32 and 35% for ciprofloxacin, bezafibrate, ofloxacin, azithromycin and sulfamethoxazole, respectively.

Chapter 5

- Both the PhACs removal percentages and the fluence-based degradation rate constants of UV/PDS and UV/PMS technologies resulted to be compound-specific. Removal efficiencies ranged between 40% and 100% for both systems, while K_{obs} varied in the ranges of 0.6 – 6.2 cm^2/J and 1.1 – 20.4 cm^2/J for UV/PDS and UV/PMS, respectively. No pH adjustments were needed.

- On the other hand, the presence of higher concentrations of inorganic anions produced varying effects on kinetics and degradation efficiencies. In particular, increasing chloride and nitrate concentration did not alter the oxidation capacity of UV/PDS and UV/PMS in terms of removal efficiency, but affected K_{obs} values. More bicarbonates allowed for faster degradation kinetics and greater removal values. On the contrary, the high competition between PhACs and effluent organic matter (EfOM) decreased the efficiencies of both processes.

- The pilot plant investigation demonstrates that sulfate based-AOPs are applicable to remove PhACs from municipal wastewater effluents, reaching 84% and 85% removal respectively for

UV/PDS and UV/PMS. These values were obtained with 416 mJ/cm² of UV fluence and 0.4 mM of oxidant. Direct photolysis only had a minor role in PhACs degradation.

- UV/PMS proved to be more energy efficient than UV/PDS, even though in the range 0.5 – 0.7 kWh/m³, both processes were able to reach removal efficiencies greater than 70%.

- The calculated electrical energy per order (EEO) were : UV/PMS (0.8 kWh/m³/order) < UV/PDS (0.9 kWh/m³/order) < UV alone (5.3 kWh/m³/order).

Chapter 6

- From the operating cost comparison, UV/PDS resulted to have the lowest operating cost (0.14 €/m³), followed by BAC-UF process (0.18 €/m³) and then by UV/PMS (0.32 €/m³). In the case of BAC-UF, the most relevant contribution was given by purchase of GAC and energy required for the pilot plant operation. With regard to sulfate based-AOPs, the costs were primarily determined by the energy demand of the UV-C reactor and by the oxidant demand.

- The life cycle assessment impact of the BAC-UF process indicates the most impacting factors being as follows : electricity consumption (50.5%) > GAC reactivation (25.2%) > citric acid consumption (8.6%) > GAC production (5.8%) > transport (4.5%). The impact on climate change, ozone depletion, terrestrial acidification, human toxicity and fossil depletion was calculated to be 0.371 kg CO_2 eq., 6.6 X 10^{-8} kg CFC-11 eq., 1.03 x 10^{-3} kg SO_2 eq., 0.070 kg 1.4 DB eq. and 0.108 kg of oil eq.; respectively. In this context, GAC reactivation is associated with a smaller environmental footprint than using fresh material after every breakthrough event.

- The two main factors with the greatest environmental footprint for UV/PDS process were PDS production (52.9%) and electricity consumption (33.4%). Only a smaller impact was associated to the UV lamp production (7%) and the transport of all chemicals and materials used (4.9%). The total climate change impact was quantified as 0.424 kg/CO_2 eq. With respect to ozone depletion, the total emission was calculated to be 1.00 x 10^{-7} kg/CFC-11 eq. Terrestrial acidification was impacted by 2.08 x 10^{-3} kg/SO_2 equivalent. The emission of 0.199 kg of 1.4-DB eq. was the impact on human toxicity and 0.131 kg of oil equivalent represented fossil depletion.

- The PMS production accounted for 85% of the total environmental impact of UV/PMS while the second factor, the electricity, only was responsible for the 11.2%. The total environmental impacts regarding the five chosen midpoint categories (climate change, ozone depletion, terrestrial acidification, human toxicity and fossil depletion) were 1.569 kg CO_2 eq., 1.63 X 10^{-7} kg CFC-11 eq., 9.49 x 10^{-3} kg SO_2 eq., 0.797 kg 1.4 DB eq. and 0.471 kg of oil eq., respectively.

- The environmental impact provided by the single-score-endpoint analysis for the proposed technologies (calculated for 1m³ of treated wastewater with 80% average PhACs removal) showed that BAC-UF yielded the lowest environmental footprint of 34.4 mpt, UV/PDS was characterized by an environmental footprint of 45.4 mpt and, finally, UV/PMS significantly exceed the score of the previous ones with 166.4 mpt.

References

[1] J.C. Pasqualino, M. Meneses, F. Castells, Life Cycle Assessment of Urban Wastewater Reclamation and Reuse Alternatives, J. Ind. Ecol. 15 (2011) 49–63. doi:10.1111/j.1530-9290.2010.00293.x.

[2] D. Fatta-Kassinos, C. Manaia, T.U. Berendonk, E. Cytryn, J. Bayona, B. Chefetz, J. Slobodnik, N. Kreuzinger, L. Rizzo, S. Malato, L. Lundy, A. Ledin, COST Action ES1403: New and Emerging challenges and opportunities in wastewater REUSe (NEREUS), Environ. Sci. Pollut. Res. 22 (2015) 7183–7186. doi:10.1007/s11356-015-4278-0.

[3] L.H. Leal, N. Vieno, H. Temmink, G. Zeeman, C.J.N. Buisman, Occurrence of xenobiotics in gray water and removal in three biological treatment systems, Environ. Sci. Technol. 44 (2010) 6835–6842. doi:10.1021/es101509e.

[4] JRC, Minimum quality requirements for water reuse in agricultural irrigation and aquifer recharge - Towards a water reuse regulatory instrument at EU level, 2017. doi:10.2760/887727.

[5] M. Meneses, J.C. Pasqualino, F. Castells, Environmental assessment of urban wastewater reuse: Treatment alternatives and applications, Chemosphere. 81 (2010) 266–272. doi:10.1016/j.chemosphere.2010.05.053.

[6] J.E. Drewes, T. Heberer, K. Reddersen, Fate of pharmaceuticals during indirect potable reuse, Water Sci. Technol. 46 (2002) 73–80.

[7] A. Gózd-Barszczewska, M. Kozioł-Montewka, A. Sikora, P. Barszczewski, M. Kozioł, Rola mikroflory jelitowej w patogenezie otyłošci i chorób kardiologicznych, Int. Rev. Allergol. Clin. Immunol. 20 (2014) 95–100. doi:10.1007/698.

[8] X. Garcia, D. Pargament, Reusing wastewater to cope with water scarcity: Economic, social and environmental considerations for decision-making, Resour. Conserv. Recycl. 101 (2015) 154–166. doi:10.1016/j.resconrec.2015.05.015.

[9] N. Le-Minh, S.J. Khan, J.E. Drewes, R.M. Stuetz, Fate of antibiotics during municipal water recycling treatment processes, Water Res. 44 (2010) 4295–4323. doi:10.1016/j.watres.2010.06.020.

[10] EEA - European Environment Agency, Resource-efficient green economy and EU policies, 2014. doi:10.2800/18514.

[11] J. Rivera-Utrilla, M. Sánchez-Polo, M.Á. Ferro-García, G. Prados-Joya, R. Ocampo-Pérez, Pharmaceuticals as emerging contaminants and their removal from water. A review, Chemosphere. 93 (2013) 1268–1287. doi:10.1016/j.chemosphere.2013.07.059.

[12] D. Dolar, M. Gros, S. Rodriguez-Mozaz, J. Moreno, J. Comas, I. Rodriguez-Roda, D. Barceló, Removal of emerging contaminants from municipal wastewater with an integrated membrane system, MBR-RO, J. Hazard. Mater. 239–240 (2012) 64–69. doi:10.1016/j.jhazmat.2012.03.029.

[13] V. Osorio, M. Imbert-Bouchard, B. Zonja, J.L. Abad, S. Pérez, D. Barceló, Simultaneous determination of diclofenac, its human metabolites and microbial nitration/nitrosation transformation products in wastewaters by liquid chromatography/quadrupole-linear ion trap mass spectrometry, J. Chromatogr. A. 1347 (2014) 63–71. doi:10.1016/j.chroma.2014.04.058.

[14] C.G. Daughton, I.S. Ruhoy, Environmental footprint of pharmaceuticals: the significance of factors beyond direct excretion to sewers., Environ. Toxicol. Chem. 28 (2009) 2495–2521. doi:10.1897/08-382.1.

[15] M. Carballa, F. Omil, J.M. Lema, M. Llompart, C. García-Jares, I. Rodríguez, M. Gómez, T. Ternes, Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant, Water Res. 38 (2004) 2918–2926. doi:10.1016/j.watres.2004.03.029.

[16] A. Joss, E. Keller, A.C. Alder, A. Göbel, C.S. McArdell, T. Ternes, H. Siegrist, Removal of pharmaceuticals and fragrances in biological wastewater treatment, Water Res. 39 (2005) 3139–3152. doi:10.1016/j.watres.2005.05.031.

[17] European Commission, Commission Implementing Regulation (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council, Off. J. Eur. Union. L78/40 (2015) 20–30. doi:http://eur-lex.europa.eu/pri/en/oj/dat/2003/l_285/l_28520031101en00330037.pdf.

[18] R.N. Carvalho, L. Ceriani, A. Ippolito, T. Lettieri, Development of the first Watch List under the Environmental Quality Standards Directive, 2015. doi:10.2788/101376.

[19] P. Verlicchi, M. Al Aukidy, E. Zambello, Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment-A review, Sci. Total Environ. 429 (2012) 123–155. doi:10.1016/j.scitotenv.2012.04.028.

[20] D. Serrano, S. Suárez, J.M. Lema, F. Omil, Removal of persistent pharmaceutical micropollutants from sewage by addition of PAC in a sequential membrane bioreactor, Water Res. 45 (2011) 5323–5333. doi:10.1016/j.watres.2011.07.037.

[21] Y. Luo, W. Guo, H.H. Ngo, L.D. Nghiem, F.I. Hai, J. Zhang, S. Liang, X.C. Wang, A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, Sci. Total Environ. 473–474 (2014) 619–641. doi:10.1016/j.scitotenv.2013.12.065.

[22] A. Jelic, M. Gros, A. Ginebreda, R. Cespedes-Sánchez, F. Ventura, M. Petrovic, D. Barcelo, Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment, Water Res. 45 (2011) 1165–1176. doi:10.1016/j.watres.2010.11.010.

[23] D.N. Bulloch, E.D. Nelson, S.A. Carr, C.R. Wissman, J.L. Armstrong, D. Schlenk, C.K. Larive, Occurrence of halogenated transformation products of selected pharmaceuticals and personal care products in secondary and tertiary treated wastewaters from Southern California, Environ. Sci. Technol. 49 (2015) 2044–2051. doi:10.1021/es504565n.

[24] S.K. Behera, H.W. Kim, J.E. Oh, H.S. Park, Occurrence and removal of antibiotics, hormones

and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea, Sci. Total Environ. 409 (2011) 4351–4360. doi:10.1016/j.scitotenv.2011.07.015.

[25] M.J. García Galán, M.S. Díaz-Cruz, D. Barceló, Removal of sulfonamide antibiotics upon conventional activated sludge and advanced membrane bioreactor treatment, Anal. Bioanal. Chem. 404 (2012) 1505–1515. doi:10.1007/s00216-012-6239-5.

[26] B. Drury, J. Scott, E.J. Rosi-Marshall, J.J. Kelly, Triclosan exposure increases triclosan resistance and influences taxonomic composition of benthic bacterial communities, Environ. Sci. Technol. 47 (2013) 8923–8930. doi:10.1021/es401919k.

[27] H. V. Lubarsky, S.U. Gerbersdorf, C. Hubas, S. Behrens, F. Ricciardi, D.M. Paterson, Impairment of the bacterial biofilm stability by triclosan, PLoS One. 7 (2012). doi:10.1371/journal.pone.0031183.

[28] D.F.-K. K.Kummerer, D.D. Dionysiou, Advanced Treatment Technologies for Urban Wastewater Reuse, Hdb Environ. Chem. 45 (2016) 291–300. doi:10.1007/698.

[29] J. Rivera-Utrilla, M. Sánchez-Polo, M.Á. Ferro-García, G. Prados-Joya, R. Ocampo-Pérez, Pharmaceuticals as emerging contaminants and their removal from water. A review, Chemosphere. 93 (2013) 1268–1287. doi:10.1016/j.chemosphere.2013.07.059.

[30] S.O. Ganiyu, E.D. Van Hullebusch, M. Cretin, G. Esposito, M.A. Oturan, Coupling of membrane filtration and advanced oxidation processes for removal of pharmaceutical residues: A critical review, Sep. Purif. Technol. 156 (2015) 891–914. doi:10.1016/j.seppur.2015.09.059.

[31] J.E. Drewes, M. Reinhard, P. Fox, Comparing microfiltration-reverse osmosis and soil-aquifer treatment for indirect potable reuse of water, Water Res. 37 (2003) 3612–3621. doi:10.1016/S0043-1354(03)00230-6.

[32] B. Van Der Bruggen, L. Lejon, C. Vandecasteele, Reuse, treatment, and discharge of the concentrate of pressure-driven membrane processes, Environ. Sci. Technol. 37 (2003) 3733–3738. doi:10.1021/es0201754.

[33] F.I. Hai, K. Tessmer, L.N. Nguyen, J. Kang, W.E. Price, L.D. Nghiem, Removal of micropollutants by membrane bioreactor under temperature variation, J. Memb. Sci. 383 (2011) 144–151. doi:10.1016/j.memsci.2011.08.047.

[34] Y. Yoon, P. Westerhoff, S.A. Snyder, E.C. Wert, J. Yoon, Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes, Desalination. 202 (2007) 16–23. doi:10.1016/j.desal.2005.12.033.

[35] U. Von Gunten, Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine, Water Res. 37 (2003) 1469–1487. doi:10.1016/S0043-1354(02)00458-X.

[36] K. Ikehata, N. Jodeiri Naghashkar, M. Gamal El-Din, Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: A review, Ozone Sci. Eng. 28 (2006) 353–414. doi:10.1080/01919510600985937.

[37] S. Koepke, M. Krauss, C.S. Mcardell, Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-Scale Post-Ozonation Followed by Sand Filtration, 43 (2009) 7862–7869. doi:10.1021/es9014629.

[38] J. Margot, C. Kienle, A. Magnet, M. Weil, L. Rossi, L.F. de Alencastro, C. Abegglen, D. Thonney, N. Chèvre, M. Schärer, D.A. Barry, Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon?, Sci. Total Environ. 461–462 (2013) 480–498. doi:10.1016/j.scitotenv.2013.05.034.

[39] J. Reungoat, B.I. Escher, M. Macova, F.X. Argaud, W. Gernjak, J. Keller, Ozonation and biological activated carbon filtration of wastewater treatment plant effluents, Water Res. 46 (2012) 863–872. doi:10.1016/j.watres.2011.11.064.

[40] M. Bourgin, B. Beck, M. Boehler, E. Borowska, J. Fleiner, E. Salhi, R. Teichler, U. von Gunten, H. Siegrist, C.S. McArdell, 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 Res. 129 (2018) 486–498. doi:10.1016/j.watres.2017.10.036.

[41] W.T. Plants, Technology : Ozone Disinfection, (1998).

[42] F. Benstoem, A. Nahrstedt, M. Boehler, G. Knopp, D. Montag, H. Siegrist, J. Pinnekamp, Performance of granular activated carbon to remove micropollutants from municipal wastewater—A meta-analysis of pilot- and large-scale studies, Chemosphere. 185 (2017) 105–118. doi:10.1016/j.chemosphere.2017.06.118.

[43] K. Yapsakli, F. Çeçen, Effect of type of granular activated carbon on DOC biodegradation in biological activated carbon filters, Process Biochem. 45 (2010) 355–362. doi:10.1016/j.procbio.2009.10.005.

[44] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, Carbon N. Y. 42 (2004) 83–94. doi:10.1016/j.carbon.2003.09.022.

[45] M. Rattier, J. Reungoat, J. Keller, W. Gernjak, Removal of micropollutants during tertiary wastewater treatment by biofiltration: Role of nitrifiers and removal mechanisms, Water Res. 54 (2014) 89–99. doi:10.1016/j.watres.2014.01.030.

[46] X.T. Bui, T.P.T. Vo, H.H. Ngo, W.S. Guo, T.T. Nguyen, Multicriteria assessment of advanced treatment technologies for micropollutants removal at large-scale applications, Sci. Total Environ. 563–564 (2016) 1050–1067. doi:10.1016/j.scitotenv.2016.04.191.

[47] M. Mulder, D. Antakyali, S. Ante, Costs of Removal of Micropollutants from Effluents of Municipal Wastewater Treatment Plants, STOWA and Waterboard the Dommel, The Netherlands. (2015) 55. http://www.tapes-interreg.eu/uploads/Stowa TAPES Final report.pdf.

[48] A.M. Kennedy, A.M. Reinert, D.R.U. Knappe, I. Ferrer, R.S. Summers, Full- and pilot-scale GAC adsorption of organic micropollutants, Water Res. 68 (2015) 238–248. doi:10.1016/j.watres.2014.10.010.

[49] C.O. Lee, K.J. Howe, B.M. Thomson, State of Knowledge of Pharmaceutical, Personal Care

Product, and Endocrine Disrupting Compound Removal during Municipal Wastewater Treatment, (2009) 284. doi:10.1007/10503050.

[50] J. Ann, Activated Carbon for Water and Wastewater Treatment Related Titles Ozonation of Water and Waste Water A Practical Guide to Understanding Ozone and its Applications, (2011).

[51] F. Fdz-Polanco, E. Méndez, M.A. Urueña, S. Villaverde, P.A. García, Spatial distribution of heterotrophs and nitrifiers in a submerged biofilter for nitrification, Water Res. 34 (2000) 4081–4089. doi:10.1016/S0043-1354(00)00159-7.

[52] J. Reungoat, B.I. Escher, M. Macova, J. Keller, Biofiltration of wastewater treatment plant effluent: Effective removal of pharmaceuticals and personal care products and reduction of toxicity, Water Res. 45 (2011) 2751–2762. doi:10.1016/j.watres.2011.02.013.

[53] M. Rattier, J. Reungoat, W. Gernjak, J. Keller, A. Joss, Investigating the role of adsorption and biodegradation in the removal of organic micropollutants during biological activated carbon filtration of treated wastewater, J. Water Reuse Desalin. 2 (2012) 127–139. doi:10.2166/wrd.2012.012.

[54] D. Zhang, W. Li, K. Wang, H. Gong, Bacterial community dynamics and its effects during biological activited carbon filter process for drinking water treatment, (2010) 0–5.

[55] Ç. Kalkan, K. Yapsakli, B. Mertoglu, D. Tufan, A. Saatci, Evaluation of Biological Activated Carbon (BAC) process in wastewater treatment secondary effluent for reclamation purposes, Desalination. 265 (2011) 266–273. doi:10.1016/j.desal.2010.07.060.

[56] S. Velten, M. Boller, O. Köster, J. Helbing, H.U. Weilenmann, F. Hammes, Development of biomass in a drinking water granular active carbon (GAC) filter, Water Res. 45 (2011) 6347–6354. doi:10.1016/j.watres.2011.09.017.

[57] A. Justo, O. González, C. Sans, S. Esplugas, BAC filtration to mitigate micropollutants and EfOM content in reclamation reverse osmosis brines, Chem. Eng. J. 279 (2015) 589–596. doi:10.1016/j.cej.2015.05.018.

[58] S. Zhang, S.W. Gitungo, L. Axe, R.F. Raczko, J.E. Dyksen, Biologically active filters – An advanced water treatment process for contaminants of emerging concern, Water Res. 114 (2017) 31–41. doi:10.1016/j.watres.2017.02.014.

[59] D. Gerrity, S. Gamage, J.C. Holady, D.B. Mawhinney, O. Quiñones, R.A. Trenholm, S.A. Snyder, Pilot-scale evaluation of ozone and biological activated carbon for trace organic contaminant mitigation and disinfection, Water Res. 45 (2011) 2155–2165. doi:10.1016/j.watres.2010.12.031.

[60] L. Paredes, E. Fernandez-Fontaina, J.M. Lema, F. Omil, M. Carballa, Understanding the fate of organic micropollutants in sand and granular activated carbon biofiltration systems, Sci. Total Environ. 551–552 (2016) 640–648. doi:10.1016/j.scitotenv.2016.02.008.

[61] D.B. Miklos, C. Remy, M. Jekel, K.G. Linden, J.E. Drewes, U. Hübner, Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review, Water Res. (2018). doi:10.1016/j.watres.2018.03.042.

[62] M.I. Stefan, Advanced Oxidation Processes for Water Treatment - *Fundamentals and Applications*, 2017. doi:10.2166/9781780407197.

[63] S. Giannakis, F.A. Gamarra Vives, D. Grandjean, A. Magnet, L.F. De Alencastro, C. Pulgarin, Effect of advanced oxidation processes on the micropollutants and the effluent organic matter contained in municipal wastewater previously treated by three different secondary methods, Water Res. 84 (2015) 295–306. doi:10.1016/j.watres.2015.07.030.

[64] L. Rizzo, S. Malato, D. Antakyali, V.G. Beretsou, M.B. Đolić, W. Gernjak, E. Heath, I. Ivancev-Tumbas, P. Karaolia, A.R. Lado Ribeiro, G. Mascolo, C.S. McArdell, H. Schaar, A.M.T. Silva, D. Fatta-Kassinos, Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater, Sci. Total Environ. 655 (2019) 986–1008. doi:10.1016/j.scitotenv.2018.11.265.

[65] D. Fatta-Kassinos, M.I. Vasquez, K. Kümmerer, Transformation products of pharmaceuticals in

surface waters and wastewater formed during photolysis and advanced oxidation processes - Degradation, elucidation of byproducts and assessment of their biological potency, Chemosphere. 85 (2011) 693–709. doi:10.1016/j.chemosphere.2011.06.082.

[66] H. V. Lutze, R. Bakkour, N. Kerlin, C. von Sonntag, T.C. Schmidt, Formation of bromate in sulfate radical based oxidation: Mechanistic aspects and suppression bydissolved organic matter, Water Res. 53 (2014) 370–377. doi:10.1016/j.watres.2014.01.001.

[67] USEPA, Wastewater Technology Fact Sheet - Disinfection for Small Systems, Water Technol. Fact Sheet. (2002).

[68] J.C. Kruithof, P.C. Kamp, B.J. Martijn, UV/H2O2 treatment: A practical solution for organic contaminant control and primary disinfection, Ozone Sci. Eng. 29 (2007) 273–280. doi:10.1080/01919510701459311.

[69] Y. Yang, J.J. Pignatello, J. Ma, W.A. Mitch, Comparison of halide impacts on the efficiency of contaminant degradation by sulfate and hydroxyl radical-based advanced oxidation processes (AOPs), Environ. Sci. Technol. 48 (2014) 2344–2351. doi:10.1021/es404118q.

[70] W. Yang, H. Zhou, N. Cicek, Treatment of organic micropollutants in water and wastewater by UV-based processes: A literature review, Crit. Rev. Environ. Sci. Technol. 44 (2014) 1443–1476. doi:10.1080/10643389.2013.790745.

[71] J. Wang, S. Wang, Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants, Chem. Eng. J. 334 (2018) 1502–1517. doi:10.1016/j.cej.2017.11.059.

[72] L. Lian, B. Yao, S. Hou, J. Fang, S. Yan, W. Song, Kinetic Study of Hydroxyl and Sulfate Radical-Mediated Oxidation of Pharmaceuticals in Wastewater Effluents, Environ. Sci. Technol. 51 (2017) 2954–2962. doi:10.1021/acs.est.6b05536.

[73] S. Yang, P. Wang, X. Yang, L. Shan, W. Zhang, X. Shao, R. Niu, Degradation efficiencies of azo dye Acid Orange 7 by the interaction of heat, UV and anions with common oxidants:

Persulfate, peroxymonosulfate and hydrogen peroxide, J. Hazard. Mater. 179 (2010) 552–558. doi:10.1016/j.jhazmat.2010.03.039.

[74] P. Hu, M. Long, Cobalt-catalyzed sulfate radical-based advanced oxidation: A review on heterogeneous catalysts and applications, Appl. Catal. B Environ. 181 (2016) 103–117. doi:10.1016/j.apcatb.2015.07.024.

[75] M.G. Antoniou, A.A. de la Cruz, D.D. Dionysiou, Degradation of microcystin-LR using sulfate radicals generated through photolysis, thermolysis and e-transfer mechanisms, Appl. Catal. B Environ. 96 (2010) 290–298. doi:10.1016/j.apcatb.2010.02.013.

[76] Y. Fu, X. Gao, J. Geng, S. Li, G. Wu, H. Ren, Degradation of three nonsteroidal anti-inflammatory drugs by UV/Persulfate: degradation mechanisms, efficiency in effluents disposal, Chem. Eng. J. (2018). doi:10.1016/J.CEJ.2018.08.013.

[77] J.M. Monteagudo, A. Durán, J. Latorre, A.J. Expósito, Application of activated persulfate for removal of intermediates from antipyrine wastewater degradation refractory towards hydroxyl radical, J. Hazard. Mater. 306 (2016) 77–86. doi:10.1016/j.jhazmat.2015.12.001.

[78] I. Michael-Kordatou, M. Iacovou, Z. Frontistis, E. Hapeshi, D.D. Dionysiou, D. Fatta-Kassinos, Erythromycin oxidation and ERY-resistant Escherichia coli inactivation in urban wastewater by sulfate radical-based oxidation process under UV-C irradiation, Water Res. 85 (2015) 346–358. doi:10.1016/j.watres.2015.08.050.

[79] M. Mahdi-Ahmed, S. Chiron, Ciprofloxacin oxidation by UV-C activated peroxymonosulfate in wastewater, J. Hazard. Mater. 265 (2014) 41–46. doi:10.1016/j.jhazmat.2013.11.034.

[80] M. Nihemaiti, D.B. Miklos, U. Hübner, K.G. Linden, J.E. Drewes, J.-P. Croué, Removal of trace organic chemicals in wastewater effluent by UV/H2O2 and UV/PDS, Water Res. (2018). doi:10.1016/J.WATRES.2018.08.052.

[81] E.A. Serna-Galvis, F. Ferraro, J. Silva-Agredo, R.A. Torres-Palma, Degradation of highly consumed fluoroquinolones, penicillins and cephalosporins in distilled water and simulated

hospital wastewater by UV254 and UV254/persulfate processes, Water Res. 122 (2017) 128–138. doi:10.1016/j.watres.2017.05.065.

[82] J. Rodríguez-Chueca, E. Laski, C. García-Cañibano, M.J. Martín de Vidales, Encinas, B. Kuch, J. Marugán, Micropollutants removal by full-scale UV-C/sulfate radical based Advanced Oxidation Processes, Sci. Total Environ. 630 (2018) 1216–1225. doi:10.1016/j.scitotenv.2018.02.279.

[83] J. Rodríguez-Chueca, C. García-Cañibano, R.J. Lepistö, Encinas, J. Pellinen, J. Marugán, Intensification of UV-C tertiary treatment: Disinfection and removal of micropollutants by sulfate radical based Advanced Oxidation Processes, J. Hazard. Mater. (2018) 0–1. doi:10.1016/j.jhazmat.2018.04.044.

[84] J. Rodríguez-Chueca, S.V. Della Giustina, J. Rocha, T. Fernandes, C. Pablos, Á. Encinas, D. Barceló, S. Rodríguez-Mozaz, C.M. Manaia, J. Marugán, Assessment of full-scale tertiary wastewater treatment by UV-C based-AOPs: Removal or persistence of antibiotics and antibiotic resistance genes?, Sci. Total Environ. 652 (2018) 1051–1061. doi:10.1016/j.scitotenv.2018.10.223.

[85] B. Kirk, C. Etnier, E. Karman, S. Johnstone, Methods for Comparing Wastewater Treatment Options, (2005) 206.

[86] S. Morera Carbonell, Sadurní, Comprehensive inventories for Life Cicle Assessment in urban wastewater systems, 2016. http://dugi-doc.udg.edu/handle/10256/12246?show=full.

[87] L. Corominas, J. Foley, J.S. Guest, A. Hospido, H.F. Larsen, S. Morera, A. Shaw, Life cycle assessment applied to wastewater treatment: State of the art, Water Res. 47 (2013) 5480–5492. doi:10.1016/j.watres.2013.06.049.

[88] R.H.C. EMMERSON, G.K. MORSE, J.N. LESTER, D.R. EDGE, The Life-Cycle Analysis of Small-Scale Sewage-Treatment Processes, Water Environ. J. 9 (1995) 317–325. doi:10.1111/j.1747-6593.1995.tb00945.x.

[89] P.J. Roeleveld, A. Klapwijk, P.G. Eggels, W.H. Rulkens, W. Van Starkenburg, Sustainability of municipal wastewater treatment, Water Sci. Technol. 35 (1997) 221–228. doi:10.1016/S0273-1223(97)00199-6.

[90] C. Baresel, L. Dahlgren, M. Almemark, A. Lazic, Municipal wastewater reclamation for non-potable reuse - Environmental assessments based on pilot-plant studies and system modelling, Water Sci. Technol. 72 (2015) 1635–1643. doi:10.2166/wst.2015.373.

[91] I.M. Ortiz, Life Cycle Assessment as a Tool for Green Chemistry: Application to Different Advanced Oxidation Processes for Wastewater Treatment Tesi Doctoral, Doctor. (2006).

[92] C. Remy, U. Miehe, B. Lesjean, C. Bartholomäus, Comparing environmental impacts of tertiary wastewater treatment technologies for advanced phosphorus removal and disinfection with life cycle assessment, Water Sci. Technol. 69 (2014) 1742–1750. doi:10.2166/wst.2014.087.

[93] E. Carré, J. Beigbeder, V. Jauzein, G. Junqua, M. Lopez-Ferber, Life cycle assessment case study: Tertiary treatment process options for wastewater reuse, Integr. Environ. Assess. Manag. 13 (2017) 1113–1121. doi:10.1002/ieam.1956.

[94] L. Høibye, J. Clauson-Kaas, H. Wenzel, H.F. Larsen, B.N. Jacobsen, O. Dalgaard, Sustainability assessment of advanced wastewater treatment technologies, Water Sci. Technol. 58 (2008) 963–968. doi:10.2166/wst.2008.450.

[95] H. Wenzel, H.F. Larsen, J. Clauson-Kaas, L. Høibye, B.N. Jacobsen, Weighing environmental advantages and disadvantages of advanced wastewater treatment of micro-pollutants using environmental life cycle assessment, Water Sci. Technol. 57 (2008) 27–32. doi:10.2166/wst.2008.819.

[96] C. Köhler, S. Venditti, E. Igos, K. Klepiszewski, E. Benetto, A. Cornelissen, Elimination of pharmaceutical residues in biologically pre-treated hospital wastewater using advanced UV irradiation technology: A comparative assessment, J. Hazard. Mater. 239–240 (2012) 70–77.

doi:10.1016/j.jhazmat.2012.06.006.

[97] S. Foteinis, J.M. Monteagudo, A. Durán, E. Chatzisymeon, Environmental sustainability of the solar photo-Fenton process for wastewater treatment and pharmaceuticals mineralization at semi-industrial scale, Sci. Total Environ. 612 (2018) 605–612. doi:10.1016/j.scitotenv.2017.08.277.

[98] R.R. Zepon Tarpani, A. Azapagic, Life cycle environmental impacts of advanced wastewater treatment techniques for removal of pharmaceuticals and personal care products (PPCPs), J. Environ. Manage. 215 (2018) 258–272. doi:10.1016/j.jenvman.2018.03.047.

[99] APHA/AWWA/WEF, Standard Methods for the Examination of Water and Wastewater, Stand. Methods. (2012) 541. doi:ISBN 9780875532356.

[100] S. Velten, F. Hammes, M. Boller, T. Egli, Rapid and direct estimation of active biomass on granular activated carbon through adenosine tri-phosphate (ATP) determination, Water Res. 41 (2007) 1973–1983. doi:10.1016/j.watres.2007.01.021.

[101] ISO [International Organization for Standardization], Determination of the specific surface area of solids by gas adsorption - BET method (ISO 9277:2010(E)), Ref. Number ISO. 9277 (2010) 30 pp. doi:10.1007/s11367-011-0297-3.

[102] J.R. Bolton, K.G. Linden, Standardization of Methods for Fluence (UV Dose) Determination in Bench-Scale UV Experiments, J. Environ. Eng. 129 (2003) 209–215. doi:10.1061/(ASCE)0733-9372(2003)129:3(209).

[103] L. Paredes, C. Alfonsin, T. Allegue, F. Omil, M. Carballa, Integrating granular activated carbon in the post-treatment of membrane and settler effluents to improve organic micropollutants removal, Chem. Eng. J. 345 (2018) 79–86. doi:10.1016/j.cej.2018.03.120.

[104] M. Goedkoop, R. Heijungs, M. Huijbregts, A. De Schryver, J. Struijs, R. Van Zelm, ReCiPe 2008, Minist. van Volkshuisvesting, Ruimtelijke Ordening En Milieubeh. (2009) 1–44. doi:10.029/2003JD004283.

[105] E. Chatzisymeon, S. Foteinis, D. Mantzavinos, T. Tsoutsos, Life cycle assessment of advanced

oxidation processes for olive mill wastewater treatment, J. Clean. Prod. 54 (2013) 229–234. doi:10.1016/j.jclepro.2013.05.013.

[106] C. Teodosiu, A.F. Gilca, G. Barjoveanu, S. Fiore, Emerging pollutants removal through advanced drinking water treatment: A review on processes and environmental performances assessment, J. Clean. Prod. 197 (2018) 1210–1221. doi:10.1016/j.jclepro.2018.06.247.

[107] M. Gros, S. Rodríguez-Mozaz, D. Barceló, Fast and comprehensive multi-residue analysis of a broad range of human and veterinary pharmaceuticals and some of their metabolites in surface and treated waters by ultra-high-performance liquid chromatography coupled to quadrupole-linear ion trap tandem, J. Chromatogr. A. 1248 (2012) 104–121. doi:10.1016/j.chroma.2012.05.084.

[108] L. Li, P. Zhang, W. Zhu, W. Han, Z. Zhang, Comparison of O3-BAC, UV/O3-BAC and TiO2 /UV/O3-BAC processes for removing organic pollutants in secondary effluents, J. Photochem. Photobiol. A Chem. 171 (2005) 145–151. doi:10.1016/j.jphotochem.2004.09.016.

[109] F. Meinel, A. Sperlich, M. Jekel, Pilot-scale study of powdered activated carbon recirculation for micropollutant removal, Water Sci. Technol. 74 (2016) 927–934. doi:10.2166/wst.2016.273.

[110] L. Li, W. Zhu, P. Zhang, Q. Zhang, Z. Zhang, AC/O3-BAC processes for removing refractory and hazardous pollutants in raw water, J. Hazard. Mater. 135 (2006) 129–133. doi:10.1016/j.jhazmat.2005.11.045.

[111] T. Lin, W. Chen, L. Wang, Particle properties in granular activated carbon filter during drinking water treatment, J. Environ. Sci. 22 (2010) 681–688. doi:10.1016/S1001-0742(09)60163-7.

[112] A. Magic-Knezev, D. van der Kooij, Optimisation and significance of ATP analysis for measuring active biomass in granular activated carbon filters used in water treatment, Water Res. 38 (2004) 3971–3979. doi:10.1016/j.watres.2004.06.017.

[113] S.A. Snyder, S. Adham, A.M. Redding, F.S. Cannon, J. DeCarolis, J. Oppenheimer, E.C. Wert, Y. Yoon, Role of membranes and activated carbon in the removal of endocrine disruptors and

pharmaceuticals, Desalination. 202 (2007) 156–181. doi:10.1016/j.desal.2005.12.052.

[114] G. Knopp, C. Prasse, T.A. Ternes, P. Cornel, Elimination of micropollutants and transformation products from a wastewater treatment plant effluent through pilot scale ozonation followed by various activated carbon and biological filters, Water Res. 100 (2016) 580–592. doi:10.1016/j.watres.2016.04.069.

[115] V. Kårelid, G. Larsson, B. Björlenius, Pilot-scale removal of pharmaceuticals in municipal wastewater: Comparison of granular and powdered activated carbon treatment at three wastewater treatment plants, J. Environ. Manage. 193 (2017) 491–502. doi:10.1016/j.jenvman.2017.02.042.

[116] X. Yang, R.C. Flowers, H.S. Weinberg, P.C. Singer, Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant, Water Res. 45 (2011) 5218–5228. doi:10.1016/j.watres.2011.07.026.

[117] J. Reungoat, B.I. Escher, M. Macova, J. Keller, Biofiltration of wastewater treatment plant effluent: effective removal of pharmaceuticals and personal care products and reduction of toxicity, Water Res. 45 (2011) 2751–2762. doi:10.1016/j.watres.2011.02.013.

[118] M. Weemaes, G. Fink, C. Lachmund, A. Magdeburg, D. Stalter, C. Thoeye, G. De Gueldre, B. Van De Steene, Removal of micropollutants in WWTP effluent by biological assisted membrane carbon filtration (BioMAC), Water Sci. Technol. 63 (2011) 72–79. doi:10.2166/wst.2011.011.

[119] D.J. De Ridder, A.R.D. Verliefde, S.G.J. Heijman, J.Q.J.C. Verberk, L.C. Rietveld, L.T.J. Van Der Aa, G.L. Amy, J.C. Van Dijk, Influence of natural organic matter on equilibrium adsorption of neutral and charged pharmaceuticals onto activated carbon, Water Sci. Technol. 63 (2011) 416–423. doi:10.2166/wst.2011.237.

[120] R. Mailler, J. Gasperi, Y. Coquet, C. Derome, A. Buleté, E. Vulliet, A. Bressy, G. Varrault, G. Chebbo, V. Rocher, Removal of emerging micropollutants from wastewater by activated carbon adsorption: Experimental study of different activated carbons and factors influencing the

adsorption of micropollutants in wastewater, J. Environ. Chem. Eng. 4 (2016) 1102–1109. doi:10.1016/j.jece.2016.01.018.

[121] P. Westerhoff, Y. Yoon, S. Snyder, E. Wert, Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes, Environ. Sci. Technol. 39 (2005) 6649–6663. doi:10.1021/es0484799.

[122] Q. Jiang, H.H. Ngo, L.D. Nghiem, F.I. Hai, W.E. Price, J. Zhang, S. Liang, L. Deng, W. Guo, Effect of hydraulic retention time on the performance of a hybrid moving bed biofilm reactor-membrane bioreactor system for micropollutants removal from municipal wastewater, Bioresour. Technol. 247 (2017) 1228–1232. doi:10.1016/j.biortech.2017.09.114.

[123] G. Ersan, Y. Kaya, O.G. Apul, T. Karanfil, Adsorption of organic contaminants by graphene nanosheets, carbon nanotubes and granular activated carbons under natural organic matter preloading conditions, Sci. Total Environ. 565 (2016) 811–817. doi:10.1016/j.scitotenv.2016.03.224.

[124] J. Müller, J.E. Drewes, U. Hübner, Sequential biofiltration – A novel approach for enhanced biological removal of trace organic chemicals from wastewater treatment plant effluent, Water Res. 127 (2017) 127–138. doi:10.1016/j.watres.2017.10.009.

[125] C. Sheng, A.G.A. Nnanna, Y. Liu, J.D. Vargo, Removal of Trace Pharmaceuticals from Water using coagulation and powdered activated carbon as pretreatment to ultrafiltration membrane system, Sci. Total Environ. 550 (2016) 1075–1083. doi:10.1016/j.scitotenv.2016.01.179.

[126] J. Hu, A. Aarts, R. Shang, B. Heijman, L. Rietveld, Integrating powdered activated carbon into wastewater tertiary filter for micro-pollutant removal, J. Environ. Manage. 177 (2016) 45–52. doi:10.1016/j.jenvman.2016.04.003.

[127] C. Bertelkamp, J. Reungoat, E.R. Cornelissen, N. Singhal, J. Reynisson, A.J. Cabo, J.P. van der Hoek, A.R.D. Verliefde, Sorption and biodegradation of organic micropollutants during river bank filtration: A laboratory column study, Water Res. 52 (2014) 231–241.

doi:10.1016/j.watres.2013.10.068.

[128] R. Mailler, J. Gasperi, Y. Coquet, A. Buleté, E. Vulliet, S. Deshayes, S. Zedek, C. Mirande-Bret, V. Eudes, A. Bressy, E. Caupos, R. Moilleron, G. Chebbo, V. Rocher, Removal of a wide range of emerging pollutants from wastewater treatment plant discharges by micro-grain activated carbon in fluidized bed as tertiary treatment at large pilot scale, Sci. Total Environ. 542 (2016) 983–996. doi:10.1016/j.scitotenv.2015.10.153.

[129] S.K. Maeng, S.K. Sharma, C.D.T. Abel, A. Magic-Knezev, G.L. Amy, Role of biodegradation in the removal of pharmaceutically active compounds with different bulk organic matter characteristics through managed aquifer recharge: Batch and column studies, Water Res. 45 (2011) 4722–4736. doi:10.1016/j.watres.2011.05.043.

[130] H. Xiang, X. Lu, L. Yin, F. Yang, G. Zhu, W. Liu, Microbial community characterization, activity analysis and purifying efficiency in a biofilter process, J. Environ. Sci. (China). 25 (2013) 677–687. doi:10.1016/S1001-0742(12)60089-8.

[131] J. Altmann, D. Rehfeld, K. Träder, A. Sperlich, M. Jekel, Combination of granular activated carbon adsorption and deep-bed filtration as a single advanced wastewater treatment step for organic micropollutant and phosphorus removal, Water Res. 92 (2016) 131–139. doi:10.1016/j.watres.2016.01.051.

[132] K. Beijer, B. Björlenius, S. Shaik, R.H. Lindberg, B. Brunström, I. Brandt, Removal of pharmaceuticals and unspecified contaminants in sewage treatment effluents by activated carbon filtration and ozonation: Evaluation using biomarker responses and chemical analysis, Chemosphere. 176 (2017) 342–351. doi:10.1016/j.chemosphere.2017.02.127.

[133] C.M.G. Carpenter, D.E. Helbling, Removal of micropollutants in biofilters: Hydrodynamic effects on biofilm assembly and functioning, Water Res. 120 (2017) 211–221. doi:10.1016/j.watres.2017.04.071.

[134] M. Kim, P. Guerra, A. Shah, M. Parsa, M. Alaee, S.A. Smyth, Removal of pharmaceuticals and

personal care products in a membrane bioreactor wastewater treatment plant, Water Sci. Technol. 69 (2014) 2221–2229. doi:10.2166/wst.2014.145.

[135] A. Joss, S. Zabczynski, A. Göbel, B. Hoffmann, D. Löffler, C.S. McArdell, T.A. Ternes, A. Thomsen, H. Siegrist, Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme, Water Res. 40 (2006) 1686–1696. doi:10.1016/j.watres.2006.02.014.

[136] T.A. Ternes, C. Prasse, C.L. Eversloh, G. Knopp, P. Cornel, U. Schulte-Oehlmann, T. Schwartz, J. Alexander, W. Seitz, A. Coors, J. Oehlmann, Integrated Evaluation Concept to Assess the Efficacy of Advanced Wastewater Treatment Processes for the Elimination of Micropollutants and Pathogens, Environ. Sci. Technol. (2016) acs.est.6b04855. doi:10.1021/acs.est.6b04855.

[137] P. Falås, A. Wick, S. Castronovo, J. Habermacher, T.A. Ternes, A. Joss, Tracing the limits of organic micropollutant removal in biological wastewater treatment, Water Res. 95 (2016) 240–249. doi:10.1016/j.watres.2016.03.009.

[138] J. Deng, Y. Shao, N. Gao, S. Xia, C. Tan, S. Zhou, X. Hu, Degradation of the antiepileptic drug carbamazepine upon different UV-based advanced oxidation processes in water, Chem. Eng. J. 222 (2013) 150–158. doi:10.1016/j.cej.2013.02.045.

[139] Y. Yang, X. Lu, J. Jiang, J. Ma, G. Liu, Y. Cao, W. Liu, J. Li, S. Pang, X. Kong, C. Luo, Degradation of sulfamethoxazole by UV, UV/H2O2and UV/persulfate (PDS): Formation of oxidation products and effect of bicarbonate, Water Res. 118 (2017) 196–207. doi:10.1016/j.watres.2017.03.054.

[140] S. Wacławek, H. V. Lutze, K. Grübel, V.V.T. Padil, M. Černík, D.D. Dionysiou, Chemistry of persulfates in water and wastewater treatment: A review, Chem. Eng. J. 330 (2017) 44–62. doi:10.1016/j.cej.2017.07.132.

[141] J.A. Khan, X. He, N.S. Shah, H.M. Khan, E. Hapeshi, D. Fatta-Kassinos, D.D. Dionysiou, Kinetic and mechanism investigation on the photochemical degradation of atrazine with

activated H2O2, S2O82-and HSO5-, Chem. Eng. J. 252 (2014) 393–403. doi:10.1016/j.cej.2014.04.104.

[142] J.A. Khan, X. He, N.S. Shah, M. Sayed, H.M. Khan, D.D. Dionysiou, Degradation kinetics and mechanism of desethyl-atrazine and desisopropyl-atrazine in water with[rad]OH and SO4[rad]−based-AOPs, Chem. Eng. J. 325 (2017) 485–494. doi:10.1016/j.cej.2017.05.011.

[143] M. Mahdi Ahmed, S. Barbati, P. Doumenq, S. Chiron, Sulfate radical anion oxidation of diclofenac and sulfamethoxazole for water decontamination, Chem. Eng. J. 197 (2012) 440–447. doi:10.1016/j.cej.2012.05.040.

[144] Y. Yang, J.J. Pignatello, J. Ma, W.A. Mitch, Effect of matrix components on UV / H 2 O 2 and UV / S 2 O 2 8 advanced oxidation processes for trace organic degradation in reverse osmosis brines from municipal wastewater reuse facilities, Water Res. 89 (2016) 192–200. doi:10.1016/j.watres.2015.11.049.

[145] Y. Chen, C. Hu, X. Hu, J. Qu, Indirect photodegradation of amine drugs in aqueous solution under simulated sunlight, Environ. Sci. Technol. 43 (2009) 2760–2765. doi:10.1021/es803325j.

[146] X. Ao, W. Liu, W. Sun, M. Cai, Z. Ye, C. Yang, Z. Lu, C. Li, Medium pressure UV-activated peroxymonosulfate for ciprofloxacin degradation: Kinetics, mechanism, and genotoxicity, Chem. Eng. J. 345 (2018) 87–97. doi:10.1016/j.cej.2018.03.133.

[147] Y.H. Guan, J. Ma, X.C. Li, J.Y. Fang, L.W. Chen, Influence of pH on the formation of sulfate and hydroxyl radicals in the UV/Peroxymonosulfate system, Environ. Sci. Technol. 45 (2011) 9308–9314. doi:10.1021/es2017363.

[148] G. V. Buxton, M. Bydder, G. Arthur Salmon, Reactivity of chlorine atoms in aqueous solution Part 1, J. Chem. Soc. Faraday Trans. 94 (1998) 653–657. doi:10.1039/a707377a.

[149] W.L. Wang, Q.Y. Wu, N. Huang, T. Wang, H.Y. Hu, Synergistic effect between UV and chlorine (UV/chlorine) on the degradation of carbamazepine: Influence factors and radical species, Water Res. 98 (2016) 190–198. doi:10.1016/j.watres.2016.04.015.

[150] Z. Wu, J. Fang, Y. Xiang, C. Shang, X. Li, F. Meng, X. Yang, Roles of reactive chlorine species in trimethoprim degradation in the UV/chlorine process: Kinetics and transformation pathways, Water Res. 104 (2016) 272–282. doi:10.1016/j.watres.2016.08.011.

[151] M. Kwon, Y. Yoon, S. Kim, Y. Jung, T.M. Hwang, J.W. Kang, Removal of sulfamethoxazole, ibuprofen and nitrobenzene by UV and UV/chlorine processes: A comparative evaluation of 275 nm LED-UV and 254 nm LP-UV, Sci. Total Environ. 637–638 (2018) 1351–1357. doi:10.1016/j.scitotenv.2018.05.080.

[152] C. Liang, Z.S. Wang, N. Mohanty, Influences of carbonate and chloride ions on persulfate oxidation of trichloroethylene at 20 °C, Sci. Total Environ. 370 (2006) 271–277. doi:10.1016/j.scitotenv.2006.08.028.

[153] R. Zhang, P. Sun, T.H. Boyer, L. Zhao, C.H. Huang, Degradation of pharmaceuticals and metabolite in synthetic human urine by UV, UV/H2O2, and UV/PDS, Environ. Sci. Technol. 49 (2015) 3056–3066. doi:10.1021/es504799n.

[154] M. Jiang, J. Lu, Y. Ji, D. Kong, Bicarbonate-activated persulfate oxidation of acetaminophen, Water Res. 116 (2017) 324–331. doi:10.1016/j.watres.2017.03.043.

[155] O.S. Keen, K.G. Linden, Degradation of antibiotic activity during UV/H2O2 advanced oxidation and photolysis in wastewater effluent, Environ. Sci. Technol. 47 (2013) 13020–13030. doi:10.1021/es402472x.

[156] Y. Liu, X. He, Y. Fu, D.D. Dionysiou, Kinetics and mechanism investigation on the destruction of oxytetracycline by UV-254 nm activation of persulfate, J. Hazard. Mater. 305 (2016) 229–239. doi:10.1016/j.jhazmat.2015.11.043.

[157] Y. Yang, Y. Cao, J. Jiang, X. Lu, J. Ma, S. Pang, J. Li, Y. Liu, Y. Zhou, C. Guan, Comparative study on degradation of propranolol and formation of oxidation products by UV/H2O2 and UV/persulfate (PDS), Water Res. 149 (2019) 543–552. doi:10.1016/j.watres.2018.08.074.

[158] H. Yu, E. Nie, J. Xu, S. Yan, W.J. Cooper, W. Song, Degradation of Diclofenac by Advanced

Oxidation and Reduction Processes: Kinetic Studies, Degradation Pathways and Toxicity Assessments, Water Res. 47 (2013) 1909–1918. doi:10.1016/j.watres.2013.01.016.

[159] X. Lu, Y. Shao, N. Gao, J. Chen, Y. Zhang, H. Xiang, Y. Guo, Degradation of diclofenac by UV-activated persulfate process: Kinetic studies, degradation pathways and toxicity assessments, Ecotoxicol. Environ. Saf. 141 (2017) 139–147. doi:10.1016/j.ecoenv.2017.03.022.

[160] H. Guo, T. Ke, N. Gao, Y. Liu, X. Cheng, Enhanced degradation of aqueous norfloxacin and enrofloxacin by UV-activated persulfate: Kinetics, pathways and deactivation, Chem. Eng. J. 316 (2017) 471–480. doi:10.1016/j.cej.2017.01.123.

[161] L. Rizzo, Bioassays as a tool for evaluating advanced oxidation processes in water and wastewater treatment, Water Res. 45 (2011) 4311–4340. doi:10.1016/j.watres.2011.05.035.

[162] C. Fang, D. Xiao, W. Liu, X. Lou, J. Zhou, Z. Wang, J. Liu, Enhanced AOX accumulation and aquatic toxicity during 2,4,6-trichlorophenol degradation in a Co(II)/peroxymonosulfate/Cl- system, Chemosphere. 144 (2016) 2415–2420. doi:10.1016/j.chemosphere.2015.11.030.

[163] Y. Ji, L. Wang, M. Jiang, J. Lu, C. Ferronato, J.M. Chovelon, The role of nitrite in sulfate radical-based degradation of phenolic compounds: An unexpected nitration process relevant to groundwater remediation by in-situ chemical oxidation (ISCO), Water Res. 123 (2017) 249–257. doi:10.1016/j.watres.2017.06.081.

[164] G.R. Peyton, The free-radical chemistry of persulfate-based total organic carbon analyzers, Mar. Chem. 41 (1993) 91–103. doi:10.1016/0304-4203(93)90108-Z.

[165] G. V Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (?OH/?O ? in Aqueous Solution, J. Phys. Chem. Ref. Data. 17 (1988) 513–886. doi:10.1063/1.555805.

[166] G. V Buxton, G.A. Salmon, N.D. Wood, A pulse radiolysis study of the chemistry of oxysulphur radicals in aqueous solution, in: Physico-Chemical Behav. Atmos. Pollut., Springer Netherlands, 1990: pp. 245–250.

[167] C. Liang, H.-W. Su, Identification of sulfate and hydroxyl radicals in thermally activated persulfate, Ind. Eng. Chem. Res. 48 (2009) 5558–5562. doi:10.1021/ie9002848.

[168] Y. Ahn, D. Lee, M. Kwon, I. hwan Choi, S.N. Nam, J.W. Kang, Characteristics and fate of natural organic matter during UV oxidation processes, Chemosphere. 184 (2017) 960–968. doi:10.1016/j.chemosphere.2017.06.079.

[169] G.G. Jayson, B.J. Parsons, A.J. Swallow, Some simple, highly reactive, inorganic chlorine derivatives in aqueous solution, J.Chem.Soc.Faraday Trans. 69 (1973) 1597–1607.

[170] T.N. Das, Reactivity and Role of $SO_5^{\bullet -}$ Radical in Aqueous Medium Chain Oxidation of Sulfite to Sulfate and Atmospheric Sulfuric Acid Generation, J. Phys. Chem. A. 105 (2001) 9142–9155. doi:10.1021/jp011255h.

[171] X.Y. Yu, J.R. Barker, Hydrogen peroxide photolysis in acidic aqueous solutions containing chloride ions. II. Quantum yield of $H\dot{O}$(Aq) radicals, J. Phys. Chem. A. 107 (2003) 1325–1332. doi:10.1021/jp026666s.

[172] O.P. Chawla, An electron spin resonance study of the mechanism and kinetics of photochemical reactions in aqueous solutions, Carnegie-Mellon University, 1973.

[173] C.M. Sharpless, K.G. Linden, UV photolysis of nitrate: Effects of natural organic matter and dissolved inorganic carbon and implications for UV water disinfection, Environ. Sci. Technol. 35 (2001) 2949–2955. doi:10.1021/es002043l.

[174] U.K. Klaning, K. Sehested, E.H. Appelman, Laser flash photolysis and pulse radiolysis of aqueous solutions of the fluoroxysulfate ion, SO4F-, Inorg. Chem. 30 (1991) 3582–3584. doi:10.1021/ic00018a040.

[175] O.S. Keen, N.G. Love, K.G. Linden, The role of effluent nitrate in trace organic chemical oxidation during UV disinfection, Water Res. 46 (2012) 5224–5234. doi:10.1016/j.watres.2012.06.052.

[176] R.E. Huie, C.L. Clifton, Temperature dependence of the rate constants for reactions of the sulfate

radical, SO4-, with anions, J. Phys. Chem. 94 (1990) 8561–8567. doi:10.1021/j100386a015.

[177] L. Paredes, F. Omil, J.M. Lema, M. Carballa, What happens with organic micropollutants during UV disinfection in WWTPs? A global perspective from laboratory to full-scale, J. Hazard. Mater. 342 (2018) 670–678. doi:10.1016/j.jhazmat.2017.08.075.

[178] D.B. Miklos, R. Hartl, P. Michel, K.G. Linden, J.E. Drewes, U. Hübner, UV/H2O2process stability and pilot-scale validation for trace organic chemical removal from wastewater treatment plant effluents, Water Res. 136 (2018) 169–179. doi:10.1016/j.watres.2018.02.044.

[179] J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, Figures-of-Merit for the Technical Development and Application of Advanced Oxidation Processes, J. Adv. Oxid. Technol. 73 (1995) 627–637. doi:10.1515/jaots-1996-0104.

[180] D. Mousel, L. Palmowski, J. Pinnekamp, Energy demand for elimination of organic micropollutants in municipal wastewater treatment plants, Sci. Total Environ. 575 (2017) 1139–1149. doi:10.1016/j.scitotenv.2016.09.197.

[181] I.A. Katsoyiannis, S. Canonica, U. von Gunten, Efficiency and energy requirements for the transformation of organic micropollutants by ozone, O3/H2O2and UV/H2O2, Water Res. 45 (2011) 3811–3822. doi:10.1016/j.watres.2011.04.038.

[182] B. Cédat, C. de Brauer, H. Métivier, N. Dumont, R. Tutundjan, Are UV photolysis and UV/H2O2process efficient to treat estrogens in waters? Chemical and biological assessment at pilot scale, Water Res. 100 (2016) 357–366. doi:10.1016/j.watres.2016.05.040.

[183] C.P. James, E. Germain, S. Judd, Micropollutant removal by advanced oxidation of microfiltered secondary effluent for water reuse, Sep. Purif. Technol. 127 (2014) 77–83. doi:10.1016/j.seppur.2014.02.016.

[184] Y. Mery, L. Tiruta-Barna, I. Baudin, E. Benetto, E. Igos, Formalization of a technical procedure for process ecodesign dedicated to drinking water treatment plants, J. Clean. Prod. 68 (2014) 16–24. doi:10.1016/j.jclepro.2014.01.011.

[185] R. de Oliveira Schwaickhardt, Ê.L. Machado, C.A. Lutterbeck, Combined use of VUV and UVC photoreactors for the treatment of hospital laundry wastewaters: Reduction of load parameters, detoxification and life cycle assessment of different configurations, Sci. Total Environ. 590–591 (2017) 233–241. doi:10.1016/j.scitotenv.2017.02.218.

[186] J.B. Guinée, Handbook on Life Cycle Assessment, n.d.

[187] D. Vogna, R. Marotta, R. Andreozzi, A. Napolitano, M. D'Ischia, Kinetic and chemical assessment of the UV/H2O2treatment of antiepileptic drug carbamazepine, Chemosphere. 54 (2004) 497–505. doi:10.1016/S0045-6535(03)00757-4.

[188] S. Sakshaug, K. V. Thomas, M. Grung, S. Skurtveit, T. Källqvist, Environmental assessment of Norwegian priority pharmaceuticals based on the EMEA guideline, Ecotoxicol. Environ. Saf. 71 (2007) 328–340. doi:10.1016/j.ecoenv.2007.10.015.

[189] I. Muñoz, A. Rodríguez, R. Rosal, A.R. Fernández-Alba, Life Cycle Assessment of urban wastewater reuse with ozonation as tertiary treatment, Sci. Total Environ. 407 (2008) 1245–1256. doi:10.1016/j.scitotenv.2008.09.029.

[190] E. Igos, A. Biwer, R. Moeller, E. Benetto, S. Venditti, A. Cornelissen, Is it better to remove pharmaceuticals in decentralized or conventional wastewater treatment plants? A life cycle assessment comparison, Sci. Total Environ. 438 (2012) 533–540. doi:10.1016/j.scitotenv.2012.08.096.

[191] S. Lundie, G.M. Peters, P.C. Beavis, Life cycle assessment for sustainable metropolitan water systems planning, Environ. Sci. Technol. 38 (2004) 3465–3473. doi:10.1021/es034206m.

Annex 1

One sample T-test

The one sample T-test has been applied to determine whether the mean Kobs obtained during the "standard conditions" experiments where greater or smaller than the mean values obtained during the "new conditions" experiments. With reference to Table A1, we compared experiments 3 (standard condition UV/PDS) with experiment 14, 16, 18, 22 concerning UV/PDS process. while we compared experiment 4 (standard condition UV/PMS) with experiment 15, 17, 19, 23. The statistical procedure has been applied according to the following steps:

1. Calculation of $K_{obs\text{-}expE}$ and $K_{obs\text{-}expG}$ for each PhAC
2. Calculation of the percent difference between $K_{obs\text{-}expE}$ and $K_{obs\text{-}expG}$ ($K_{obs\text{-}E/G}$) for each PhAC.
3. Calculate the mean of all the differences (e.g. $K_{obs\text{-}E/G\text{-}ATNL}$, $K_{obs\text{-}E/G\text{-}CBZ}$ and so on).
4. Verify whether this mean value is positive (> 0).
5. If it is positive, then $K_{obs\text{-}expE} > K_{obs\text{-}expG}$

The statistical significance of this test is determined by looking at the p-value. If p-value is smaller than the chosen cut off value ($\alpha = 0.05$), then the hypothesis can be considered significant.

Table A1: T-test results

	PDS	**PMS**
pH		
Kobs (pH8.2) > Kobs (pH6)	YES $p = 0.0011$	YES $p = 0.012$
Cl^-		
Kobs (9mM) > Kobs (27mM)	YES $p = 0.0021$	YES $p = 0.005$
NO_3^-		
Kobs (10mM) > Kobs (1mM)	YES $p = 0.0032$	YES $p = 0.0026$
EfOM		
Kobs (EfOM=0) > Kobs (EfOM)	YES $p = 0.00005$	YES $p = 0.001$

Annex 2

Table A2 : K_{obs} and Removal values

	ATNL		CBZ		CPFX		DZP		MTPL		SMX		VLFX		NDL		OFXC	
N°	K_{obs} (cm²/J)	R (%)	K_{obs} (cm²/J)	R (%)	K_{obs} (cm²/J)	R (%)	K_{obs} (cm²/J)	R (%)	K_{obs} (cm²/J)	R (%)	K_{obs} (cm²/J)	R (%)	K_{obs} (cm²/J)	R (%)	K_{obs} (cm²/J)	R (%)	K_{obs} (cm²/J)	R (%)
1	18.32	100.00	9.07	100.00	8.56	93.67	11.36	94.00	16.86	98.41	19.87	98.87	15.98	100.00	6.23	100.00	18.56	100.00
2	9.84	90.42	4.10	72.42	11.93	93.48	4.55	66.70	10.23	85.77	18.73	98.88	9.13	89.29	6.11	80.17	11.36	93.64
3	2.98	54.60	4.40	54.00	6.20	93.30	1.30	23.50	0.64	39.90	2.96	69.90	1.30	54.60	1.90	66.20	3.90	99.00
4	1.30	42.90	5.10	61.00	20.40	97.30	1.10	34.50	1.60	64.80	3.40	96.40	1.90	76.45	2.90	73.60	6.90	98.80
5	0.02	1.29	0.41	18.11	0.41	19.03	0.02	1.29	0.09	4.00	1.06	59.76	0.08	5.83	0.41	19.03	0.46	18.34
6	1.24	32.27	4.58	44.00	4.58	90.00	1.26	20.49	0.22	17.00	1.21	60.00	2.15	30.00	2.07	32.00	2.15	72.00
7	2.06	52.13	4.96	52.00	4.96	94.00	1.41	20.79	0.43	27.00	1.21	61.00	2.22	42.00	2.75	49.00	2.22	91.00
8	2.15	52.84	7.93	52.00	7.93	96.00	1.50	21.47	0.63	37.00	1.38	65.00	2.31	49.00	2.75	58.00	2.31	98.00
9	2.35	68.58	10.52	72.00	10.52	96.00	1.63	21.77	1.51	70.00	2.88	97.00	2.38	84.00	3.44	94.00	2.38	100.00
10	2.27	34.68	5.14	43.00	4.21	93.00	0.74	11.60	0.61	2.26	1.58	64.70	1.96	39.00	0.86	18.78	11.89	32.37
11	2.57	39.39	5.15	46.00	4.93	95.00	0.94	16.20	0.74	3.56	2.00	72.80	2.33	29.00	0.95	21.36	12.18	36.89
12	3.49	45.59	5.27	46.00	6.90	95.00	0.96	16.70	0.76	3.37	2.40	80.10	2.52	44.00	1.00	26.13	12.39	43.02
13	4.59	49.28	5.86	50.00	9.50	96.00	0.97	17.50	0.78	4.29	3.22	88.60	2.55	50.00	1.00	32.51	16.00	47.74
14	0.97	42.05	3.58	44.14	5.68	92.55	0.45	13.61	0.08	6.30	1.77	88.53	0.82	57.39	0.56	20.06	3.89	100.00
15	1.12	32.22	7.41	60.89	12.57	96.38	0.55	15.53	0.45	23.66	3.18	86.95	0.97	44.56	2.24	33.28	2.75	82.90
16	1.74	51.90	2.68	27.90	4.41	81.30	1.97	20.00	0.90	53.60	1.60	73.40	1.42	58.30	1.64	75.00	4.14	100.00
17	1.18	65.00	3.89	52.70	13.10	96.00	0.79	29.00	1.16	63.00	2.38	86.90	2.08	82.40	0.61	65.50	4.48	97.60
18	1.03	45.96	4.20	48.20	12.60	96.33	1.94	26.48	0.66	43.00	1.30	67.33	1.64	51.40	1.11	39.11	3.87	100.00
19	2.71	80.79	5.89	55.62	25.20	97.43	1.92	24.71	1.84	67.99	2.78	84.11	2.91	82.76	1.76	68.45	24.26	91.64
20	23.89	84.34	8.12	61.01	28.66	98.22	4.61	44.31	11.28	82.88	24.79	97.08	14.26	87.86	15.32	87.93	14.42	83.55
21	8.46	53.71	6.66	44.78	28.06	95.04	3.10	28.48	8.61	54.60	36.40	97.76	15.20	69.13	9.04	61.50	22.86	90.75
22	5.01	71.70	6.31	74.00	11.90	93.60	1.41	29.10	4.98	59.30	0.85	15.40	7.60	76.00	6.45	74.60	16.84	97.40
23	2.80	31.30	6.01	60.20	8.84	93.60	1.28	29.30	5.19	25.30	18.78	98.60	9.09	76.00	3.50	39.00	15.16	95.90

Annex 3

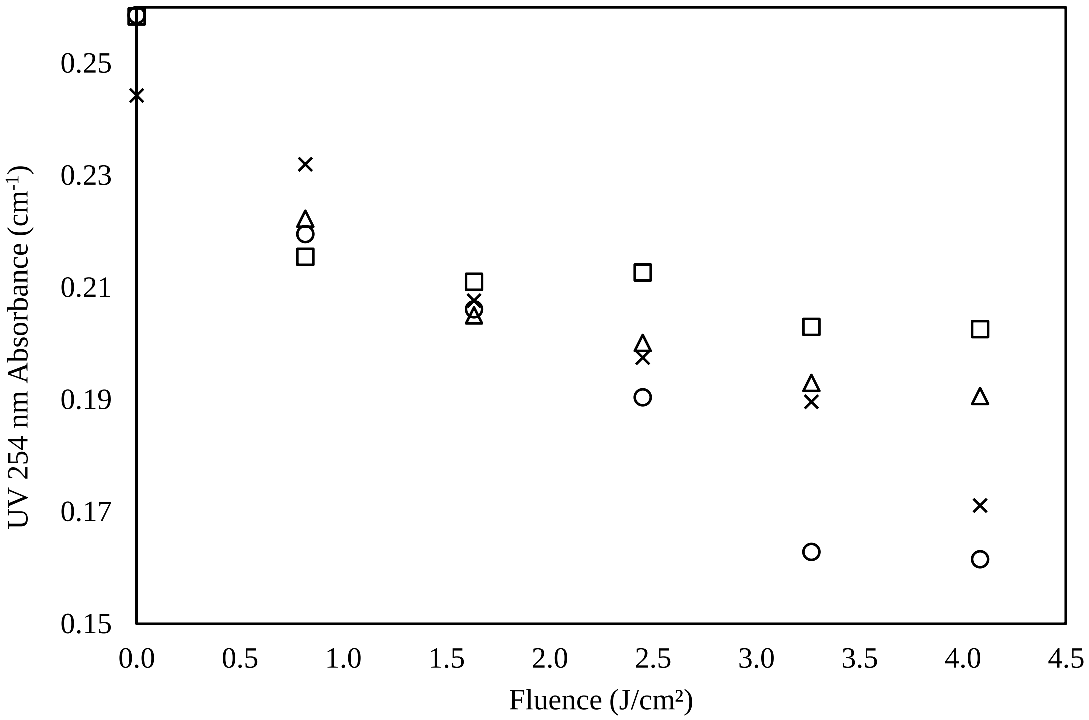


Figure A1 : Change in UV 254 nm absorbance during UV/PDS-0.4mM X, UV/PMS-0.4mM ○, UV/PDS-0.8mM Δ, UV alone □. ([PhAC]0 = 10 µg/L; pH = 8.2).