PHARMACEUTICAL AND PERSONAL CARE PRODUCTS REMOVAL BY ADVANCED TREATMENT TECHNOLOGIES

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Universitat
de Girona

DOCTORAL THESIS

Pharmaceutical and Personal Care Products removal by advanced treatment technologies

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2018

Water Science and Technology Doctoral Programme

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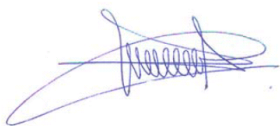Dr. Joaquim Comas Matas (University of Girona)

Certificate:

The thesis entitled *Pharmaceutical and Personal Care Products removal by advanced treatment technologies* presented by **Mariem Chtourou** has been supervised by Dr. Hector Monclús Sales and Dra. Victòria Salvadó Martín from University of Girona and Dr. Walha Khaled from Sfax University and it fulfil the requirements for the degree of Doctor from the University of Girona and Sfax University

This certificate, original and signed by the supervisors, proves that the doctoral candidate has carried out the research work under the supervisor's guidance.

In Girona, on Monday, 30 July 2018

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Nomenclature

AC	Activated carbon
AnMBR	Anaerobic membrane bioreactor
AMO	Ammonia monooxygenase
AOB	Ammonia oxidizing bacteria
AOP	Advanced oxidation process
BOD	Biochemical oxygen demand
AOP	Advanced oxidation processes
BR	Batch reactor
BSA	Bovine serum albumin
BV	Bed volume
CAF	Caffeine
CAS	Conventional activated sludge
CBZ	Carbamazepine
CNT	Carbon nanotube
COA	Coagulation
COD	Chemical oxygen demand $(mg.L^{-1})$
CPB	Cetylpyridinium bromide
CST	Capillarity suction time (s)
CTDs	Chlorinated triclosan derivatives
DCF	Diclofenac
DOM	Dissolved organic matter
DWCNTs	Double-walled carbon nanotubes
DWTPs	Drinking water treatment plants
EBCT	Empty bed contact time
ECs	Emerging contaminants
EDCs	Endocrine disrupting compounds
EMPs	Emerging micropollutants
EfOM	Effluent organic matter
EU	European union
Fe(VI)	Ferrate
Fe^{3+}	Ferric
Fe^{2+}	Ferrous
FS	Flat sheet
GAC	Granular activated carbon

GC	Gas chromatography
HF	Hollow fiber
HPLC	High performance liquid chromatography
H$_2$O$_2$	Hydrogen peroxide
HRT	Hydraulic retention time (h)
KET	Ketoprofen
LC	Liquid chromatography
LC–MS/MS	Liquid chromatography– mass spectrometry in tandem
LOD	Limit of detection
LOQ	Limit of quantification
Log Kow	Octanol-water partition coefficient
MBR	Membrane bioreactor
MF	Microfiltration
MLSS	Mixed liquor suspended solids (g.L^{-1})
MP	Micropollutant
MPB	Methyl paraben
MT	Multi-tube
MW	Molecular weight
MWCNTS	Multi-walled carbon nanotubes
MWCO	Molecular weight cut-off
N	Nitrogen (mg.L^{-1})
N. europaea	Nitrosomonaseuropaea
NO$_2^-$-N	Nitrites (mg.L^{-1})
NO$_3^-$-N	Nitrates (mg.L^{-1})
NAP	Naproxen
NF	Nanofiltration
NH$_4^+$-N	Ammonium (mg.L^{-1})
NO$_X^-$-N	Oxidized nitrogen (mg.L^{-1})
NOM	Natural organic matter
NSAIDs	Non-steroidal anti-inflammatory drugs
NZ	Natural Zeolite (NZ)
OZs	Organo-zeolites
PAC	Powdered activated carbon
PCPs	Personal care products
PDMS	Polydimethylsiloxane
PP	Pharmaceutical products
pK$_a$	-log K$_a$ (K$_a$=Ionization constant)

PPCPs	Pharmaceuticals and Personal Care Products
RO	Reserve osmosis
ROC	Reserve osmosis concentrate
SEM	Scanning electron microscopy
SLS	Sodium lauryl sulphate surfactant
SPE	Solid-phase extraction
SR	Silicone rod
SRT	Sludge retention time (day)
TCS	Triclosan
TiO$_2$	Titanium dioxide
TKN	Total Kjeldahl nitrogen (mg.L^{-1})
TMP	Trans membrane pressure (bar)
TOC	Total organic carbon
TrOCs	Trace organic contaminants
UF-HF	Ultrafiltration hollow fibre
UPLC	Ultra-performance liquid chromatography
US	United States
WCNTs	Single walled carbon nanotubes
WWTPs	Wastewater treatment plants
ZnO	Zinc oxide

The following publication has been included as part of this doctoral thesis:

M. Chtourou, M. Mallek, M. Dalmau, J. Mamo, E. Santos-Clotas, A. Ben Salah, K. Walha, V. Salvadó, H. Monclús. (2018). Triclosan, carbamazepine and caffeine removal by activated sludge system focusing on membrane bioreactor. Process Safety and Environmental Protection 118, 1-9. https://doi.org/10.1016/j.psep.2018.06.019

The following publication has resulted from this work:

M. Mallek, **M. Chtourou**, M. Portillo, H. Monclús, K. Walha, A. Ben Salah, V Salvadó. (2018). Granulated cork as biosorbent for the removal of phenol derivatives and emerging contaminants. Journal of Environmental Management 223, 576-585. https://doi.org/10.1016/j.jenvman.2018.06.069

Summary:

Wastewater treatment plant (WWTPs) effluent is one of the most important sources of contaminants entering aquatic environment because they are designed only to eliminate organic matter, nitrogen and phosphorous.

The presence of anthropogenic chemical substances such as some non-steroidal anti-inflammatory drugs (naproxen, diclofenac and ibuprofen), neutral pharmaceuticals such as carbamazepine, endocrine disruptors such as triclosan, anthropogenic markers such as caffeine and antimicrobial agents such as methyl paraben are among some of the many other compounds detected at trace levels in WWTP effluent.

Advanced treatments such as membrane bioreactor (MBR) and adsorption process allow the elimination of pharmaceutical products to be improved, but their efficiency depends on the physicochemical properties of the pollutants, the characteristics of the water, the operating conditions and the types of treatment that have been applied. In this thesis, different wastewater treatments have been evaluated to assess the efficiency of pharmaceutical and cosmetic product removal. To remove contaminants, sorption is often the preferred separation process for aqueous systems. The most widely used sorbent is activated carbon but the high cost of this sorbent is its major drawback. A more economic, practical and efficient alternative adsorbent is cork.

Firstly, a state-of-art revision of advanced treatment technology for removing Triclosan (TCS) from waste water was carried out in an attempt to evaluate the most favourable technologies and discern any major limiting factors. The technological categories evaluated were: (i) adsorption, (ii) advanced oxidation processes, and (iii) membrane technology.

The results found in the second chapter are based on treating three PPCP compounds in a cyclic anoxic/aerobic membrane bioreactor. In fact, the target compounds selected for this study were specifically carbamazepine, caffeine and triclosan. The ultrafiltration membrane bioreactor process was an efficient and

appropriate technology for chemical oxygen demand removal, as it achieved a removal average of 97%, removal rate for caffeine reaching up to 93.7 ± 9.7 and 89.7 ± 8.3 % for triclosan. In the case of carbamazepine, removal was lower (36.2 ± 6.8%) due to its recalcitrance. Low ammonia removal efficiencies were observed in both experimental systems suggesting that nitrification was inhibited by the presence of triclosan. The deterioration of sludge characteristics induced a fouling increment which forced several chemical cleanings to be carried out.

The last section is focused on cork and evaluates its potential as a sorbent material. The cork was firstly characterized to discern its structure. Then a fixed-bed column was chosen as the most suitable technology with which to evaluate the cork adsorption. Four pharmaceuticals (diclofenac, ketoprofen, naproxen and carbamazepine) and two cosmetic compounds (triclosan and methylparaben) were treated in wastewater effluent by using a fixed-bed column. Furthermore, a novel, simple, selective and low-cost method for the pre-concentration sample before chromatography was performed in real wastewater effluent. This methodology is based on a silicone rod micro extraction combined with HPLC-DAD to simultaneous determine the concentration levels of six compounds. The adsorption capacities of cork followed this order: TCS >CBZ and MPB> KET and NAP > DCF. This behaviour could be explained by the fact that the removal of PPCPs by cork is based on hydrophobicity and the charge of the PPCP molecules. Generally, the cork showed a much higher capacity for TCS sorption, minimizing the concentrations of triclosan and avoiding the inhibition effect into biological systems, as well as minimizing fouling in MBRs.

In the last part of this thesis, two different proposals were selected as the most suitable treatment technologies for treating wastewater with high concentrations of PPCPs. However, further analyses are required to evaluate the hybrid systems.

Resum:

Els afluents de les Estacions Depuradores d'Aigües Residuals (EDARs) son una de les fonts d'entrada de contaminants més importants al medi aquàtic degut a que l'objectiu d'aquestes recau tan sols en l'eliminació de Carboni, Nitrogen i Fòsfor.

La presència de compostos antropogènics com són els compostos anti-inflamatoris no esteroïdals (naproxè, diclofenac i ibuprofè), fàrmacs com la carbamazepina, disruptors endocrins com el triclosan, marcadors antropogènics com la cafeïna i agents antimicrobians com el metil-paraben estan entre els compostos detectats a nivell traça tant a l'aigua d'entrada de les EDARs com a l'aigua de sortida.

Tractaments avançats com els bioreactors de membrana (MBR) i processos d'adsorció permeten la millora en l'eliminació de compostos farmacèutics però l'eficiència en l'eliminació dependrà de les característiques físic-químiques dels contaminants, de les característiques de l'aigua, de les condicions d'operació i del tipus de tractament aplicat. En aquesta tesi doctoral, diferents tractament avançats s'han avaluat amb l'objectiu de conèixer els rendiments, limitacions d'operació i avantatges dels tractaments.

Primerament, una estat de l'art sobre els diferents tractaments per eliminar triclosan ha permès establir quines tipologies de tractament podrien ser els més rendibles tant a nivell operacional com de costos. Els tractaments avaluats han estat a) adsorció, b) processos d'oxidació avançada, i c) tractament per filtració amb membrana.

La tecnologia de membrana va ser una de les tecnologies escollides per analitzar la capacitat per eliminar els productes farmacèutics i cosmètics, així com per poder establir les causes de l'embrutiment de les membranes. Els compostos escollit en aquest estudi van ser el triclosan, la carbamazepina i la cafeïna. Els rendiments d'eliminació van ser elevats pel triclosan i al cafeïna (>90%), mentre

que la carbamazepina va ser molt inferior degut a seu poder recalcitrant (<40%). En l'experimentació també es va detectar una inhibició del procés de nitrificació, degut a la presència de triclosan. Aquesta inhibició és va confirmar en un estudi complementari on es va quantificar la pèrdua de la capacitat nitrificant en un 60%.

El darrer capítol es centra en l'avaluació de l'adsorció com a tecnologia de tractament. En aquest cas s'ha utilitzat el suro com a material adsorbent i s'han presentat resultats de caracterització del material i resultats de capacitat d'adsorció. Per dur a terme l'experimentació es va triar la tecnologia de llit fix per tractar quatre composts farmacèutics (diclofenac, fetoprofen, naproxen i carbamazepina) i dos productes cosmètics (triclosan i metilparaben). La metodologia d'anàlisi va ser la micro-extracció en tub de silicona amb HPLC-DAD. Els resultats obtinguts van demostrar que el triclosan era el compost amb major capacitat de ser eliminat i el diclofenac el que presentava menors rendiments.

TCS> CBZ i MPB> KET i NAP> DCF

Finalment la tesi presenta una proposta de tractament on es pretén minimitzar les limitacions de cada tecnologia i fer front al tractament dels productes farmacèutics i cosmètics en base als resultats obtingut al llarg dels tres capítols de resultats.

Résumé

Les effluents des stations d'épuration des eaux usées (STEP) sont l'une des sources les plus importantes d'entrée de contaminants dans le milieu aquatique. Ces stations sont conçues essentiellement pour l'élimination des matières organiques, nitrogène et phosphores.

Les effluents d'alimentation des stations d'épuration contiennent des substances chimiques anthropiques : quelques anti-inflammatoires non stéroïdiens (comme le naproxène NAP, diclofénac DCF et Ketoféne KTF) de produits pharmaceutiques (la carbamazépine CBZ), de perturbateurs endocriniens (le triclosan TCS), de marqueurs anthropiques (la caféine) et d'agents antimicrobiens (le méthylparabène MPB). Les composés détectés dans les eaux usées sont à l'état de traces.

Différentes technologies de traitement des eaux usées peuvent être utilisées. Il s'agit de (i) l'adsorption, (ii) l'oxydation et l'oxydation avancée (Ozonation (O3), procédé Fenton et Photo-Fenton), (iii) les procédés membranaires et plus particulièrement les bioréacteurs à membrane (MBR). L'efficacité d'un procédé dépend des propriétés physico-chimiques des polluants, des caractéristiques physico-chimiques de l'eau à traiter et des conditions opératoires.

Pour l'élimination des contaminants, l'adsorption est souvent le processus de séparation préféré des systèmes aqueux. L'adsorbant le plus utilisé est le charbon actif mais le coût élevé de cet adsorbant est son principal inconvénient. La recherche d'un adsorbant plus économique, pratique et efficace est souhaitable. Le liège peut être une bonne alternative au charbon actif.

Dans ce travail, deux types de traitement sont utilisés pour le traitement des eaux usées synthétiques contenant les produits pharmaceutiques et cosmétiques. Nous avons procédé par le bioréacteur à membrane BRM et par adsorption sur le liège pour évaluer l'efficacité de chacun de ces deux procédés pour l'élimination des produits pharmaceutiques et cosmétiques des eaux usées synthétiques.

Comme nous avons déjà dit que les produits pharmaceutiques existent à l'état de traces. À cet effet, il est nécessaire d'utiliser des méthodes analytiques capables de détecter et de quantifier les produits pharmaceutiques et de soins personnels (cosmétiques) contenus à des faibles concentrations dans des échantillons d'eaux synthétiques. Une méthode innovante, simple, sélective et à faible coût a été utilisée. La méthode analytique utilisée est basée sur une micro-extraction de tige de silicone (SR) combinée à la méthode HPLC-DAD.

Nous avons procédé au traitement par bioréacteur à membrane BRM (anoxique / aérobie cyclique), équipé d'une membrane d'ultrafiltration, d'une eau contenant trois composés (la carbamazépine, la caféine et le triclosan). Ce procédé s'est avéré être une technologie efficace et appropriée pour diminuer en moyenne 97% de la demande chimique en oxygène DCO. Les taux d'élimination sont respectivement de 93,7 et 89,7% pour la caféine et le triclosan. Pour la carbamazépine, l'élimination était plus faible (36,2%) en raison de sa récalcitrance. De faible élimination de l'ammoniac ont été observées dans BRM. Ce qui suggère que la nitrification était probablement inhibée en raison de la présence de triclosan.

La dernière partie est basée sur l'adsorption en utilisant le liège (un biomatériau, nouveau adsorbant). Tout d'abord, la structure du liège a été caractérisée afin de mieux comprendre le phénomène d'adsorption. Le traitement d'une eau synthétique contenant quatre produits pharmaceutiques (Diclofinac DCF, Kétoprofène KET, Naproxène NAP et Carbamazépine CBZ) et deux composés cosmétiques (Triclosan TCS et Méthylparabène MPB) a été réalisé en utilisant une colonne (lit fixe) contenant l'adsorbant. Les ordres d'adsorption sont les suivants:

TCS> CBZ et MPB> KET et NAP> DCF

Les capacités d'adsorption peuvent être expliquées que les absorptions de PPSP par le liège reposent sur l'hydrophobie et la charge des molécules PPSP. Une étude comparative a été réalisée en utilisant le charbon actif granulé.

En perspective, nous envisagerons de faire la combinaison du MBR et l'adsorption sur le liège. Ce dernier a permis d'une part une diminution plus élevée de la teneur en triclosan et d'autre part il empêche l'inhibition de la nitrification dans MBR et par conséquent l'encrassement de la membrane (biofouling).

Resumen:

Los efluentes de las Estaciones Depuradoras de Aguas Residuales (EDARs) son una de las fuentes de entrada de contaminantes en el medio acuático receptor debido a que el objetivo principal de las EDARs es la eliminación de Carbono, Nitrógeno y Fósforo.

La presencia de compuestos antropogénicos como son los compuestos anti-inflamatorios no esteroidales (naproxeno, diclofenaco e ibuprofeno), fármacos como la carbamazepina, disruptores endocrinos como el triclosan, marcadores antropogénicos como la cafeína y agentes antimicrobianos como el metil paraben estén entre los compuestos detectados a nivel traza en los efluentes de las EDARs.

Tratamientos avanzados como los biorreactores de membrana (MBR) y procesos de adsorción permiten la mejora en la eliminación de fármacos pero su eficiencia de eliminación dependerá de las características físico-químicas de los contaminantes, de las características del agua a tratar, de las condiciones de operación y del tipo de tratamiento aplicado. En esta tesis doctoral, diferentes tratamientos avanzados se han evaluado con el objetivo de conocer los rendimientos, sus limitaciones y sus ventajas.

Primeramente, un estado del arte sobre los tratamientos avanzados para eliminar el triclosan ha permitido establecer que tipos de tratamiento podrían ser los más rentables tanto a nivel operacional como a nivel de coste. Los tratamientos considerados han sido a) adsorción, b) procesos de oxidación avanzada y c) tratamiento por filtración por membrana.

La tecnología de membrana fue la tecnología escogida para analizar la capacidad para eliminar los fármacos y productos cosméticos, así como para también establecer las causas del ensuciamiento de las membranas. Los compuestos escogidos para el estudio fueron el triclosan, carbamazepina y la cafeína. Los rendimientos de eliminación de la demanda química de oxígeno fueron muy altos llegando a alcanzar una eliminación promedio del 97%. Para la cafeína y para el

triclosan también fueron elevados pero en menor medida alcanzando 93% y 90%, respectivamente. En cambio, la carbamazepina, debido a su poder recalcitrante solo se pudo eliminar en un 36%. Con la experimentación también se detectó que el triclosan inhibe la nitrificación, reduciendo el poder nitrificante en un 60%.

El último capítulo de resultados se centra en la evaluación del corcho como material adsorbente. Primeramente se caracterizó para conocer su estructura y posteriormente se escogió la tecnología de lecho-fijo para tratar cuatro fármacos y dos productos cosméticos. La metodología de extracción fue la micro-extracción en tubo de silicona y posteriormente analizado por HPLC-DAD. Los resultados con este adsorbente permitieron conseguir rendimientos muy elevados para el triclosan y rendimientos muy bajos para el diclofenaco.

TCS> CBZ y MPB> KET y NAP> DCF

Finalmente, en la discusión final de la tesis se presenta un posible esquema de tratamiento con el que se pretende minimizar las limitaciones de cada tecnología escogida para el tratamiento de estos compuestos siendo la tecnología híbrida MBR-corcho como la que puede presentar mayores rendimientos.

1. INTRODUCTION

1.1. Pharmaceuticals and Personal Care Products in the environment

Pharmaceuticals and Personal Care Products (PPCPs) are widely used in daily life and have been identified as a potential risk to the environment since the late 1990s (Daughton and Ternes 1999). PPCPs are included in the family of emerging contaminants (ECs), including pharmaceutical products (PP), personal care products (PCPs), endocrine disrupting compounds (EDCs), surfactants, pesticides, flame retardants, and industrial additives.

However, the presence of these contaminants was first identified in surface and wastewaters in the United States and Europe in 1960s (Kyzas *et al.* 2015). PPCPs are becoming ubiquitous in the environments because they cannot be effectively removed by the conventional wastewater treatment plants due to their toxic and recalcitrant performance potential in a high spectrum PPCPs. The discharge of hospital effluent into the municipal wastewater treatment plants (WWTP) (even at diluted pharmaceutical concentrations) decreases the biodegradation process of the organic contaminants. Continuous introduction of diclofenac in anoxic sludge treatment process has been reported to reduce the gas production and reduce the denitrifying potential of microbial community present in WWTP (Tiwari *et al.* 2017).

PPCPs include analgesics, lipid regulators, antibiotics, diuretics, non-steroidal anti-inflammatory drugs (NSAIDs), stimulant drugs, antiseptics, beta blockers, antimicrobials, cosmetics, sun screen agents, food supplements, fragrances and their metabolites and transformation products. PPCP are metabolised in the human body and then excreted and released via urine or faeces into the environment. Other physicochemical and biological transformations can take place in the WWTP or waterworks, giving place to a diversity of by-products (Mompelat *et al.* 2009).

The primary sources of PPCPs in the environment are pharmaceutical and cosmetic industries, hospitals, animal waste, research activities utilizing target compounds and discharge of expired medicine or compounds in the

environment. Hospitals are one the major contributors of pharmaceuticals release in the environment. Also veterinary PhACs, urban and industrial activities can contribute realising into the media some pathogen, pharmaceutical residues and their metabolites, drug conjugates, radioactive elements and other chemicals.

PPCPs can enter in surface water by runoff of bio-solids spread on agricultural land and also with some irrigation using contaminated water sources. In the latter case, the contaminants can reach the groundwater by leaching or bank filtration. Within the surface water compartment, sediment can adsorb the PPCPs because it has a variety of binding sites or can arrive into the soil by the irrigation with the treated or untreated wastewater containing PPCPs (Wang and Wang 2016). This can affect water quality and potentially affect drinking water supplies, ecosystem and human health (Figure 1. 1). So, it is important to avoid the presence of the most widespread PP such as carbamazepine and NSAIDs in the main drinking water networks (Mompelat, Le Bot et al. 2009).
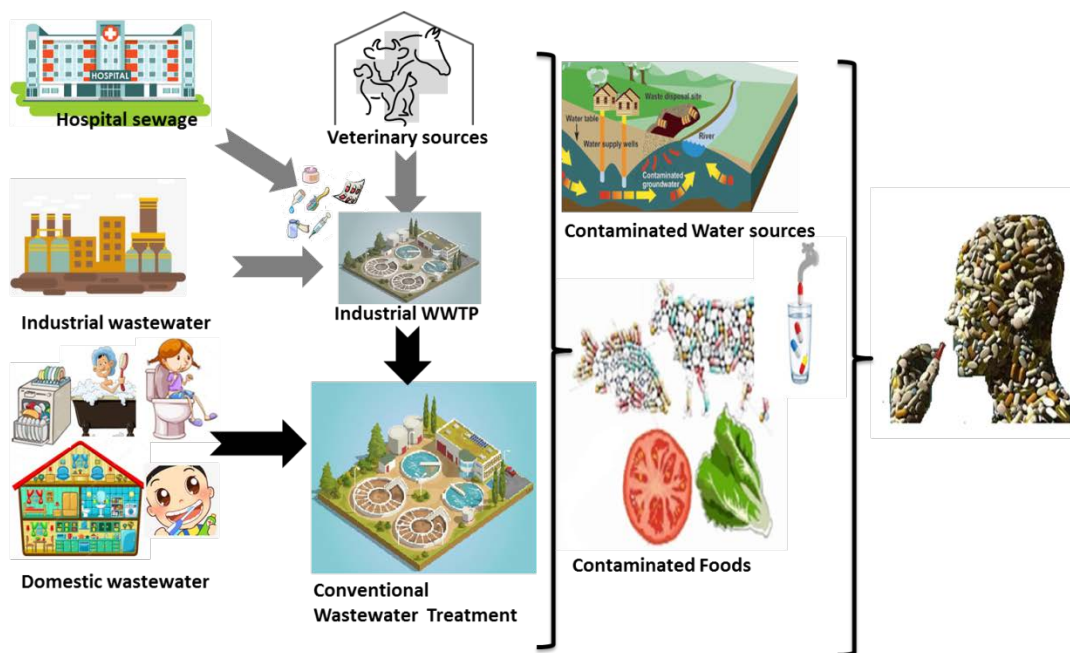
Figure 1. 1 Major Pathways of PPCPs release into the environment which cause PPCPs resistance for human

1.1.1. Environmental impacts of PPCP presences in the environment

The presence of PPCP in the receiving environment has adverse effects, causing disturbance of aquatic flora and fauna and risk to human health (Verlicchi et al., 2012). These substances are identified as emerging organic contaminants in environmental waters (Kumar and Xagoraraki 2010) and can be toxic and bioaccumulate. Bioaccumulation is typically associated with the high lipid solubility property of a compound and its ability to accumulate in the fatty tissues of living organisms for a long time period. These persistent compounds move up the food chain, and they increase in concentration as they are processed and metabolized in certain tissues of organisms, increasing their toxicity in the environment (Grandclément *et al.* 2017a).

Many short-term toxicity studies reported that drug molecules in low concentration do not have an acute toxic effect on aquatic organisms, but their constant release and exposure to aquatic biota can have long-term (chronic) effects (Tiwari, Sellamuthu et al. 2017). These effects include aquatic toxicity, pathogen-resistant development and genotoxicity (Bruce *et al.* 2010). These impacts include fish (male and female) damage to the digestive glands, deterioration on the male reproductive health of mussel (Gonzalez-Rey and Bebianno 2012) and clam DNA modification (Milan *et al.* 2013). Other laboratory studies have shown that egg production in zebra (female) fish was reduced to 50%, when they were exposed to treated wastewater for 7 days (L Lister and Kraak 2009).

Long term exposure could decline the vulture population. An study carried out in Asia demonstrated that the presence of veterinary drug diclofenac in their food caused visceral gout and renal failure (Tiwari, Sellamuthu et al. 2017). Pharmaceuticals are large and chemically complex molecules. The wide range of chemical classes represented in this group makes generalisations on their behaviour in the environment very difficult. One example is the impact resulting from discharge of chemotherapeutic drugs into the environment, given the high incidence of cancer in the population (Franquet-Griell *et al.* 2017). Numerous

environmental impacts may occur, including acute or chronic toxicity (Enick and Moore 2007), endocrine disruption (Sumpter 2005), interference with detoxification systems (Daughton and L Jones-Lepp 2001; Epel and Smital 2001), stimulation of reproductive processes (Fong 2001) and inhibition of primary productivity (Halling-Sørensen *et al.* 1998).

1.1.2. Uses and fate of PPCP in water bodies

In this section the PPCP uses and their fate into water bodies have been described. Some of the key parameters and their chemical structure have been detailed in Table 1. **1** and Figure 1.2 respectively:

1.1.2.1. Disinfectants

Triclosan (TCS): TCS is an antimicrobial agent used in PPCPs. It is an endocrine disruptor. It can combine with chlorine in water to form chloroform which is a carcinogen (Sioufi *et al.* 1977). TCS has already been a concern of scientific communities and regulatory authorities, especially in western countries. As a result, European Union (EU) has disapproved the use of TCS in biocidal products on 27 January 2016 due to its unacceptable environmental risk (EU 2016). In US, over-the-counter (OTC) consumer antiseptic wash products containing TCS can no longer be marketed after 2 September 2016 (FDA 2016).

Nowadays, antimicrobial active component TCS can be found in many consumer care products such as toothpaste, mouthwash and soaps, household cleaners and even in textiles, such as sportswear, bed clothes, shoes and carpets, acting as antifungal and antibacterial. The TCS content in these products was found to be in the range of 0.1–0.3% in weight (Sabaliunas *et al.* 2003; Schweizer 2001; Singer *et al.* 2003). TCS has been reported in wastewater and in surface water ranging from 9 ng/L to 6.7 µg/L (Ying *et al.* 2009).

1.1.2.2. Anticonvulsant

Carbamazepine (CBZ): CBZ is an anti-epileptic drug and it is also prescribed as an antidepressant. It is ubiquitously present in municipal wastewater and, due to its chemical stability; it is not significantly removed during conventional biological treatment. Therefore, it was found to be a recalcitrant pharmaceutical discharged to surface waters with secondary effluents (Zhang *et al.* 2008). CBZ is denoted as indicator PhACs by regulation internationally (Kårelid *et al.* 2017). The concentrations of CBZ in WWTP influents are typically in the 437–673 ng/L range (Santos *et al.* 2013).

1.1.2.3. Stimulant

Caffeine (CAF): CAF is an alkaloid of the methylxanthine family. Their sources are usually coffee, tea, soft and energy drinks. Caffeine is also used as a stimulant or adjuvant in psychoactive medicine (Nehlig *et al.* 1992), which explain why it is usually detected at high concentration in raw sewage (Luo *et al.* 2014). Since CAF is so frequently observed in the aquatic environment, including wastewater, surface water and ground water (Qi *et al.* 2014) , it can be an anthropogenic marker for contaminated source water (Buerge *et al.* 2003) and have been listed as an emerging organic contaminant (Rodriguez-Narvaez *et al.* 2017). The concentrations of CAF in WWTP influents are typically in the range 102 ng/L-113.2µg/L (Tran *et al.* 2018).

1.1.2.4. Non-steroid anti-inflammatory drugs (NSAIDs)

a) **Diclofenac (DCF):** DCF is one of the most widely prescribed NSAID. The DCF has been found in drinking water at concentrations below 10 ngL[-1](Rigobello *et al.* 2013). DCF was highlighted by the EU Water framework directive of 2015 as a prioritized substance for monitoring (Kårelid, Larsson et al. 2017). Studies point out that DCF has effects on different organisms even at low concentrations and that it has the highest acute toxicity on aquatic organisms among anti-inflammatory drugs (Brozinski *et al.* 2012). Moreover, DCF is listed in the high priority category by Global Water Research

Coalition. The concentrations of DCF in WWTP influents can range from below the limit of detection to 269 ng/L (Santos, Gros et al. 2013).

b) **Naproxen (NAP):** NAP is one of the most common NSAID drug. Continuous discharge of NAP into the aquatic environment could pose high risks to non-target organisms (Ding *et al.* 2017) .The high detection frequency and levels of NAP in natural waters is likely due to the low removal efficiency (below 15%) by wastewater treatments such as conventional activated sludge processes and granular activated carbon processes (Paredes *et al.* 2016). The concentrations of NAP in WWTP influents are typically in the 8.84–1617ng/L range (Santos, Gros et al. 2013).

c) **Ketoprofen (KET):** KET is widely used in medical care because it is able to treat inflammatory diseases and musculoskeletal injuries (Zunngu *et al.* 2017). Because of the large quantity of ketoprofen consumed by humans, the compound is widely detected with other NSAIDs in wastewater and surface water (Yu *et al.* 2013). The concentrations of KET in WWTP influents are typically in the 289-589 ng/L range (Santos, Gros et al. 2013).

1.1.2.5.Preservative

Methyl Paraben (MPB): MPB is widely used as antimicrobial agents in pharmaceutical preparations, cosmetic and toiletries consumer products. MPB has been banned or restricted by the Cosmetic Directive, as announced in the Official Journal of the European Union. Methylparaben-free labels are popping up on beauty products recently (Steter et al. 2016). The average concentrations of MPB in WWTP influents was 6.4 mg/L (Haman *et al.* 2015).

Table 1. 1. Overview of the physical and chemical properties of the target PPCP

Compounds	Category	Physical-chemical properties			
		MW [a]	WS[b]	pKa[c]	Log K$_{ow}$[d]
TCS	Disinfectants	289.55	$1.0 \cdot 10^{-2}$	8.14	4.76
CBZ	Anticonvulsant	236.28	$1.77 \cdot 10^{-2}$	13.90	2.45
CAF	Stimulant	194.19	21.6	10.40	-0.07
SodiumDCF	NSAID	318.13	2.37	4.30	3.91
NAP	NSAID	230.27	$1.59 \cdot 10^{-2}$	4.15	3.18
KET	NSAID	254.29	$5.1 \cdot 10^{-2}$	4.45	3.12
MPB	Preservative	152.15	2.45	8.40	1.93

[a] Molecular weight (g mol^{-1}).
[b] Water solubility (25 °C) (g L^{-1}).
[c] Ionization constant (pKa).
[d] Octanol-water partition coefficient (log Kow). SRC physical properties database.
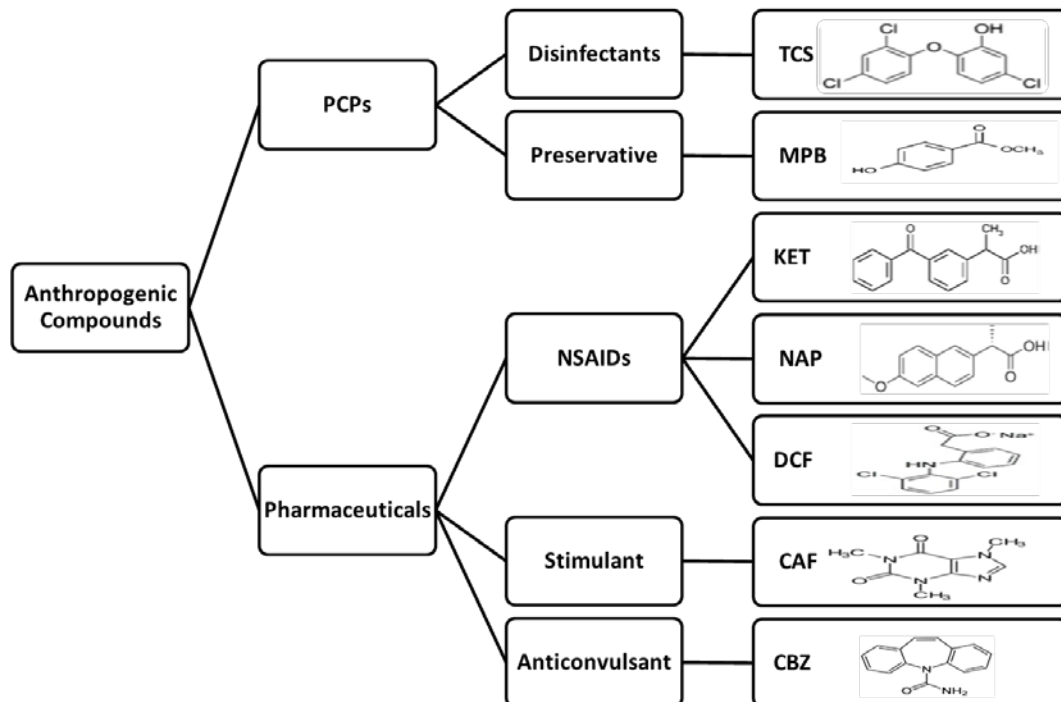
Figure 1.2 Classification and Chemical structures of the target emerging contaminants

1.2. Natural Removal mechanisms for emerging contaminants

Emerging contaminants (EC), also referred as micropollutants, are present in nature in low concentrations and high diversity. Some ECs are partly removed in WWTP via conventional treatment methods through sorption (including adsorption and absorption) and biodegradation onto activated sludge. This is considered the most important removal mechanisms for ECs.

Absorption involves the incorporation of the pollutant into the sorbent. Some examples are algal uptake and hydrophobic interactions characterized by the K_{ow} value. Adsorption is the physical adherence of molecules or ions of the micropollutant onto the surface of a sorbent. These mechanism takes place with electrostatic interactions characterized by the dissociation constant (pKa) (Gruchlik *et al.* 2018). Finally, biodegradation refers to the degradation of organic compounds by microorganisms (e.g. bacteria, fungi, algae) into simpler chemical structures. This can occur under aerobic, anoxic and anaerobic conditions, resulting sometimes in complete mineralization. The biodegradability of EC depends on the complexity of the compound structure (e.g. monocyclic or polycyclic) and also on the functional groups (e.g. halogen groups), which play an important role (Gruchlik, Linge et al. 2018).

1.3. Treatment processes for emerging contaminants removal

In light of the known risks to water quality and ecosystem health, there is currently a significant international interest in the identification of treatment technologies that are capable of effectively remove EC at trace concentrations from sewage. Most of them can easily escape a conventional treatment in a WWTP and thus, are present in the discharged effluent. For example, carbamazepine is hardly eliminated in any treatment other than advanced oxidation. Therefore, advanced methods such as (i) adsorption, (ii) oxidation and advanced oxidation processes (Ozonation(O_3), O_3-based advanced oxidation

processes, Fenton and photo fenton oxidation), (iii) membrane processes, and (iv) membrane bioreactors (MBR), become technologies that should be considered.

MBR is widely considered as being a state-of-the-art technology for municipal and industrial wastewater treatment. The main advantage of MBRs is that they can be adapted to a wide range of influent fluctuation ensuring the complete elimination of many PPCPs and providing a high quality effluent free of microorganisms and suspended solids, with a low organic matter concentration (Bui et al. 2016).

Physical techniques remain the most appropriate treatment option (Mailler et al 2015). Among them, adsorption is the most promising one since it is efficient, simple to design, unaffected by toxicity and inexpensive. The performance of an adsorption process is affected by an adsorbent's characteristics (Kyzas, Fu et al. 2015).

1.4. Removal PPCPs by membrane bioreactor systems

1.4.1. Membrane separation processes

Membrane processes used in WWTPs are microfiltration (MF), ultrafiltration (UF) but sometimes are up-graded with nanofiltration (NF) and reverse osmosis (RO) if the effluent wants to be reuse (Figure 1. 3). Filtration and adsorption on the membrane are the key removal mechanisms for membrane processes. The rejection rate depends on both MPs (molecular size and weight, charge and hydrophobicity) and membrane characteristics. With the smallest membrane pore sizes, RO is the most effective membrane process to remove MPs (Bui, Vo et al. 2016)

Atomic Microscope	Laser Microscope Scanner	Optical Microscope

REVERSE OSMOSIS — MICROFILTRATION
NANOFILTRATION
ULTRAFILTRATION — DEPTH FILTRATION

$0{,}0001\,\mu m$ — $0{,}001\,\mu m$ — $0{,}01\,\mu m$ — $0{,}1\,\mu m$ — $1\,\mu m$ — $10\,\mu m$

Free atoms

Small organic monomers
Sugars
Herbicides
Pesticides

Colloids:
Albumen protein
Colloidal silica

Virus

Bacteria (to ~ 40µm)

Crypto-sporidia

Dissolved Salts

Endotoxins/pyrogens

Red blood cells

Figure 1. 3. Membrane separation processes overview. Adapted from Monclús (2011).

MF and UF are frequently used to support other EC treatment technologies rather than being used *per se* because their membrane pores are larger than EC molecular sizes.

1.4.2. Membrane bioreactor (MBR) Technology

MBR technology combines biodegradation removal mechanisms as in Conventional Activated Sludge (CAS) systems with a solid–liquid separation using membrane filtration, usually using MF or UF (Figure 1. 4).
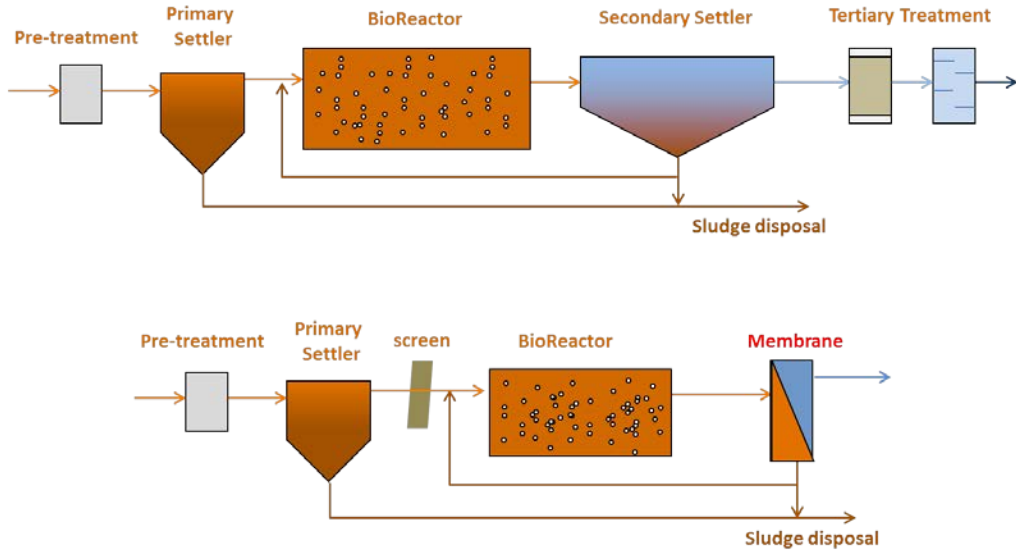
Figure 1. 4 Conventional Activated Sludge (CAS) Systems and MBR technology

Membrane bioreactor (MBR) technologies employed for wastewater treatment can be classified according to membrane configuration: flat sheet (FS), hollow fiber (HF), and multitube (MT) (Figure 1. 5). The choose of a specific configuration attends to: (a) a high membrane area to module bulk volume ratio (or packing density), (b) a high degree of turbulence for mass transfer promotion on the feed side, (c) a low energy expenditure per unit product water volume, (d) a low cost per unit membrane area, (e) a design that facilitates cleaning and (f) a design that permits modularization. The modules must permit turbulence to scour the membrane surface together with regular effective cleanings. Turbulence promotion can arise through passing either the feed water or an air/water mixture along the surface of the membrane to aid the passage of permeate through it (Simon Judd 2011).
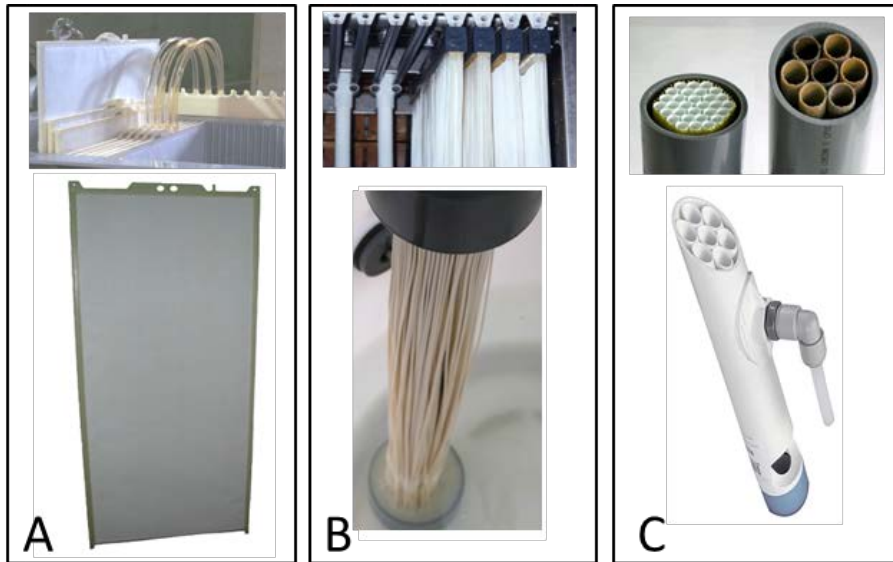
Figure 1. 5 Membrane modules configurations: (A) FS, (B) HF (c) MT

1.4.3. MBR configurations

MBRs are categorized into two configurations depending on the location of the membrane unit: submerged (or immersed) and side stream (or external) (Figure 1. 6). In submerged MBRs, the membrane module is fitted inside the reactor whereas in the sidestream configuration, the membrane is outside the reactor and the sludge is recirculated to the aeration tank. In a sidestream MBR, sufficiently high cross flow velocities need to be maintained to overcome flux decline due to fouling. The absence of a high-flow (Ng and Kim 2007) recirculation pump in a submerged MBR results in a more compact, low cost, and energy saving system.
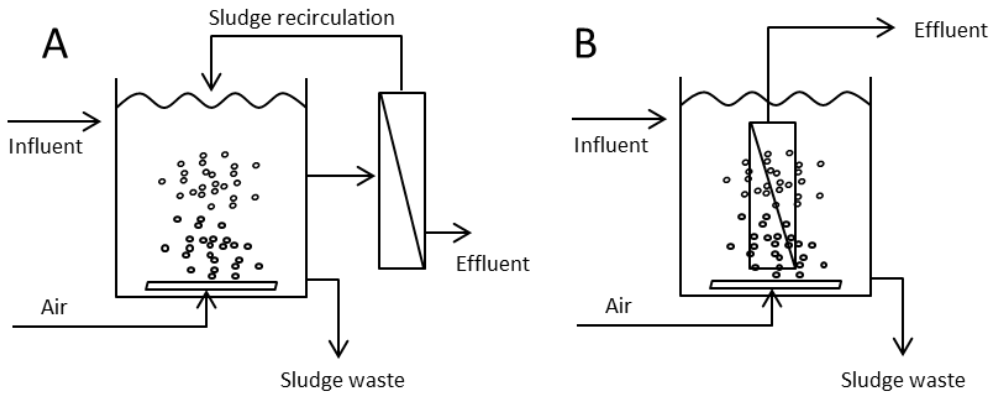
Figure 1. 6 MBR configurations: external (A) and submerged (B)

1.4.4. Fouling phenomena

Fouling of membranes remains a major challenge in the advancement of MBR technology, taking into account membrane material costs and energy demand associated with the prevention of fouling.

Membrane fouling is usually caused by interactions between foulants and membrane properties. Organic foulants are extensively involved in the hydrophobic interactions between foulants and membrane (or between foulant and foulant) for fouling (Xiao *et al.* 2011). Great efforts have been made to enhance the hydrophilicity of different membrane materials. Hydrophilic membranes have been shown to exhibit improved antifouling performance and have given rise to superior fouling-resistant membranes (Liang *et al.* 2018).

The cake formation, which is inevitable on the membrane surface, becomes one of the factors that lead to membrane fouling. In a general, the side stream of MBR has higher fouling tendency than submerged MBR. This is because the side stream of MBR needs high energy of pumping that produces high flux that will lead to repeating the fouling compared with submerged MBR. Standard blocking and cake filtration models have been indicated as the most suited for predicting initial flux decline during filtration (Figure 1. 7) (Judd 2011).
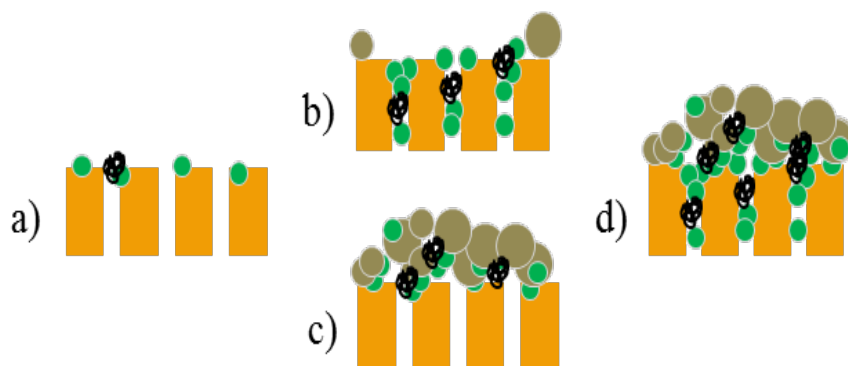
Figure 1. 7 Fouling mechanisms: (a) Started blocking, (b) standard blocking, (c) intermediate blocking and (d) cake filtration. Adapted from Monclús (2010).

There are two types of fouling. One the one hand the removable fouling, also named reversible fouling, is caused by loosely attached foulants and can be easily eliminated by implementation of physical cleaning (e.g., backwashing). On the other hand, irremovable fouling requires chemical cleaning to be eliminated. Irremovable fouling is caused by pore blocking and strongly attached foulants during filtration. The irrecoverable or permanent fouling is a permanent fouling which cannot be removed by any approaches. In general, removable fouling is attributed to the formation of cake layer, and the irremovable fouling is attributed to pore blocking (Figure 1. 8).
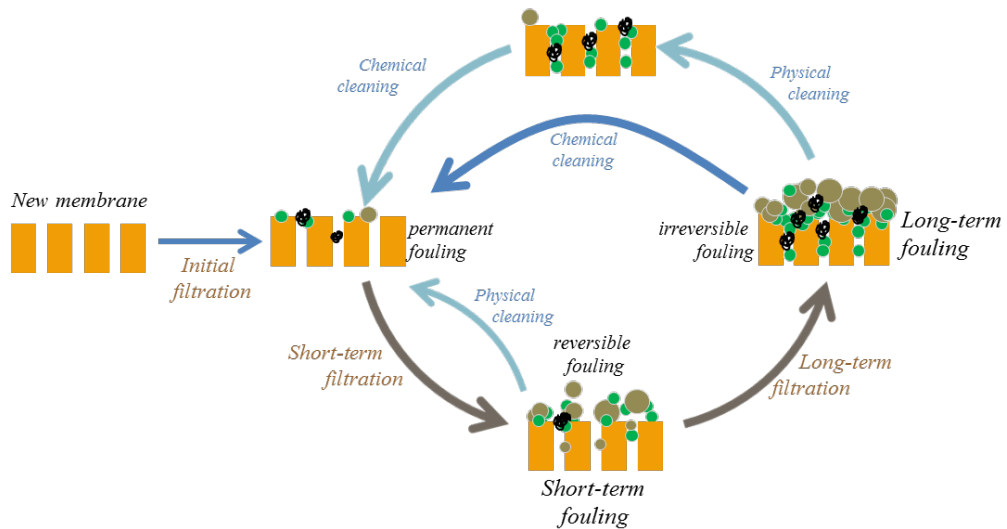
Figure 1. 8. Schematic illustration of the formation and removal of removable and irremovable fouling in MBRs.

1.4.5. Emerging contaminants removal by MBR technology

MBRs have been shown to be one of the more promising advanced secondary treatment processes, achieving high removal efficiencies for micropollutants, and thus producing higher quality effluents than that obtained by conventional activated sludge processes (Luo, Guo et al. 2014). Overall, it can be said that among ECs, EDCs show the greater removal efficiency in MBR followed by pharmaceuticals, beta blockers, PHPs and last, pesticides. When looking specifically at the pharmaceuticals group, analgesics generally show the greatest removal followed by antibiotics, anti-inflammatory, stimulants and other pharmaceuticals. The efficiencies of diverse microbial populations in the elimination of selected pesticides and ECs (especially pharmaceuticals) and the optimization of design and operating parameters are needed to provide focus for further research (Ahmed *et al.* 2017).

EC removal in MBRs largely relies on (i) microorganism consortia to metabolise MPs, (ii) sorption capacity of sludge and (iii) rejection rate of the specific membrane (Bui, Vo et al. 2016). MBR generally improves the degradation of EC

compared to conventional activated sludge (CAS) system, because it allows reaching different values for process parameters such as hydraulic retention time (HRT) or sludge retention time (SRT). MBRs operate generally at higher SRTs (at least 15 days) than CAS systems (15 days at the most) (Grandclément *et al.* 2017b) (Figure 1. 9).
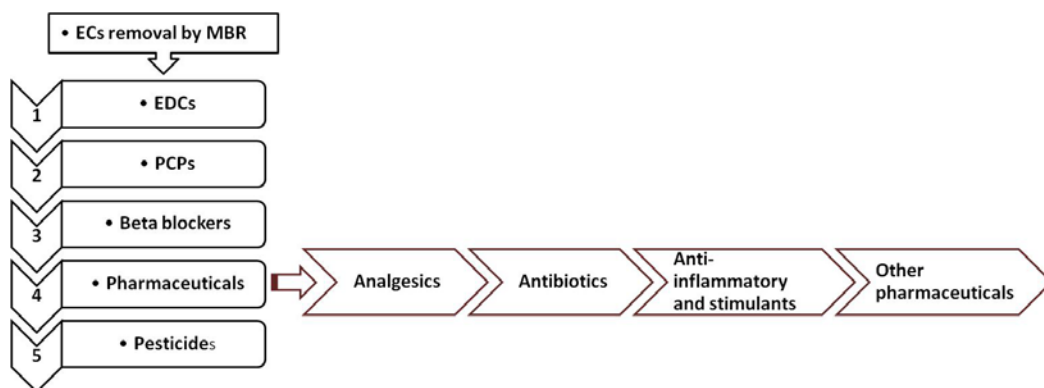
Figure 1. 9 ECs removal by MBR

1.4.5.1. MBR operating conditions effect on the elimination of pharmaceutical micropollutants

The removal of ECs in MBR systems can be affected by several factors, including sludge age, organic load, temperature, pH and conductivity. The longer sludge age or SRT of an MBR can (i) provide sufficient time for the growth of slow-growing bacteria (such as nitrifiers) and (ii) allow for the development of specialized microbial species capable of decomposing compounds of lower biodegradability. The organic loading of the wastewater plays an important role in membrane fouling and sludge filterability (Krzeminski *et al.* 2012). The operating temperature plays also an important role in both biotransformation and adsorption processes within the MBR. Several compounds increase their sorption at the time that is temperature decreasing (Alidina *et al.* 2015) and biotransformation efficiency is reduced at lower temperature (Cirja *et al.* 2008). pH has also been reported to play a critical role on the sorption of ionisable pharmaceuticals. The pKa determines in these cases the fraction of the protonated relative to the deprotonated form that exists at a given pH (Mestre *et*

al. 2009). Finally, conductivity has been shown to impact biological wastewater treatment processes. This is caused because the presence of salt may reduce bioavailability of compounds used for bacterial metabolism, inhibit degradation processes and produce harmful metabolites which could persist and accumulate in the bioreactor. Thus, the increase of salinity would limit the nitrogen removal processes (Rodriguez-Sanchez *et al.* 2018).

1.5. Removal PPCPs by physical adsorption

There are different kinds of adsorbents for removal of pharmaceutical residuals from water: Activated carbon, graphene, graphene oxide and carbon nanotube (Wang and Wang 2016). Activated carbon technologies are preferred by EU countries as an upgrading option for their WWTPs because they can remove most of the micropollutants found in urban WWTP effluents. Granular activated carbon (GAC) is often utilized as a filtration medium and as fixed beds (Sotelo *et al.* 2012). Despite activated carbon adsorption is simple to establish and operate, it bears a high capital investment and variable costs (Bui, Vo et al. 2016). Due to the relatively high cost of activated carbons, there have been attempts to utilize low cost, naturally occurring sorbents such as cork, that do not represent an economic cornerstone for the large scale implementation to remove trace organic and inorganic contaminants from water and wastewater.

1.5.1. Adsorption by cork

Powdered and granulated cork is the major sub-product of the cork industry, one of the leading economic activities in Portugal and other Mediterranean countries. Many applications have been envisaged for this product due to the fact that this natural product can be used as a sorbent without preliminary treatments and that is cheaper compared to activated carbon There are many applications envisaged for this product, that go from the production of cork stoppers and the incorporation in agglomerates and briquettes, to the use as an adsorbent in the treatment of gaseous emissions, waters and wastewaters (Figure 1. 10) (Pintor *et al.* 2012). Research is increasing on this subject and there is still a lot of room for

advances. New applications can be investigated and scale-up of the existing technologies could be designed.

Figure 1. 10. Stoppers for wine bottling wine and granulated cork

The chemical composition of cork consists primarily of suberin and lignin, the other organic constituents being polysaccharides (cellulose and hemicellulose) and extractives (waxes and tannins) (Pintor, Ferreira et al. 2012). The interaction of cork with organic pollutants, which are essentially hydrophobic, can be explained by its structure, especially its aromatic domain of suberin and lignin. The fact that cork is hydrophobic by itself has an advantage of affinity over other natural materials for the removal of organic pollutants. Cork powder and granules can also be used as a precursor for activated carbons with good surface properties such as surface area and porosity. The cork as a new adsorbent there are not regulations for disposal and at the moment it has to be treated as a solid waste or hazardous waste with their specific regulation if the cork has been used as absorbent.

2. OBJECTIVES

2.1. Research hypothesis

Municipal WWTPs are designed to control a wide range of substances, such as particulates, carbonaceous substances, nutrients and pathogens. While these substances can be efficiently and consistently eliminated, the removal of micropollutants is often insufficient. Hence, the evaluation of the fate and removal of micropollutants, especially Triclosan, as a selected compound for its toxicity in bio-treatments during wastewater treatment and an evaluation of new advanced technologies will make a step forward into the improvement of PPCP removal and the optimization of treatment processes. This will potentially prevent the release of these potentially harmful micropollutants in the aquatic environment.

To achieve it, it will be necessary to work on the following issues:

- To compare and to acquire knowledge on the different physical, chemical and biological methodologies for PPCP treatment
- To improve the knowledge on biological treatment technologies for PPCP removal.
- To evaluate the effect of high PPCP concentration into activated sludge processes.
- To evaluate new technologies for PPCP removal.

2.2. Thesis Objective

The main objective of this thesis is:

> **To evaluate the advanced and alternatives treatments for Pharmaceuticals and Personal Care Products elimination**

In order to accomplish this main objective, it has been defined different sub-objectives.

A. To make an overview of the state of the art of Triclosan removal technologies in wastewater.

    a. To compare and to evaluate advanced methods such as (i) adsorption, (ii) oxidation and advanced oxidation processes (Ozonation(O_3), O_3-based advanced oxidation processes, Fenton and Photo-Fenton oxidation), (iii) membrane technology (including membrane bioreactors (MBR)).

B. To apply the MBR technology for PPCP rich-influent treatment

    a. To evaluate the membrane fouling.

    b. To find the causes of membrane fouling and the capability to remove PPCP

    c. To evaluate the biological activity of the activated sludge treating high-rich triclosan influent.

C. To evaluate the cork as a new adsorbent.

    a. To characterise cork as an adsorbent (structure and characteristics)

    b. To evaluate granulated cork for PPCP removal in wastewater effluents

    c. To apply a silicon rod method for PPCP analysis in real WWTP influent

The thesis structure is detailed as follows in Figure 2. 1.
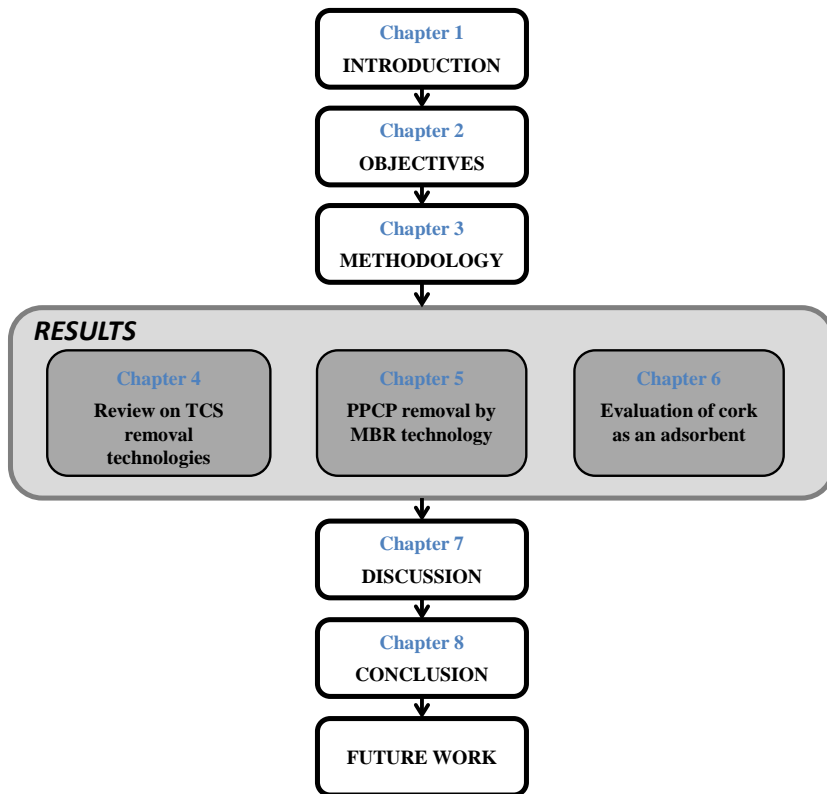
Figure 2. 1. Thesis road map

3. METHODOLOGY

This chapter describes the research methodology followed in this thesis. Firstly, the lab-scale MBR system and materials are presented for experimental studies. Secondly, the reagents and solutions are listed. Finally, the analytical methods are described.

3.1. Experimental systems

3.1.1. Lab-scale Membrane bioreactor (MBR)

The lab-scale membrane bioreactor (**Figure.3.1**), located at the Scientific and Technology Park of the University of Girona (Girona, NE Spain), consisted of a 33 L anoxic tank connected to a 26 L membrane tank (working volume) with a ZW-10 submerged ultrafiltration hollow fibre (UF-HF) membrane module (Zenon/Suez) with a nominal pore size of 0.04 μm and a total membrane area of 0.93 m^2 (*Table 3. 1*) (Monclús et al. 2011)..

The system was fed with a synthetic influent prepared twice a week and stored under mixing conditions in a 150 L tank at 4 °C, which has been described in previous studies (Table 5. 1) (Puig et al. 2007). The composition of this influent was intended to simulate municipal sewage and was continuously pumped into the reactor using a peristaltic pump (Watson-Marlow, UK). Permeate was obtained using a gear pump (Micropump, USA) controlled by a pressure transducer (Endress+Hauser, Sweden) to create a vacuum pressure drop over the membranes and monitoring the transmembrane pressure (TMP) to evaluate the fouling phenomena.

Table 3. 1 Membrane and module specification

Description	ZENON (ZW-10)
Type	HF UF
Membrane material	PVDF
Pore size, μm	0.04
Internal fibre diameter, mm	0.8
External fibre diameter, mm	1.9
Dimensions of module (LxWxH), mm	109.54x109.54x692.15
Total effective membrane surface area, m^2	0.93

The wastewater was pumped from the buffer tank into the reactor using a peristaltic pump (Watson-Marlow). The permeate was obtained by applying a vacuum pressure drop over the membranes using a gear pump (Micropump) controlled by a pressure transducer; the trans-membrane pressure (TMP) values were stored in the Supervisory Control And Data Acquisition (SCADA). The permeate was collected in the permeate tank to ensure constantly sufficient water for backwashing the membranes. Ultimately, the treated effluent collected in the permeate tank is discharged from the lab-scale plant to the sewer Figure 3. 1. All the data is accessible on-line by a developed access control system (www.colmatar.es).
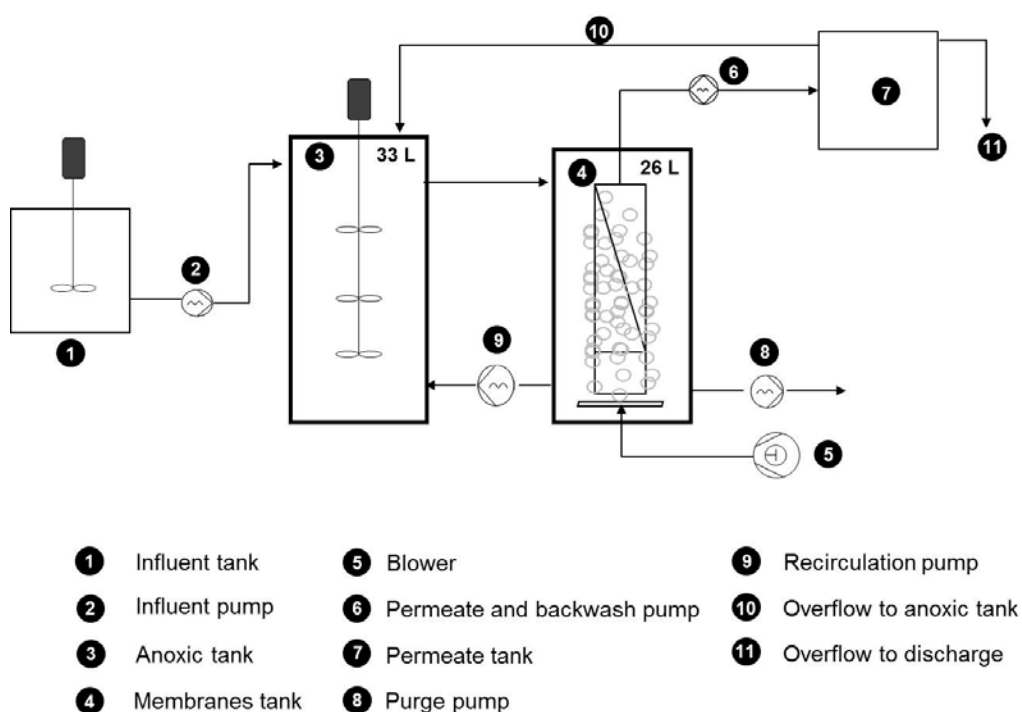
Figure 3. 1 Schematic diagram of the lab-scale membrane bioreactor

3.1.1.1. Membrane cleaning protocol

Acid and basic chemical cleanings were carried out for the membrane when required. For basic cleaning the membrane was submerged ex-situ in a 0.05% wt hypochlorite solution and for acid cleaning, the same procedure was undertaken

using a 0.5-1% wt oxalic acid solution. The membrane photos (Figure 3. 2) shown the efficacy of the membrane cleaning.

Figure 3. 2. Membrane before cleaning (left) and after cleaning (right)

3.1.2. Batch reactors (BRs)

Three batch reactors (BRs) with a total volume of 1.5L, equipped with external water jackets to maintain a constant temperature of 20°C (Figure 3. 3), were employed in the batch tests. Air was injected into each reactor by means of a plastic tube connected to air-stones to generate fine air bubbles and to facilitate oxygen transfer to microorganisms (Monclús *et al.* 2010; Puig *et al.* 2010).

The experiment consisted of a 24-hour aerobic phase and samplings were carried out periodically from each BR in order to monitor the nutrients and PPCP concentrations.
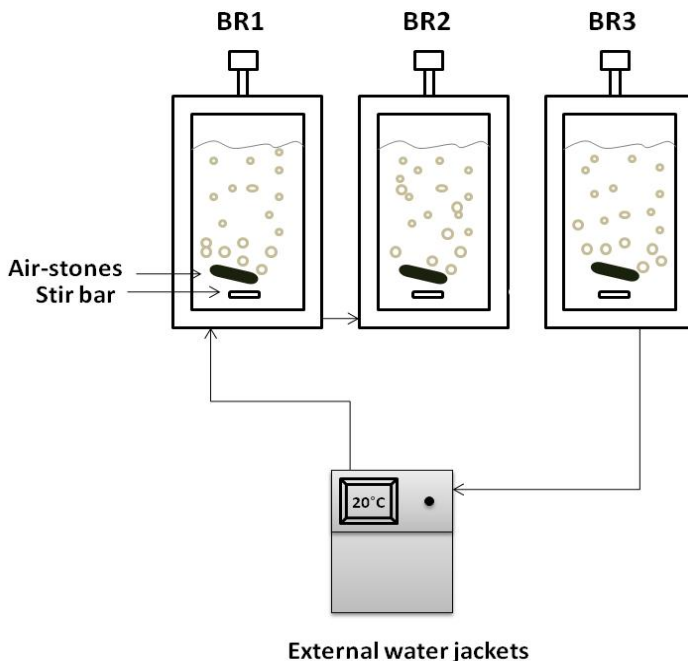
Figure 3. 3. Schematic diagram of BRs

3.1.3. Fixed-bed column

The solutions have been carried out in shaking flask (AFORA, Spain) of volume 1L in a rotary shaker (250 rpm). The column fixed-bed (Alco SuministresPerALaboratori S.A) had an internal diameter of 3.2 cm and an active length of48 cm, resulting in a bed volume (BV) of 410mL. The second column fixed bed (AFORA. Spain) had a volume of 40 cm^3 (0.5 cm i.d., 0.8 cm o.d).

The substrate solution from the bioreactor was fed in fixed-bed reactor by a peristaltic pump (Watson Marlow, UK) through the column in an up-flow mode via a peristaltic pump (Masterflex L/S, USA)under aerobic conditions (without forced aeration) .The picture of the experimental setup is shown in Figure 3. 4.
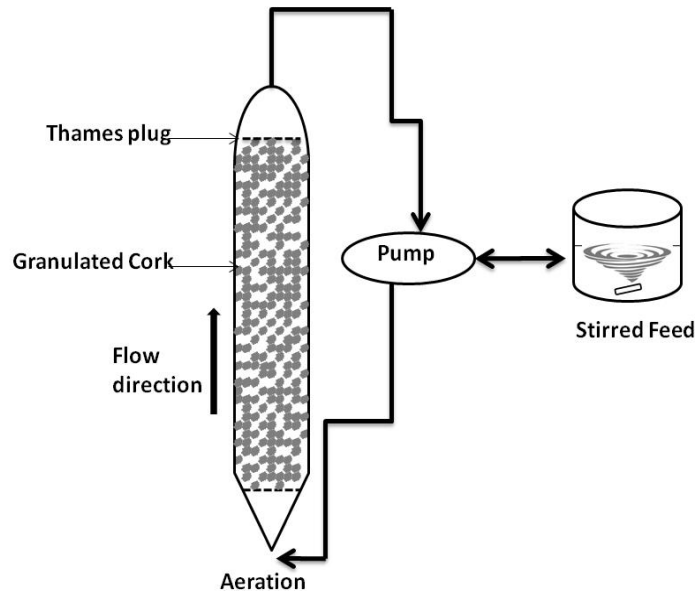
Figure 3. 4. Schematic diagram of the column fixed bed

3.1.3.1. Adsorbents

The cork, kindly supplied by the Cork Centre (Palafrugell, Girona), was sifted to attain powder particles of 2-3.5mm, cleaned three times thoroughly with bi-distilled water, and air dried before use. The type of GAC—coal-based Calgon Filtrasorb 100 (F100) (Pittsburgh, PA, USA) was selected for evaluation. The individual fractions of GAC vary in both volume and mass since it was not possible to withdraw exactly defined volume or weight fractions. The fractions were subsequently dried at 105 °C until weight constancy around 12h prior to storage in a desiccator until use. It was sieved manually using mesh seize 2 mm.

Table 3. 2. Summary of experimental systems used in this doctoral thesis

Experimental systems	Chapter	Section
Membrane bioreactor (MBR)	Chapter 5	5.2.1
Batch reactors (BR)	Chapter 5	5.2.3
Fixed-bed column	Chapter 6	6.2.1

3.2. Reagents and solutions

3.2.1. PPCPs and solutions

TCS, CBZ, CAF, NAP, KET, DCF sodium salt and MPB were purchased from Sigma Aldrich (Spain).

A standards stock solution (250 mg.L^{-1}) containing all these compounds was prepared in methanol, stored in brown glass bottles and kept at 4°C in order to avoid degradation during the test period. This solution was prepared monthly. Working standard solutions of 0.5 and 1 mg.L^{-1} were prepared daily by diluting this stock solution with ultrapure water obtained from a Millipore purification system (Millipore, USA). Chromatographic grade acetonitrile was provided by Fisher (USA) and sodium acetate and acetic acid were from Sigma Aldrich (Spain). NaOH and HCl solutions were used for the pH adjustment of the test solutions. All chemicals used in this study were of analytical grade.

3.2.2. Composition of synthetic wastewater

3.2.2.1. Composition of synthetic wastewater of MBR experiment

The system was fed with a synthetic influent prepared twice a week and stored under mixing conditions in a 150 L tank at 4 °C, which has been described in previous studies (Puig *et al.* 2007) (Table 3. 3 and Table 3. 4).

Table 3. 3. Composition of synthetic wastewater

Compounds	Quantity in 150 L	Compounds	Quantity in 150 L
CH_3CH_2OH	40.5mL	K_2HPO_4	2.7g
Meat extract	84g	Na_2HPO_4	2.1g
Milk	60mL	KH_2PO_4	1.05g
$NaHCO_3$	42g	NH_4Cl	27.4g
Leachate	1995mL	Micronutrients	200 ml

Table 3. 4. Composition of micronutrients

Compounds	Concentration (g/L)
$MnCl_2 \cdot 4H_2O$	1.4245
$ZnCl_2 \cdot 2\ H_2O$	0.0135
$CoCl_2 \cdot 2\ H_2O$	0.1642
$MgSO_4 \cdot 7\ H_2O$	49.2720
$FeCl_3 \cdot 6\ H_2O$	5.4046
$CaCl_2 \cdot 2\ H_2O$	8.8200

3.2.2.2. Composition of synthetic wastewater of BRs experiment

Synthetic wastewater was prepared with 4.0 g of $NaCH_3COO$, 0.6 g of $NaHCO_3$, 0.4 g of NH_4Cl, and 0.5 mL of micronutrients per 500 mL to obtain a standard influent with the required proportions of sodium bicarbonate to avoid alkalinity limitation (Monclús *et al.* 2009). A nitrate solution was prepared by dissolving 0.61 g of $NaNO_3$ in 100 mL of tap water.

3.3. Analytical Methods

3.3.1. Determination of basic parameters

Standard methods (APHA, 2005) were performed to determine the following parameters (Table 3. 5).

Table 3. 5 Analytical methods used for the determination of the influent and effluent concentration

Total suspended solids (TSS)	APHA standard method 2540D
Volatile suspended solids (VSS)	APHA standard method 2540E
Chemical oxygen demand (COD)	APHA standard method 5220B
Total Kjeldahl nitrogen (TKN)	APHA standard method 4500-Norg B. using boric acid and destillatorBüchi (postfach, Switzerland)
Ammonium (NH_4^+-N)	APHA standard method B324, using boric acid and destillatorBüchi (postfach, Switzerland)
Nitrites (NO_2^--N) and nitrates (NO_3^--N)	APHA standard method 4110B, using ionic chromatography (Metrohm 761-Compact)
Alkalinity (Alk)	APHA standard method 2320B

Off-line pH was measured with pH meter (pH-Meter Basic 20+, Crison PLC, Spain).

3.3.2. Activated Sludge characterisation

The dewaterability of the different sludge samples was evaluated by measuring the capillarity suction time (CST) (Triton electronics, type 304 B) with CST papers and the 6mL sludge sample (Scholz *et al.* 2007). The capability of the sludge to be filtered (filterability) was determined by means of the paper filtration test method (Kubota 2004) (Dalmau et al. 2014) (Table 3. 6).

Table 3. 6 Activated Sludge characterisation techniques

Total suspended solids (TSS)	APHA standard method 2540D
Volatile suspended solids (VSS)	APHA standard method 2540E
Capillarity Suction Time (CST)	APHA standard method 2710G
Filterability	Measure of time for 6mL sludge sample filtration

3.3.3. PPCP analysis

3.3.3.1. Liquid chromatography–mass spectrometry in tandem (LC–MS/MS) analysis
Solid and phase extraction (SPE)

Micropollutant concentrations were determined by a previously described analytical method (Garcia-Rodríguez et al. 2015). The analytes were extracted by using 6 mL-Oasis HLB solid phase extraction (SPE) cartridges containing 200 mg of poly (divinylbenzene-co-N-pyrrolidone) (Waters, Milford, MA, USA). In order to determine the best SPE extraction conditions, cartridges were first conditioned with 3 ml of Ethyl acetate and 3 ml of methanol following by 3ml of Milli-Q. A volume of 100 ml of influent and 200 ml of permeate filtered were percolated through the cartridges (acidify the sample at pH =1,5 with acid sulfuric). After extraction, the cartridges were washed with 3ml of water with 5% aqueous Methanol and dried under vacuum for 15 min. The samples were then eluted using 1ml of ethyl acetate; and the extracts were evaporated to dryness under nitrogen stream in the fume hood. Samples were reconstituted in 750µl of methanol: water solution (25:75).

Chromatographic analysis was then performed in an ultra-performance liquid chromatography(UPLC) (Agilent TM 1290 Infinity, Palo Alto, CA, USA) coupled to a 6430 triple quadrupole mass spectrometer detector (Agilent Technologies, Palo Alto, CA, USA) and equipped with a Kinetex C18column (100Å, 50mm x 2.10 mm x 2.6 µm) (Phenomenex, Spain). Chromatographic

separation of three compounds (TCS, CBZ and CAF) was carried out at a flow rate of 0.4 ml/min with mobile phase gradient program: 0- 2min (A:B) 80:20, 2-10 min (A:B) 15:85, 10-18 min (A:B) 0:100. An injection volume of 5μ L was kept constant for all the analyses (Table 3. 7).

Table 3. 7. Chromatographic and MS parameters of LC–MS/MS method and LODs for the target compounds.

Compound	Retention Time (min)	Transitions (m/z)	Fragmentor voltage (V)	Collision energy (V)	Ionization mode	LOD µg.L^{-1}
Caffeine	1.95	195 → 138	135	20	Positive	5
Carbamazepine	6.55	237 → 194.1	135	20	Positive	6
Triclosan	9.80	287 → 35	80	5	Negative	2

3.3.3.2. *Chromatographic high performance liquid chromatography (HPLC-DAD) analysis*

The Agilent 1200 series high performance liquid chromatography system equipped with two pumps (G13128), a degasser (G1379B), an auto-sampler (G1329B) and a DAD detector (G4212A), system control and data acquisition were performed using Agilent Chem Station software. The column was C18 Kinetik column (2.6µm, 50×2.10 mm i.d.) (Phenomenex,USA) (Figure 3. 5). The analytes were separated in a C18 Luna column (50 × 2 mm, 2.5 µm) (Phenomenex, USA) using a mobile phase in gradient mode consisting of (A) 0.1 % acetic acid and 0.3852g of sodium acetate in Milli-Q water, and (B) acetonitrile (Table 3. 8).

Figure 3. 5 HPLC –DAD system

Table 3. 8. HPLC-DAD retention times and wavelength values of compounds

Compounds	Retention time (min)	Wavelength (nm)	LOD ($\mu g.L^{-1}$)
Triclosan	17.4	242	5.45
Diclofenac	15.5	280	3.99
Ketoprofen	13.8	242	2.42
Naproxen	13.3	250	3.65
Carbamazepine	11.12	242	4.48
Methyl paraben	7.63	250	3.44

3.3.4. Silicone rod extraction of emerging organic contaminants

The commercial polydimethylsiloxane (PDMS) rod pre-concentration techniques have been applied to pharmaceuticals and personal care products. The determination of the range of compounds was carried out by Chromatographic HPLC-DAD.

3.3.4.1. PDMS rod extraction

Commercial 10 mm elastomer PDMS rods were cut from the PDMS cord (Figure 3. 6). These were then cleaned and stored in methanol and, immediately prior to use, were dried with a lint-free tissue. The different parameters to be studied affecting the extraction of the analytes (volume of solution, pH, ionic strength (addition of salt), organic modifiers…) and the desorption (solvent, volume, desorption time and sonication).
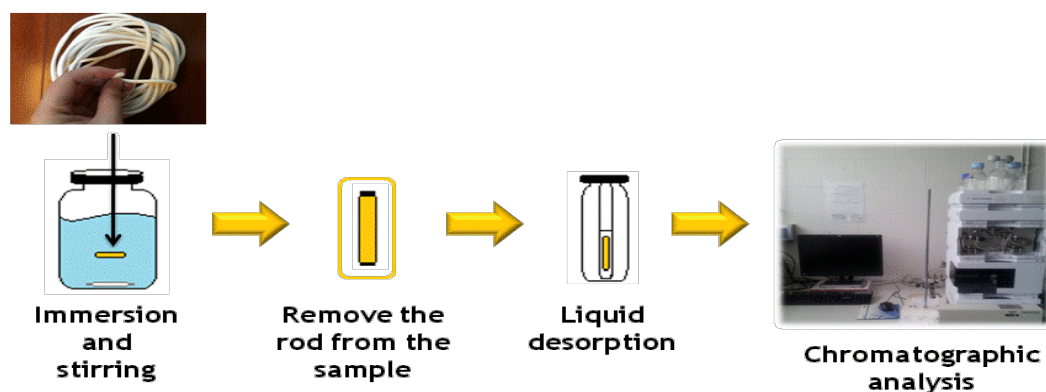
Figure 3. 6. Silicone rod method

3.3.4.2. Development of the sorptive extraction of pharmaceutical and cosmetic products

Commercial 10 mm elastomer PDMS rods (appx. 0.037 g) were cut from the PDMS cord. These were then cleaned and stored in methanol and, immediately prior to use, were dried with a lint-free tissue. In a typical assay, the PDMS rod was immersed in a 125 mL amber vial containing 50 mL of a 100 μgL^{-1} of all the compounds in ultrapure water and 15% w/v of NaCl. The pH was adjusted to 2. The vial was then closed and the extraction was performed for different periods of time (3, 5, 8 and 10 h).The experiments were performed three times using a ten-point magnetic shaker (MultiMix D, Ovan, Badalona, Spain) at 200 rpm. After extraction, the PDMS rod was removed with clean tweezers and then dried with a lint-free tissue. The rod was then placed into a tapered glass insert containing 200µL of MeOH. The Verex-EU vial (9mm screw, 2ml amber) (Phenomenex, USA) was closed allowing the desorption process to take place for

times 30 min with sonication in ultrasonic bath (J.P. Selecta, Spain). The PDMS rod was removed and 10µL of the extract was then injected into the liquid chromatograph.

3.3.5. **Scanning electron microscopy (SEM)**

The morphology was observed by a scanning electron microscope (SEM) (Model ZEISS DSM-960A). Samples were examined at a magnification range of 20x to 500x.

Representative pictures of cork samples were taken and particle size distribution was determined from these using the Feret diameter (Figure 3. 7) with a resolution of 3,5 nm and image logging using digitizing card I Querc PCI program. The Signal detectors are Secondary electrons (SE), Backscattered electrons (BSE) and Catheter-luminescence (CL). The X-ray detector for energy separation (EDX) is Oxford Link Isis L200B, equipped with ultra-thin windows Beryllium, silicon detector (li) and resolution of 135. The detection of elements of an atomic number was equal to or greater than 6 (C).
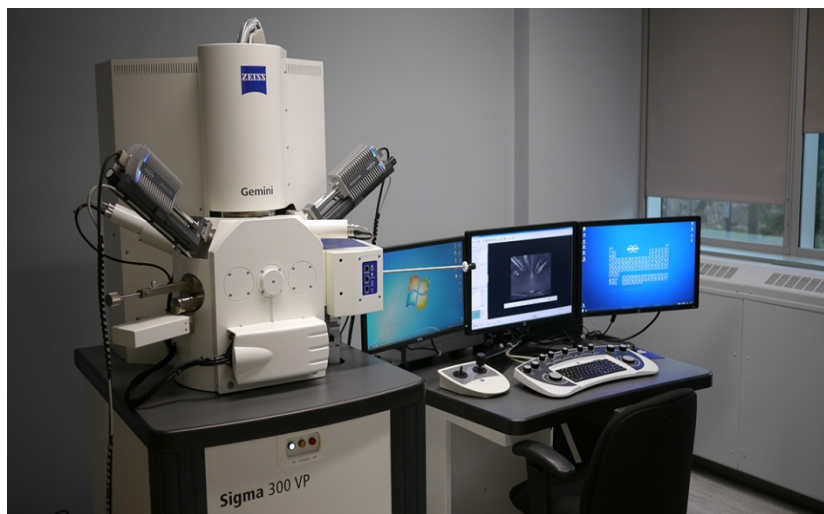
Figure 3. 7 Scanning electron microscopy (SEM)

RESULTS

4. Advanced technologies for Triclosan removal in wastewater: A state-of-the-art review

4.1. Background, motivation and objectives

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol) is a common synthetic antimicrobial agent that has been incorporated into more than 700 different industrial and personal care products. Today, triclosan (TCS) can be found in personal hygiene products (e.g. toothpaste, mouthwash and soaps), in household cleaners and textiles (e.g. sportswear and bedclothes) as well as in shoes and carpets, where it acts as antifungal and antibacterial agent. The amount found in such products ranges from 0.1–0.3% (Sabaliunas *et al.* 2003; Schweizer 2001; Singer *et al.* 2003). TCS is a product intended for external use on the human body and is subjected to very few metabolic alterations which means TCS can be released into the environment at various stages of its life-cycle.

In EU environmental regulations, pharmaceuticals and hormones are a highly controversial group of compounds. TCS is an endocrine disruptor and can combine with chlorine in water to form chloroform which is a carcinogen (Sioufi *et al.* 1977). However, TCS is considered more of an evolving risk, as information about the contaminant is still emerging and it has only recently been restricted within the EU ((COM) 2014) and the US ((USFDA) 2015). This review focuses solely on this common antimicrobial drug because of widespread interest in TCS among regulators and the public alike.

On disposal by consumers, TCS is washed down the drain and primarily conveyed to wastewater treatment plants (WWTPs) and then removed by conventional treatment techniques (J Benotti *et al.* 2009). However, due to the incomplete removal by these treatment processes, residual TCS is continuously being released into receiving waters through wastewater discharge. In their study, Ying *et al.* (2009) reported concentration rates in surface water ranging from 9 ng·L^{-1} to 6.7 μg·L^{-1}.

TCS exhibits a tendency to accumulate and persist in biosolids, and it has been estimated that up to 50% of the TCS in WWTP influent will remain in the biosolids of the WWTPs themselves [10, 11]. Consequently, applying biosolids containing residues of TCS as agro-fertilizers for land, poses a potential risk to

the ecosystem and eventually to humans (Chalew and Halden 2009). TCS is a hydrophobic compound with a high $logK_{OW}$ of 4.76 (see **Table 1** for its physical–chemical properties) and it is likely to be adsorbed into organic particles in sewage sludge treatment process and then be transported to the land sludge applications (van Pinxteren *et al.* 2010).

This highlights the importance wastewater and sludge management strategies have and which is why wastewater treatment using advanced methods like (i) adsorption, (ii) oxidation and advanced oxidation processes AOP, (iii) membrane processes, (iv) membrane bioreactors MBR (v) combined processes: MBR and powder activated carbon (MBR/PAC), AOP/PAC and/or AOP/membrane to remove TCS have been studied extensively in recent decades.

So far, no published reviews have focussed on comparing the overall effectiveness of major sewage treatment technologies in eliminating a range of TCS, or on identifying the potential of increasing TCS elimination by enhancing existing treatment processes.

4.2. TCS removal technologies

4.2.1. TCS removal by adsorption.

To enhance the adsorption capacity for TCS, different adsorbents have been researched and developed to adsorb TCSs in aqueous solution. This section will focus on carbon-based adsorptive materials, including activated carbon, graphene and carbon nanotubes (known as graphene sheets) that are considered as a highly promising adsorption technique. The different adsorbents' TCS removal efficiencies are summarized in Table 4. 1.

Table 4. 1. The removal of TCS by adsorption

Adsorbent	Medium	Influent concentration	Conditions	Removal efficiency (%)	References
PAC	Effluent wastewater	135ng/L	Q=10mg/L,	~23	(Mailler *et al.* 2015)
	Wastewater	2.4µg/L	pH 7.5, T 20.1°C Q=100mg/L	100	(Sheng *et al.* 2016a)
	Surface water	10-250ng/L	pH 8.2, Q=5mg/L, time 4h	98	(Westerhoff *et al.* 2005)
GAC	secondary effluent	108 ± 14ng/L	Q=20 g µGAC/ m3 Time = 10 and 20 min	19	(Mailler *et al.* 2016)
	Synthetic secondary effluent [15]	1-40 (µg/L)	pH7.3-7.8,25°C,35min	100	(Paredes et al. 2016)
	Grey water [16]	2 .032(µg/L)	29g,2h,25°C pH8.4,Grey water	95	(Hernández-Leal et al. 2011)
CNT	Synthetic water	50-2000µg/L	pH7, Q=0.5-2.0mg Qm=105,4-558.2 mg/g	-	(Cho *et al.* 2011)
Organo-zeolites	Synthetic water	40mg/L	Q=10mg,pH6.71	~100	(Lei *et al.* 2013)
Biochar	secondary effluent	300µg/L	Q=0.4g/L	32	(Tong *et al.* 2016)
Dried sludge	secondary sedimentation	20 µg/L	Q=100ml, pH6.5, T 25°C, Time 6h	~100	(Tohidi and Cai 2016)
Magnetic activated carbon	River water	20mg/L	Q=50mg/L	43	(Liu *et al.* 2014)

4.2.2. Activated carbon

The common materials for the synthesis of activated carbon (AC) are petroleum residue and natural coal wood that are used as adsorbent and AC is one the important treatments for removing residual micropollutants (Theydan and Ahmed 2012). In recent years, AC has undergone an evolution in its composition, size and the operating conditions. This technology is preferred by EU countries as an upgrading option for their WWTPs because they can remove 80% of the micropollutants found in municipal WWTP effluents (Bui *et al.* 2016). The removal performance of AC is governed by the physicochemical properties of the sorbent (surface area, pore size distribution, surface charge, oxygen content) and the properties (shape, size, charge, and hydrophobicity) of the solute (Jung *et al.* 2015b). AC comes in two forms: powdered activated carbon (PAC) and granular activated carbon (GAC).

TCS resistant to conventional processes can be removed by adsorption after meticulously selecting the adsorbent and operating conditions. GAC tends to adsorb hydrophobic organic compounds and successfully removes 100% (or very close to) of TCS (Hernández-Leal *et al.* 2011; Katsigiannis *et al.* 2015; Paredes *et al.* 2016) due to the hydrophobicity of TCS and, hence, a higher affinity for carbonaceous structures (Patiño *et al.* 2015).

PAC 100 mg/L and 50 mg/L efficiently removes 100% and 95%, respectively, of TSC. Decreasing the amount of PAC, decreases the amount of TCS removal i.e. 75% elimination if 10mg/L is used (Sheng *et al.* 2016a). While a high dose of PAC allows very high TCS removal rates to be attained (>90%), it is at a much higher cost (Mailler *et al.* 2015).

The external surface area of the adsorbent materials and the availability of mesoporous volume have been shown to be decisive in the amount of adsorbate retained (Patiño et al. 2015). TCS removal is influenced by the combination of $logK_{OW}$ solute and pKa values because it is hydrophobic and has a high pKa value (>7) which means it has high adsorption by AC (Shanmuganathan *et al.*

2015b). Increasing the amount of oxygen-containing functional groups on the surface of the AC decreases the adsorption of organic solutes, indicating preferential adsorption for water molecules over organic solutes at these sites (Li *et al.* 2002).

Pore blockage and direct site competition are considered to be the most common mechanisms that would affect activated carbon sorption in the presence of natural organic matter (NOM) (Behera *et al.* 2010). The inorganic constituents of water, such as Ca, form complexes with the natural organic matter in water or precipitate as $CaCO_3$, thus reducing the adsorption capacity of the activated carbon filters (Pastrana-Martínez *et al.* 2010). The residual TCS in secondary effluent can barely be removed by the fixed-bed of GAC(Ma *et al.* 2017). In the case of GAC, screening, with respect to hydraulic capacity and carbon usage rate, is a necessity if the specific product being used has not previously been tested on similar wastewater. If the explicit task is to remove as much pharmaceutical residue as possible from new wastewater, then using PAC would be recommended. However, the high performing GAC process can also reach the same performance levels as PAC can(Kårelid *et al.* 2017).

4.2.3. Nanotubes

Several different types of carbon nanotubes (CNTs) are currently being produced. The standard industrial types are: 1) single-walled carbon nanotubes (SWCNT) which are composed of a single cylinder, 2) double-walled carbon nanotubes (DWCNT), which are made up of two layers and 3) multi-walled carbon nanotubes (MWCNT) which are composed of multiple layers of graphene sheets rolled into a long, thin, hollow cylinder with a nanoscale outer diameter that is typically 1-30 nm (Figure 4. 1) (Jackson *et al.* 2013). The adsorption properties of CNTs depend on various factors, including adsorption site, surface area, purity, and surface functional groups. CNT bundles have four potential sites for the adsorption of different pollutants: (i) the *internal sites* i.e., the hollow interior of individual nanotubes (available only if the caps are removed and the

open ends are unblocked), (ii) the *interstitial channels* i.e., the channels between individual nanotubes in the bundles, (iii) the *grooves* i.e., the grooves present on the periphery of a nanotube bundle and the exterior surface of the outermost nanotubes where two adjacent parallel tubes meet, and (iv) the *outside surface* which is the curved surface of individual nanotubes on the outside of the nanotube bundles (Jung et al. 2015b) . The surface chemistry of CNTs, the chemical properties of PPCPs, and aqueous solution chemistry (pH, ionic strength, dissolved organic matter) all play an important role in CNT PPCP sorption.
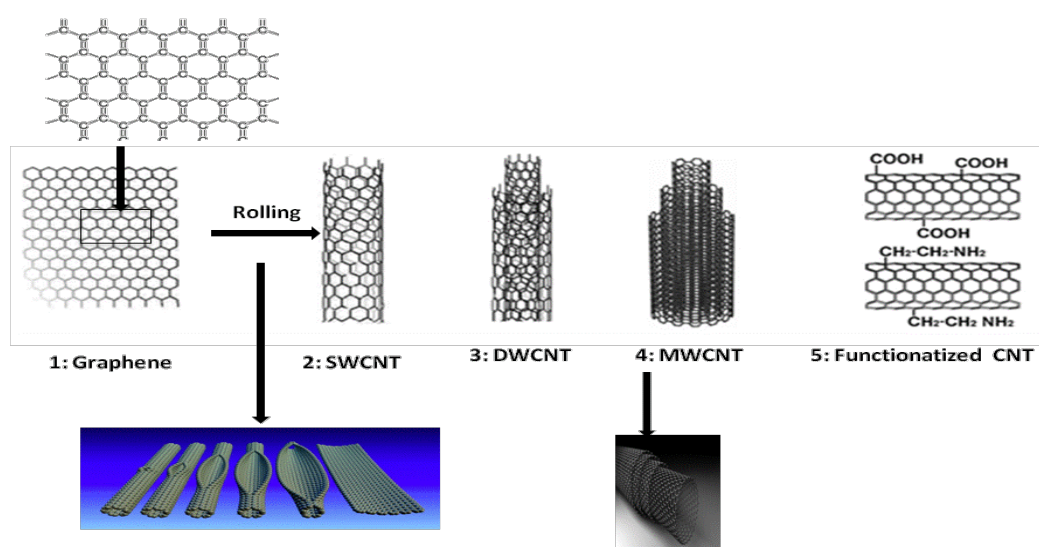
Figure 4. 1. Different kind of Carbon nanotubes (CNT)

For all types of CNTs, sorption decreased with the increase of pH due to the electrostatic repulsion between TCS and CNTs (Li et al. 2016). Specifically, when using SWCNT and MWCNT, the electrostatic interactions also motivated greater TCS removal at pH 4 than at pH 10 and pH 7 (Castro *et al.* 2017; Wang *et al.* 2015). The specific surface area also plays a key role in the capacity to remove TCS. For instance, Cho *et al.* (2011) demonstrated higher TCS removal using SWCNT than MWCNT, while Wang et al. (2016) reported that MWCNT can effectively remove TCS and that the efficiency levels increase as feeding concentrations decrease.

Different studies have demonstrated that pH plays a vital role. The pH effect is greater for non-functionalized CNTs (NF-CNT) than functionalized CNTs (F-CNT). The surface charge density of F-CNTs is more negative than NF-CNTs at acidic and neutral pH levels, which decreases the sorption capacity of NF-CNTs. Li *et al.* (2016) compared the TCS adsorption with one NF-CNT and with two F-CNT (CNTs-OH, CNTs-COOH), demonstrating that TCS sorption decreased in the following order: NF-CNTs, CNTs-OH, CNTs-COOH.

However, with respect to CNTs with curve graphene layers, the influence aromaticity seems to be the most relevant parameter, whereas in the other cases, it is the functional groups seem to be the most relevant parameters (Patiño et al. 2015).

CNTs may possess different sorption sites for hydrophobic PPCP compounds (Cho et al. 2011). It has also been reported that larger molecules, such as TCS, have a much greater adsorption rate than smaller molecules do because smaller molecules need to be diffused to the inner sites of MWNTs, which is time consuming and results in extremely low diffusivities (Jung et al. 2015a). The competitive sorption effects of natural organic material are affected by the hydrophobicity and concentration of TCS compounds and are pronounced except in high equilibrium concentrations for hydrophobic TCS compounds with strong affinity to CNTs (Cho et al. 2011). Special functional groups that are capable of forming specific bonding with the targeted PPCP, attach to the surface of the MWCNT thus eliminating the NOM competition or the pre-coagulation phase that is commonly employed to enhance NOM removal (Wang et al. 2016).

Carbon nanotubes are very promising for TCS adsorption because they are sensitive to the presence of TCS molecules and, therefore, could be used as a filter system for wastewater treatment (Castro et al. 2017).

4.2.4. Other sorbents

Despite the abundance of studies in published research on the removal of pollutants with various adsorbents, there are very few about the use of adsorption as a treatment process for pharmaceutical compounds (Kyzas *et al.* 2015).

Dried sludge can be considered an effective potential sorbent for TCS removal from wastewater as sludge tends to adsorb considerable amounts of this compound. However, the importance of sludge management strategies should be highlighted because pH, temperature and adsorbent concentrations can affect sorption considerably. For instance, decreasing the pH to induce acidic conditions, as well as lowering the temperature, enhances TCS sorption capacity. Although the uptake of compounds improved with an increase in sludge concentration, the adsorption capacity dropped significantly. Most of the newly introduced adsorbents are neither economical nor applicable to real conditions, whereas sludge is abundant, cheap and easy to use (Tohidi and Cai 2016).

Organo-zeolites (OZs) were prepared by loading cetylpyridinium bromide onto natural zeolite to remove TCS from an aqueous solution. Lei *et al.* (2013) found that the TCS adsorption capacities are strongly dependent on the pH solution and the nature of the surface charge of the OZs, which are a little higher in acidic and neutral pH conditions. OZs could be used as effective adsorbents for TCS removal from wastewater

The sorption capacity of clays, kaolinite and montmorillonite for TCS removal was higher in acidic rather than alkaline conditions (Behera et al. 2010). In the case of vermiculite and acid-modified montmorillonite K10 and K30, the sorption of TCS was not significantly affected by pH which is crucial in wastewater treatment (Styszko *et al.* 2015).

Biochar characterization indicated that adsorption may occur mainly due to high surface area, hydrophobicity, and potential interaction between biochar and TCS functional groups including hydrogen bonding and π-stacking. In wastewater,

acid-treated biochar also effectively adsorbs TCS, although at a decreased capacity and removal rate because of the competition from other organic constituents (Tong *et al.* 2016).

While adsorption of TCS onto AC, CNT and other adsorbents is considered to be a promising technique, several problems must be solved to pave the way for large scale application. For instance, TCS with a high molecular weight is more sensitive to competition of organic matter. Furthermore, high pH levels could inhibit TCS adsorption on all the standard adsorbents and attention should also be paid to recycling and regenerating adsorbents.

4.3. TCS removal using the advanced oxidation process (AOP)

The most commonly used AOPs techniques are ozonation, heterogeneous photocatalysis with semiconductors, Fenton and photo-Fenton(Klavarioti *et al.* 2009). Table 4. 2 outlines the different TCS removal processes using AOPs.

Table 4. 2. The removal of TCS by chemical advanced oxidation process

Method	Medium	Initial Conc.	Conditions	Removal Efficiency (%)	References
Ozonation	Effluent wastewater	5mg/L	4 mg/L (8,3 x10^{-5} mol/L) O_3, 7,5 mg/L of DOC,	100	(Suarez *et al.* 2007)
	STP effluent	246 ng/L	ozone of 0.34 mmol/L pH 7.63 15min	78	(Rosal *et al.* 2010)
	River water	102 ng/L	O_3 dose of 2.5 mg/L Ph 7	99	(Snyder *et al.* 2006)
	Grey water	48ng/L	O_3 10mg/L 20min	>87	(Hernández-Leal *et al.* 2011)
Fenton	water	10mg/L	H_2O_2 20mg/L Fe^{3+} 1mg/L 1h T25°C	~100	(Munoz *et al.* 2012)
	water	34.4µmol/L	H_2O_2 10mmol/L $BiFe0_3$ 0.5mg/L 180min T25°C	82.7	(Song *et al.* 2012)
	Wastewater	151ng/L	H_2O_2 60mg/L Fe^{2+} 5mg/L 1h T25°C 20 min	>90%	(Chi Tangyie *et al.* 2013)
	Effluent wastewater	100µg/L	H_2O_2 50mg/L Fe^{2+} 5mg/L 280min pH3	88	(Klamerth *et al.* 2010a)
	Effluent wastewater	100µg/L	H_2O_2 50mg/L Fe^{2+} 5mg/L 280min	87	(Klamerth *et al.* 2010b)
Photo Fenton	Effluent wastewater	135 ng/L	550 w/m^2, 17°C, pH 2.5, Fe^{2+} 5mg/L ,H_2O_2 = 50 mg/l, 10min	100	(De la Cruz *et al.* 2012)
	Synthetic wasteater	5mg/L	4.2 mW cm-^{2} 2 mM Fe^{2+} and 5 mM H2O2 60min	~100	(Son *et al.* 2010)

Method	Medium	Initial Conc.	Conditions	Removal Efficiency (%)	References
Photolysis UV	Secondary effluent	150µg/L	pH 7.85, UV range (290-400 nm)	62	(Wang et al. 2017)
	Effluent wastewater	135 ng/L	550 w/m^2, 17°C, pH 2.5, H$_2$O$_2$ = 50 mg/l, 30 min	100	(De la Cruz et al. 2012)
	Synthetic wastewater	0.5 µg/L	1.4w/cm^2, 20°C, pH 7.4, , 7.5 min	85	(Nguyen et al. 2013)
photocatalyst UV/TiO2	Effluent wastewater	100 µg/L	Solar UV lamp (30 W, b400 nm); Time 90min	100	(Miranda-García et al. 2011)
	Synthetic water	31.8 mg/L.	[TiO2] = 200 mg/L pH = 6.5 UV lamp (λ= 300–400 nm) Time 240min	99.7	(Constantin et al. 2017)
	Water	9 mg/L	[TiO2] = 100 mg/L UV lamp (λ= 365 nm) Time 240min,Time 6h	95%	(Yu et al. 2006)
UV/ZnO	water	10 mg/L	125 W mercury vapor lamp 200 to 300 nm; Time 90min	>90	(Kosera et al. 2017)

4.3.1. Ozonation (O$_3$)

The electrophilic nature of ozone means it specifically reacts with molecular sites with a strong density such as unsaturated bonds and aromatics, whereas the HO$^·$ radical is less specific and oxidizes with all kinds of organic functional groups. However, in water these radicals can be scavenged because of substances present in the matrix such as HCO3 $^-$, CO$_3$ $^{2-}$, NO$_3^-$, NO$_2^-$, Cl$^-$, Br$^-$ or NOM (Gomes *et al.* 2017b).

Direct triclosan-O$_3$ reaction, which results in the phenol ring of triclosan being oxidised and the consequent elimination of the parent compound's antibacterial activity, appears to be maintained even during ozonation of wastewaters containing relatively high dissolved organic carbon (DOC) concentrations (Hübner *et al.* 2015). This suggests that municipal wastewater ozonation can provide an efficient means of eliminating the antibacterial activity of dissolved TCS molecules (Suarez *et al.* 2007).

TCS is rapidly oxidized (90% at ~5 min) when it directly reacts with ozone (Rozas *et al.* 2017). This is because the hydroxyl group donates an electron to the benzene ring, activating the aromatic system and so facilitating oxidative attack by ozone (Nakada *et al.* 2007).

The presence of DOC is an important limiting factor. Nearly 100% TCS depletion was achieved when applied to wastewater containing 7.5 mg/L of DOC, and ~58% depletion for a wastewater containing 12.4 mg/L of DOC, even when the amount of O3 is increased by 50% (Suarez et al. 2007). This is due to the latter's water having a substantially higher concentration of DOC and so it can compete with the target compound for O$_3$, as well as for $^·$OH generated by O$_3$ decomposition and reactions with matrix constituents.

To completely eliminate TCS from surface water with 1-5 mg/L TCS via continuous ozonation at 5 mg/L, requires 20-30 min ozonation time depending

on the pH. For the complete oxidation of triclosan and its by-products, the ozone demand was calculated as being 13.04 mg ozone per mg of triclosan (Orhon *et al.* 2017).

This treatment process can convert TCS into different products: 2,4-dichlorophenol, chlorocatechol, chlororesorcinol, monohydroxy-TCS and dihydroxy-TCS (Figure 4. 2) (Chen *et al.* 2012). It is important to point out that within the framework of the EU surface water directive 76/464/EC (European Commission 1976) 2,4-dichlorophenol is considered to be a dangerous substance and is classified as being "harmful to aquatic organisms" and "may cause long term adverse effects in the aquatic environment" (Chen et al. 2012).
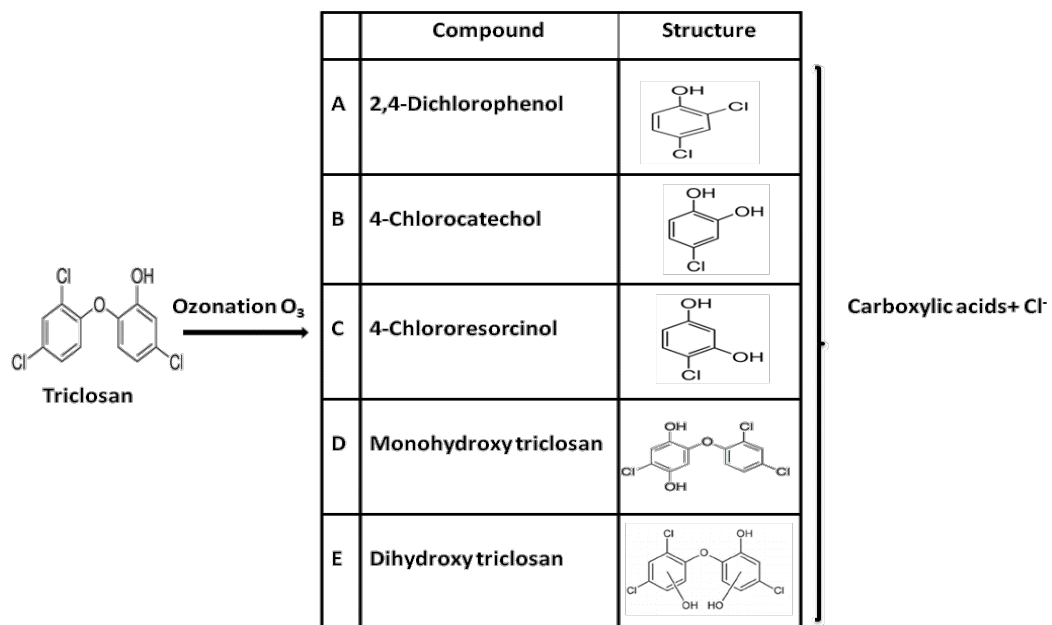
Figure 4. 2. Proposed reaction pathway for ozonation of TCS.

Ozonation appears to provide an effective technique for enhancing the removal of TCS after biological treatment (Suarez et al. 2007). It enables up to 99% of the water to be recovered with no waste production. When reactors are being

designed, the formation of oxidation by-products should be taken into account with the specific aim to reduce them. Higher ozone doses or greater retention times will facilitate the transformation into hydroxylated aromatic compounds (Figure 2) (Gomes et al. 2017a). Such reactions are typically fast because these compounds react more readily than the parent compound does (Hübner et al. 2015). Nevertheless, the operating costs are dependent on the ozone dose (Chen et al. 2012) which means that this technology comes at a higher cost. To reduce this, a combination of the biological treatment technologies might not only be suitable, but lower the operation costs as well (Gomes et al. 2017a).

4.3.2. Fenton and photo-Fenton oxidation

Homogeneous oxidation with Fenton's Reagent occurs in the presence of ferrous (Fe^{2+}) or ferric (Fe^{3+}) ions and hydrogen peroxide (H_2O_2) via a free radical chain reaction which produces hydroxyl radicals. It is a metal-catalysed oxidation reaction in which iron acts as the catalyst. The oxidation efficiency may be enhanced in the presence of UV irradiation as more hydroxyl radicals are produced in the so-called photo-Fenton reaction (Klavarioti et al. 2009). Fenton oxidation in acidic conditions is an important oxidation treatment method for removing the pollutants (Wang and Wang 2016) and consequently photo-Fenton oxidation processes have been developed in the recent years as a tertiary treatment to remove micropollutants at relatively low concentrations (ng/L–g/L) (Prieto-Rodríguez *et al.* 2013).

Fenton degradation could be a fast process if the UV/H_2O_2 process facilitating the cleavage of H_2O_2 molecules into hydroxyl radicals is used (Klamerth *et al.* 2010b), which, in turn, implies Fe $^{3+}$ being reduced to Fe^{2+} (Klamerth et al. 2010b). The lower the concentration of Fe applied is, the lower the TCS degradation. However, higher or complete TCS degradation could be reached if H2O2 is dosed resulting in less mineralization of the overall organic content of the municipal WWTP. This means that TCS is easily degraded by $^•OH$ and that the organic content of the WWTP does not significantly compete with TCS (Klamerth *et al.* 2010a). Only 4.1% of TCS was removed when applying only

Fenton and 17.6% with only UV-C (254 nm light). Removal efficiencies (up to 68%) can be reached after only 20 min in photo-Fenton (Son *et al.* 2010).

The high removal of total organic carbon (TOC) together with the high generation of ˙OH radicals through photo-Fenton improves TCS degradation because competition from organic matter has been reduced (De la Cruz *et al.* 2012; Son et al. 2010). However, because of the presence of humic acids, TCS degradation in real wastewater samples is greater than in synthetic wastewater. These solvate electrons and hydroxyl radicals upon irradiation, which contributes to the radicals produced by photo-Fenton (Klamerth et al. 2010b). Klamerth et al., (2010) completely removed TCS (spiking 5 μg L^{-1} of TCS) in a real wastewater, whereas removal efficiency was reduced to 87% when using synthetic wastewater.

When applying only the Fenton process, TCS removal is unsatisfactory compared to other oxidation processes such as photo-Fenton. Therefore, the use of a catalyst, solar or any other light source is required to promote TCS removal from the wastewater.

Employing ferrous or ferric salts usually suffers from two major drawbacks associated to (a) the narrow pH operating range required to avoid the formation and subsequent precipitation of iron oxyhydroxides and (b) the need to recover dissolved ions from the treated solution, thus requiring an additional stage using homogeneous Fenton and photo-Fenton systems after the treatment has been completed (Klavarioti et al. 2009). When the photo-Fenton method is used to decompose hazardous water contamination, the possibility of more toxic intermediates forming increases, nevertheless photo-Fenton treatment does enhance the biodegradability of wastewater (Gmurek *et al.* 2017).

The combined reaction of Fe^{2+} and UV-C can overcome the disadvantages (for instance, the use of expensive H$_2$O$_2$, pH adjustment and sludge production) the Fenton reaction has because the presence of dissolved organic matter (DOM) exposed to light induced transformation pathways of organic contaminants. This

transformation is mainly initiated by the absorption of light by water components and various Fe species, leading to the formation of several primary and secondary reactive species that are able to react with organic compounds (Wenk *et al.* 2011), making the combined reaction more practical than the Fenton reaction alone (De la Cruz et al. 2012; Son et al. 2010).

4.3.3. Photolysis

Photolysis is when artificial or natural light interacts with target molecules and causes photochemical reactions that can lead to target molecule degradation to intermediate products and, when complemented with extensive light, could eventually decompose to obtain mineral end-products (Klavarioti et al. 2009).

Photolysis, both direct and indirect, has been shown to cause the breakdown of many emerging contaminants. In direct photolysis, the contaminant itself absorbs photons and is degraded (Zepp and Cline 1977), while in indirect photolysis, degradation occurs via the compound reacting to a reactive species generated by photosensitizers which can absorb radiation to reach an excited state (Andreozzi *et al.* 2003). DOM and nitrate are two wastewater components which have been recognized as being important photosensitizers, and play key roles during the indirect photolysis of micropollutants within the aquatic system (Yufei Wang *et al.* 2017). The efficiency of photolytic degradation depends on several factors such as the absorbance spectrum of the pharmaceutical in question, the quantum yield of photolysis, the concentration of H_2O_2 employed and the water matrix (Klavarioti et al. 2009).

Rapid degradation for TCS is achieved when photolysis is applied. Tixier et al. (2002) obtain high removal efficiency (97%) after 4 h irradiation in pure water. The combination of radiation (254/185 nm) results in faster TCS photolysis than when only applying one radiation 254 nm (Yuval *et al.* 2017). The functional group phenoxy of TCS molecules plays an important role in photolysis which can absorb solar radiation. TCS also contains an acid functional group (phenol) with a pKa value of 8.1 (Sanchez-Prado *et al.* 2006; Tixier et al. 2002), which is

close to the pH of the water matrix making TCS more reactive and photodegradable due to it being in anionic form (Martínez-Zapata *et al.* 2013).

TCS photodegradation rates in secondary effluent are reduced by 62% compared with Milli-Q water. The TCS degradation rate decreased with indirect photolysis which plays a negative role in TCS removal due to the presence of photosensitizers that can absorb the available light thus shielding the target compounds from photodegradation. In the presence of light, nitrate could act as photosensitizer producing hydroxyl radicals. This seems to facilitate and improve the TCS photodegradation but TCS removal pathways are higher with direct photolysis than indirect photolysis with nitrates and DOM (Yufei Wang et al. 2017).

A limiting factor has been detected when solar irradiation is present. For instance, Agüera et al., (2003) observed that the presence of TCS in surface water can form highly toxic dioxin-type derivatives because TCS is a halogenated compound and could be involved in dealkylation mechanisms (Nguyen *et al.* 2013b)

Photocatalysis is a process based on the excitation of a semiconductor through light. This excitation generates electron-hole pairs that, in the presence of oxygen and water, photo-generate hydroxyl radicals. The most important photocatalysts are titanium dioxide (TiO2) and zinc oxide (ZnO), as they are strong oxidizers and TCS can be oxidized (Yu *et al.* 2006).

The photocatalyst using TiO_2 showed a very efficient degradation and the total disappearance of TCS is obtained with sufficient irradiation time (i.e. 60 min). The degradation pathways involve the homolytic scission of the C–O bond and the hydroxylation of the phenolic group. The former process leads to the formation of 2,4-dichlorophenol which represents 25% of TCS conversion.

No dioxin derivatives were detected and they are only exclusively formed if TCS, in its anionic form, absorbs light at < 300 nm. *Son et.al* (2009) showed that TCS oxidation by OH radicals can greatly reduce the production of dioxin-group intermediates as well as generate the effective mineralization of TCS. Thus, photocatalysis of TCS may be an effective abatement process for TCS in water. *Yu et al.*, (2006) found that the hydroquinone and quinone species were at least 10 times fewer than those of dichlorophenol. Detection of 2,4-dichlorophenol suggested the cleavage of ether linkage occurred in the TCS degradation process. Based on the identification of intermediates in TCS degradation, we can conclude that the dechlorination reaction was not an important step in the photocatalytic reaction. Finally, photocatalytic degradation by UV at 365 nm was found to be a feasible approach for treating TCS.

TCS mineralisation by using the photocatalyst by employing TOC decrement was efficient in both pure and natural waters (Rafqah *et al.* 2006). Previous studies show that TCS concentrations (100µg/L) in water can be successfully degraded with immobilized TiO_2 under solar irradiation on a pilot-plant scale, not only in simulated effluents from municipal WWTP, but also in spiked real effluent. These results open the way to applying TiO_2 photocatalysis to the reuse of treated wastewater (Constantin *et al.* 2017; Miranda-García *et al.* 2011). A new photocatalyst based on nano-sized TiO_2 supported on SWCNTs with tailored photocatalytic properties upon irradiation by both UV and solar simulated light, was successfully employed for the degradation of TCS in real secondary wastewater effluent (Murgolo *et al.* 2015).

In the wurtzite phase, using ZnO as the catalyst for CS degradation and mineralization may be an interesting alternative to TiO2 since, when compared with photolysis, it also showed an increased efficiency, particularly in the mineralization process. The immobilization of ZnO in calcium alginate spheres further highlights the application possibilities heterogeneous photocatalysis have in processes for treating water contaminated with TCS, since the separation of the photocatalyst in the final stage is greatly facilitated and does not impair the activity of ZnO as a photocatalyst. Kosera et al. (2017) used ZnO spheres for 18

h to achieve TCS mineralization of more than 50%, but if 24 h of photolysis is applied 90% is achieved.

Many organic substances absorb radiation primarily below 250 nm, which is a small percentage of solar radiation. Therefore, photolysis occasionally occurs in the environment, often supported by natural photosensitizers called humic acids. Unfortunately, this process is inefficient and is associated with a long reaction time and low quantum yields (Gmurek et al. 2017).

TiO_2 is found to effectively degrade TCS by photocatalysis with the formation of 2,4-dichlorophenol, chlorocatechol, 5-chloro-2-(4-chlorophenoxyl) phenol as by-products or intermediates (Rafqah et al. 2006). TCS can be transformed into dioxin intermediates due to its high sensitivity to photolysis. Therefore, effective treatment is needed not only to remove TCS, but also to minimize the production of dioxin-type intermediates. Using ZnO instead of TiO_2 achieved good degradation levels, presenting another alternative to lowering the costs of photocatalysis and using renewable energy; something which is very attractive from an environmental perspective (Kosera et al. 2017).

The main limitation of the heterogeneous photocatalysis is the difficulty in separating the catalysts in the final treatment stage, especially when the catalyst is used in powdered form (Lee *et al.* 2016). Because of this, alternatives for immobilizing the catalysts by using different supports have been studied, for example in activated carbon fibres (Liang *et al.* 2016) and glass plates (Yahia Cherif *et al.* 2014). The chemical technologies can achieve high TCS removal efficiency but usually result in a high cost as well and frequently generate toxic intermediate products (Wang and Wang 2016). Therefore, the environmental risks they pose need to be assessed to confirm whether the photocatalysis process represents a safe alternative to conventional wastewater treatment processes or not.

4.4. Physical separation by membrane process

Membrane processes are becoming prominent in wastewater reclamation/reuse and drinking water treatments because they are effective in removing both macro and micro organic pollutants. That said, only nanofiltration/reverse osmosis (NF/RO) has been reported as being efficient in removing PPCPs and other dissolved contaminants from wastewater because the size and molecular weight (MW) of most PhACs is smaller than the molecular weight cut-off of most microfiltration (MF) and ultra-filtration (UF) membranes. MF and UF processes can only be employed as pre-treatment process to remove colloids and natural organic matter (NOM) (Ganiyu *et al.* 2015). The NF membrane removal efficiency is very close to that of the RO membranes (Luo *et al.* 2014).

Nearly complete rejection of TCS by the NF270 membrane, which is a loose NF membrane, at pH 7 has also been reported by Nghiem and Coleman (2008), and Sudhakaran et al. (2013) reported that NF removed 90% of TCS. However, the combination of membranes with UV irradiation did not enhance removal. The ceramic NF membrane used has the same capability of removing TCS as the polymeric NF membranes do (Fujioka *et al.* 2014).

On the other hand, using RO did not show higher removal percentages when compared with NF. This is important in terms of WWTP operating costs. However, TCS removal by RO is sometimes slightly higher than NF (Table 4. 4) because the adsorption of TCS to the membrane surface is a precursor for the diffusion of this compound through the membrane. Furthermore, NF is highly influenced by electrostatic and hydrophobic interaction and TCS interactions are systematically related to the compound's physicochemical properties, the membranes and the pH solution. It is worth noting that even when TCS was fully dissociated at pH 10, TSC adsorption to the membrane could still occur to an appreciable extent (Nghiem and Coleman 2008).

Table 4. 3. The removal of TCS by membrane (NF/RO)

Process	Medium	Initial conc.	Removal (%)	References
NF Membrane	Wastewater	74ng/L	>95	(Kim et al. 2007)
	Synthetic water	300ng/L	90	(Fujioka et al. 2014)
RO Membrane	Wastewater	74ng/L	>95	(Kim et al. 2007)
	Synthetic water	500 µg/L	99	(Xie et al. 2012)
	Synthetic water	750µg/L	100	(Nghiem and Coleman 2008)

The formation of a hydrophobic fouling layer on the membrane surface could interfere with the solute–membrane interaction and thus reduce the diffusive transport of TCS across the membrane because the concentration polarization was enhanced by the presence of humic acid or calcium ions (Chang *et al.* 2012a). The NOM had a positive effect on TCS removal due to the TCS–humic acid complex formation that limits TCS permeation through the membrane. On the other hand, NOM was found to increase molecular weight cut-off, but did not result in a decrease in TCS rejection due to the humic acid –TCS complex forming. NOM lead to an increase in TCS removal mainly by sorption into the membrane (Ogutverici *et al.* 2016). Consequently, significant enhancement in TCS rejection was observed when the membranes were pre-fouled with the three model organic foulants: bovine serum albumin (BSA), alginate and humic acid (Nghiem and Coleman 2008).

RO is used widely in wastewater reclamation plants as the final treatment stage (Umar *et al.* 2015). The resulting product from the plants is then used for irrigation and replenishing river water. While these RO plants lead to high quality reusable water, they also produce large volumes of reverse osmosis concentrate rich in dissolved organics. The direct disposal of reverse osmosis concentrate into water bodies can pose a severe eco-toxicological risk, threaten aquatic organisms and cause serious environmental problems. Consequently, its

proper treatment, sustainable management and safe disposal are mandatory requirements (Sun *et al.* 2014).

The high energy consumption of RO together with high waste production, low water recovery and high maintenance tasks due to for example membrane RO fouling, have dismissed RO as a promising technology for TCS treatment (Carson O. Lee *et al.* 2012). NF is a less cost-effective technique for removing low-molecular-weight micropollutants from water at an operating pressure lower than that of RO (Chang *et al.* 2012b).

4.5. The MBR process

MBR technology combines biodegradation using activated sludge with a solid–liquid separation using membrane filtration (usually MF or UF). MBRs are categorized into two configurations depending on the location of the membrane unit: submerged (or immersed) MBRs and side-stream (or external) MBRs. The full-scale MBR sustained high and stable nutrient removal (>95% for both total nitrogen, TN and phosphate, PO_4^{3-}-P) (Phan *et al.* 2015).

It was found that when a submerged MBR with capillary UF membranes and an isolated bacterial consortium with initial concentrations of 4.20 - 5.5 $mg \cdot L^{-1}$ were used, the average removal efficiency of TCS was >90 % (Banerjee *et al.* 2016). Previous studies have shown removals of > 95% in an anoxic-aerobic MBR treatment with initial concentrations of 5 $\mu g \cdot L^{-1}$ (Phan *et al.* 2014; Phan *et al.* 2016; Wijekoon *et al.* 2013). The MBR process can be induced under anaerobic conditions (in the absence of both molecular oxygen and nitrate) and/or anoxic (in the absence of molecular oxygen but in the presence of nitrate) and aerobic (in the presence of molecular oxygen) (**Table5**). Consequently, anaerobic conditions seem to be the most unfavourable conditions as they only achieved a TCS reduction of 70%, whereas if aerobic or aerobic/anoxic conditions are applied, higher removal efficiencies are reached (90%).

Table 4. 4. The removal of TCS by MBR process

MBR	Membrane	Medium	Influent conc.	Removal (%)	Ref.
Aerobic	HF UF	Synthetic wastewater	2µg/L	>91.8	(Tadkaew *et al.* 2011)
Anaerobic	HF UF	Synthetic wastewater	594 ± 361ng/L	90.2	(Monsalvo *et al.* 2014)
Anaerobic	Ceramic membrane	Synthetic wastewater	5µg/L	70	(Wijekoon *et al.* 2015)
Anoxic - Aerobic	HF UF	Synthetic wastewater	5µg/L	>90	(Phan *et al.* 2014)

TCS removal is increased with increased temperature, as well as with increased hydraulic retention time (HRT) and sludge retention time (SRT) (Armstrong *et al.* 2018). Trinh et al. (Trinh *et al.* 2016) found that TCS removal via biodegradation increased during summer sampling (24°C) as opposed to winter sampling (15°C). Conversely, TCS removal via sorption to sludge increased in the winter, concurrent with the decrease in biodegradation removal rate. An increased SRT allows a more diverse microbial population with more diverse physiological capabilities to develop, since the increased residence time allows for slow-growing microbes that would not have had time to establish populations and proliferate during reduced time periods.

The degradation of pharmaceuticals from laboratory bioreactor studies simulating activated sludge determined that in an MBR, and a submerged attached biofilter, a reduction in HRT resulted in reduced pharmaceutical removal efficiencies due to a reduction in the time the compounds were exposed to microbial populations (Armstrong et al. 2018).

Biological treatments have attracted a great deal of attention. Until now, several microorganisms, such as *Sphingomonas sp.* Rd1(Hay *et al.* 2001), *Nitrosomonaseuropaea* (Roh *et al.* 2009), *Sphingopyxis* (Do Gyun Lee *et al.* 2012) and *Trametes versicolor* (Hundt *et al.* 2000) have been demonstrated to be capable of degrading TCS. Among these strains, *Sphingopyxis* achieves a 100% removal of TCS and complete dechlorination based on the stoichiometric release of chloride when the initial concentration of TCS is 5 mg/L (Shizong Wang *et al.* 2017).

Membrane fouling is one of the factors that most limits MBR technology. It results from the high organic matter content in wastewater which, in turn, requires high amounts of energy to process and causes significant maintenance costs. Submerged membrane systems need frequent air scouring to reduce cake deposit and to generate localized cross-flow conditions along the membrane surface (Grandclément *et al.* 2017). Furthermore, at high concentrations, TCS causes serious damage to the cell membrane of *Nitrosomonaseuropaeaas* and the ammonia monooxygenase enzyme is not efficient enough to degrade the entire organic toxin. Therefore, the non-growth metabolism of *N. Europaea* is inhibited which, in turn, stops nitrification activity (Qiu *et al.* 2015). At lower TCS concentrations, increasing ammonia oxidation activity has been found to enhance TCS removal in nitrifying activated sludge (Huang *et al.* 2016)

4.6. Discussion

4.6.1. The advantages and challenges of the different TCS removal technologies

On the one hand, adsorption presents a wide range of TCS removal efficiencies, together with the removal of residuals, disinfection and oxidation products, but its greatest advantages is that it does not generate toxins. On the other hand, there are some limitations which, in a nutshell, are its and high maintenance, re-generation and AC product costs (Table 4. 5).

AOP processes present high removal efficiency as well as adsorption, and they also improve reaction time. However, despite this they consume very high amount of energy consumption. Furthermore, AOPs generate some non-desirable toxics due to the oxidation capacity of the process (Table 4. 5).

As the membrane separation process depends on the pore size of the membrane, NF and RO are the most promising configurations. RO presents slightly better TCS removal than NF does, so it would seem to be the most appropriate membrane technology.

Thanks to the combination of biological activated sludge and membrane separation MBR is highly effective. Several microorganisms are capable of TCS removal but membrane pore size also has a key role in completing TCS removal. Furthermore, MBR demands high energy consumption to cope with air-scouring and backwashing. And, as TCS has some toxicity into the biomass that could result in being a nitrification inhibition, the MBR may require some pre-treatment to avoid the activated sludge not working as it should.

Table 4. 5. Advantages and challenges of different technologies in the removal of TCS

Treatment process	Advantages	Challenges	References
Adsorption	-A wide range of TCS removal from wastewater. -Removal of residual disinfection/oxidation products -Not generating toxic active products of TCS	- Relatively high cost in operation and maintenance -Regeneration and disposal issues of high sludge -Depend of quantity - with high molecular weight is more sensitive to the competition of organic matter	(Behera et al. 2010; Mailler et al. 2015; Nguyen et al. 2013; Sheng et al. 2016b)
AOP	-High removal efficiency -Short degradation rate	-Energy consumption issues, operational & maintenance cost -Formation of toxic disinfection by-products	(Chen et al. 2012; Gomes et al. 2017; Nakada et al. 2007)
Membranes (NF/ RO)	Fully effective in removing TCS as pore sizes less larger than TCS.	-High cost of operation -High energy demand, membrane fouling and disposal issue	(Kim et al. 2007; Carson O. Lee et al. 2012)
MBR	-Effective for the removal of TCS . - Several microorganisms capable of degrading TCS.	-High energy consumption and fouling, control of heat and mass transfer -High aeration cost and robustness of membrane - High concentration of TCS inhibit the nitrification, TCS pre-treatment would be necessary.	(Aun Ng et al. 2006; Hay et al. 2001; Huang et al. 2016; Hundt et al. 2000; Do Gyun Lee et al. 2012; Nguyen et al. 2013; Phan et al. 2014; Qiu et al. 2015; Roh et al. 2009)

4.6.2. TCS removal by hybrid and combined treatments

The technologies above all have some advantages and some limitations. Here we introduce the hybrid treatments designed to reduce long-term treatment, and high energy costs, all except MF+GAC achieved complete TCS mineralization (Table 4. 6).

Table 4. 6. The removal of TCS by combined treatments

Process	Medium	Influent conc.	Removal (%)	References
PAC-MBR / MBR-GAC	Synthetic wastewater	5µg/L	> 95%	(Nguyen et al. 2013)
MF+GAC	Sewage effluent	11 ng/L	54.5%	(Shanmuganathan et al. 2015)
PAC+O$_3$	Synthetic water	2.3 mg/L	100%	(Rozas et al. 2017)
Coagulation + MWCNT membrane	Wastewater effluent	1 mg/L	93%	(Wang et al. 2018)
Activated sludge+ sand filtration+O$_3$	Wastewater	316 ng/L	>97.4%	(Nakada et al. 2007)

MBRs remove TCS well and maintain this high level of removal throughout both the MBR–GAC and PAC–MBR operations. The PAC–MBR system can outperform an MBR–GAC system in terms of adsorbent consumption and, furthermore, the direct addition of PAC into an MBR may also reduce membrane cleaning and membrane fouling, thus increasing membrane life-time (Aun Ng *et al.* 2006).

When using an AC, it is important to understand that after use, its adsorption capacity could be exhausted. This can be detected by a gradual decrease in TCS

removal efficiency, requiring an AC replacement or regeneration if GAC was used (Nguyen *et al.* 2013a).

In anaerobic MBR (AnMBR) without PAC, TCS was moderately biodegraded and partially biotransformed. The one-time addition of PAC into the AnMBR improved TCS biotransformation into easily biodegradable TCS over long-term experiments (>80 days), thus resulting in constant removal 93.2 ± 6.6% (Xiao *et al.* 2017), Furthermore, the scouring effect of PAC contributed to reducing fouling in the AnMBR (Park *et al.* 1999).

The hydrophobic compounds can be adsorbed to NF/RO membranes and then diffused through the dense polymeric matrix, resulting in a considerable transportation of these compounds across the ultra-thin active skin layer. On the contrary, most of these hydrophobic compounds can be effectively removed by an MBR. TCS had been substantially removed by the preceding MBR treatment process (Alturki *et al.* 2010). But TCS appears to be permeable through these membranes, so a complete removal is not achieved. Even when membrane bioreactor (MBR) treatment is combined with NF or RO membrane filtration for TCS removal, there were detectable (albeit low) TCS levels even in the permeate of NF membranes (Alturki et al. 2010). Therefore, coupling MBR with NF/RO or UV does not lead to enhanced TCS removal. The NF/RO membrane or UV treatment, complement MBR treatment very well, including in the removal of some persistent TrOCs (i.e., diclofenac and fenoprop) (Nguyen et al. 2013b).

One of the limitations MBRs have is fouling. Shanmuganathan et al. (2015b) applied NF as the post-treatment of an MF-GAC, demonstrating no TMP increment and no flux reduction in the NF membrane and achieving 54.5% and 90% TCS removal, respectively.

Applying a pre-treatment step using coagulation does not enhance the filtration processes and reduces treatment efficiency by around 4% (Sheng *et al.* 2016b). Pre-coagulation of wastewater effluent effectively mitigated the competitive adsorption of effluent organic matter (EfOM) and increased the removal

efficiencies of an MWCNT membrane by 11–34%. The pre-coagulation primarily removed biopolymers and humic substances in EfOM which, in turn, enhances TCS removal when employing an MWCNT-membrane. Biopolymer removal, on the other hand, resulted in reduced membrane fouling during the filtration of pre-coagulated wastewater (Wang *et al.* 2018).

Applying ozone to the PAC process decreases its basic properties but considerably improves acute toxicity removal (Rozas et al. 2017). The addition of AC to the ozonation process contributed to accelerating the oxidation of the transformed compounds that cause toxicity at lower ozone doses. Thus, this carbon based-AOP is a promising candidate to be integrated into water treatment to effectively remove emerging organic pollutants.

The combination of conventional activated sludge treatments, sand filtration, and ozonation is effective in reducing the risks associated with TCS in sewage effluent and TCS removal was highly efficient (>95%).

4.7. Conclusions

Due to the diversity in nature of TCS, one single treatment technology is incapable of controlling it because each treatment method has their own drawbacks that need to be resolved. As a result, combining different advanced methods is an interesting research topic. Reviewing the different methods for TCS removal has revealed that future research should focus on combining ozonation and AC adsorption for TCS removal. In addition to this, widely implemented and extensively accepted technologies such as MBR, could be upgraded with AC, thus facilitating TCS biodegradation, reducing the non-desirable sub-products generation, while also avoiding some of the limiting factors that occurs when the MBR technology is used separately.

5. Triclosan, carbamazepine and caffeine removal by activated sludge system focusing on membrane bioreactor

5.1. Background, motivation and objective

The synthetic chemical industry produces effluents with high chemical oxygen demand (COD), high level of salinity and a high concentration of micropollutants. The treatment of these effluents by biological processes is not recommended since the presence of some PPCP compounds and their metabolites can inhibit the biological activity of microorganisms present in activated sludge (Li et al. 2004). In recent studies, the overall removal of organic micropollutants to as low as $\mu g \cdot L^{-1}$ concentration levels by MBR treatments has been investigated (Phan et al. 2014, Phan et al. 2016, Wijekoon et al. 2013).

Hospital effluents are generally treated with urban wastewaters within the same WWTPs, giving no special attention to their higher load in pharmaceutical compounds (ranges up to 50 $\mu g \cdot L^{-1}$) and to their potentially dangerous nature. The necessity of more specific management and treatment of this kind of effluents is crucial for a better protection of the environment (Verlicchi et al., 2012). In that sense, a wastewater treatment using MBR technology for treating PPCP has to demonstrate its viability and capability of operation, risk assessment and management. For this reason the present study aims to evaluate the impact of commercial drugs and cosmetic products (at $mg \cdot L^{-1}$ concentration levels) into an MBR biological system treating the selected PPCPs. The sub-objectives of the study were, firstly, to evaluate the performance of an MBR system treating a synthetic influent with high content of the selected PPCPs, monitoring the fouling and biomass characteristics and secondly, to demonstrate the inhibitory nitrification effect of TCS in biomass activity.

5.2. Materials and Methods

Two different experimental set-ups were used in this study: a lab-scale MBR to evaluate the effect into the filtration process treating wastewater with a high content of three micropollutants (carbamazepine, caffeine and triclosan) and a batch reactor (BR) to corroborate the effect of triclosan on biological treatment.

5.2.1. Membrane bioreactor set-up

The lab-scale membrane bioreactor (Figure 3. 1), located at the Scientific and Technology Park of the University of Girona (Girona, NE Spain), consisted of an anoxic tank of 33 L connected to a membrane tank of 26 L (working volume) with a ZW-10 submerged ultrafiltration hollow fibre (UF-HF) membrane module (Suez) with a nominal pore size of 0.04 μm and a total membrane area of 0.93 m^2 (Monclús et al. 2011).

The system was fed with a synthetic influent prepared twice a week and stored under mixing conditions in a 150 L tank at 4 °C, which has been described in previous studies (Table 5. 1) (Puig et al. 2007). The composition of this influent was intended to simulate municipal sewage and was continuously pumped into the reactor using a peristaltic pump (Watson-Marlow, UK). Permeate was obtained using a gear pump (Micropump, USA) controlled by a pressure transducer (Endress+Hauser, Sweden) to create a vacuum pressure drop over the membranes and monitoring the transmembrane pressure (TMP) to evaluate the fouling phenomena.

Table 5. 1. Characteristics of synthetic wastewater

Quality parameters	Unit	Influent (phase I)	Influent (phase II)
pH	-	7.6	7.4
Chemical oxygen demand (COD)	mg·L^{-1}	416.4	1615
Nitrogen (N)	mg·L^{-1}	49.2	58.3
Alkalinity	mg·L^{-1}	409	547
CAF	mg·L^{-1}	-	~1
CBZ	mg·L^{-1}	-	~1
TCS	mg·L^{-1}	-	~3.2

The experiment was planned to have two different phases in order to study the impact on fouling and biological activity. Initially the lab-scale plant was inoculated with nitrifying biomass collected at Quart WWTP (NE Spain).Phase I corresponded to the start-up period (from day 1 to day 22) working under constant operational conditions reaching 4 g·L^{-1} of mixed liquor suspended solids (MLSS) concentration. Then Phase II, for PPCP treatment (from day 23 to day 60), different target compounds were provided. Commercial caffeine and carbamazepine crushed pills and toothpaste containing 0.3 % triclosan were added to the synthetic wastewater twice a week. The crushed pills of the commercial drugs contained 617 mg of caffeine and 710 mg of carbamazepine per pill. By adding 210 mg and 243 mg, respectively, the influent concentration of each compound was around 1 mg·L^{-1}. 160.9 g of toothpaste containing 0.3% triclosan were continuously added to the synthetic influent wastewater, resulting in a triclosan concentration of 3.2 mg·L^{-1}.

The permeate flow was maintained under a constant flux of 14.4 L·m^{-2}·h^{-1} (LMH) throughout this study, permeating for 9 minutes and backwashing at the same flux for 1 minute. In these operating conditions, the sludge retention time (SRT) was 50 days and the hydraulic retention time (HRT) was 33 hours. In order to evaluate the fouling character (reversible or irreversible), physical control actions were modified. From day 41 to day 60, the backwash time was increased from 1 minute to 2 minutes, while filtration cycles were decreased to periods of 7 minutes. Additionally, permeate flux was reduced to 9.6 LMH. The average inflow was 50.4 L·day^{-1} during both phases achieving an organic loading rate (OLR) of 0.36 Kg COD·m^{-3}·day^{-1} in phase I and 1.38 Kg COD·m^{-3}·day^{-1} in phase II. The Nitrogen Loading Rate (NLR) was 0.042 and 0.05 Kg N·m^{-3}·day^{-1} respectively (**Table 5. 2**).

Table 5. 2. Loading rates and operating conditions of MBR lab-scale plant

Quality parameters	Unit	Phase I	Phase II
Feeding rate	L·day^{-1}		50.4
Organic loading rate (OLR)	Kg COD·m^{-3}·day^{-1}	0.36	1.38
Nitrogen loading rate (NLR)	Kg N·m^{-3}·day^{-1}	0.042	0.05
Permeate flux	L·m^{-2}·h^{-1}	14.4	9.6
MBR cycle (permeate/backwash)	minutes	9/1	9/1 - 7/2
HRT	hours		28
SRT	days		50

5.2.2. Membrane cleaning protocol

Acid and basic chemical cleanings were carried out for the membrane when required. For basic cleaning the membrane was submerged ex-situ in a 0.05% wt hypochlorite solution and for acid cleaning, the same procedure was undertaken using a 0.5-1% wt oxalic acid solution (Monclús et al. 2010b).

5.2.3. Batch Tests

The batch reactor used in this study are detailed in section 3.1.2. Each BR was fed with synthetic wastewater and filled with activated sludge. The first BR was used as a control. The second BR was fed with 5 mg·L^{-1} standard solution of triclosan, and 2.5 g of toothpaste were added to the third to obtain a triclosan concentration of 5 mg·L^{-1} (Table 5. 3). The experiment consisted of a 24-hour aerobic phase and samplings were carried out periodically from each BR in order to monitor the nutrients and PPCP concentrations.

Table 5. 3. Content of each Batch Reactor (BR)

	Control BR	**BR-1**	**BR-2**
Activated sludge ($3\ g\ MLSS \cdot L^{-1}$)	1430 mL	1430 mL	1430 mL
Synthetic wastewater	70 mL	70 mL	70 mL
Influent compound	-	triclosan ($5mg \cdot L^{-1}$)	toothpaste containing triclosan ($5mg \cdot L^{-1}$)

Synthetic wastewater was prepared with 4.0 g of $NaCH_3COO$, 0.6 g of $NaHCO_3$, 0.4 g of NH_4Cl, and 0.5 mL of micronutrients per 500 mL to obtain a standard influent with the required proportions of sodium bicarbonate to avoid alkalinity limitation (Monclús et al., 2009). A nitrate solution was prepared by dissolving 0.61 g of $NaNO_3$ in 100 mL of tap water. 50 mL of synthetic water and 20 mL of the nitrate solution were added to each batch reactor together with activated sludge from the municipal WWTP of Quart (Girona, NE Spain).

5.2.4. Analytical Methods

5.2.4.1. Determination of basic parameters

The following parameters were analysed and the method used is detailed in chapter 3 (Table 3. 5 and Table 3. 6).:

- Mixed liquor suspended solids (MLSS),
- chemical oxygen demand (COD),
- Total Kjeldahl Nitrogen (TKN) and
- Ammonium concentration (NH_4^+-N). Nitrites (NO_2^--N) and nitrates (NO_3^--N).
- Sludge dewaterability and Capillarity suction time (CST)
- (Triton electronics, type 304 B) (Scholz et al. 2007).

5.2.4.2. PPCP analysis

Influent and MBR effluent samples were collected twice a week and immediately filtered through 0.2 µm cellulose acetate membrane filter. The membrane permeate samples were not further filtered. All samples were placed in glass-stoppered flasks of 0.5 L and stored at 4°C prior to their analysis. Stock solutions of triclosan, carbamazepine and caffeine (Sigma–Aldrich, Germany) were prepared in pure methanol at a concentration of 250 mg·L^{-1}, stored in brown glass bottles and kept at 4°C in order to avoid degradation during the test period. Standard solutions containing equal parts of the three stock solutions were prepared daily by dilution with Milli-Q water (Millipore, Express 40, USA). The main characteristics of the selected micropollutants are detailed in the supplementary material.

Table 5. 4. Table of selected PPCP characteristics

	Compound	Molecular formula	M. W.	pKa	Log K$_{OW}$
Cosmetic compounds	**Triclosan**	$C_{12}H_7C_{13}O_2$	289.54	7.8	4.76
Pharmaceutical compounds	**Caffeine**	$C_8H_{10}N_4O_2$	194.19	10.4	-0.07
	Carbamazepine	$C_{15}H_{12}N_2O$	236.26	13.9	2.45

[a] Molecular weight (g·mol^{-1})
[b] ionization constant (pKa)
[c] Octanol-water partition coefficient (log K$_{OW}$)

Micropollutant concentrations were determined by a previously described analytical method (Garcia-Rodríguez et al. 2015). The analytes were extracted by using 6 mL-Oasis HLB solid phase extraction (SPE) cartridges containing 200 mg of poly (divinylbenzene-co-N-pyrrolidone) (Waters, Milford, MA, USA). Chromatographic analysis was then performed in an ultra-performance liquid chromatography (UPLC) (Agilent TM 1290 Infinity, Palo Alto, CA, USA) coupled to a 6430 triple quadrupole mass spectrometer detector (Agilent

Technologies, Palo Alto, CA,USA) and equipped with a Kinetex C18 column (100Å, 50mm x 2.10 mm x 2.6 µm) (Phenomenex, Spain). All samples were analyzed in duplicate.

5.3. Results and discussion

5.3.1. Removal of PPCPs

The average removal efficiency in the MBR system for triclosan was of 89.7 ± 8.3 % with an influent concentration of 3.2 mg·L^{-1} (Figure 5. 1A). Similar triclosan removal efficiencies were found in a submerged MBR with capillary UF membranes and an isolated bacterial consortium with initial concentrations of 4.20 - 5.5 mg·L^{-1} (Banerjee et al. 2016). Previous studies have reported removals of 75% applying aerobic conditions (Chen et al. 2011) and more than 95% removal in anoxic-aerobic MBR treatment with influent concentrations of 5 µg·L^{-1} (Phan et al 2016). Biodegradation and sorption are assumed to be the main mechanisms for the removal of PPCPs by MBR that comprises a combination of CAS process with ultrafiltration membrane separation (Tran et al. 2016). High MLSS concentration developed in MBRs combined with long SRTs, has been regarded as one of the most important parameters promoting the biodegradation of PPCPs (Sipma et al. 2010). On the other hand, sorption can be maximized by larger surface areas in the MBR and smaller floc sizes (Fernandez-Fontaina et al. 2013). Biodegradation is considered to be the main removal mechanism of PPCPs in MBR in the case of hydrophilic substances. However, the hydrophobic character of triclosan ($logK_{0W}> 3.2$) results in its higher affinity to be adsorbed into the sludge as a natural phenomenon (Tohidi & Cai 2016).
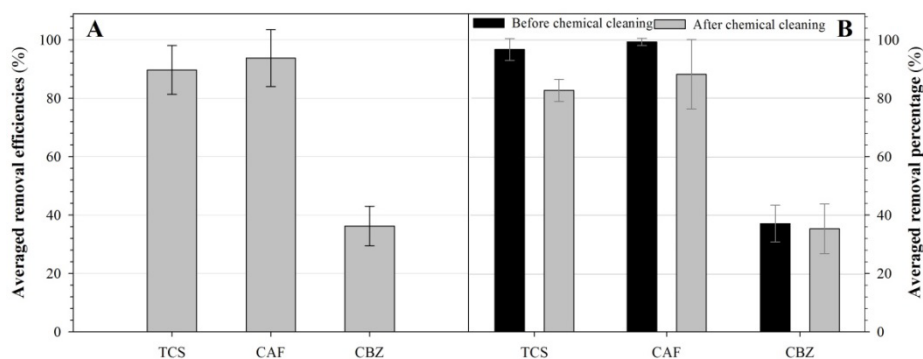
Figure 5. 1. Removal efficiencies of PPCPs. A) Averaged removal efficiencies throughout all MBR period. B) Comparison of removal efficiencies before and after chemical cleaning

The removal efficiency of caffeine, a rather hydrophilic compound (log $K_{0W} <$ 3.2 at a pH=7), was 93.7 ± 9.7 % (Figure 5. 1A), which is in agreement with Phan et al. (2015). Using membrane bioreactor technology, a reduction of 99.9% was observed when the compost leachate contained 1.33 mg·L^{-1} of caffeine (Brown et al. 2013). Several reports point out that high removal efficiencies for caffeine in MBRs are mainly accomplished due to biodegradation or biotransformation by microorganisms (Phan et al 2015, Trinh et al 2016). Operation at short contact times reduces the capability of biodegradation achieving lower total removal efficiencies (Anumol et al. 2016).

On the other hand, the average removal efficiency of carbamazepine was 36.2 ± 6.8 % (Figure 5. 1A). This result is similar to the 38.9 % removal by anoxic-aerobic MBR obtained by Phan et al. (2016), who reported a greater CBZ removal in anoxic conditions than in aerobic conditions. They attributed this improvement to the different microbial composition of the seed sludge used. When the MBR is operated in anoxic–aerobic conditions, the oxygen transfer from the aerated compartments to the anoxic zone due to sludge recirculation may influence the removal efficiency. Anoxic conditions benefit carbamazepine removal, showing that its degradation is sensitive to the operating conditions (Hai et al. 2011a). The low removal efficiency of carbamazepine could be attributed to a combination of its hydrophobicity (log K_{0W} =2.45), which partially favours its sorption (Wijekoon et al. 2013), and its resistance to

biodegradation. Fernandez-Fontaina et al. (2013) reported higher carbamazepine removal efficiencies when high SRT and MLSS concentrations were present in MBRs. Moreover, Hai et al. (2014) suggested that the low removal efficiency of CBZ by CAS or MBR processes are due to the presence of strong electron-withdrawing groups or the absence of electron-donating groups in the compound.

Alternative technologies for treating recalcitrant compounds are needed rather than biotechnologies. Ultrafiltration processes were established as an efficient and appropriate technology for synthetic pharmaceutical and cosmetic industrial effluent treatment with high concentrations of triclosan and caffeine. This study offers a unique insight into the impact of applying anoxic and aerobic treatments to influents containing high concentrations of the three compounds. These removals confirmed the efficiency of MBR treatment for PPCP-rich synthetic influent. In order to reduce the concentration of carbamazepine in the permeate, it is necessary to combine the MBR process with other treatments such as adsorption. This was observed in a recent study reporting >90% removal efficiency for carbamazepine through direct dosing of powdered activated carbon (PAC) (Alvarino et al. 2017).

5.3.2. MBR performance monitoring

Fouling indicators were monitored in order to evaluate and to identify the fouling in the MBR system treating high content of PPCPs. During phase I, the TMP was stable between 0.076 and 0.09 bars, and permeability values ranged between 147 and 193 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ (Fig. 3). Throughout the phase II, the TMP increased progressively until day 32, and afterwards the TMP increased faster achieving 0.48 bars at day 40 when a chemical recovery was applied. In order to evaluate if fouling was reversible an increase of physical recovery control actions were applied such as increasing the backwash time (from 1 min. to 2 min.) and decreasing the permeate flux (from 14.4 LMH to 9.6 LMH). The TMP decreased as a consequence of the operating conditions changes but it increased again after two days, requiring another chemical cleaning at day 50 (Figure 5. 2). Inefficiency of physical actions compared to the high efficiency of chemical actions demonstrated the presence of irreversible fouling. During this second

phase the permeability decreased to 30 L·m^{-2}·h^{-1}·bar^{-1} at day 40 and after the recovery control action the permeability dropped off again to 30 L·m^{-2}·h^{-1}·bar^{-1}.

Li et al. (2015) reported that the addition of 90 µg·L^{-1} of carbamazepine resulted in an increase in the TMP after 8 days due to the modification of extracellular polymers concentration. In the present study, TMP increased after 15 days of the addition of 1 mg·L^{-1} carbamazepine so the fouling appeared later than in Li et al. (2015). This variance could be explained by the differences on feed quality, organic load, permeate flux and/or the sludge capabilities to be filtered (filterability) (Dalmau et al., 2014).
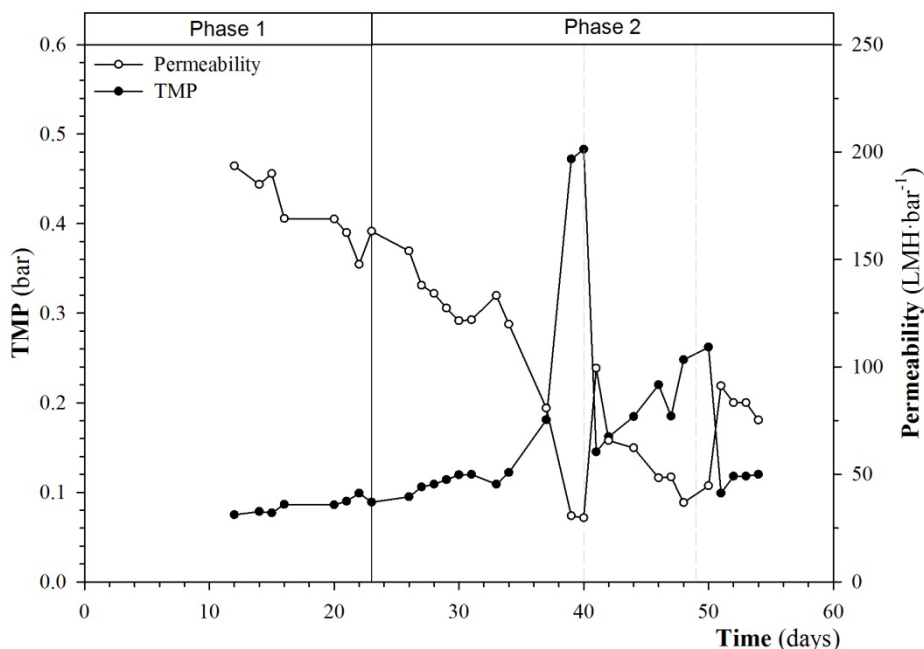
Figure 5. 2. Evolution of TMP and permeability treating PPCP rich influent by lab-scale MBR

According to the irreversible fouling observed, the authors evaluated in detail the removal efficiency of PPCP before and after the chemical cleanings (Figure 5. 1B) and related it with the membrane pore size distribution. When irreversible fouling is present in the membrane, a reduction of the pore size distribution due

to the pore blocking can be assumed (Marti et al. 2011). Consequently, a decrease of removal efficiencies of PPCPs is demonstrated after a chemical cleaning. Removal efficiencies for triclosan and caffeine were sligthly reduced (14% and 11% respectively) after chemical cleaning and no changes were detected for carbamazepine removal efficiencies (Figure 5. 1B).

The high presence of irreversible fouling might be explained by the sludge properties, which could be affected by sodium lauryl sulphate (SLS), a surfactant used as a foaming agent, coming from the toothpaste added. This compound together with triclosan could damage the cellular membrane with the consequent production of extracellular polymers (Jenkins 2004). The deterioration of some sludge indicators would give more information about the fouling precursor capability.

5.3.3. Sludge characteristics' evolution

The MLSS concentration and sludge characteristics (i.e. CST and filterability) might be the main precursors for membrane fouling development. Navaratna et al. (2011) reported that 6 g·L^{-1} of MLSS was the maximum level from which fouling increased significantly. Within this study the MLSS concentration increased from 2 to 6 g·L^{-1} (Figure 5. 3), which was considered a standard concentration for MBR operation. In that sense, the effect of fouling regarding the sludge concentration (sludging) could be assumed as almost negligible (Gabarrón et al., 2013; Monclús et al., 2012).

In phase II, there was an increase in CST from 122 s at day 30 to 1282 s at day 41. Filterability also decreased from 25.5 mL to 1.13 mL in the same period, corresponding to the rise in the irreversible fouling potential. After day 41, the value of CST was not measurable and the low sludge filterability decreased up to 95.5 % (Figure 5. 3). This low filterability together with the increase in the MLSS observed in this study resulted in an increase of the TMP from 0.15 to 0.45 bars (Figure 5. 2). The greater alkalinity in the influent, due to the composition of the toothpaste, might have contributed increasing the membrane

fouling due to the multiple layers of inorganic crystal-like foulants (Chang et al. 2011).
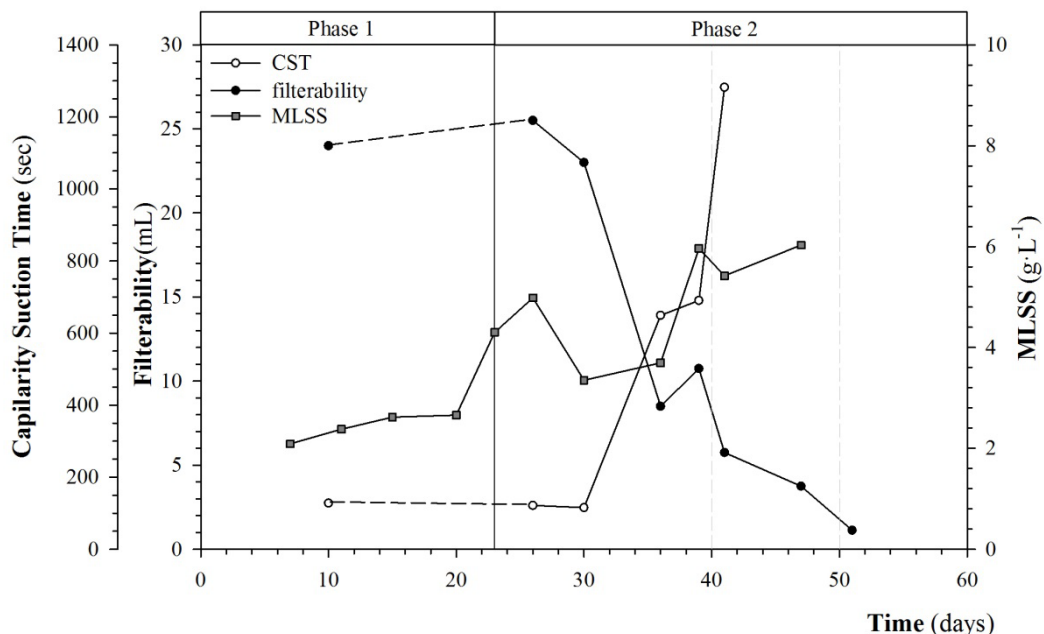
Figure 5. 3. Monitoring activated sludge characteristics throughout the experimental period

Since the sludge characteristics were deteriorated (in terms of filterability) affecting directly the MBR performance, a pre-treatment by means of adsorption or hybrid processes (e.g. GAC or PAC) (Nguyen et al., 2013) would avoid a deterioration of sludge characteristics improving the overall performance of the MBR.

5.3.4. Biological removal efficiencies

5.3.4.1. Carbon and nitrogen removal efficiencies in the MBR

In phase I, the average COD concentration was 416.4 mg $O_2 \cdot L^{-1}$ in the influent and 37.84 mg $O_2 \cdot L^{-1}$ in the effluent, giving a removal efficiency of over 90%. In phase II, the average influent COD concentration increased to 1615 mg $O_2 \cdot L^{-1}$

(due to the PPCP addition), but the effluent COD remained below 72.73 mg $O_2 \cdot L^{-1}$. Hence, COD removal efficiencies ranged between 88% and 97%. COD removal efficiencies were high during the whole study thanks to the versatility of the reactor operating at high SRTs and so avoiding washouts, and also to the capacity of the ultrafiltration membrane retaining all the particulate COD (Falahti-Marvast & Karimi-Jashni 2015).

The average influent alkalinity concentration in phase I was of 409 mg$\cdot$L^{-1}, whereas the effluent concentration decreased to 222 mg$\cdot$L^{-1}, demonstrating an average reduction of 46%. In phase II the influent alkalinity was 541 mg$\cdot$L^{-1} and in the effluent 380 mg$\cdot$L^{-1} achieving a reduction in alkalinity of around 29%. This change in the alkalinity of the effluent was proportional to the loss of nitrification (Figure 5. 4).
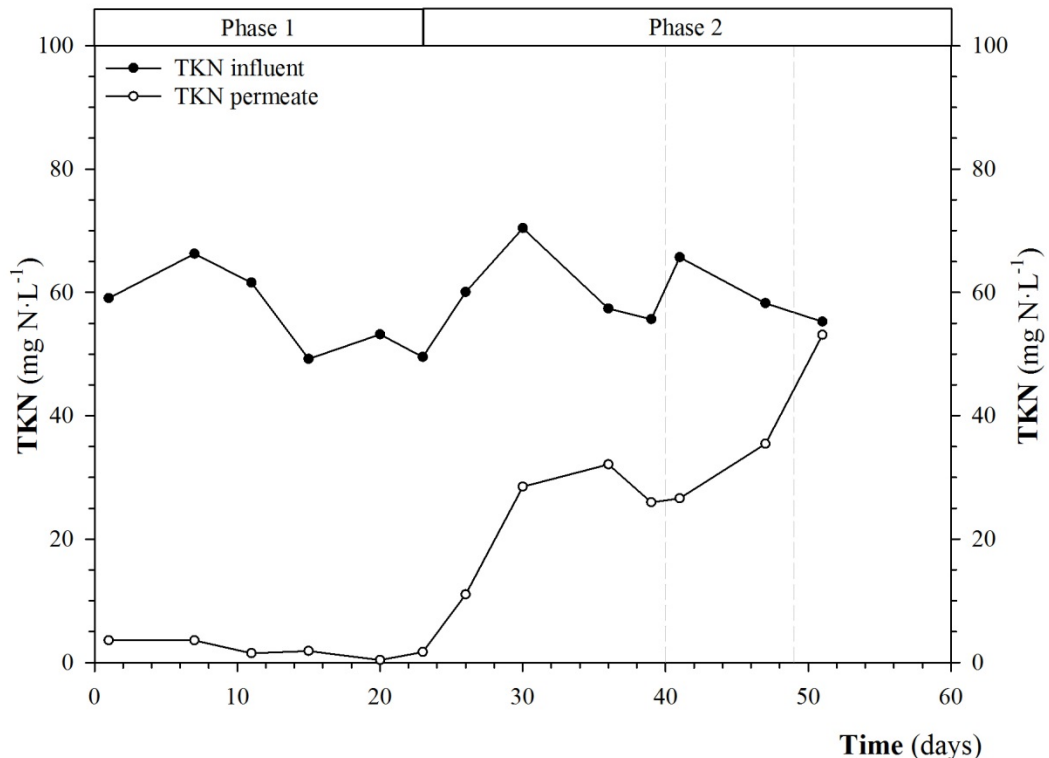
Figure 5. 4. TKN concentration evolution treating PPCP rich influent by MBR

Finally, the influent TKN in phase I presented an average of 49.2 mg N·L^{-1}, while effluent concentration was 2.61 mg N·L^{-1}, giving a removal efficiency of 94.6 %, which agrees with other MBR studies (Fraga et al. 2016). In phase II, the effluent TKN concentration kept increasing until reaching parity with the influent on day 57. This TKN accumulation in the effluent, together with the accumulation of alkalinity, could be explained by a reduction of nitrification due to an inhibitory effect (Figure 5. 4).

5.3.4.2. Complimentary nitrification experiments

Since different studies have evaluated how carbamazepine and caffeine directly affect the biological activity of ammonia-oxidizing bacteria (AOB) (Wang & Gunsch 2011), this paper focuses only in studying the effect of TCS-containing toothpaste and standard TCS on the biological performance of AOB. Batch tests were carried out using three batch reactors (BRs) (Table 5. 3) to find out the main cause of the inhibition of nitrification by comparing the effect of the addition of a TCS standard solution with that of TCS-containing toothpaste. In order to know the capability of the biomass to treat an influent with high content of TCS, new sludge from urban WWTP was used to validate these tests. The influent triclosan concentration was fixed at 5 mg·L^{-1} in BR-1 and BR-2. COD removal efficiencies were 71.4% in the case of the control BR, 75% in BR-1 and 72% in BR-2 (Figure 5. 5). The COD influent concentration of BR-2 was six times higher (8854 mg·L^{-1}) than control BR and BR-1 (1304.8 and 1491.2 mg·L^{-1}, respectively), due to the toothpaste addition. These results showed that the COD removal efficiencies in each BR were similar regardless of the influent concentration.

The removal efficiencies of NH_4^+-N in control BR, BR-1 and BR-2 were 89.5, 13 and 33%, respectively (Figure 5. 5). The difference between NH_4^+-N removal efficiency in BR-2 and BR-1 was related to the interactions between the compounds of the toothpaste, which could have a greater effect in minimizing the inhibition of nitrification than standard triclosan. The results of BR-2 demonstrated the same behaviour observed during phase II in the MBR experiments where the effluent TKN concentration increased (Figure 5. 5). Since

alkalinity was provided in excess (Monclús et al., 2009) for the ammonia concentration in the synthetic feed, the alkalinity could not be the reason of the differences between BR-1 and BR-2.
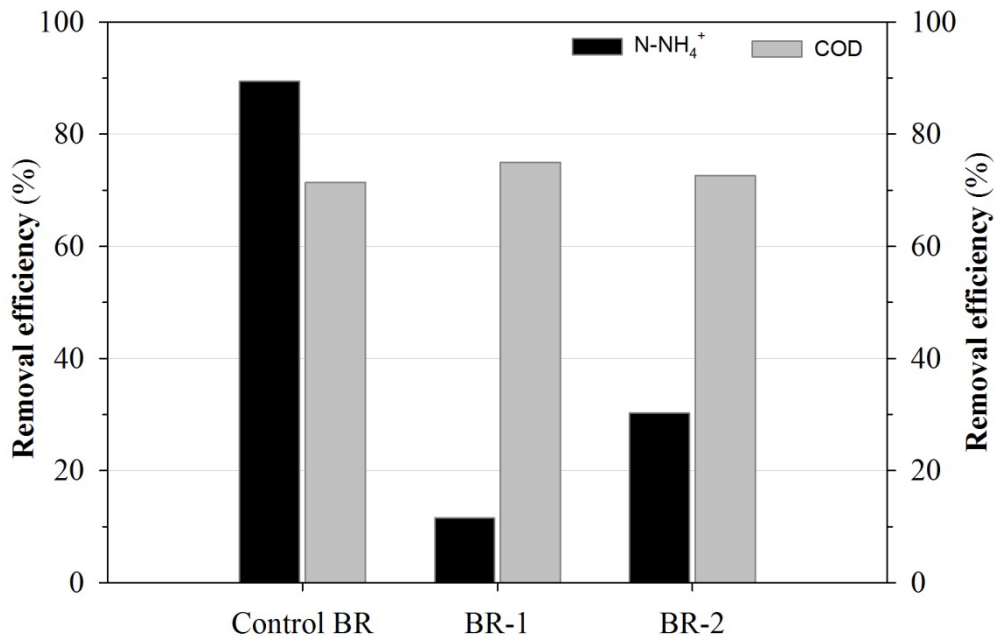
Figure 5. 5. Removal efficiency of COD and NH4+-N in each batch reactor

The evolution of the concentration of oxidized nitrogen species ($NO_x^- $-$N = NO_2^- $-$N + NO_3^- $-$N$) in these tests also showed a reduction of nitrification in BR-1 and BR-2. In the control BR, the rate of production of these species was 0.22 mg NO_x-N·g $MLSS^{-1}$·h^{-1} while in BR-1 the rate was 0.09 mg NO_x-N·g $MLSS^{-1}$·h^{-1} and 0.01 mg NO_x-N·g $MLSS^{-1}$·h^{-1} for BR-2.

The MBR also presented higher COD removal efficiencies (around 93%), compared to the 70% that was found in BR tests, due to the use of an ultrafiltration unit (Viero et al. 2008). Furthermore, triclosan did not appear to have any effect on the heterotrophic biomass responsible for COD removal.

The reduction of nitrification might be explained by the combination of competitive inhibition between ammonia and triclosan for the ammonia monooxygenase (AMO) enzyme, which oxidizes ammonia to nitrite, and its consequent effect on nitrite-oxidizing bacteria (Dokianakis et al. 2004). The low level of nitrification found in this study suggests that the adverse effects were directly caused by the addition of 5 mg·L^{-1} of triclosan to the BR, both as the standard solution and as a component of toothpaste.

Previous studies have demonstrated that triclosan is biodegraded by several microorganisms, including a gram-negative bacterium called Nitrosomonas europaea (N. europaea) (Lee et al. 2014, Qiu et al. 2015). When triclosan is added at low concentrations (<1.0 mg·L^{-1}) it promotes non-growth metabolism and extends the life of N. europaea cells. However, at high concentrations, the presence of triclosan causes serious damages to its cell membrane, as the AMO is not efficient enough to degrade all of the organic toxins. Therefore, the non-growth metabolism of N. Europaea is inhibited (Qiu et al. 2015). The capability of recovering the nitrification activity after a period of acclimation would not solve the problem with the low filterability measured in the sludge characterization (Stasinakis et al. 2007).

It is important to remove triclosan when biological processes are used in treating wastewater in order to avoid disturbing the biological activity. MBR systems are capable of obtaining high removal efficiencies (90.0 ± 7.6 %), which makes this technology interesting in the treatment of cosmetic industry effluents.

5.4. Conclusions

This work evaluates the biodegradability, refractory and inhibitory character of some commercial drugs frequently found in wastewater effluents from the pharmaceutical and cosmetic industries, including caffeine, carbamazepine and triclosan. A synthetic influent has been prepared and treated in a cyclic anoxic/aerobic MBR operated for 57 days. The MBR demonstrated efficiency removals as high as 93.1 ± 9.4 and $90 \pm 7.6\%$ for caffeine and triclosan respectively, and $36.9 \pm 6.5\%$ for carbamazepine, which is known to be a rather recalcitrant compound.

These results are similar to those found in other studies, confirming that the MBR process is an efficient and appropriate technology for the treatment of pharmaceutical and cosmetic industrial effluents. One of the main challenges of MBRs is the avoidance of membrane fouling, which has become a major obstacle for the wide-scale application of MBRs. However, it was observed in this work that the irreversible fouling increased the capacity to remove PPCPs due to pore blocking phenomena. Moreover, during the MBR operation, the use of a long SRT (50 days) promoted, as well, the removal of PPCPs treating high influent organic loads.

Triclosan inhibited nitrification, reducing 63% its activity. However, the MBR system was capable of eliminating this compound up to 90%. For this reason, a pre-treatment like adsorption techniques or hybrid processes (adsorption combined with biological treatment) would be necessary prior to its treatment.

Future studies will be needed to couple adsorption techniques with other treatments to minimize the concentrations of triclosan, preventing not only nitrification inhibition but also fouling while improving carbamazepine removal.

6. Evaluation of Cork as an adsorbent

6.1. Background, motivation and objectives

In a previous study, cork, a lignocellulosic natural material, has been used as a biosorbent to remove micropollutants from water (Mallek et al. 2018). Removal percentages of 100% for sodium diclofenac, 100 % for triclosan (TCS), 82% for naproxen (NAP), 57% for ketoprofen (KET), 50% for carbamazepine (CBZ), and 50% for methyl paraben (MPB) were obtained using small amounts of cork (5-10 mg) and 1 mg L^{-1} solution. These results are explained by hydrophobic interactions between the target contaminants and granulated cork as the adsorption capacities followed the order of hydrophobicity: TCS and DCF>NAP>KET> CBZ and MPB. Moreover, the hydrophobic interaction of these compounds with the cork are complemented by the π–π interactions between the aromatic moieties of the compounds and the aromatic rings of lignin (Olivella *et al.* 2015). The study was performed at equilibrium conditions and the adsorption process was almost complete after 30 minutes for all the micropollutants tested. The high efficiency of granulated cork in adsorbing the target micropollutants as well as the fast kinetics of the adsorption process led us to evaluate the use of a fixed bed technology for the removal of four pharmaceutical products (DCF, NAP, KET and CBZ) and two ingredients of personal care products (TCS and MPB) from water. Granulated cork are proposed to be an alternative to the use other expensive adsorbents such us granulated activated carbon that can be used to remove these contaminants prior the biological treatment in order to avoid the inhibition of the biological activity by TCS. The great advantages of using granulated cork as an adsorbent are that, unlike other adsorbents, no pre-treatment is required and, given that it is currently treated as a waste product within the industry, it can be acquired for little or no cost.

The scope of this research is to evaluate the capacity of granulated cork to remove four pharmaceuticals (diclofenac, ketoprofen, naproxen and carbamazepine) and two cosmetics compounds (triclosan and methylparaben) in a wastewater effluent by using fixed bed technology. In order to accomplish the main objective, different sub-objectives were defined:

- Characterization of the cork structure and surface.

- Evaluation of the fixed bed technology for removing the target contaminants using granulated cork as biosorbent.

- Evaluation of the fixed bed technology for removing the target contaminants using granulated activated carbon.

- A comparison was also made between removal efficiencies attained with this biosorbent and those obtained with other biosorbent in previous studies.

Ultimately, the results of this study may provide an evaluation on the potential of this biomaterial to be used as post-treatment technologies of secondary effluents or pre-treatment it will be combined by another process, especially in wastewater treatment plants located near the cork industries resulting in reduced transportation costs.

6.2. Materials and methods

6.2.1. Experimental conditions (set-up)

The solutions were prepared in 1L tank mixed by magnetic stirrer at 250 rpm. A solution containing 1 mg.L^{-1} of each compound was recirculated for 24h through the fixed-bed setup in absence of cork and in aerobic conditions (without forced aeration) in order to evaluate the system adsorption capacity. The fixed bed column (Alco S.A., Spain) had an internal diameter of 3.2 cm and an active length of 48 cm resulting in a bed volume (BV) of 410 mL.

During the experiments with cork, the column was partially packed with 15 g, 30 g or 34 g of granulated cork, previously washed with deionized water. The experiments performed using granulated activated carbon as the sorbent (10 mg·L^{-1}) were carried out in a 40 mL fixed bed column (0.5 cm i.d., 0.8o.d.). The test solutions were recirculated for the fixed-bed reactor using a peristaltic pump

(WatsonMarlow, UK) in an up-flow mode at a flow rate of 100 mL·min^{-1} (equivalent to 14.6 BV·h^{-1}), this pump was resulting in an empty bed contact time (EBCT) of 4.1 min in column. A diagram of the fixed-bed setup is presented in Figure 3.4.

The test solutions, prepared in ultrapure water and secondary effluent wastewater, contained 0.5 mg·L^{-1} of CBZ and MPB, and 0.1 mg·L^{-1} of DCF, NAP, KET and TCS. The test concentrations were selected taking into account the sensitivity of the analytical methodology as well as the efficiency of granulated cork to adsorb each compound at equilibrium conditions (Mallek et *al*., 2018). Hence, higher concentrations were used in the case of CBZ and MPB that are the less hydrophobic compounds (less adsorbed). Moreover, the concentrations tested are higher than the reported concentrations in real wastewater samples in order to minimize the errors due to the possibly presence of these contaminants in the effluent wastewater and to accelerate the breakthrough of the micropollutants.

The effluent wastewater was collected at the outlet of a conventional biological treatment in the WWTP of Quart (Girona NE Spain) and was filtrated with 0.2 µm nylon membrane filter before adding the micropollutants. The main physico-chemical characteristics of this effluent (**Table 6.1)** were determined by following standard methods (APHA, 2005) (APHA). The concentration of nitrites (NO_2^--N), nitrates (NO_3^--N), cations and anions were determined by ionic chromatography.

During the operation of the system, samples of 25 mL were collected in the mixed tank at prefixed times. These samples were analysed using two different analytical methodologies that differ in their sensitivities (section 6.3.1). The amounts of micropollutants adsorbed at the different prefixed times were calculated by the difference between the initial concentration of each compound and the concentration in the sample collected at the same prefixed time. Table 6. 2. summarizes the operating conditions for each set of experiments that were performed by duplicate at room temperature.

Table 6. 1. Characterization of Quart WWTP effluent

Quality parameters	Unit	Effluent
pH	-	7.7
Conductivity	$\mu S \cdot cm^{-1}$	1661
COD	mg L^{-1}	51
Cl$^-$	mg L^{-1}	266.17
PO$_4^{3-}$	mg L^{-1}	1.54
SO$_4^{2-}$	mg L^{-1}	17.035
NO$_2^-$-N	mg L^{-1}	-
NO$_3^-$-N	mg L^{-1}	2.98
NH$_4^+$-N	mg L^{-1}	-
Na$^+$	mg L^{-1}	175.23
K$^+$	mg L^{-1}	16.85
Mg^{2+}	mg L^{-1}	15.85
Ca^{2+}	mg L^{-1}	65.83

Table 6. 2. Operation conditions in fixed bed column experiments

Test	Solution	pH	Adsorbate	Initial concentration (mg·L^{-1})	Adsorbent Amount (g)	Volumetric flow rate (L h^{-1})	Length of experiment (h)	Analysis
1	Milli-Q water	5.5	TCS,KET,NAP,DCF, MPB and CBZ	1	-	6	24	HPLC-DAD
2	Milli-Q water	5.5	TCS,KET,NAP,DCF, MPB and CBZ	0.5	34 cork	6	24	HPLC-DAD
3	Milli-Q water	5.5	TCS,KET,NAP and DCF MPB and CBZ	0.1 0.5	30 cork	6	5	SR extraction/concentration HPLC-DAD
4	Milli-Q water	5.5	TCS,KET,NAP and DCF MPB and CBZ	0.1 0.5	15 cork	6	5	SR extraction/concentration HPLC-DAD
5	WWTP effluent	7.7	TCS,KET,NAP and DCF MPB and CBZ	0.1 0.5	0.01 GAC	1.8	5	SR extraction/concentration HPLC-DAD

6.2.2. Reagents and materials

TCS, NAP, KET, CBZ, DCF sodium salt and MPB were purchased from Sigma–Aldrich (USA). A 500 mg·L^{-1} stock solution containing all these compounds was prepared in methanol, stored in brown glass bottles and kept at 4°C in order to avoid degradation during the test period. This solution was prepared monthly. Standard working solutions were prepared daily by diluting this stock solution with Milli-Q water obtained from a Millipore purification system (Millipore, Express 40, USA).

Chromatographic grade acetonitrile was provided by Fisher (USA) and sodium acetate and acetic acid were from Sigma Aldrich (Germany). HCl solutions were used for the pH adjustment of the test solutions.

The cork, kindly supplied by the Cork Centre (Palafrugell, Girona), was sifted to attain particle sizes of < 2 mm, cleaned three times thoroughly with bi-distilled water, and air dried before use. Granulated activated carbon (GAC—coal-based) was from Calgon Filtrasorb 100 (F100) (Pittsburgh, PA, USA). A GAC fraction was dried at 105 °C for approximately 12 h. until constant weight and then stored in a desiccator until use. The GAC was sieved using a 2 mm mesh seize.

6.2.3. Cork characterization

The morphology was observed by a scanning electron microscope (SEM) (Model ZEISS DSM-960A). Samples were examined at a magnification range of 20x to 500x. Pictures of representative cork samples were taken and particle size distribution was determined from these using the Feret diameter.

6.2.4. Chromatographic analysis

The determination of CBZ, NAP, KET, DCF, TCS, and MPB was performed with an Agilent 1200 series high performance liquid chromatography system equipped with two pumps (G13128), a degasser (G1379B), an autosampler

(G1329B) and a DAD detector (G4212A), system control and data acquisition were performed using Agilent ChemStation software.

The detection wavelength was set at 242 nm for CBZ, NAP and TCS; 250 nm for KET and MPB, and 280 nm for DCF. The parameters (intensity, peaks area, peak shape and retention time) affecting the chromatographic analysis were studied in order to improve the detection sensitivity and the analyte separation. Different mobile phase compositions and gradients as well as flow rates were tested in order to find out the best resolutions between the peaks, especially in the case of NAP and KET that have similar retention times. Moreover, two different chromatographic columns, C18 Luna (50×2 mm, 2.5 µm) and C18 Kinetex (50×2.10 mm; 2,6 µm) both from Phenomenex, USA, were tested.

When performing the experiments in the fixed-bed column, there were some samples in which the sensitivity of the analytical method was not sufficient to allow the determination of the micropollutants, in general, this problem occurred after recirculating the solution for several hours, as a result of the high efficiency of cork in adsorbing the contaminants. In order to increase the sensitivity of the analytical method, we performed the analysis with a new analytical methodology, recently developed and validated in the research group (Mallek et *al*., 2018). The method is based on the extraction of the analytes by a polydimethylsiloxane rod that allows enrichment factors of 10 for NAP, 24 for KET, 108 for DCF and 179 for TCS to be obtained at pH 2. The procedure consists of immersing a 10 mm-silicone rod (SR) in 25mL of a sample solution containing 15% NaCl at pH 2, allowing extraction to take place overnight. The 125 ml amber vials containing the samples were agitated at 200 rpm during this period in a ten-point magnetic shaker (MultiMix D, Ovan, Badalona, Spain). After extraction, the PDMS rod was removed with clean tweezers and then dried with a lint-free tissue. The rod was then placed into a "tapered" glass insert containing 200 µL of methanol and sonicated for 30 min. 10 µL of the extract was then injected into the HPLC-DAD system for analysis. This silicone rod (SR) microextraction method allows the achievement of detection limits in the 0.47 to 1.02 µg·L^{-1} range, except 3.40 µg·L^{-1} for CBZ

6.3. Results and discussions

6.3.1. Analytical methodologies

The first point before to start the study of the performance of cork for the removal of micropollutants in a fixed bed column is to select the analytical methodology that will allow the monitoring of the target compounds during the removal process. Checking previous (Ahmad et al. 2017; Almeida et al. 2017; Kim et al. 2013; Patrolecco et al. 2013; Silva and Nogueira 2008; Silva et al. 2008) published articles in the determination of PPCPs by liquid chromatography with a diode array detection (HPLC-DAD), it was found that they differ in the mobile phase composition. However, most of these methodologies are based on reversed-phase liquid chromatography using C18 columns of 10-15 cm-long and particle sizes of 5 µm. Our objective was to reduce the analysis time and to improve the resolution of the peaks with a 5 cm-C18 column having particle sizes of 2.5 µm.

In order to determine the best chromatographic conditions to improve the sensitivity and selectivity of the instrumental determination, three different methods were tested (Table 6. 3).

The main difference between the three methods is the composition of mobile phase A. In the case of Method 1, the resolution between the peaks of NAP and KET was not good and the addition of potassium dihydrogen phosphate caused clogging problems in the chromatographic system. To avoid these problems, a new composition of mobile phase A, which consisted of ultrapure water acidified with 0.1 % of acetic acid, was tested resulting in a worst separation (overlapping of the NAP and KET peaks) and background hampering as can be seen in Figure 6. 1.

Table 6. 3. HPLC conditions for PPCPs analyses

	Method 1		Method 2		Method 3	
Flux	0.5 mL·min^{-1}		0.3 mL·min^{-1}		0.3 mL·min^{-1}	
Column	C18 Kinetex 100A		C18 Kinetex column		C18 Luna column	
Column size	50×2.10 mm; 2.6 µm		50×2.10 mm; 2.6 µm		50×2 mm; 2,5 µm	
Injection Volume:	20µL		20µL		10µL	
Mobile phase A:	Water + 50 mMKH_2PO_4		Water + 0.1% acetic acid		Water + 0.1% acetic acid + 0.3852g of sodium acetate	
Mobil Phase B:	Acetonitrile		Acetonitrile		Acetonitrile	
	Time	**%**	**Time**	**%**	**Time**	**%**
	0	15	0	10	0	10
	6	25	5	25	5	25
Gradient based on %of B	10	45	15	45	15	45
	15	45	20	80	20	80
	20	15	21	45	23	45
			25	10	25	10
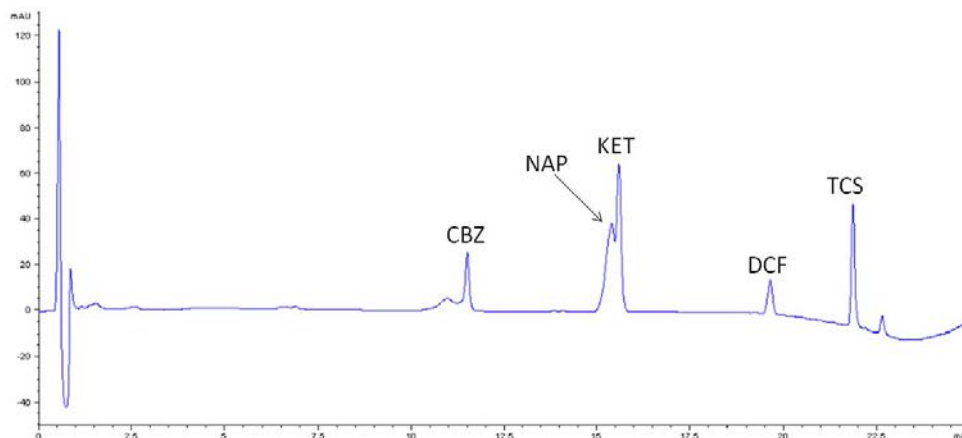
Figure 6. 1. Chromatogram of a 400µgL^{-1} standard obtained with Method 2

In Method 3, to obtain a good resolution of NAP and KET peaks, a buffer solution at pH 4, composed of 0.1% acetic acid + 0.3852 g of sodium acetate, was employed as mobile phase A and de gradient was slight modified. Moreover, the chromatographic column was also changed in order to improve the form of the peaks. In these conditions, a good resolution of ketoprofen and naproxen was obtained (Figure 6. 2).
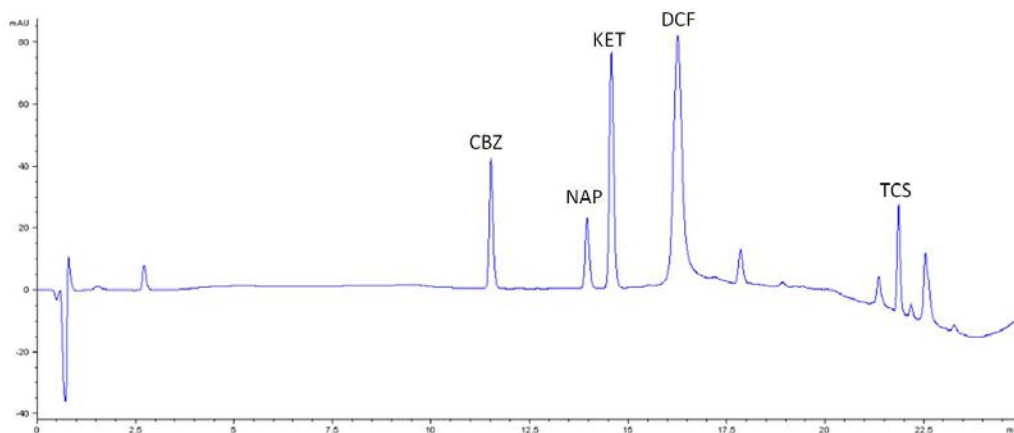
Figure 6. 2. Chromatogram of a 250 µgL^{-1} standard solution obtained with Method 3.

The chromatographic conditions of Method 3 were used to perform the chromatographic analysis of the water samples.

Linearity was evaluated by analyzing five standard solutions of different concentration levels ranging from 75 to 400 µg·L^{-1} of NAP, KET, CBZ, DCF, and TCS by triplicate (**Table 6.4**). The method was linear for all compounds and determination coefficients (r^2) were higher than 0.990. The LODs and LOQs were calculated using the Excel regression analysis tool and considering a signal-to-noise ratio of 3 and 10, respectively. LODs ranged from 2.42 to 5.45 µg·L^{-1} and LOQs from 7.35 to 16.76 µg·L^{-1}. The precision of the method, expressed as RSD%, was evaluated by replicate analysis ($n = 6$) of two standard solutions of 100 and 400 µg·L^{-1}. Intraday precision was in the range of 0.2–1.2% and 0.3-0.8% and interday precision was between 3.8-10 and 4.7-18.8%.

The LODs of this method were improved by introducing a pre-concentration step based on silicone rod (SR) microextraction. The development and validation of the SR-based method for the determination of KET, NAP, DCF, CBZ and TCS was performed by Mallek, et al. (2018). The method was validated for river waters, but in this study, it was applied to analyse secondary effluent wastewaters showing a good performance.

Table 6. 4. Equations of calibration curves. Linearity, LODs, LOQs and precision obtained for the five compounds.

Compounds	Retention time (min)	Equations of calibration curve	Linearity (R^2)	RSD interday (%) (n=6) 25 $\mu g \cdot L^{-1}$	100 $\mu g \cdot L^{-1}$	RSD intraday (%) (n=6) 100 $\mu g \cdot L^{-1}$	400 $\mu g \cdot L^{-1}$	LOD $\mu g \cdot L^{-1}$	LOQ $\mu g \cdot L^{-1}$
KET	13.8	$y = 9.647\,x - 19.21$	0.998	3.8	4.7	1.2	0.3	1.1	3.36
TCS	17.5	$y = 27.58\,x - 11.38$	0.999	4.5	4.7	0.6	0.5	1.08	3.3
NAP	13.3	$y = 4.963\,x - 7.207$	0.999	10.2	10.5	0.2	0.8	1.4	4.3
DCF	15.5	$y = 11.82\,x - 26.29$	0.999	5.9	5.6	0.3	0.3	0.8	2.5
CBZ	11.12	$y = 0.708\,x - 2.714$	0.994	8	18.8	0.8	0.3	6.28	19.04

6.3.2. Cork structure and morphology

Cork is mainly composed of two hydrophobic biopolymers, suberin and lignin, and hydrophilic polysaccharides cellulose and hemicellulose. Although highly variable with tree maturity and geographical area, the typical chemical composition of cork is approximately 40% of suberin, 22% lignin, 18% polysaccharides and 15% extractives (Pereira 2013). The content of suberin is the chemical fingerprint of cork and it is directly related to most of its typical properties (Pereira 2015).

The structural features of cork were observed by SEM at different magnifications. The irregular shape of the granulated cork particles can be observed in the Figure 6. 3A. The structure of cork is compact and presents a regular arrangement of cells without intercellular spaces. The aspect of this arrangement in the transverse section (the plane perpendicular to the plant axis) is similar to a brick-wall and the cells present a rectangular form (Figure 6. 3B) while in the tangential section (the plane perpendicular to a radius) the cork cells appear polygonal, mostly as hexagons with a alveolar (honeycomb-like) structure (Figure 6. 3B).
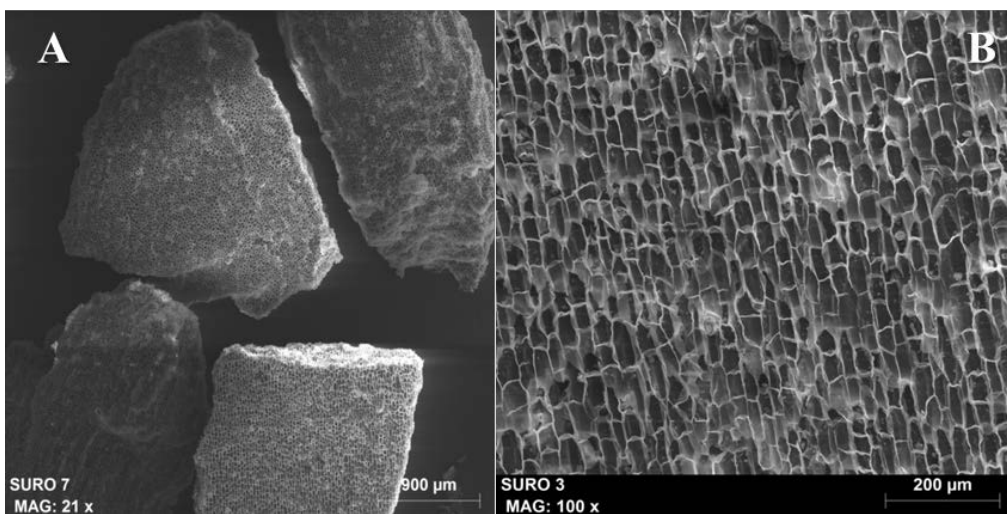
Figure 6. 3. Scanning electron micrographs (SEM) of cork granules. A) SEM 21x and B) 100x

SEM observation of cork also showed that, in a radial section, cork cells appear as, predominantly 4, 5 and 6-sided polygons shapes (Figure 6. 4A). Either three or four cell walls meet at each vertex of the network (Dordio *et al.* 2011). On average the cell prism height is 30–40 µm and the cell wall thickness 1–1.5 µm (Figure 6. 4B). An important characteristic of prismatic cork cells is that their lateral faces are corrugated (Figure 6. 4) with two or three complete corrugations per cell that probably result from compression during cell and bark growth.
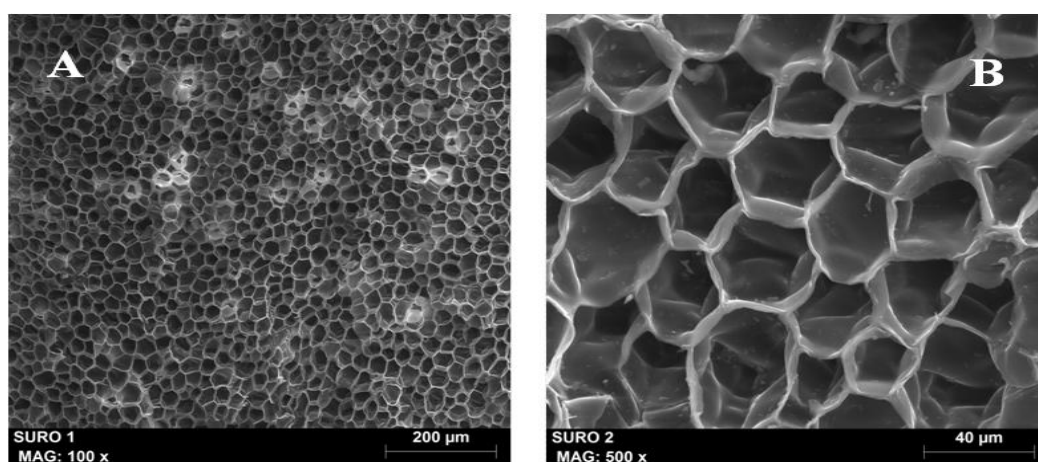
Figure 6. 4. Scanning electron micrographs (SEM) of cork granules. A) SEM 100x and B) 500x

The granulated cork used in this study was sieved to obtain particle sizes smaller than 2 mm but due to its irregular shape some larger particles could cross the sieve. Particle size distribution was obtained from the SEM images from measuring the areas of the particles (Figure 6. 5A) an applying a statistical calculation. As can be seen in this Figure 6. 5B, 94 % of the particles have diameters within 2.25–3.5 mm.
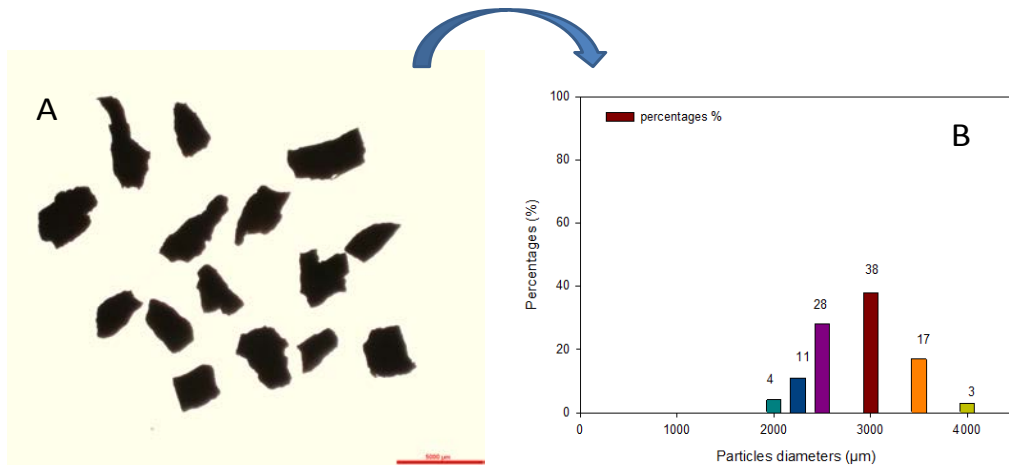
Figure 6. 5. Particle size distribution

Surface area for 1-2mm granulates was 16.3 $m^2 \cdot g^{-1}$ and for 3-4 mm granulates 10.7 $m^2 \cdot g^{-1}$. The mean pore diameter was calculated to be around 1-1.34 mm, which indicates the presence of macropores. The pore volume was 2.83 $cm^3 \cdot g^{-1}$ for 1-2 mm granulates and 2.24 $cm^3 \cdot g^{-1}$ for 3-4 mm granulates (Domingues et al. 2005) The fact that surface area and pore volume decrease when the particle size decreases confirms that the cork cells are closed making the interior spaces inaccessible and only the external surface area is available for sorbing the contaminants.

The apparent porosity is quite large, due not only to inter-granules void space but also to the porous cellular surface (Figure 6. 3). The extensively porous nature of this material is also responsible for a very low bulk density, which raises some practical problems in terms of maintaining compactness of cork bed sat high flooding rates. The density of cork can vary by as much as a factor of 2 (120–240 Kg m^3), depending mostly on it sage (virgin or reproduction) and treatment (natural or boiled).

6.3.3. Equilibrium contact time and kinetic studies

In a previous study (Mallek et al. 2018), batch experiments were carried out in order to characterize the adsorption isotherms of PPCPs by granulated cork. Removal percentages and uptakes of 82% (3.56 mg·g^{-1}) for naproxen, 57% (2.31 mg·g^{-1}) for ketoprofen, 50% (1.84 mg·g^{-1}) for carbamazepine, 50% (1.78 mg·g^{-1}) for methyl paraben, 100% for sodium diclofenac, and 100 % for triclosan, were obtained using 5 mg of cork and a 1 mg L-1 solution of each compound. The adsorption process was almost complete after 30 minutes for all the micropollutants and followed Freudlinch isotherm model:

$$\log q_e = \log K_F + \frac{1}{n} \log C_{eq} \qquad \text{Equation 6.1}$$

where K_F (L$^{1/n}$ mg$^{(1-1/n)}$ g^{-1}) represents the sorption capacity when the equilibrium concentration equals 1 mg·L^{-1} and it is characteristic of the sorption system (adsorbent and adsorbate).The Freundlich 1/n value, which is calculated from the slope of eq.6.1, determines the degree of non-linearity between solution concentration and adsorption. The estimated adsorption capacities (K_F) and n values for NAP, KET, CBZ and MPB were found to be 3.68, 2.92, 2.96 and 2.72, and 1.98, 1.03, 1.25 and 1.34, respectively. These results suggest that small amounts of cork possess a relatively high removal capacity for all these compounds, and especially for TCS and DCF, which were completely adsorbed, and for NAP, which gave the highest K_F and n values, following their hydrophobicity order.

The results obtained in equilibrium conditions were considered in order to define the experimental conditions to be selected in the fixed bed tests. The first experiment was performed in the set-up using described in section 6.2.1, using 34 mg of granulated cork and an aqueous solution containing 0.5 mg·L^{-1} of each compound at pH 5.5. The sorption process was monitored by analysing samples that were collected at prefixed periods of time. Preliminary experiments were carried out to determine the contact time needed by the system to reach equilibrium (Figure 6. 6), the adsorption process was almost complete after 3 hours under a constant flux 124.4 L·h^{-1}·m^{-2} for the four PPCPs this time was

chosen for performing the subsequent adsorption experiments. TCS and DCF were not detected in the samples at the first 10 minutes.
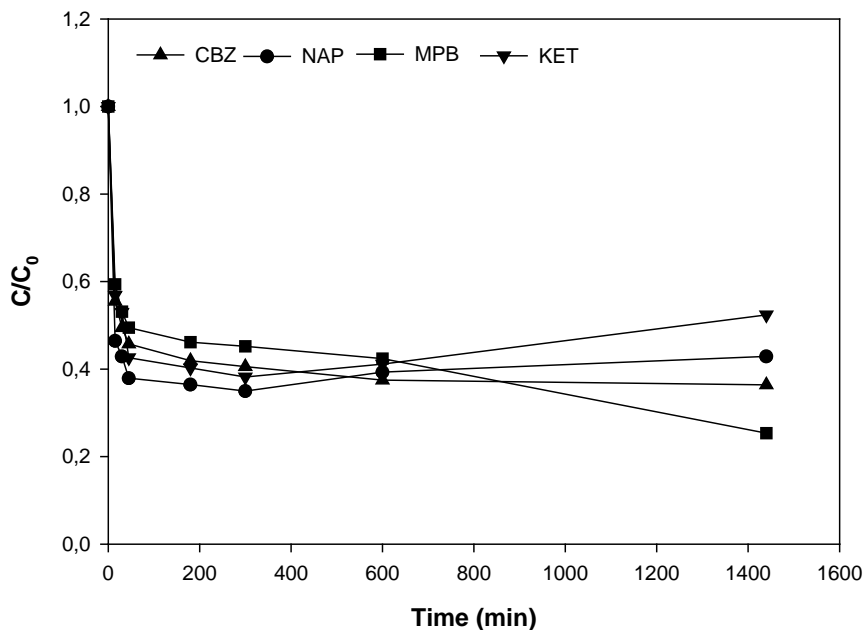
Figure 6. 6. Adsorption kinetics of NAP, KET, CBZ and MPB with 34 g. of cork. Initial concentration: 0.5 mg·L^{-1} at pH 5.5

The adsorption rises steeply at high amount so the removal increased as the cork mass was raise from 15 to 30 g. In the first 10 minutes, the initial concentration of CBZ in the aqueous solution decreased of 40%, for MPB decreased of 30% and for NAP and KET decreased more than 50%. TCS and DCF were not detected in the samples as their concentrations were lower than the detection limits of the instrumental chromatography method (Table 6. 4). The subsequent experiments were performed with different amounts of cork, 15 and 30 mg, and initial concentrations of 0.5 mg·L^{-1} of CBZ and MPB, which are the less hydrophobic compounds, and 0.1 mg·L^{-1} of NAP, KET, TCS and DCF. The solutions were prepared in ultrapure water (pH 5.5). To improve the sensitivity of the determination of all the target compounds during the experiments, the samples were analyzed by the SR micro-extraction method (section 3.3.3). The results obtained are represented in Figure 6. 7 showing that the removal decreased as the cork amount was reduced from 30 to 15 mg. The removal

percentage for NAP and KET increased from 45% to 71% and from 16 % to 59%, respectively, but in the case of CBZ and MPB, removal remained almost the same (Table 6. 5). The initial concentration of CBZ and MPB fell by about 45% and 30% respectively in the first 5 minutes, but a part of these compounds was desorbed from the cork leaving the remaining concentrations of the two both compounds. At 5h, those compounds were at around 50% of the initial concentrations. TCS and DCF can be considered as having been completely adsorbed by the cork given that these compounds were not detected in the testing solution.
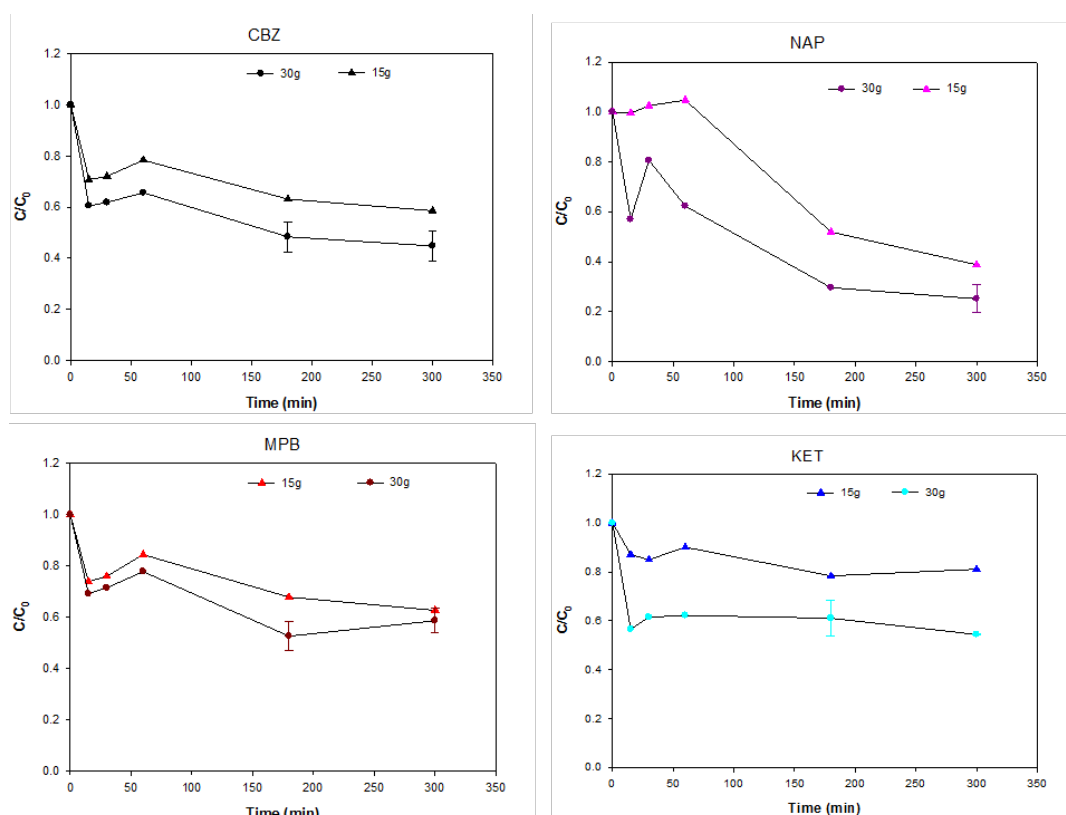
Figure 6. 7. Adsorption kinetics of NAP, KET, CBZ and MPB with amounts of cork 30 g. and 15 g. Initial concentration of KET and NAP 0.1 mg·L-1 and CBZ and MPB 0.5 mg·L^{-1} at pH 5.5 in Milli-Q water

The fixed bed column experiments were then performed with secondary effluent wastewater that was filtrated through an 0.2 µm filter to eliminate the particulate matter in order to avoid it to compete with granulate cork in adsorbing the micropollutants. 5 mg·L^{-1} of each compound, CBZ and MPB, and 0.1mg·L^{-1} of TCS, DCF, NAP and KET were added to the filtrated wastewater (pH 7.7). As can be seen in Table 6. 5, the removal efficiencies in ultrapure water for NAP and KET, MPB and CBZ were 75%, 44.89 %, 60% and 54%, respectively after 3 h. In the case of TCS and DCF, nearly quantitative removals were obtained at the first 10 minutes. When comparing these results with those obtained in the batch experiments (Mallek et *al*., 2018), the results obtained are very similar in terms of removal efficiencies but differ in the uptake values as the amount of cork used in the bed fixed column was higher. According the results in the batch experiments (Mallek et *al*., 2018) when the amount of cork increased the uptake decreases one half.

The hydrophobic properties of TCS and DCF (logK$_{0W}$> 3.2) result in them being mostly completely adsorbed by the cork. In the case of NAP and KET, which have similar log K$_{OW}$, the higher adsorption capacity obtained by NAP in comparison with KET can be explained by the higher water solubility of the latter.

In effluent wastewater, the removal efficiencies for TCS, CBZ and MPB are similar to those obtained in ultrapure water. However, for DCF, NAP and KET, the removal efficiencies are much lower with values of approx.30% for DCF and NAP and 20% for KET. These results are explained by the acidic properties of these pharmaceuticals (DCF pKa =4.3, NAP pK$_a$=4.15, KET pK$_a$=4.45), which are present in their ionic forms at pH>pKa and the ionic species are not suitable to be adsorbed by a hydrophobic sorbent such as cork.

Table 6. 5. Removal of six PPCPs by fixed bed cork after 3 hours (this study): amounts of cork 30g .Initial concentration of TCS, DCF, KET and NAP 0.1 mg·L^{-1} and CBZ and MPB 0.5 mg·L^{-1}.

Target compound	Milli-Q water (pH 5.5)		Effluent water (pH 7.7)	
	Removal (%)	qe (mg·g^{-1})	Removal (%)	qe (mg·g^{-1})
TCS	97.55±0.54	0.0032	96.1±1.11	0.0030
DCF	97±2.21	0.0032	26±9	0.0006
CBZ	54.33±5	0.0080	51.56±0.12	0.0086
MPB	60.24±4.4	0.0098	59.2±2	0.0096
NAP	75.3±4	0.0024	31.99±1.86	0.0011
KET	44.89±0.38	0.0019	18.4±9	0.0006

In this case, a simple operation of pH adjustment in the effluent can be maintaining the same removal as in Milli-Q water experiment.

The amount adsorbed from distilled water was largest at high PPCPS solution concentrations, because there was no competition between inorganic ions (Table 6. **1** and Table 6. 5) and PPCPs molecules.

Interestingly, CBZ, which was not eliminated to any appreciable degree during activated sludge treatment, was eliminated quite well by the cork, suggesting that there was still some sorption capability available in the bed. The accumulation and the adsorption of TCS into the biomass directly affected the performance of the MBR. Moreover the high concentration of TCS inhibited the nitrification reducing the capability to remove Nitrogen from wastewater. The hybrid of cork-MBR can be obtained a good result, this adsorbent can adsorb the TCS and decrease the TCS concentration in the solution then the MBR remove completely the TCS without inhibition of nitrification process
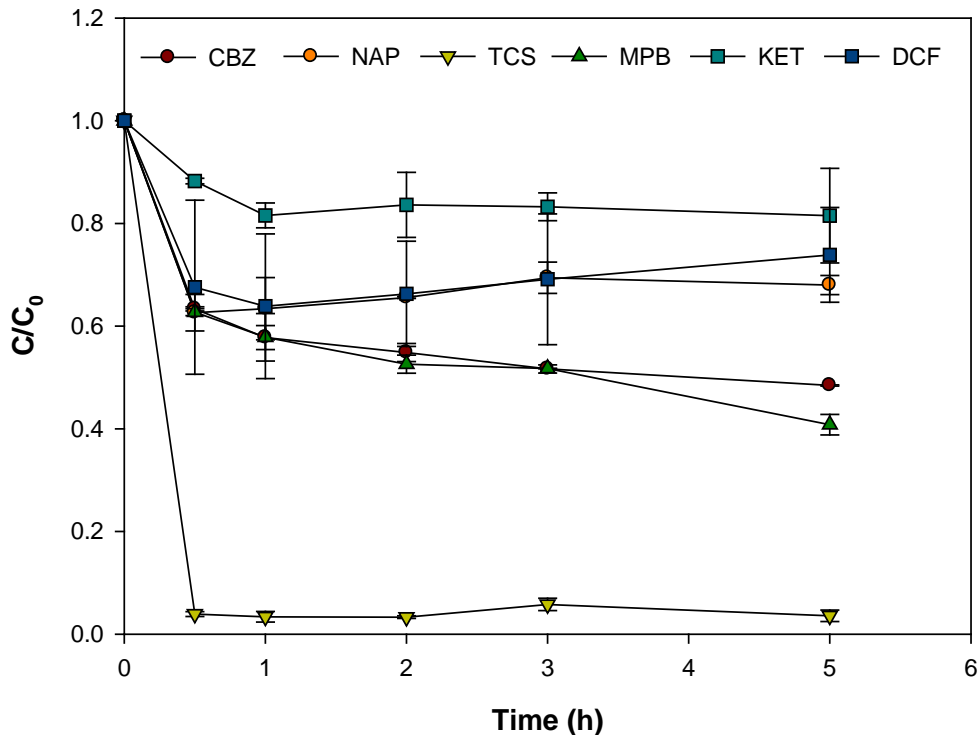
Figure 6. 8. Adsorption kinetics of NAP, KET, CBZ,MPB, TCS and DCF with amounts of cork 30g .Initial concentration of KET, NAP, TCS and DCF 0.1 mg.L-1 and CBZ and MPB 0.5 mg·L^{-1} at pH 7.7 in effluent

The granulated activated carbon GAC filtration is generally implemented at final stages of water treatment process for eliminating residual micropollutants and it is also widely used in drinking water treatment plants (Knopp et al. 2016). In this study, GAC has been tested for the removal of TCS, DCF, CBZ, MPB, NAP and KET in ultrapure water and secondary effluent wastewater at the same concentrations employed in the experiments performed with granulated cork. As it has been explained in the methodology, the experimental set-up (dimensions of the fixed bed column) was different as the amount of GAC was of 10 mg. All the micropollutants were removed from the effluent wastewater as they were not detected in all the samples collected after 30 minutes of recirculation of the wastewater through the fixed bed column containing the GAC (Figure 6. 8).

Results obtained show the high capacity of this type of GAC in removing the micropollutants.

Table 6. 6. Removal of six PPCPs by fixed bed GAC after 10 minutes (this study): amounts of GAC 10mg .Initial concentration of TCS, DCF, KET and NAP 0.1 mg·L⁻¹ and CBZ and MPB 0.5 mg·L⁻¹.

Target compound	Effluent water (pH 7.7) Removal (%)
TCS	100
DCF	100
CBZ	100
MPB	100
NAP	100
KET	100

Paredes *et al*. (2016) shows that the faster removal of TCS and DCF (100%) at 35min by GAC adsorption the same than in this study (Table 6. 7). All late researches (Kårelid et al. 2017; Nguyen et al. 2016; Nguyen et al. 2013a; Nguyen et al. 2013b; Nguyen et al. 2012; Paredes et al. 2016; Rigobello et al. 2013) found before 1h that the GAC was a good adsorbent (> 93%) for DCF. It was observed that the results of Cork showed a linear dependence between amount of sorbent and initial concentration that play an important role to accelerate and increase the removal

Table 6. 7. Removal of six PPCPs by fixed bed adsorption onto various kinds of GAC

Adsorbate	GAC Adsorbent	Adsorption conditions	C_0 $\mu g \cdot L^{-1}$	Removal (%)	References
CBZ	F400	<41mg/L, 15.5°C , 51min, WWTP effluent	0.221	>95	Kårelid et al. 2017
		25mg/L, 15min, WWTP effluent	0.067	74	Yang et al. 2011
	1200	7.5g, 7min, pH7.2-7.5, 20/22°C, synthetic wastewater	4.3	~100	Nguyen et al. 2013b☐
			5	>95	Nguyen et al. 2013a Nguyen et al. 2012
	F100	10mg/L , 30min, pH7.7, WWTP effluent	500	100	This study
DCF	F400	<41mg/L, 15.5°C, 51min, WWTP effluent	0.287	> 93	Kårelid et al. 2017
	n.i.	pH 7.3-7.8, 25°C, 35 min, secondary effluent	1-40	>90	Paredes et al. 2016
		pH 4.9 , 4.5mg/L, 20°C, 20min, synthetic water	1000	99.7	Rigobello et al. 2013
	1200	7.5g, 7min, pH7.2-7.5, 20/22°C, synthetic wastewater	3.75	~100	Nguyen et al. 2013b
			5	>95	Nguyen et al. 2013a Nguyen et al. 2012
	F100	10mg/L , 30min, pH7.7, Effluent	100	100	This study

	n.i.	pH7.3-7.8,25°C,35min synthetic secondary effluent	1-40	>90	Paredes et al. 2016
NAP	1200	7.5g, 7min, pH7.2-7.5, 20/22°C, synthetic wastewater	3.75	~100	Nguyen et al. 2013b
			5	>95	Nguyen et al. 2013a Nguyen et al. 2012
	F100	10 mg/L , 30min, pH 7.7, WWTP effluent	100	100	This study
KET	1200	7.5g, 7min, pH (7.2-7.5), 20-22°C, synthetic wastewater	3	~100	Nguyen et al. 2013b
			5	>95	Nguyen et al. 2013a Nguyen et al. 2012
	F100	10mg/L , 30min, pH7.7, WWTP effluent	100	100	This study
TCS	n.i.	pH (7.3-7.8), 25°C, 35min, synthetic secondary effluent	1-40	100	Paredes et al. 2016
	F100	10mg/L , 30min, pH7.7, WWTP effluent	100	100	This study
MPB	NRS Carbon EA 0.5-1.5 Norit	29 g., 2h ,25°C pH 8.4, Grey water	0.189	72	Hernández-Leal et al. 2011
	F100	10mg/L , 30min, pH7.7, Effluent	500	100	This study

n.i.: not identified

The adsorption of specific PPCPs onto GAC is dependent on the physical-chemical properties of the individual PPCPs and GAC tends to adsorb hydrophobic organic compounds(Yang et al. 2011).At pH<pKa, the net charge on activated carbon surface is positive when the solution pH is less than pHpzc =7 and the hydrophobic compound is mainly non-dissociated. Thus, repulsive electrostatic interactions are minimized and sorption is enhanced.(Behera et al. 2010)

The different types of GAC (Table 6. 7) present high removal of KET, NAP, CBZ, MPB and DCF using GAC than cork in the effluent. High removal of the hydrophilic compounds can be explained by the fact that hydrophobicity-independent mechanisms such as ion exchange, surface complexation and hydrogen bonding also play significant roles in sorption of trace organics onto GAC. In addition to hydrophobic partitioning, various other mechanisms such as hydrogen bonding π- π interaction between aromatic rings, and van der Waals forces (e.g., dipole-dipole interaction, London dispersion force) can contribute towards the adsorption of a compound onto a specific adsorbent (Nguyen et al. 2013b).

However, the differences between amounts adsorbed by cork and by GAC were much pronounced for DCF, NAP and KET but with a simple operation of pH adjustment in the effluent can be maintaining the removal of DCF by cork (97%) and increasing the removal of NAP. In fact, KET was removed in larger extent by GAC than it was by cork.

In the case of both GAC and cork, screening with respect to adsorption capacity and carbon usage rate is a necessity if the specific product has not previously been tested on similar wastewater. If the specific task is the removal of as much as possible of pharmaceutical residues in uncharted wastewater the recommendation is also here in terms of carbon to use GAC taking caution that it should be selected well according its varied capacities of each kind before using, as indicated by our results. However well -performing nature cork product could

approach the performance of GAC for certain well-defined PPCPs (TCS, MPB and DCF).

The important adsorption onto Cork of the compounds resistant can ensured that the combined with another process will result in an overall near complete removal of the compounds.

6.4. Conclusions

The results obtained with this work showed that granulate cork presents good sorption qualities for the removal of some PPCPs from aqueous solutions. This material was shown to remove extensively three of the six pharmaceuticals tested, TCS and DCF and NAP during the full period of contact with cork (3h), although CBZ and MPB were removed more the half of amount and the lowest adsorption capacity was for KET. This behavior of TCS, CBZ and MPB was observed in all the tested conditions (in waters). However, there was some loss of removal efficiency in the effluent, where the adsorbed amounts of DCF, NAP and KET were reduced, due to the ionic forms and the dissolved organic matter in effluent.

Cork showed a high capacity for TCS sorption. GAC showed a much higher capacity in removing the micropollutants. Equilibrium was also attained slightly faster for GAC in comparison with cork granules.

This work represents only a first step in the study of its use as post-treatment technologies of secondary effluents or pretreatment. The combination of cork adsorption together with another process could be a good hybrid treatment process or combined technology. Further tests are still necessary in order to evaluate aspects such as its suitability for plants development and the cost implications that cannot be assessed as breakthrough times of micropollutants were not achieved in the cork columns operated in this study.

7. GENERAL DISCUSSION

7.1. General discussion

The results chapters presented in this doctoral thesis have focused on the treatment technologies for pharmaceutical and personal care product removal:

- Review of treatment technologies for TCS removal (**Chapter 4**)

- PPCP removal using MBR technology (**Chapter 5**)

- Evaluation of cork as a natural adsorbent (**Chapter 6**)

Each study has also allowed the knowledge required to address the main objective of this doctoral thesis to be extracted. Thus, the main outputs acquired during each study have been the base for a technology treatment proposal for PPCP removal where TCS is the selected target compound.

7.1.1. Review of treatment technologies for TCS removal:

The main goal of this chapter was to identify the limitations to and the advantages of treatment technologies for TCS removal in wastewater effluent. As TCS is a common synthetic antimicrobial agent and can generate disinfection-by-products such as chloroform, its treatment must be considered to prevent its toxicity entering receiving the media.

Activated sludge systems are the cheapest technology to consider but they are not capable of removing a high percentage of TCS and even less complete removal. Therefore, CAS systems are one of the technologies that should be considered but need to be complemented with another advanced technology.

Adsorption based on active carbon is the most suitable technology for TCS treatment, although the most limiting factor is the high costs of the operating conditions resulting from CAG regeneration or replacement requirements.

AOP processes are another technology that can facilitate high removal efficiencies for TCS removal but the operating costs are also high due to the use

of oxidants or oxidant formation in-situ. Furthermore, AOPs have another important limiting factor which is the generation of non-desirable sub-products due to the potential for high oxidation.

Finally, MBR technology is the most promising technology as it is a hybrid system. This technology combines a conventional activated sludge process together with a solid-liquid separation process through ultrafiltration or a microfiltration membrane. It is true that the smaller the pore size distribution of the membrane, the more efficient TCS removal is, but MBR usually requires MF or UF membranes. This technology also has high operating conditions for minimizing membrane fouling.

7.1.2. PPCP removal by MBR technology

In this chapter the MBR technology has been evaluated for its suitability. In this study MBR has demonstrated high removal efficiency of PPCP but the most limiting factor was the high fouling phenomena which resulted in a high TMP episode that provoked several chemical cleanings. One of the fouling causes identified during this study was attributed to the activated sludge degradation in terms of filterability. Consequently, the accumulation and the adsorption of TCS into the biomass directly affected the performance of the MBR. Furthermore, high TCS concentration inhibited nitrification and thus reduced the capacity to remove the nitrogen from the wastewater.

7.1.3. Evaluation of cork as a natural adsorbent

Granular cork has shown a good adsorption capacity for some PPCPs in water solutions. Cork was high efficient in removing TCS, DCF and NAP. Furthermore, it demonstrated a high capacity for TCS.

While cork costs are undoubtedly much lower than other AC adsorbents, studies on other complementary technologies are required to ensure a good combined system to treat PPCPs in wastewater.

7.2. A step-forward to a combined system for PPCP treatment with a focus on Triclosan

In this section a combination of different technology processes has been proposed to, on the one hand, address technology limitations, costs and other drawbacks and, on the other hand, to increase the removal efficiencies. Along these lines, AOP processes have been discarded due to their very high operating costs and potential for non-desirable products to be produced.

As has been demonstrated, adsorbents (i.e. AC or cork) are very promising treatments for TCS adsorption because TCS is hydrophobic and has a high pKa value (>7). However, AC materials have high operating costs that result from the regeneration and replacement requirements.

A system that combines the most suitable technologies that were evaluated in this thesis could improve the whole wastewater treatment process by not only reducing the amount of PPCPs, but also by lowering operating costs.

MBR technology is a highly efficient technology for biodegrading organic matter, and eliminating nutrients such as N and P. By incorporating a membrane separation process, effluent quality is improved and complete retention of solids and particulates ensured. It can also help with the biodegradation of some slow-rate emerging contaminants. The capability of increasing SRT and the concentration solids in the MBR without affecting the whole process, would improve PPCP biodegradation and consequently the removal efficiency of PPCPs.

The combination of the AC process together with the MBR technology can overcome two different limiting factors. In terms of AC, the high costs of replacement or re-generation could be mitigated by biomass which has a high capability for bio-adsorption and bio-degradation. Furthermore, the adsorbents (i.e. CAG/PAC or cork) could act as a mitigation agent for fouling because of their capacity to scour the membrane surface. However, AC adsorbents could

reduce its life-time due to the presence of biomass. To overcome this, two different proposals for adsorption-MBR treatment are selected for PPCP treatment and detailed in Figure 7. 1 and Figure 7. 2
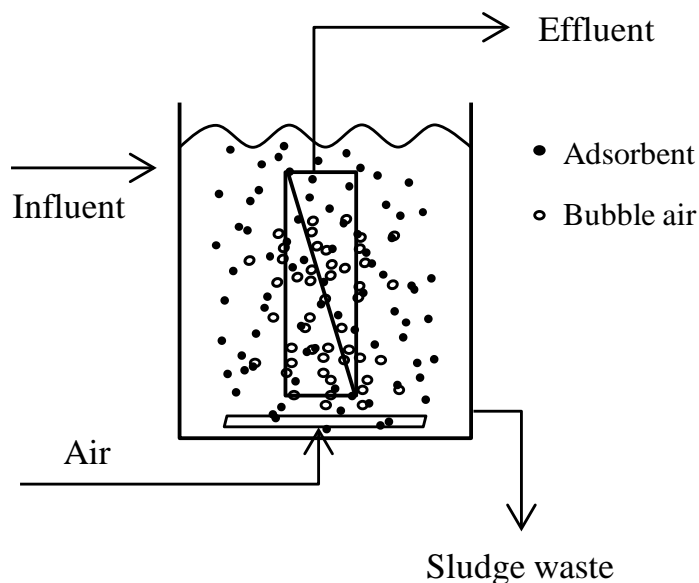
Figure 7. 1. Hybrid combined system (PAC/GAC/cork-MBR)

This first hybrid technology proposal would reduce the inhibition potential of some PPCPs due to the adsorption capacity of the adsorbents and biomass. Also, a second advantage is the reduction in fouling thanks to the scouring effect along the membrane's surface. Meanwhile, costs would be lower when compared with all the other advanced treatments for wastewater (i.e. AC and AOPs).
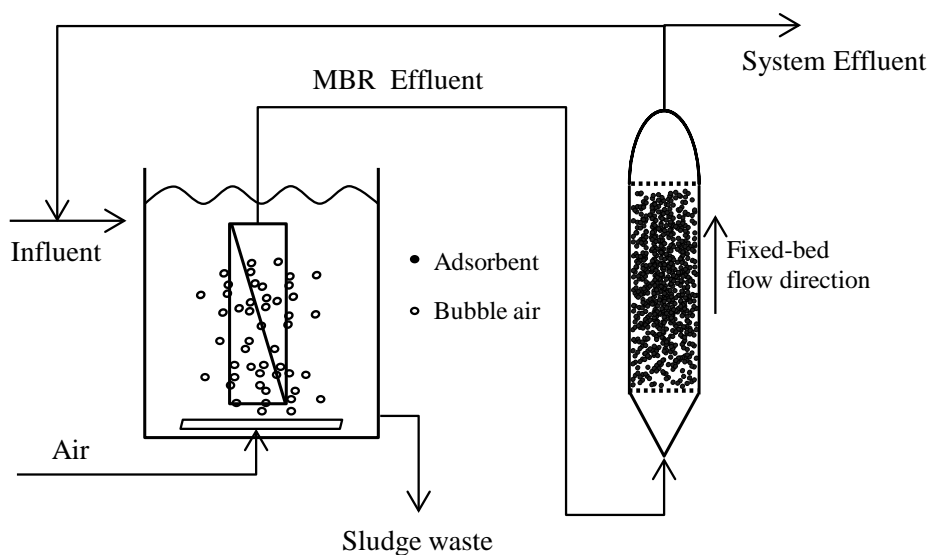
Figure 7. 2. External combined system (MBR–GAC/cork)

This second option would place the adsorption separately from the MBR. This option attempts to lengthen the life-time of the adsorbent minimising its saturation. The inhibitory effect due to the high concentration of PPCP in the MBR could be solved if the fixed-bed effluent is partially returned into the influent in the system, thus diluting influent concentrations Figure 7. 2.

The following Table 7. 1 aims to summarise the two different options proposed in this sections in terms of capital costs, operating costs, removal efficiency of PPCP and nutrients. This Table 7. 1 is based on qualitative criteria between all five configurations involved.

Table 7. 1. Qualitative summary of the technologies proposed in the discussion

Category	Sub-category	Hybrid system			Externally coupled system	
		PAC+MBR	GAC+MBR	Cork+MBR	MBR-GAC	MBR-Cork
CAPEX	Adsorbent	👎👎👎	👎👎👎	👍	👎👎	👍
	Equipment and proves	👎	👎	👎	👎👎	👎👎
	Frame and structure	👎	👎	👎👎	👎	👎👎
Technology	Compactness	👍	👍	👎	👎	👎
OPEX	Adsorbent	👎👎	👎👎	👎	👎👎	👎
	Maintenance	👎	👎	👍	👎	👍
	Operating	👎	👎	👎	👎	👎👎
Efficiency	Nutrients	👍	👍	👍	👍	👍
	PPCP	👍👍	👍👍	👍	👍👍	👍
Limitations		Costs	Costs	Proof of concept	Costs	Proof of concept
Advantages		Fouling reduction		Costs	Less saturation of adsorbent	

8. CONCLUSIONS

8.1. General conclusions

This thesis takes a step towards evaluating advanced treatment technologies for eliminating Pharmaceutical and Personal Care Products (PPCP). The most important conclusions drawn from this work are detailed as follows:

- AC is very promising treatment for TCS adsorption because TCS is hydrophobic. However, several problems must be solved such as high pH levels, the competition of organic matter and the recycling and regeneration of AC.

- The most important advanced oxidation processes are ozonation and photo Fenton which appear to provide an effective technique for enhancing the removal of TCS. The main limitations of those processes are the formation of oxidation by-products and the high operating costs.

- The membrane (nanofiltration / reverse osmosis) and membrane bioreactor sustained high TCS removal but membrane fouling is one of the most limiting factors. MBR has demonstrated high removal efficiency of PPCPs.

- The high concentration of TCS inhibited the nitrification reducing the capability to remove nitrogen from wastewater and caused a deterioration in the sludge characteristics, thus increasing the membrane fouling.

- The alveolar (honeycomb-like) structure of the cork material are made up of thin-walled cells that are closed and hollow, forming shapes of predominantly 4, 5 and 6-sided polygons, without intercellular space.

- Cork removed with high efficiency TCS, DCF and NAP in water solutions. In WWTP effluent, cork showed a higher capacity for TCS compared with the other PPCPs.

- The method developed using a silicone rod was applied successfully, as a first time, to real wastewater effluent that was collected from municipal WWTP in Quart (Girona NE Spain).

- After three hours the adsorption process was almost complete, achieving an effluent concentration of 13.45 µg TCS $\cdot L^{-1}$, 75 µg NAP$\cdot L^{-1}$, 66.68 µg KET$\cdot L^{-1}$, 80.38 µg DCF$\cdot L^{-1}$, 211.04 µg MPB$\cdot L^{-1}$ and 242.62 µg CBZ$\cdot L^{-1}$.

As a general conclusion:

A hybrid system coupling MBR technology with cork adsorbent could be a suitable treatment technology for PPCP removal. It would reduce not only fouling but the operating costs as well and PPCP concentration would be substantially reduced.

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Chapter 9. References