TESE DE DOUTORAMENTO

A COMPARISON OF NOVEL AND CONVENTIONAL SEWAGE TREATMENT PLANTS IN TERMS OF ENERGY REQUIREMENTS, OPERATIONAL COSTS AND ORGANIC MICROPOLLUTANTS REMOVAL

Antón Taboada Santos

ESCOLA DE DOUTORAMENTO INTERNACIONAL

PROGRAMA DE DOUTORAMENTO EN
ENXEÑARÍA QUÍMICA E AMBIENTAL

SANTIAGO DE COMPOSTELA

2019

DECLARACIÓN DO AUTOR DA TESE

A COMPARISON OF NOVEL AND CONVENTIONAL SEWAGE TREATMENT PLANTS IN TERMS OF ENERGY REQUIREMENTS, OPERATIONAL COSTS AND ORGANIC MICROPOLLUTANTS REMOVAL

D. Antón Taboada Santos

Presento a miña tese, seguindo o procedemento axeitado ao Regulamento, e declaro que:

1) A tese abarca os resultados da elaboración do meu traballo.

2) De selo caso, na tese faise referencia ás colaboracións que tivo este traballo.

3) A tese é a versión definitiva presentada para a súa defensa e coincide coa versión enviada en formato electrónico.

4) Confirmo que a tese non incorre en ningún tipo de plaxio doutros autores nin de traballos presentados por min para a obtención doutros títulos.

Santiago de Compostela, a 27 de setembro de 2019

Asdo. Antón Taboada Santos

AUTORIZACIÓN DOS DIRECTORES DA TESE

A COMPARISON OF NOVEL AND CONVENTIONAL SEWAGE TREATMENT PLANTS IN TERMS OF ENERGY REQUIREMENTS, OPERATIONAL COSTS AND ORGANIC MICROPOLLUTANTS REMOVAL

Dna. Marta Carballa Arcos, Profesora Contratada Doutora e D. Juan M. Lema Rodicio, Profesor Emérito de Enxeñaría Química

INFORMAN

Que a presente tese, correspóndese co traballo realizado por D. **Antón Taboada Santos**, baixo a nosa dirección, e autorizamos a súa presentación, considerando que reúne os requisitos esixidos no Regulamento de Estudos de Doutoramento da USC, e que como directores desta non incorre nas causas de abstención establecidas na Lei 40/2015.

Santiago de Compostela, a 27 de setembro de 2019

Asdo. Marta Carballa Arcos   Asdo. Juan M. Lema Rodicio
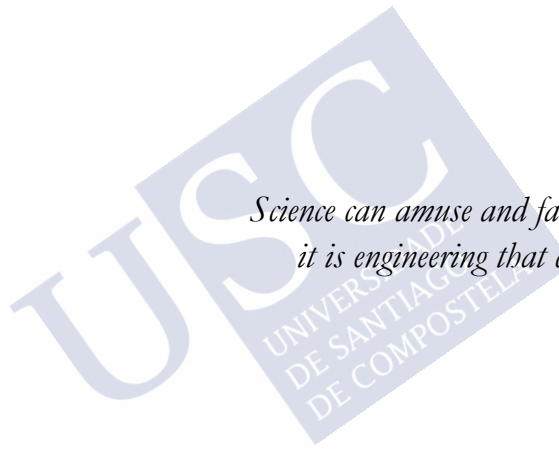
Science can amuse and fascinate us all, but it is engineering that changes the world.

Isaac Asimov

Abstract

Conventional sewage treatment plants (STPs) are expected to be replaced by a new generation which is aimed to be more energetically efficient. These novel STPs consist on a first stage for maximum organic matter capture followed by a partial nitritation-anammox unit. The organic matter recovered as sludge is further transformed into biogas during anaerobic digestion, whose production is enhanced by applying a sludge pretreatment technology such as thermal hydrolysis. However, the different technologies included in novel configurations have not been sufficiently tested, and moreover, they have not been integrated to holistically determine the energy requirements, the operational costs and the fate of organic micropollutants (OMPs).

Therefore, the goal of this Thesis is to evaluate the energy requirements, the operational costs and the OMPs removal in different novel STP configurations based on rotating belt filters, chemically enhanced primary treatment and high-rate activated sludge or combinations for organic matter recovery and to compare the results with those of a conventional STP configuration.

This thesis demonstrates that the different novel STP configurations evaluated significantly decrease the energy requirements in comparison with conventional STPs due to two reasons, the lower aeration demand and the higher self-produced electricity obtained from biogas combustion. Thermal hydrolysis before anaerobic digestion also contributes to decrease the STP energy demand, although a higher degree of thickening is required than in conventional configurations. Yet, the energy self-sufficiency is not reached in any of the studied configurations.

This thesis also highlights that the energetic analysis must be accompanied by an economical evaluation since lower energy requirements do not necessarily mean a reduction of the operational costs. For example, novel STPs based on chemically enhanced primary treatment for organic matter recovery lead to the lowest energy demand but to the highest operational costs, even higher than those of a conventional configuration. In contrast, the alternative based on high-rate activated sludge reaches very comparable energy demand and also considerably lower operational costs than the other evaluated configurations.

In terms of OMPs, all the studied novel STP configurations reach similar removal efficiencies from wastewater for most them, indicating that the technology used for organic matter recovery does not affect OMPs elimination in the water line. However, it strongly affects the presence of hydrophobic OMPs in the sludge line, and subsequently, in digested sludge. Among the studied alternatives, the

novel STP configurations based on the high-rate activated sludge reactor achieve the lowest presence of OMPs in digested sludge.

In conclusion, the STP configurations based on high-rate activated sludge for organic matter recovery become the preferable option from a holistic point of view because, although it presents similar OMPs removal efficiency from wastewater and slightly a higher energy demand than the other novel configurations, it achieves the lowest operational costs and presence of OMPs in digested sludge.

Keywords: anaerobic digestion, chemically enhanced primary treatment, high-rate activated sludge, organic micropollutants, rotating belt filters, thermal hydrolysis.

LIST OF CONTENTS

ABBREVIATIONS AND ACRONYMS

AB: anaerobic biodegradability

AD: anaerobic digestion

ADBI: celestolide

AHTN: tonalide

BMP: biochemical methane potential

CAS: conventional activated sludge

CEPT: chemically enhanced primary treatment

CES: chemically enhanced settling

COD: chemical oxygen demands

CPT: conventional primary treatment

CTL: citalopram

DCF: diclofenac

DO: dissolved oxygen

DZP: diazepam

E1: estrone

E2: 7β-estradiol

EE2: 17α-ethinylestradiol

ERY: erythromycin

FLX: fluoxetine

HHCB: galaxolide

HRAS: high-rate activated sludge

HRT: hydraulic retention time

IBP: ibuprofen

IC: inorganic carbon

k_{biol}: kinetic constant

K_D: partition coefficient

LOQ: limits of quantification

NPX: naproxen

OLR: organic loading rate

OMPs: organic micropollutants

PN-AMX: partial nitritation-anammox

RBF: rotating belt filter

ROX: roxithromycin

SMX: sulfamethoxazole

SPE: solid phase extraction

SRT: sludge retention time

STPs: sewage treatment plants

TCS: triclosan

TH: thermal hydrolysis

TKN: total Kjeldahl nitrogen

TMP: trimethoprim

TAN: total ammonium nitrogen

TS: total solids

TSS: total suspended solids

VFA: volatile fatty acids

VS: volatile solids

VSS: volatile suspended solids

RESUMEN

Capítulo 1. Introducción y objetivos

Las estaciones depuradoras de aguas residuales (EDARs) han sido utilizadas de manera satisfactoria durante las últimas décadas para eliminar contaminantes presentes en el agua residual tales como materia orgánica, sólidos suspendidos y nutrientes, evitando que importantes cantidades de estos contaminantes fueran vertidos a aguas superficiales.

Estas depuradoras han estado basadas tradicionalmente en los reactores de nitrificación-desnitrificación. Sin embargo, este proceso presenta una alta demanda energética principalmente debida a la aireación necesaria para oxidar el amonio (NH_4^+) a nitrito y posteriormente a nitrato, la cual representa entre el 45 y el 75% del consumo energético de la EDAR. El nitrato producido en este proceso es eliminado mediante su conversión a nitrógeno gas, proceso en el que parte de la materia orgánica, medida como demanda química de oxígeno (DQO) presente en el agua residual se pierde en forma de dióxido de carbono. El resultado de esto es que las EDARs presentan habitualmente una alta demanda energética en el rango 0,3-0,6 kWh/m³ de agua tratada.

Sin embargo, la implantación del proceso nitritación parcial-anammox para la eliminación autótrofa del NH_4^+ permite reducir hasta en un 60% las necesidades de aireación de las EDAR, ya que solo el 50% del NH_4^+ debe ser oxidado a nitrito, y además se evita la oxidación hasta nitrato. Al tratarse de un proceso autótrofo la materia orgánica ya no es necesaria para la desnitrificación y puede ser capturada en forma de fango para aumentar la producción de biogás mediante la digestión anaerobia (DA) del mismo. Aunque numerosos procesos basados en tecnología anammox ya son ampliamente utilizados para tratar los sobrenadantes de la DA, su implementación en la línea de aguas supone todavía un desafío debido a la menor temperatura y concentración de NH_4^+, y debe asegurarse una buena eliminación de materia orgánica antes de esta etapa ya que de lo contrario puede causar la inhibición del proceso.

La primera etapa de estas EDARs innovadoras consiste en la recuperación y concentración de DQO del agua residual, seguida de un reactor nitritación parcial-anammox. Esta DQO puede recuperarse mediante procesos físicos, tales como los filtros de banda rotatoria; químicos, por medio de un tratamiento primario mejorado químicamente; o biológicos, tales como reactores de lodos activos de alta carga. Independientemente de la tecnología utilizada para la recuperación de DQO, los lodos producidos son tratados para la obtención de biogás en procesos de DA. Además, en los últimos años se han desarrollado diversas tecnologías para el pretratamiento de los fangos previo a la DA. Entre ellos, los procesos de hidrólisis térmica son los más atractivos dado su potencial para ser integrados energéticamente en las EDAR, dado que no solo aumentan

el rendimiento de biogás sino que también permiten la recuperación de calor del motor de biogás. Además, la HT aumentar la deshidratación de los fangos, reduce las emisiones de olores y elimina patógenos, obteniendo un fango esterilizado de alta calidad, el cual puede ser utilizado en agricultura sin una posterior etapa de higienización, reduciendo notablemente los costes de operación de las EDARs.

Por otra parte, el consumo de compuestos orgánicos tales como productos de cuidado personal, fármacos, pesticidas, hormonas o compuestos químicos industriales ha aumentado drásticamente en las últimas décadas. Consecuentemente, estos compuestos están presentes en las aguas residuales pero también en los suelos agrícolas dada la utilización de los fangos de EDAR como fertilizantes. Aunque estos compuestos están presentes en concentraciones muy bajas, muchos son recalcitrantes y tienden a bioacumularse, por lo que sus efectos para el medio ambiente y la salud humana pueden ser nocivos. Estos compuestos son conocidos como microcontaminantes orgánicos (MCOs), y su eliminación del agua residual está considerado como un gran objetivo. La eliminación de estos MCOs en EDARs convencionales ha sido ampliamente estudiada en las últimas dos décadas, sin embargo, hasta el momento la eliminación de MCOs en EDARs innovadoras es un tema que permanece prácticamente inexplorado en la bibliografía. Además, parte de los MCOs presentan un alto comportamiento hidrofóbico (alta afinidad por absorberse en el fango) y son eliminados durante la DA, lo cual es especialmente importante en países tales como Portugal, Irlanda, Reino Unido, España o Dinamarca en los cuales el fango es utilizado como fertilizante en agricultura. A pesar de que no existe una legislación a nivel europeo para limitar la presencia de estos compuestos ni en los efluentes de EDAR ni en los fangos, algunos países ya han adoptado medidas de carácter nacional mitigar su presencia.

Así, el objetivo de esta tesis es comparar las EDAR innovadoras con las convencionales desde un punto de vista de la demanda energética, los costes de operación y la eliminación de MCOs. Para alcanzar este amplio objetivo, se establecieron los siguientes objetivos específicos que al mismo tiempo sirven para estructurar la tesis:

- Evaluar técnica, energética y económicamente el potencial de los filtros de banda rotatoria para la recuperación de materia orgánica del agua residual mediante su combinación con un tratamiento químico, determinando la eliminación de MCOs en el proceso (Capítulo 2).

- Comparar la demanda energética, los costes de operación y la eliminación de MCOs entre un sistema de precipitación química y otro

de lodos activos de alta carga para determinar la mejor alternativa desde un punto de vista holístico (Capítulo 3).

- Analizar el efecto de los procesos de hidrólisis térmica y digestión anaerobia en la eliminación de MCOs (Capítulo 4).

- Determinar cómo afecta al balance energético y económico de EDARs innovadoras y convencionales. la instalación de una planta de hidrólisis térmica (Capítulo 5).

- Evaluar la eliminación de MCOs en EDARs innovadoras realizando una comparación con una EDAR convencional (Capítulo 6).

Capítulo 2. Oportunidades de los filtros de banda rotatoria en EDARs innovadoras.

En este capítulo se examinaron los filtros de banda rotatoria en diferentes configuraciones para identificar sus oportunidades en las EDAR innovadoras. Estos filtros son operados habitualmente con un tamaño de malla de 350 μm, permitiendo la recuperación de aproximadamente entre el 22 y el 37% de la DQO del influente. y la eliminación de entre el 34-56% de los MCOs hidrofóbicos tales como triclosán, galaxolide, tonalide y celestolide, mientras que los MCOs hidrofílicos, incluyendo antiinflamatorios, neurodrogas u hormonas no fueron eliminados en porcentajes significativos. Sin embargo, dada la baja recuperación de DQO alcanzada con estos filtros, los efluentes de estas unidades, con ratios DQO- NH_4^+ muy superior a 2, no son adecuados para ser tratados en un reactor nitritación parcial-anammox debido al crecimiento de biomasa desnitrificante heterótrofa, que compite con la biomasa AMX por el nitrito.

El tratamiento primario mejorado químicamente permitió superar estas limitaciones, y generar un efluente con un ratio DQO/NH_4^+ apropiado para una unidad nitritación parcial-anammox, alcanzando un aumentando la eficiencia de eliminación de MCOs hidrofóbicos hasta 73-94%, nuevamente sin eliminaciones significativas de MCOs hidrofílicos. Sin embargo, para ello se requirió una alta dosis de 300 mg / L de cloruro férrico que provocó un consumo de alcalinidad de 66 g de carbon inorgánico (CI) por m³ de agua residual, lo cual podría inhibir también el proceso nitritación parcial-anammox ya que éste demanda un ratio mínimo de1-1,25 g IC por g NH_4^+ para prevenir la acidificación del sistema.

La combinación de filtros de banda rotatoria y el tratamiento primario mejorado químicamente permitió nuevamente generar efluentes apropiados para ser tratados en unidades PN-AMX, pero disminuyendo notablemente el consumo de alcalinidad hasta 22 g IC por m³ de agua residual y la dosis de cloruro de férrico

hasta 100 mg/L, obteniendo eliminaciones de MCOs y DQO comparables al tratamiento con 300 mg/L de cloruro férrico. El rendimiento de metano de la combinación de ambos lodos fue 184 L (N) CH_4/ kg DOQ en el agua residual, el cual resultó un 75% mayor que el obtenido en el tratamiento convencional de aguas residuales (105 L (N) CH_4 / kg DQO en el agua residual). La demanda eléctrica del tratamiento disminuyó desde 0,54 hasta 0,41 kWh / m^3 de agua residual.

Tras considerar el potencial de recuperación de metano de los lodos generados, los cálculos energéticos mostraron que una EDAR que incorpore este tratamiento combinado podría alcanzar la autosuficiencia energética, disminuyendo drásticamente la demanda de eléctrica que presentan las EDAR convencionales. Además, la configuración propuesta alcanzó unos costes de operación que resultaron un 26% menor que en el tratamiento convencional (4,3 frente a 5,7 c € / m^3 de aguas residuales), siempre y cuando se asegure en el efluente del tratamiento combinado una relación mínima de alcalinidad a amonio de 1-1.25 g IC por g NH_4^+.

Capítulo 3. Comparación entre los tratamientos primarios mejorado químicamente y los reactores de lodos activos de alta carga en EDARs innovadoras

El objetivo de este capítulo es comparar dos alternativas diferentes tales como el tratamiento primario mejorado químicamente y los lodos activos de alta carga en términos de demanda energética, costes de operación y eficiencia de eliminación de MCOs y virus en esquemas de EDARs innovadores.

Para este propósito se operó una planta piloto para el tratamiento primario mejorado químicamente con un tiempo de retención hidráulica de 30 minutos y un reactor continuo de tanque agitado de lodos activos de alta carga a escala de laboratorio, con un tiempo de retención hidráulica de 2 horas y un tiempo de retención de sólidos de 1 día. Se determinó una dosis mínima de 150 mg / L de cloruro férrico para conseguir disminuir el ratio g DQO / g NH_4 por debajo de 2, (requisito para un reactor de nitritación parcial-anammox). Bajo estas condiciones se alcanzó una recuperación de DQO del 84% y una eliminación de fosfato superior al 99%. En el reactor de lodos activos de alta carga se obtuvo una eliminación comparable de DQO, generando también efluentes aptos para ser tratados en la unidad de nitritación parcia-anammox. Sin embargo, la oxidación parcial de la misma provocó que su recuperación fuese sensiblemente inferior, de un 70%. En este sistema biológico la eliminación de fosfato fue muy inferior (13%) a la alcanzada en la alternativa química, pero mediante la adición de 30 mg/L de cloruro férrico se aumentó hasta un valor superior al 99%. Ambos fangos presentaron una biodegradabilidad anaerobia similar de

aproximadamente 50%. Así, la alternativa basada en el tratamiento primario mejorado químicamente se identificó como la más favorable energéticamente, presentando una demanda de 0.07 kWh / m³ de agua residual, frente a los 0.13 kWh / m³ de agua residual de la opción biológica. Sin embargo, los costes operacionales de la alternativa química resultaron notablemente más elevados que los correspondientes a la alternativa biológica (6,0 frente 3,8 c€ / m³ de agua residual).

Con respecto a los MCOs, para aquellos que presentan k_{biol}> 10 L / g_{VSS} d en el reactor de lodos activos de alta carga tales como estrona, estradiol, ibuprofeno, galaxolide, tonalide, celestolide y triclosán se lograron eficiencias de eliminación considerablemente más altas en la alternativa biológica (80-90%) que en el tratamiento primario mejorado químicamente (4-55%). Para MCOs tales como naproxeno, roxitromicina, diazepam o etinilestradiol la eliminación fue más alta en el sistema biológico que en el químico, pero en ambas por debajo del 55%, mientras que otros como sulfametoxazol, eritromicina, citalopram, diclofenaco y carbamazepina alcanzaron una eliminación inferior al 25% en ambas tecnologías.

Finalmente, el tratamiento primario mejorado químicamente también fue menos eficiente que el reactor de lodos activos de alta carga para la eliminación de los virus estudiados (norovirus y sapovirus, ya que el virus de la hepatitis A no fue detectado) . La evaluación holística de los resultados permite concluir que el reactor de lodos activos de alta carga seguido de la precipitación de fosfato en el clarificador es una mejor alternativa que el tratamiento primario mejorado químicamente para la recuperación de DQO en EDARs innovadoras.

Capítulo 4. Comportamiento de los MCOs en la hidrólisis térmica y digestión anaerobia

En los últimos años se han desarrollado diversas tecnologías para el pretratamiento de fangos antes de la DA con el objetivo de aumentar la productividad de biogás y reducir la presencia de patógenos en el lodo digerido, entre las que destaca la HT.

 El lodo es el punto final de muchos MCOs en las EDARs, lo cual implica importantes riesgos tanto ambientales como de salud humana ya que este lodo es habitualmente utilizado como fertilizante en la agricultura. El objetivo de este capítulo es determinar el comportamiento de los MCOs en la TH y posterior DA estudiando al mismo tiempo las diferencias en las poblaciones microbianas.

Los fangos de EDAR se pretrataron en una planta piloto de HT a 170ºC durante 20 minutos, en la cual se consiguió multiplicar por 3 la concentración de materia orgánica soluble en el fango. Posteriormente, se operaron dos digestores anaerobios con un volumen útil de 14 L en condiciones mesófilas, uno de ellos

tratando fango fresco y el otro fango pretratado a la misma velocidad de carga orgánica de 1,5-2 g DQO/L·d. La HT demostró ser una tecnología eficaz para eliminar entre un 30 y un 100%, dependiendo del MCO, tanto la fracción soluble de estos como la fracción absorbida en los sólidos que sí son solubilizados durante el proceso. Sin embargo, la concentración de MCOs en los sólidos que no se consiguieron solubilizar tras la HT no se vio significativamente afectada Así, se encontró que la eficiencia de eliminación de MCOs en el proceso de HT está ligada al porcentaje de solubilización de materia suspendida obtenida en el mismo.

Posteriormente, se determinó la eficiencia de biotransformación de MCOs durante la DA tanto de lodos frescos como pretratados. Se observó que la riqueza de la comunidad microbiana no se vio afectada por la HT, sin embargo, se encontró que el tipo de comunidades evolucionaron de manera diferente en ambos reactores, influenciadas por las diferentes propiedades físico-químicas del fango alimentado, pero debido a la alta redundancia funcional ambos reactores operaron de manera similar.

Así, la biotransformación anaerobia no fue significativamente diferente para la mayoría de los MCOs analizados, con excepción de las fragancias galaxolide y tonalide, que se eliminan substancialmente peor en reactores tratando lodos pretratados térmicamente. Por lo tanto, se demostró que la TH es efectiva para alcanzar una eliminación parcial de MCOs del fango, pero no para mejorar su biodisponibilidad y posterior biotransformación anaerobia.

Capítulo 5. Integración de la hidrólisis térmica en EDARs innovativas y convencionales

En las EDARs convencionales, la biodegradabilidad anaerobia de lodos se puede mejorar significativamente mediante la HT de los fangos antes de su DA. Sin embargo, en las EDARs innovadoras se espera que el impacto de la HT sobre el aumento de la producción de metano sea inferior, ya que los lodos producidos en las diferentes tecnologías de recuperación de materia orgánica son de por sí notablemente más biodegradables en condiciones anaerobias que los producidos en EDARs convencionales.

Así, en este capítulo se realizó una evaluación energética y económica de la aplicación de la HT en los esquemas innovadores de EDARs. Mientras que en las EDARs convencionales los procesos de HT compensan energéticamente cuando los fangos son espesados por encima del 5% en materia seca antes de ser pretratados, en las EDARs innovadoras esta concentración umbral aumenta hasta el 7-9%. Sin embargo, la concentración mínima de sólidos en el fango para conseguir reducir los costes de operación de las EDARs innovadoras resultó ser

de entre un 1 y un 2%. Esto se debe al hecho de que el principal impacto de la HT se atribuye a la eliminación de los costes de gestión de lodo, los cuales para una EDAR de un tamaño de 500,000 habitantes equivalentes ascienden a 300,000-430,000 € anuales, mientras que el al ahorro energético que se puede obtener resulta inferior a 60,000 € anuales incluso considerando un escenario optimizado en el cual la concentración de materia seca en el fango antes de la HT sea del 20% de materia seca.

Entre los distintos esquemas innovadores evaluados, la EDAR basada en el tratamiento químico mejorado químicamente es la que alcanza el menor consumo energético, que puede llegar a ser de 0,05 kWh/m³ de agua residual si el fango es concentrado hasta un 20% de materia seca. Así, se comprobó que la autosuficiencia energética de la EDAR resulta difícilmente alcanzable. Sin embargo, la EDAR innovadora basada en un reactor de lodos activos de alta carga + precipitación de fosfato es la alternativa de depuración que conduce a los menores costes operacionales, que resultan inferiores a 1.4 c€/m³ de agua residual si el fango se espesa por encima del 10% de materia seca.

Por último, se determinó que existe una gran economía de escala en lo referente a las plantas de HT, por lo que el tiempo de recuperación de la inversión es muy dependiente del tamaño de la EDAR. Así, el tiempo de retorno varía entre 12 y 24 años para una EDAR de 100,000 habitantes equivalentes, entre 5 y 10 años para una de 250,000 habitantes equivalentes y entre 2 y 6 años para EDARs a partir de medio millón de habitantes equivalentes.

Capítulo 6. Comportamiento de MCOs en EDARs innovadoras y convencionales

A pesar de que en las últimas décadas se han llevado a cabo numerosos trabajos de investigación para determinar la presencia de MCOs en aguas residuales y su comportamiento en EDARs convencionales, hay muy poca información disponible acerca del comportamiento de los mismos en EDARs innovadoras, y además, las distintas unidades con potencial para conformarlas las son habitualmente estudiadas por separado. Así, el objetivo de este trabajo es evaluar el comportamiento de los MCOs en tres configuraciones innovativas de EDAR, y compararlo con el obtenido en una EDAR convencional mediante un modelo empírico mecanístico que integra múltiples unidades.

Los resultados de la simulación indican que las tres configuraciones innovadoras de EDAR estudiadas, basadas en tratamiento primario mejorado químicamente, reactor de lodos activos de alta carga y una combinación de filtro de banda rotatoria y reactor de lodos activos de alta carga para la recuperación de materia orgánica, conducen a eficiencias de eliminación de MCOs del agua residual

similares. La comparativa con el escenario convencional muestra que compuestos como estrona, estradiol, ibuprofeno, triclosán, galaxolide, tonalide o celestolide son bien eliminados tanto en EDARs innovadoras como convencionales. Asimismo, compuestos que muestran un comportamiento recalcitrante en EDARs convencionales como trimetoprima, diazepam, carbamazepina o diclofenaco tampoco son eliminados en EDARs innovadoras. Por el contrario, se encontró que algunos MCOs entre los cuales se incluyen etinilestradiol, fluoxetina, roxitromicina, sulfametoxazol o eritromicina son substancialmente mejor eliminados en EDARs convencionales que en innovadoras, mostrando que es necesario incluir etapas de postratamiento en estas EDARs para alcanzar eliminaciones comparables a las de la configuración convencional.

Sin embargo, se observaron importantes diferencias en la presencia de compuestos hidrofóbicos en la línea de fangos entre las tres EDARs innovadoras analizadas. La alternativa basada en el tratamiento primario mejorado químicamente alcanzó la mayor presencia de MCOs en la línea de fangos y consecuentemente en el fango digerido. Contrariamente, la configuración basada en el reactor de lodos activos de alta carga se obtuvo la menor presencia de MCOs en la línea de fangos, alcanzando en el fango digeridos resultados muy similares a los de la EDAR convencional.

Por lo tanto, en este capítulo se identificó que en los esquemas innovadores de EDAR se logran peores eficiencias de eliminación de MCOs que en las convencionales. Entre las tres alternativas evaluadas se concluyó que la basada en el reactor de lodos activos de alta carga es la opción preferible, ya que logra eficiencias de eliminación de MCOs del agua residual comparables a las obtenidas en otras alternativas innovadoras pero alcanza la menor carga de MCOs en el lodo digerido.

Capítulo 7: Discusión general y conclusiones

En este capítulo se integran los principales resultados de la tesis y son discutidos juntamente con algunos de los estudios más relevantes publicados en este campo científico.

En resumen, se demostró que, de las tres tecnologías evaluadas para la recuperación de materia orgánica del agua residual, los filtros de banda rotatoria resultan claramente insuficientes para una posterior etapa de eliminación autótrofa de nitrógeno y para maximizar la recuperación de DQO, que fue tan solo de 22-37%. Por el contrario, los reactores de lodos activos de alta carga son una tecnología atractiva ya que permitieron alcanzar el valor umbral de 2 g DQO por g NH_4^+ en el influente de la unidad de nitritación parcial-anammox, aunque se produjo una oxidación parcial de alrededor de un 10% de la DQO del

influente, reduciendo su recuperación. Además, en esta tecnología se alcanza una eliminación parcial del amonio, atribuida a la alta velocidad de crecimiento de la biomasa. Desafortunadamente, la eliminación de fosfato en estas unidades resulta muy inferior a la exigida en EDARs, por lo que debe ser eliminado a través de procesos de precipitación química. Por último, los tratamientos químicos mejorados químicamente también resultan técnicamente viables para alcanzar el valor de 2 g DQO por g NH_4^+ y a su vez maximizar la recuperación de materia orgánica, aunque la dosis de coagulante necesaria resultó ser muy dependiente de las características físico-químicas del agua residual, especialmente del ratio entre la DQO soluble y la particulada. Una ventaja adicional de estos procesos es que permiten alcanzar una eliminación muy alta de fosfato., aunque el consumo de alcalinidad que implica la adición de sales metálicas podría suponer la inhibición de la unidad de nitritación parcial-anammox.

Las diferentes configuraciones innovativas de EDAR analizadas en esta Tesis permiten un considerable ahorro energético respecto a la EDAR convencional debido a dos motivos; primero por la menor demanda energética para llevar a cabo el proceso y segundo por el aumento de la autoproducción de electricidad obtenida de la combustión del biogás. Además, la instalación de una unidad de HT antes de la DA de fangos permite obtener una reducción adicional de la demanda eléctrica de las EDAR innovadoras siempre y cuando estas plantas sean operadas en condiciones óptimas, aunque esta reducción resulta inferior a la obtenida en EDARs convencionales.

Como se discute a lo largo de la tesis, todas las configuraciones innovadoras presentan menor demanda energética que las convencionales, aunque, la autosuficiencia energética no es alcanzable en ninguno de los escenarios evaluados. Sin embargo, esto no implica necesariamente que se vaya a obtener una reducción en los costes de operación, ya que se demostró que los procesos basados en la adición de productos químicos conducen a costes operacionales significativamente más altos que los basados en reactores de lodos activos de alta carga y que pueden resultar incluso más altos que los atribuidos a las EDARs convencionales. Aunque los filtros de banda rotatorios son una alternativa muy interesante para disminuir en gran medida la dosis de coagulante necesaria, esta configuración todavía alcanza mayores costes operacionales que la alternativa basada en el reactor biológico. Por lo tanto, se ha demostrado que la evaluación energética en EDARs debe ir siempre acompañada de un análisis económico. En este análisis, se identificó la HT como una tecnología crucial para reducir la demanda energética de las EDARs innovadoras, pero sobre todo para disminuir los costes operacionales mediante la obtención de un lodo de alta calidad que puede usarse para fines agrícolas evitando los altos costes de gestión de este.

Por último, en términos de MCOs, el análisis comparativo realizado entre EDARs innovadoras y convencionales indica que en las configuraciones novedosas se alcanza una menor eficiencia de eliminación de MCOs del agua residual, aunque la configuración basada en el reactor biológico de alta carga permite obtener un lodo de calidad comparable al de las EDARs convencionales.

La principal conclusión de esta tesis es que, entre las alternativas evaluadas, las EDARs innovadoras basadas en lodos activos de alta carga con precipitación de fosfato y una unidad de nitritación parcial-anammox en la línea de aguas con una planta de HT previo a la DA de fangos es, desde un punto de vista holístico, la mejor alternativa. Sin embargo, una limitación importante de este trabajo es la falta de trabajos experimentales en la literatura relativos al estudio del comportamiento de MCOs en unidades como los reactores de lodos activos de alta carga o en los de nitritación parcial-anammox. Por lo tanto, se debería realizar trabajos experimentales en el futuro que permitan obtener mayor fiabilidad en los datos de velocidad de biotransformación de MCOs para alimentar adecuadamente el modelo desarrollado, alcanzando resultados más robustos. Adicionalmente se deberían determinar los productos de transformación de los MCOs en estas configuraciones novedosas y realizar pruebas de toxicidad que permitan comparar la toxicidad de los efluentes de EDARs convencionales en innovadoras.

CHAPTER 1

GENERAL INTRODUCTION

1.1. WATER SCARCITY AND WATER POLLUTION IN THE WORLD. CURRENT SITUATION AND PERSPECTIVES

International human rights law obliges states to work towards achieving universal access to water and sanitation for all, without any discrimination, while prioritizing those most in need. To ensure water-provisioning services, such as drinking water for all, a set of preconditions are: i) water needs to be available; ii) water needs to be accessible; and iii) *water needs to be sufficiently treated.* However, worldwide, only 2.9 billion people, representing 39% of the global population used safely managed sanitation services in 2015, whereas another 2.1 billion people (29% of the total) had access to basic sanitation services (Figure 1.1). The remaining 2.3 billion, representing one out of every three people, lacked even a basic sanitation service, of which 892 million people (12% of the total) still practiced open defecation (WHO/UNICEF, 2017).
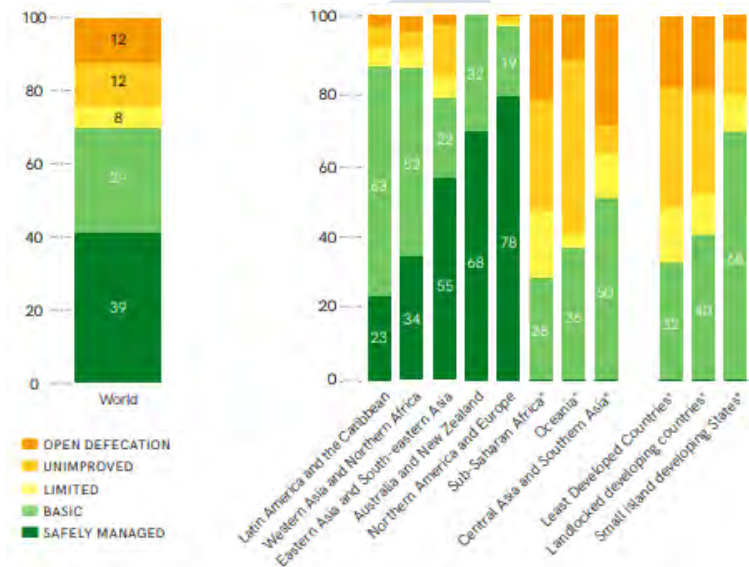
Figure 1.1. Global (left) and regional (right) sanitation coverage in 2015 (WHO/UNICEF, 2017).

In Europe the situation is better than in other regions, and approximately 97% of the people have access to basic or safely managed sanitation services The implementation of the European Directive 91/271/EEC on Urban Waste Water Treatment complemented by the EU's other pollution control and environmental protection instruments, is a major legal tool that has contributed to the progress visualized in Figure 1.2. This Directive addresses the collection, discharge and treatment of urban wastewater with the main goal of protecting

surface waters from the adverse effects of wastewater discharges. This is achieved through the requirement for collection and treatment of wastewater in all settlements with a population equivalent (p.e.) larger than 2,000. The Directive provides for the biological treatment of wastewater (secondary treatment) in agglomerations larger than 10,000 p.e. or even smaller. In catchments with particularly sensitive waters (covering nearly 75% of the territory of the EU), such as those suffering from eutrophication, tertiary wastewater treatment can be required.
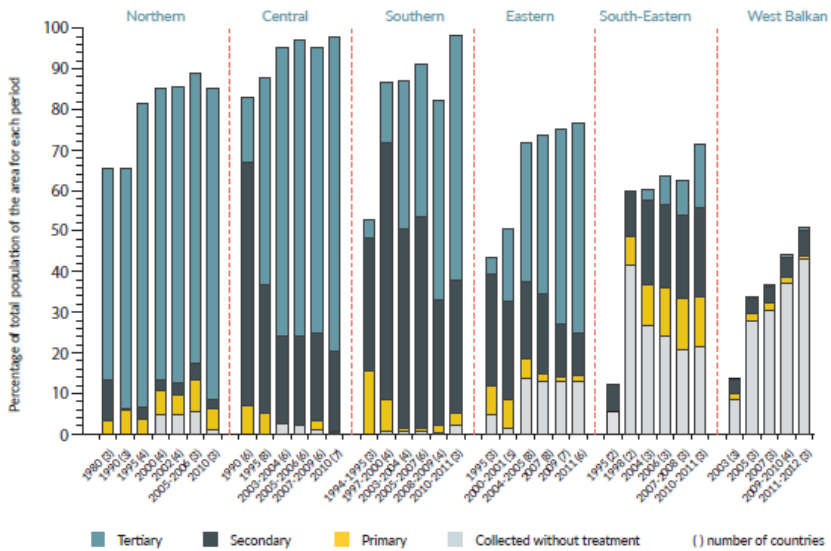
Figure 1.2. Changes in wastewater treatment in different European regions between 1980 and 2012 (WWAP, 2017).

1.2. CONVENTIONAL VS NOVEL SEWAGE TREATMENT PLANTS

To access to safely managed sanitation services, sewage treatment plants (STPs) were successfully used during decades to remove pollutants present in urban wastewater such as organic matter, suspended solids and nutrients (nitrogen and phosphorous), preventing significant amounts of these pollutants from reaching surface waters.

These STPs have been based on the nitrification/denitrification process, in which large aeration is required to oxidise of ammonium (NH_4^+) to nitrate (Figure 1.3), accounting from 45 to 75% of the plant energy expenditure (Gikas, 2017; Rosso et al., 2008). After this, nitrate is removed through a heterotrophic process, in which part of the organic matter (as chemical oxygen demand, COD) contained in wastewater is lost as carbon dioxide (CO_2) (Figure 1.3). The result

of these processes is that conventional STPs become relevant net energy consumers with a typical energy demand in the range of 0.3 to 0.6 kWh/m³ of wastewater (Gikas, 2017; Wan et al., 2016)

Although some studies have suggested that the energy contained in wastewater is nearly 5-fold the energy that is used to drive conventional wastewater treatment (Shizas and Bagley, 2004), the low COD diverted to the sludge line (due to its mineralization during denitrification) to produce methane (CH_4) and the electrical efficiency (approximately 35%) in the co-generation motor (Mills et al., 2014), results in a self-produced electricity rarely exceeding 50% of the STP demand.
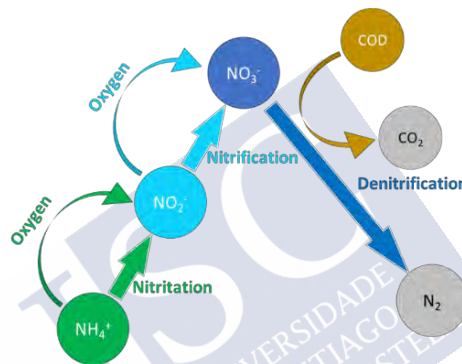
Figure 1.3. Scheme of the nitrification-denitrification process.

The discovery of the anaerobic ammonium oxidation (anammox, AMX) processes for the autotrophic removal of NH_4^+)(Mulder et al., 1995), and the subsequent development of the partial nitration-anammox (PN-AMX) technology (Figure 1.4) allows to reduce up to 60% the aeration requirements of the STP. The reason is that just 50% of the NH_4^+ must be oxidized to nitrite. Moreover, as COD is no longer required for denitrification so the removal of COD and NH_4^+ can be segregated and the former can be recovered as sludge and used to enhance CH_4 production (Gu et al., 2017; Wan et al., 2016). Actually, some researchers consider that STPs can reach the energy autarky or even become net electricity producers (Garrido et al., 2013; Siegrist et al., 2008; van Loosdrecht and Brdjanovic, 2014).

AMX-based technologies are already implemented worldwide with more than 100 installations to treat the supernatants of sludge anaerobic digestion (AD) (Lackner et al., 2014). However, the implementation of this technology in the mainstream of STPs is still t is still challenging and under development due to factors such as strict temperature requirements, the slow growth rates of AMX bacteria or the growth of fast-growing heterotrophic denitrifiers, which compete

with the slow-growing AMX microorganisms for nitrite (Gao et al., 2014; Jin et al., 2012; Xu et al., 2015). Very little work has been done to determine whether a PN-AMX unit can work in the STP mainstream (Tan and Shuai, 2015), since some authors reported a failure of the PN-AMX reactor when COD-to-NH_4^+ ratios higher than 2 were present in wastewater (Jin et al., 2012)
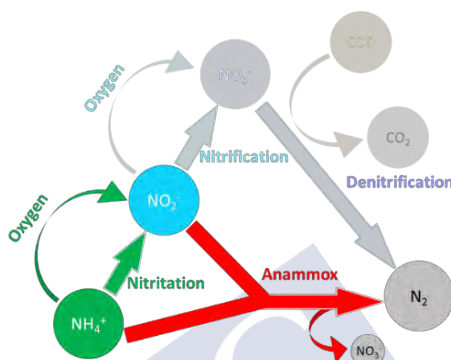
Figure 1.4. Scheme of the partial nitritation-anammox process.

The first stage in novel STPs consists on the COD recovery from the influent, followed by a PN-AMX reactor. The energy contained in wastewater can be recovered either directly in an anaerobic reactor in moderate climates (Aiyuk et al., 2006) or indirectly as sludge in technologies such as rotating belt filters (RBFs)(Ghasimi et al., 2015; Ruiken et al., 2013), chemically enhanced primary treatment (CEPT) or chemically enhanced settling (CES) (Diamantis et al., 2013; Wang et al., 2009) or high-rate activated sludge (HRAS) (Ge et al., 2017; Jimenez et al., 2015).

RBFs for municipal wastewater are commonly employed with a mesh size of 350 µm (Behera et al., 2018; Ruiken et al., 2013) and they become a low footprint solution for recovering COD. They have been successfully applied as a replacement for conventional primary treatment (CPT) in conventional STPs (Franchi and Santoro, 2015; Rusten and Ødegaard, 2006) since they achieve total suspended solids (TSS) removal efficiencies that are similar to those reported for CPT (~50%) (Carballa et al., 2004; Razafimanantsoa et al., 2014). Moreover, they present around 50% lower capital costs than CPT and operational costs can also be greatly reduced (Salsnes, 2016). However, their effluents still retain a high COD content, which is derived not only from soluble COD (COD_{sol}) that remains unaffected in the RBFs but also from particulate COD (COD_{part}) that corresponds to small TSS that pass across the RBFs. Therefore, it is required to implement additional steps to achieve an appropriate effluent quality to be treated in a PN-AMX unit (Rusten et al., 2017).

In CEPT processes, by using some chemical additives (coagulants and/or flocculants), TSS and COD removal can be eliminated up to a maximum of 90% and 70%, respectively (De Feo et al., 2008). They present additional advantages for wastewater treatment such as a small footprint and investment (Aiyuk et al., 2004), an increase in the sedimentation rate that decreases the size of the settling tank, low energy requirements (De Feo et al., 2008), ease to be operated and maintained (Jordao and Volschan, 2004) or the removal of phosphate (PO_4^{3-}) (Metcalf & Eddy, 2003). However, these processes require a considerable amount of chemicals and generate large volumes of sludge, with subsequent costs of reagents and sludge disposal (Ju et al., 2016).

The HRAS process uses high food-to-microorganism ratios and low solid retention times (SRT) and hydraulic retention times (HRT), in order to minimize the COD mineralization and maximize its recovery as sludge. The HRAS process typically uses SRT between 0.5 and 4 days and HRT between 2 and 4 hours (Ge et al., 2017; Jimenez et al., 2015). By taking advantage of the high-rate of bacterial consumption, HRAS can become a relatively affordable method of removing COD_{sol} and COD_{part} constituents from wastewater (Jimenez et al., 2007) with noticeable low energy demand (Ge et al., 2015; Smith et al., 2014). However, it must be thoroughly controlled since the efficiency of the process is greatly dependent on parameters such as dissolved oxygen (DO) concentration or SRT. The HRAS systems can be designed and operated to meet secondary effluent standards in terms of COD and TSS, however, the limited PO_4^{3-} removal efficiency makes necessary a further chemical precipitation in secondary settlers (Longo et al., 2017; Mbamba et al., 2019).

Independently of the technology or combination of technologies applied for COD capture, the recovered COD as sludge is subsequently used to produce biogas by anaerobic digestion (AD). Besides increasing the COD load in the sludge line, in recent years the application of different pretreatment techniques for sewage sludge before AD, such as ultrasounds, high pressure homogenizer, pulse electric fields or thermal hydrolysis (TH), have gained importance in order to enhance biogas yield and reduce the final volume of sludge (Carrère et al., 2010; Zhen et al., 2017). Among them, TH appears as the most attractive due to their potential to be implemented with full energy integration in STP, since they do not only increase biogas yield but also allow the recovery of heat from the biogas engine. Therefore, a better energy integration can be achieved in TH plants (Cambi, Exelys, CTH), leading to more efficient STPs (Cano et al., 2015). Additionally, this technology increases dewaterability, reduces odour emissions and viscosity and removes pathogens, obtaining a sterilized sludge that meets EPA Class A biosolids standards (Barber, 2016; Higgins et al., 2017; Wang et al., 2018). This sludge can then be used in agriculture without a further hygienization

stage, what allows to important economic savings since sludge disposal can represent up to 50% of the STP operational costs (Vázquez-Padín et al., 2011).

Most of the literature dealing with TH focuses on determining the operational conditions for maximum biogas production (Bougrier et al., 2006b; Donoso-Bravo et al., 2011; Sapkaite et al., 2017), although a minor attention has been paid to optimize the energy integration of the TH unit in the STP (Fdz-Polanco et al., 2008; Pérez-Elvira and Fdz-Polanco, 2012), since if the plant is not optimally operated it can lead to a significant increase of the STP electricity demand. Cano et al. (2015) reported that sludge concentration is the key-parameter for energy integration of TH in the STPs. This fact is very relevant since the reported biomethane potential (BMP) for sludges produced in novel STPs (from RBF, CEPT and HRAS) are higher in comparison with conventional ones (Ge et al., 2017; Ju et al., 2016; Paulsrud et al., 2014), and the impact of TH on increasing methane yield is expected to be lower, so the integration strategy of this unit on novel STPs might be significantly different in comparison conventional ones.

1.3. ORGANIC MICROPOLLUTANTS: THE NEW CHALLENGE OF SEWAGE TREATMENT PLANTS

The removal of organic micropollutants (OMPs) from wastewater is considered as a key goal promoting the upgrade of conventional STPs (WWAP, 2017). For many years, the industrial activity was considered the main contributor to introduce toxic compounds in the aquatic environment, with adverse effects on the aquatic organisms. However, the attention is currently paid to a group of polluting substances present in urban wastewater that belong to the category denominated OMPs.

The 2030 Agenda for Sustainable Development was adopted by the Member States of the United Nations in 2015 to address social, economic and environmental aspects of development. One of the 17 goals comprised in the Agenda refers to "Clean water and sanitation" and specifically to "improve water quality by reducing pollution, eliminating dumping and *minimizing release of hazardous chemicals and materials*, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally". Similarly, the European Innovation Partnership on Water (WATER, 2015) has chosen eight priority areas in the water sector within its Strategic Implementation Plan (EIP Water, 2015). Water and wastewater treatment, including recovery of resources is one of these priority areas, and the elimination of emerging pollutants is among its objectives.

1.3.1. Organic micropollutants

OMPs include a wide variety of compounds such as human and veterinary pharmaceuticals, illicit drugs, personal care products, polycyclic aromatic hydrocarbons, industrial chemicals and pesticides. The characteristics and properties of some OMPs of emerging concern which are considered in this Thesis are shown in Table 1.1.

OMPs are released worldwide into the environment through diverse sources (Ternes and Joss, 2006), mainly domestic practices, hospitals, industry and agriculture. The runoff from agriculture and livestock areas is a source of OMPs (i.e., pesticides, steroid hormones and antibiotics) that results very difficult to control. On the contrary, effluents from industries, hospitals and households end up mainly in STPs. The incomplete removal of OMPs in STPs implies that the water discharged is considered the main responsible of their presence in the aquatic environment (Kümmerer, 2010; Tijani et al., 2013). Even though OMPs are detected at trace concentrations (μg/L and even ng/L range) in sewage, surface, ground and drinking water and in biosolid-amended soils (Chen et al., 2014; Luo et al., 2014; Petrie et al., 2015), their presence is an issue of emerging concern due to their persistence, bioaccumulation and biological activity (Santos et al., 2010; Tiwari et al., 2017; Tousova et al., 2017).

The effects of OMPs can be quantified in the short-term, although the continuous exposition of the aquatic organisms to these compounds detected in rivers, oceans and lakes (Luo et al., 2014; Osorio et al., 2016) could cause unpredictable long-term effects and even irreversible changes in some of them, since a significant fraction of these substances was designed to fulfil a biological function in a specific target organism (Fent et al., 2006).

Several studies were focused on identifying and analysing the effects of OMPs on the environment (Escher et al., 2014; Macova et al., 2010; Rao et al., 2014). Antibiotic resistance of microorganisms is a topic receiving special attention due to the potential risk for global human health that can cause the migration, transformation and diffusion of antibiotic resistances genes and antibiotic resistance bacteria into the environment (Gao et al., 2018; Rizzo et al., 2013). Moreover, the presence of endocrine disrupting compounds (EDCs) is also a growing concern since different studies have shown their adverse effects on wildlife exposed at environmental concentrations (Karen et al., 2007; Schwindt et al., 2014). However, the impact of most OMPs still remains unknown (Tijani et al., 2013) and the negative impacts might even worsen due to the synergistic effects of complex mixtures of compounds (Petrie et al., 2015).

Table 1.1. Application and main physico-chemical properties of the OMPs studied in this Thesis.

OMP	Abbr.	Application	MW[a]	H[a] (atm m³/mol)	s[a] (mg/L)	pK_a [a,b,c]	log K_ow [a]
Celestolide	ADBI	Fragrance	244.4	$2.1 \cdot 10^{-4}$	0.22	-	5.9
Galaxolide	HHCB	Fragrance	258.4	$1.3 \cdot 10^{-4}$	1.8	-	5.9
Tonalide	AHTN	Fragrance	258.4	$2.6 \cdot 10^{-4}$	0.21	-	5.8
Triclosan	TCS	Antiseptic	289.5	$5.0 \cdot 10^{-9}$	10	7.7	4.7
Diclofenac	DCF	Anti-inflammatory	296.2	$4.7 \cdot 10^{-12}$	2.4	4.2	4.2
17β-estradiol	E2	Estrogen	272.4	$3.6 \cdot 10^{-11}$	3.6	10.5	4.0
Fluoxetine	FLX	Antidepressant	309.3	$8.9 \cdot 10^{-8}$	60	10.1	4.1
Ibuprofen	IBP	Anti-inflammatory	206.3	$1.5 \cdot 10^{-6}$	21	4.9	4.0
Naproxen	NPX	Anti-inflammatory	230.3	$3.4 \cdot 10^{-10}$	15.9	4.2	3.2
17α-ethinylestradiol	EE2	Contraceptive/estrogen	296.4	$7.9 \cdot 10^{-12}$	11.3	10.3	3.7
Citalopram	CTL	Antidepressant	324.4	$1.1 \cdot 10^{-9}$	31	9.6	3.7
Estrone	E1	Estrogen	270.4	$3.8 \cdot 10^{-10}$	30	10.3	3.1
Erythromycin	ERY	Antibiotic	733.9	$5.4 \cdot 10^{-29}$	1.4	8.9	3.1
Roxithromycin	ROX	Antibiotic	837.1	$5.0 \cdot 10^{-31}$	0.02	9.1	2.8
Diazepam	DZP	Anxiolytic	284.7	$3.6 \cdot 10^{-9}$	50	3.4	2.8
Carbamazepine	CBZ	Anticonvulsant	236.3	$1.1 \cdot 10^{-10}$	112	15.9	2.5
Trimethoprim	TMP	Antibiotic	290.3	$2.4 \cdot 10^{-14}$	400	6.2	0.9
Sulfamethoxazole	SMX	Antibiotic	253.3	$6.4 \cdot 10^{-13}$	610	7.1	0.9

MW: Molecular weight, H: Henry coefficient (µg m⁻³ air/µg m⁻³ wastewater); s: solubility in water at 25°C (mg L⁻¹), pK_a: acid dissociation constant; K_ow: octanol-water partition coefficient.

[a] PhysProp database [b] DrugBank database, [c] Varhanickova et al. (1995)

1.3.2. Occurrence of organic micropollutants in wastewater and fate in wastewater treatment plants

The concentration of the OMPs considered in this Thesis, widely detected in wastewater and in sewage sludge is shown in Table 1.2. The concentrations found are much dependent on their usage rates, varying strongly among countries, seasons or even STPs.

Table 1.2. Occurrence range of several OMPs in wastewater entering STPs (C_w) and in (primary/secondary) sewage sludge (C_s).

OMP	C_w (µg/L)[a]	C_s (µg/g)[b]	OMP	C_w (µg/L)[a]	C_s (µg/g)[b]
ADBI	LOQ-0.02[c]	LOQ-0.04[c]	EE2	0.002-0.07	LOQ-0.42
HHCB	0.04-13[c]	4.2-31[c,d]	CTL	-	-
AHTN	0.11-5.4[c]	0.4-9[c,d]	E1	0.002-0.67	LOQ-0.16
TCS	0.38-4.2	LOQ-17	ERY	0.06-10	LOQ-0.20
DCF	0.06-11	LOQ-7.0	ROX	0.01-0.21	LOQ-0.18
E2	0.01-3.0	LOQ-0.05	DZP	21	LOQ-0.58
FLX	0.01-2.3	LOQ-0.10	CBZ	LOQ-21	LOQ-1.7
IBP	0.8-373	LOQ-4.1	TMP	LOQ-4.7	LOQ-4.1
NPX	0.04-52	LOQ-1.0	SMX	LOQ-7.9	LOQ-68

[a] Verlicchi et al. (2012), [b] Verlicchi and Zambello (2015), [c] Clara et al. (2011), [d] Tran et al. (2018).

The removal of OMPs in conventional STPs is only partial and the efficiency of STPs for their abatement is compound-specific, being the physicochemical characteristics of each OMP and the operational conditions in the STP the main factors affecting their elimination (Fernadez-Fontaina et al., 2012; Suárez et al., 2008). Hence, the removal efficiencies observed for each OMP can differ between STPs (Table 1.3), even though some pharmaceutical compounds such as IBP or NPX, are normally highly removed in STPs (70-100%), others such as CBZ or DZP show a recalcitrant behaviour (0-60%). However, the removal of OMPs in novel STPs is a topic that still remains quite unexplored, and so far only a few works have studied their removal in the technologies in which novel STPs are expected to be based on (Alvarino et al., 2015; Kassotaki et al., 2018; Laureni et al., 2016).

Moreover, besides the removal efficiency from wastewater, it must be highlighted that the sludge line is the final point of not only lipophilic OMPs (high K_{ow}) but also of a considerable fraction of those hydrophilic (low K_{ow}) not biotransformed in the STP (Carballa et al., 2008; Gonzalez-Gil et al., 2016; Narumiya et al., 2013). The fate of OMPs during AD has been extensively studied over the last years (Carballa et al., 2007b; des Mes et al., 2008; Gonzalez-Gil et al., 2016; Malmborg

and Magnér, 2015; Narumiya et al., 2013; Samaras et al., 2014). Results are sometimes contradictory, but in general compounds such as NPX, ROX or SMX are well eliminated during AD (Table 1.4), whereas most of them are poorly removed during AD (Carballa et al., 2007b; Gonzalez-Gil et al., 2016; Narumiya et al., 2013; Phan et al., 2018). Regardless the OMPs removal efficiency in AD, there is a consensus that most of the OMPs are mainly sorbed into the solid phase of digested sludge (Carballa et al., 2008; Gonzalez-Gil et al., 2016; Narumiya et al., 2013), being this fact particularly important in those countries in which sludge use in agriculture as a fertilizer is the preferable disposal alternative, since environmental and human risks were already reported due to the accumulation of OMPs in sludge (Barron et al., 2010; Thomaidi et al., 2016). Furthermore, only few works have studied the influence of sludge pretreatment technologies on the removal of OMPs (McNamara et al., 2012; Reyes-Contreras et al., 2018; Zhang and Li, 2018), achieving again contradictory results which do not allow to conclude whether they remove OMPs and/or boost their anaerobic transformation or not.

Table 1.3. Summary of OMPs removal efficiencies in conventional STPs.

OMP	Mohapatra et al. (2016)	Luo et al. (2014)	Martínez Bueno et al. (2012)	Jelic et al. (2011)	Behera et al. (2011)
ADBI	-	-	-	-	-
HHCB	-	87	68	-	-
AHTN	-	84	68	-	-
TCS	51-100	71-99	70	-	79
DCF	0-94	0-81	64	29	81
E2	-	92-100	-	-	100
FLX	25-82	-	70	-	-
IBP	91-100	72-100	70	-	98
NPX	85-100	43-99	70	75	96
EE2	-	44-100	-	-	-
E1	-	74-91	-	-	87
ERY	-	0-82	17	-	-
ROX	-	-	-	-	-
DZP	-	-	54	41	-
CBZ	0-31	0-62	42	25	23
TMP	-	0-82	57	42	69
SMX	0-31	4-89	63	-	52

1.3.3. Current and upcoming legislation on organic micropollutants

The presence of emerging pollutants in aquatic environments has already been considered by the European Water Framework Directive 2013/39/EU (European Commission, 2013), which establishes a Priority List of substances of major concern and a Watch List in order to monitor and gain information about the potential risks of these pollutants on the aqueous environment. Whereas the concentration of priority OMPs, such as 4-nonylphenol, 4-octylphenol or polycyclic aromatic hydrocarbons is limited (EC, 2013). other 17 OMPs included in the Watch List such as pharmaceuticals (ERY, azithromycin and clarithromycin), hormones (E1, E2 and EE2), or pesticides among others only have to be monitored (EC, 2015).

However, at a national level, a country such as Switzerland has already regulated through the Ordinance on Water Protection (GSchVSchweiz, 2016) OMPs discharge thresholds in STP effluents. Others, such as Austria, Germany and The Netherlands, are considering some initiatives to increase the removal of OMPs in STPs, to achieve an overall elimination of 80% (Benstoem et al., 2017).

Moreover, since the implementation of the European Directive 91/271/EEC on Urban Waste Water Treatment the quantities of sewage sludge requiring disposal has dramatically increased. European Directive 86/278/CEE promotes the use of this sludge in agriculture in order enhance the recycling of sewage sludge nutrients, fulfilling bioeconomy and circular economy requirements. Sludge reuse in agriculture is extensively used in countries such as Ireland, Portugal, Spain, United Kingdom, Czechia, Estonia or Hungary (>70 %) (Figure 1.5). Contrary, in many countries such as Austria, Belgium, Germany, Greece, Netherlands, Croatia, Malta, Poland or Romania landfill or incineration are still the main disposal methods.

Globally, up to 4-4.5 million ton of TS of sewage sludge were used with agriculture purposes in Europe in years 2010-2012 (http://epp. eurostat.ec.europa.eu) as a fertilizer. In those countries in which landfill or incineration is the preferable option for sludge disposal the presence of pathogens and OMPs in sludge is not a crucial issue. Contrary, in those in which it is used in agriculture as fertilizer it should be minimised, since it represents another entrance pathway of OMPs in soils and indirectly in surface and groundwater (Barron et al., 2010; Thomaidi et al., 2016). Therefore, the presence of OMPs into sludge is expected to become a major issue for STP administrators in the next years.

Table 1.4. Summary of reported OMP removals during sewage sludge AD.

OMP	Phan et al. (2018)	Zhou et al. (2017)	Yang et al. (2016)	Gonzalez-Gil et al. (2016)	Malmborg & Magnér (2015)	Samaras et al. (2014)	Narumiya et al. (2013)	Paterakis et al. (2012)	Clara et al. (2011)	Carballa et al. (2007)
ADBI	-	-	-	-	-	-	-	-	5	-
HHCB	-	-	-	10	-	-	-	-	0/45	65
AHTN	-	-	-	0	-	-	-	-	0/35	60
TCS	30	74	50	20	-	65	30	-	-	-
DCF	0	66	0	-	25	95	25	-	-	0/80
E1+E2	-	-	-	0	0	-	-	50	-	80
FLX	-	-	30	65	0	-	-	-	-	-
IBP	0	-	10	30	30	95	-	-	-	45
NPX	85	-	90	100	85	85	-	-	-	85
EE2	-	-	-	75	0	-	-	20	-	40/95
CTL	-	-	-	50	-	-	-	-	-	-
ERY	-	-	-	-	-	-	45	-	-	-
ROX	-	-	-	85	-	-	65	-	-	95
DZP	-	-	-	50	-	-	-	-	-	30
CBZ	0	53	0	30	15	-	0	-	-	5
TMP	85	-	90	75	100	-	100	-	-	-
SMX	65	-	-	80	-	-	100	-	-	100
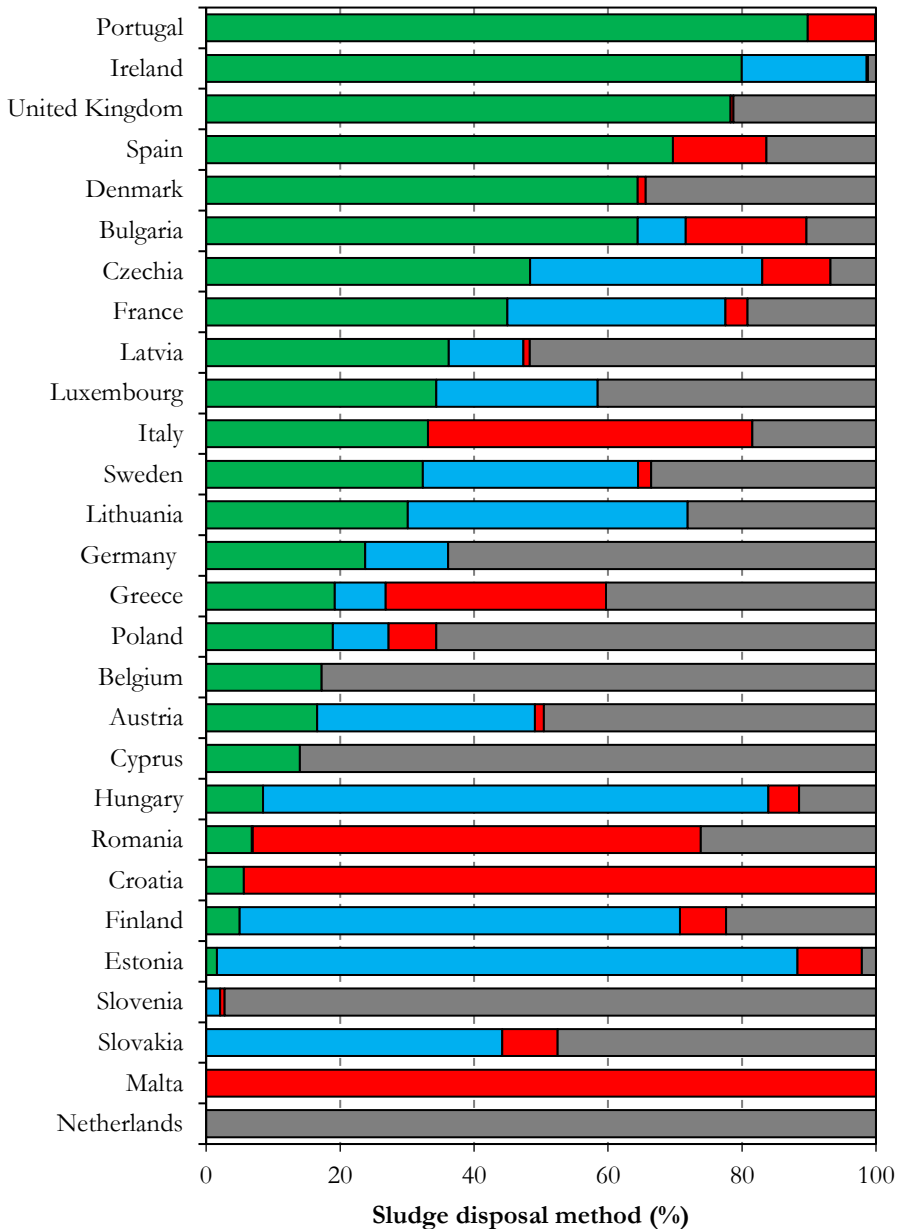
Figure 1.5. Sludge disposal methods in the UE-28: Agriculture (■), compost (■), landfill (■) and other (■) (http://epp. eurostat.ec.europa.eu).

1.4. AIMS AND SCOPE

The major goal of this Thesis is to compare conventional and novel STPs in terms of energy requirements, operational costs and OMPs removal. To achieve this broad objective, the following intermediate goals are established:

- o To technically, energetically and economically evaluate the potential of RBF to recover organic matter in novel STP configurations via its combination with a CEPT and to determine the fate of OMPs (Chapter 2).

- o To compare the energy demand, the operational costs and the fate of OMPs in CEPT and HRAS reactors in novel STPs to holistically determine the most favourable technology (Chapter 3).

- o To assess the effect of TH on the fate of OMPs and to on their biotransformation efficiency during AD (Chapter 4).

- o To determine how the energetic and economic balance in novel and conventional STPs is affected by the installation of a TH unit (Chapter 5).

- o To evaluate the fate of OMPs in novel configurations of STP and compare it with a conventional configuration (Chapter 6).

CHAPTER 2

OPPORTUNITIES FOR ROTATING
BELT FILTERS IN NOVEL
SEWAGE TREATMENT PLANTS

SUMMARY

In this chapter, rotating belt filters (RBFs) were examined in different configurations to identify their opportunities in novel sewage treatment plant (STPs). RBFs enable the recovery of 22-37% of the influent chemical oxygen demand (COD) and removal of 34-56% of hydrophobic organic micropollutants (OMPs). However, the effluent was not suitable for treatment in a partial nitritation-anammox (PN-AMX) process due to its high COD concentration. Chemically enhanced primary treatment (CEPT) enabled these limitations to be overcome and caused an increase in OMPs removal efficiency to 73-94%. However, a dose of 300 mg/L of ferric chloride was required to produce a suitable effluent for a PN-AMX reactor. The combination of RBF and CEPT not only derived effluents suitable for treatment in PN-AMX units but also decreased the alkalinity consumption and the required chemical dose 3-fold to achieve comparable COD recovery and OMPs removal. The methane yield of the combined sludges that were produced (184 L(N) CH_4/kg COD in wastewater) was 75% higher than that obtained in conventional wastewater treatment (105 L(N) CH_4/kg COD in wastewater), and the electricity requirements decreased from 0.54 to 0.41 kWh/m³ of wastewater. The energetic calculations showed that a STP incorporating this combined treatment could attain energy autarky, dramatically decreasing the STP electricity demand. Moreover, the proposed configuration achieved 26% lower operational costs than that of conventional treatment (4.3 *vs* 5.7 c€/m³ of wastewater) as long as a minimum alkalinity-to-ammonium ratio of 1-1.25 g IC to g NH_4^+ was ensured in the effluent of the combined treatment.

2.1. INTRODUCTION

Fine mesh rotating belt filters (RBFs) offer a very low footprint solution for recovering organic matter, as chemical oxygen demand (COD). They have been successfully applied as a replacement for conventional primary treatment (CPT) in conventional sewage treatment plants (STPs) (Franchi and Santoro, 2015; Rusten and Ødegaard, 2006) and achieve total suspended solids (TSS) removal efficiencies that are similar to those reported for conventional primary treatment (CPT) (~50%) (Carballa et al., 2004; Razafimanantsoa et al., 2014). A maximum of 50% dry matter content of RBF sludge can be achieved with a very high percentage of cellulose (maximum of 79% of TSS) (Ruiken et al., 2013), which facilitates its use as a soil conditioner in agriculture, fuel in a biomass-based power plant, and feed stock in the fermentation industry for the production of biofuels or chemicals, such as volatile fatty acids (VFA) (Crutchik et al., 2018). However, the most straightforward method for onsite valorisation is energy recovery by mesophilic AD (Ghasimi et al., 2015).

RBFs for municipal wastewater are commonly employed with a mesh size of 350 μm (Behera et al., 2018; Ruiken et al., 2013). Their effluents show important COD concentration, which is derived not only from soluble COD that remain unaffected in the RBFs but also from particulate COD that corresponds to small TSS that pass across the RBFs. Therefore, the implementation of additional steps prior to a partial nitritation-anammox (PN-AMX) unit is required (Rusten et al., 2017). Chemically enhanced primary treatment (CEPT) or chemically enhanced settling (CES) is an alternative that overcomes the limitations of RBF. In CEPT processes, using some chemical additives (coagulants and/or flocculants), TSS and COD removal efficiencies can be raised up to 90% and 70%, respectively. Moreover, in this technology a high phosphate removal efficiency is achieved (Diamantis et al., 2013) and a decrease of the size of the settling tank can be achieved by an increase in the sedimentation rate (De Feo et al., 2008). However, these processes require a considerable amount of chemicals and generate large volumes of sludge, with subsequent excessive costs of reagents and sludge disposal (Ju et al., 2016).

Therefore, the combination of RBF and CEPT may have a synergistic effect that overcomes the limitations of separately applying both technologies. The first effect is the incapacity of RBF to achieve high COD removal efficiencies and generate suitable effluents for PN-AMX reactors, and the second effect is the large chemical doses that are required in CEPT processes to achieve this goal (Gao et al., 2011).

The objective of this study is to assess the potential of RBFs to recover organic matter in novel STPs via its combination with a CEPT. The system was

technically, energetically and economically evaluated. An additional goal is to assess the fate of OMPs in RBFs and compare it with the removal in CPT and CEPT.

2.2. MATERIALS AND METHODS

2.2.1. Rotating belt filters system

The technical performance of two RBF systems with a mesh size of 350 μm and located in the Blaricum STP (1,600 m³/h) and Aarle-Rixtel STP (2,600 m³/h) in The Netherlands was evaluated. Influent, effluent and sludge samples were collected and stored at 4 °C in aluminium bottles prior to analysis. Wastewater samples were characterised in terms of total solids (TS, g TS/kg), volatile solids (VS, g VS/kg), total suspended solids (TSS, g TSS/kg), volatile suspended solids (VSS, g VSS/kg), total chemical oxygen demand (COD_{tot}, g O_2/L) and soluble chemical oxygen demand (COD_{sol}, g O_2/L), total Kjeldahl (TKN, g N-TKN/L), total ammonium nitrogen (g N-TAN/L) and OMPs concentrations. Dewatered RBF sludge samples were collected in both STPs, whereas STP raw RBF sludge (the sludge generated in the RBF without the dewatering process) was sampled in the Aarle-Rixtel STP. The sludge samples were characterised in terms of TS, VS, COD_{tot}, TKN and OMPs concentrations.

Eighteen commonly employed OMPs with different physico-chemical properties were considered in this study: three musk fragrances, galaxolide (HHCB), tonalide (AHTN) and celestolide (ADBI); three anti-inflammatories, ibuprofen (IBP), naproxen (NPX) and diclofenac (DCF); four anti-biotics, sulfamethoxazole (SMX), trimethoprim (TMP), erythromycin (ERY) and roxithromycin (ROX); four neurodrugs, fluoxetine (FLX), carbamazepine (CBZ), diazepam (DZP) and citalopram (CTL); one endocrine disrupting compound, triclosan (TCS); and three hormones, estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2).

2.2.2. Chemically enhanced settling tests

CES assays were carried out with both RBF influent and RBF effluent of the Aarle-Rixtel STP in a Jar-Test device with vessels that contain 1 L of liquid volume following the protocol described by Carballa et al. (2005), but without pH correction. The influence of the dose of ferric chloride (0-300 mg/L) on the removal of TSS, COD and OMPs was analysed at 25°C. The test included an initial 3 min period of rapid stirring (150 rpm) after the addition of the coagulant, followed by 5 min of slow mixing (50 rpm) for emulsion breaking and floc formation and a 1 hour period without mixing for floc separation, after which 500 mL of supernatant were collected for the characterisation.

2.2.3. Biochemical methane potential tests

The biochemical methane potential (BMP) of the RBF sludge and of the sludges generated after RBF (settling without chemicals and chemically enhanced settling using 100 mg/L of ferric chloride) was determined through the manometric method following a protocol that was described elsewhere (Holliger et al., 2016) The inoculum was flocculant biomass (11.8 g VS/L) from the sludge anaerobic digester of a STP.

The reactors were dosed with macro- and micro-nutrients, and pH was adjusted to 7.2-7.5 with NaOH or HCl. After flushing the head space with nitrogen, they were incubated at 37ºC. Methane production by each sludge was calculated as the difference between the average production in the bottles with substrate minus the average production in the blank (residual production of the inoculums). BMP was calculated as the experimental ultimate methane production, expressed in L(N)/kg VS fed, where N means normal conditions (1 atm, 0ºC). Anaerobic biodegradability (AB) was expressed as the percentage of the initial COD of the substrate converted to methane. At the end of the test, bottles were opened and pH and volatile fatty acids (VFAs) concentration were measured to confirm that no acidification occurred.

2.2.4. Solid-water distribution coefficient

A common approach to determining the fraction of OMPs sorbed onto sludge is the use of the solid–water distribution coefficient (K_D, L/kg). A spike of the 18 selected compounds was performed on raw RBF sludge at different concentrations in the three tests. Sodium azide (10 mg/L) was added to avoid biological activity. After 12 hours of mixing at room temperature to achieve equilibrium conditions, the samples were centrifuged and liquid and solid phases were separately analysed, as explained in the section analytical methods of this document.

2.2.5. Analytical methods

COD, pH, PA, TA, TSS, VSS, TS, VS, N-TKN and N-TAN were determined according to standard methods (APHA, 2005). In BMP tests, biogas production was measured by a pressure transducer (Centrepoint Electronics) and its composition was determined by gas chromatography (HP 5890 Series II). VFAs were measured by gas chromatography with flame ionisation detection (FIC, HP 5890A).

To determine the OMP concentrations in the wastewater samples, the latter were centrifuged, pre-filtered (AP4004705, Millipore) and filtered by 0.45 mm (HAWP04700, Millipore) before performing solid phase extraction (SPE) with

200 mg OASIS HLB cartridges (Waters, Milford, MA, USA) as described by Fernandez-Fontaina et al. (2013). The quantification of musk fragrances (HHCB, AHTN, ADBI), anti-inflammatories (IBP, NPX, DCF) and endocrine disrupting compound TCS was accomplished using a gas chromatograph (Varian CP-3900) coupled with an ion trap spectrometer (Varian CG-2100). Antibiotics (ERY, ROX, SMX, TMP), neurodrugs (FLX, CBZ, DZP, CTL) and hormones (E1, E2, EE2) were quantified using an Agilent G1312A liquid chromatograph with a binary pump and automatic injector HTC-PAI (CTC Analytics) connected to a mass spectrometer API 4000 triple quadrupole (Applied Biosystems)(Paredes et al., 2018).

For influents and effluents, the sample volume that was analysed was 1 L, and the final volume of the extract was 3 mL, which generated an enrichment factor of 333 $L_{supernatant}/L_{extract}$. For the liquid phase of RBF sludge, the analysed volume was 100 mL and the final volume of extract was 3 mL, which yielded an enrichment factor of 33 $L_{supernatant}/L_{extract}$. The limits of quantification (LOQ) for each case are shown in Table 2.1.

Table 2.1. Limit of quantification of OMPs in wastewater and sludge samples.

OMP	Wastewater samples		Sludge samples	
	Liquid (ng/L)	Solid (ng/g)	Liquid (ng/L)	Solid (ng/g)
ADBI, AHTN, HHCB, TCS	5	60	50	30
CTL, ERY, FLX, ROX	0.3	1.2	3	1.2
DZP, CBZ, SMX, TMP	1.5	6	15	6
E1, E2, EE2	1.5	6	15	6
IBP	6	24	20	12
NPX	7.5	30	25	15
DCF	32	120	100	60

The frozen solid phases of the influent and effluent of RBF and raw and dewatered RBF sludge were lyophilised to perform ultrasonic solvent extraction following a procedure based on the procedure described by Alvarino et al. (2014) Three sequential extractions with methanol and two sequential extractions with acetone were performed on the freeze-dried samples (0.5-1 g). In each extraction, samples were sonicated for 15 min and centrifuged at 1500 rpm for 5 min. The resulting supernatants were combined and filtered through glass wool. The resulting volume was evaporated to 1 mL (TurboVap LV, Biotage) flowing nitrogen (200 kPa, 30 ºC) and resuspended in 100 mL of Milli-Q water prior to SPE. SPE and OMPs quantification were performed as previously described for liquid samples. The enrichment factor was 166 $g_{sludge}/L_{extract}$.

2.2.6. Energetic evaluation

The potential energy in typical domestic wastewater has been estimated in the range 4.1-4.9 kWh/kg COD of wastewater, averaged at 4.5 kWh/kg COD of wastewater (Heidrich et al., 2011; Shizas and Bagley, 2004). In the biogas line, a methane heat combustion of 11 kWh/m³ (N) of methane was considered (Perry, 1984), with an electrical efficiency (η) of 0.35 in the co-generation motor (Mills et al., 2014; Zhou et al., 2013).

2.2.7. Economic evaluation

To calculate the operational costs associated with chemical addition, the $FeCl_3$ price was estimated at approximately 220 €/ton (De Feo et al., 2008) and the sodium bicarbonate price was assumed at approximately 200 €/ton (1,400 €/ton IC). For electricity, a cost of 0.12 €/kWh was assumed (STOWA, 2012). Finally, for sludge disposal, a hygienization cost of 80 €/ton dry matter was considered (Management Company, 2019). Eq. 2.1-2.3 were applied to assess digested sludge production.

$$VS_{rec} = COD_{inf} \cdot COD_{rec} \cdot \left(\frac{VS}{COD} \right)_{sl} \qquad \text{\textit{Equation 2.1}}$$

$$TS_{rec} = VS_{rec} \cdot \left(\frac{TS}{VS} \right)_{sl} \qquad \text{\textit{Equation 2.2}}$$

$$TS_{dig} = TS_{rec} - VS_{rec} \cdot AB_{sludge} \qquad \text{\textit{Equation 2.3}}$$

Where:

VS_{rec}: Volatile solids recovery in each preconcentration technology (kg VS/m³ wastewater treated).

TS_{rec}: Total solids recovery in each preconcentration technology (kg TS/m³ wastewater treated).

COD_{inf}: Total influent COD (kg COD/ m³ wastewater treated).

COD_{rec}: Total influent COD recovery (fraction of COD of the influent recovered as sludge).

$(VS/COD)_{sl}$: Volatile solids-to-total COD sludge ratio (kg VS/kg COD).

$(TS/VS)_{sl}$: Total solids-to-volatile solids sludge ratio (kg TS/kg VS).

TS_{dig}: Digested total solids production (kg TSS of digested sludge /m³ wastewater treated).

TS_{dig}: Digested total solids production (kg TSS of digested sludge /m³ wastewater treated).

TS_{prod}: TS production in each preconcentration technology (kg TSS in sludge /m³ wastewater treated).

VS_{prod}: VS production in each preconcentration technology (kg VS in sludge/m³ wastewater treated).

AB_{sludge}: anaerobic biodegradability, i.e. fraction of COD of sludge converted to CH_4 in the BMP tests (the same value was considered for VS degradation).

2.3. RESULTS AND DISCUSSION

2.3.1. Technical performance of the rotating belt filters system

The physico-chemical characterisation of the influent and effluent of the two RBFs sampled systems are shown in Table 2.2. Both influents showed similar average values of TSS (320 and 275 mg/L), VSS (300 and 255 mg /L), VS (600 and 570 mg/L), COD_{tot} (680 and 600 mg O_2/L), COD_{sol} (230 and 260 mg O_2/L) and TKN (87 and 75 mg TKN-N/L), which is consistent with previously reported values for the Blaricum STP (Ruiken et al., 2013) and for other urban STPs in The Netherlands (Puig et al., 2010). Conversely, the TS concentration in the influent of the Blaricum STP (770 mg/L) was considerably lower than that measured in the influent of the Aarle-Rixtel STP (1,260 mg/L), which indicates lower salts dissolved concentration.

Table 2.2. Physicochemical characteristics of influent and effluent in rotating belt sieves from Blaricum and Aarle-Rixtel STPs (n=3).

	Blaricum STP		Aarle-Rixtel STP	
	Influent	Effluent	Influent	Effluent
TS (mg/L)	770 ± 30	610 ± 20	1260 ± 0	1140 ± 10
VS (mg/L)	600 ± 20	440 ± 20	570 ± 5	450 ± 20
TSS (mg/L)	320 ± 10	160 ± 0	275 ± 5	145 ± 10
VSS (mg/L)	300 ± 20	150 ± 0	255 ± 10	130 ± 5
COD_{tot} (mg/L)	680 ± 10	440 ± 10	600 ± 30	470 ± 10
COD_{sol} (mg/L)	230 ± 10	220 ± 10	260 ± 20	240 ± 10
TKN-N (mg/L)	87 ± 2	75 ± 1	75 ± 4	69 ± 6
TAN-N (mg/L)	nd	nd	67 ± 3	61 ± 4

n.d.: not determined.

The removal efficiency of TSS (~50%), VSS (~50%), COD_{sol} (~0%) and TKN (~10%) were similar in both RBF systems. Regarding COD_{tot}, a higher removal efficiency (37%) was determined in the Blaricum STP than in the Aarle-Rixtel

STP (22%), which is explained by its higher COD_{sol}-to-COD_{tot} ratio. The removal efficiencies determined in this study are similar to those reported by other authors regardless of the TKN (Ruiken et al., 2013; Rusten et al., 2017), for which the removal efficiencies achieved in both scenarios were approximately 10%—a value that is slightly higher than the that reported elsewhere (~1%)(Ruiken et al., 2013).

The physico-chemical properties of dewatered RBF sludge are shown in Table 2.3. TS (21.5-27.5%), VS (20.0-25.8%), COD_{tot} (273-356 g O_2/kg) and TKN/VS ratio (12-16 mg N/g VS) are in accordance with the values reported for RBF sludge from the Blaricum STP (Ghasimi et al., 2015). VS represents approximately 95% of the TS of the sludge, and the COD_{tot}-to-VS ratio was approximately 1.3, which is in accordance with the mean values obtained by Paulsrud et al. (2014) for 19 Norwegian STPs that apply RBF technology. Ghasimi et al. (2015) reported higher COD_{tot}/VS ratios (1.6-1.8), which may be indicative of a lower cellulose concentration.

Table 2.3. Physicochemical characteristics of dewatered sieved sludge generated in rotating belt sieves of Blaricum and Aarle-Rixtel STPs (n=3).

	Blaricum STP	**Aarle-Rixtel STP**
TS (g/kg)	215 ± 10	279 ± 10
VS (g/kg)	200 ± 10	261 ± 10
COD_{tot} (g/kg)	273 ± 18	350 ± 20
TKN-N (g/kg)	3.3 ± 0.2	4.2 ± 0.1

Raw RBF sludge of the Aarle-Rixtel STP was ten times less concentrated than the dewatered RBF sludge, which shows similar physico-chemical characteristics (data not shown), as expected.

2.3.2. Technical performance of chemically enhanced settling systems

The results of applying a CES to the influent of RBFs are shown in Figure 2.1. Ferric chloride was selected as a coagulant rather than other metals salts, considering its lower price (De Feo et al., 2008) and lower required doses (Carballa et al., 2005). Effluent quality that is comparable to that obtained in RBFs was obtained after conventional settling (COD_{tot} removal and TSS removal of 36-38% and 47-49%, respectively), without removal of COD_{sol}. By the addition of 100 mg/L of ferric chloride, the removal of COD_{tot} and TSS increased to 66 and 86%, respectively. This decrease was primarily attributed to a large removal of suspended matter, considering that the maximum COD_{sol} removal achieved did not exceed 25%.

Heterotrophic denitrifiers may increase nitrogen removal efficiency in PN-AMX reactors with low influent COD/NH_4^+ ratios (Jia et al., 2018); however, system failure was reported with COD/NH_4^+-N ratios higher than 2 due to the growth of fast-growing heterotrophic denitrifiers, which compete with the slow-growing anammox bacteria for nitrite (Jin et al., 2012). To fulfil this condition, the required $FeCl_3$ dose should be increased to 300 mg/L, which is similar to that reported by Carballa et al. (2005).
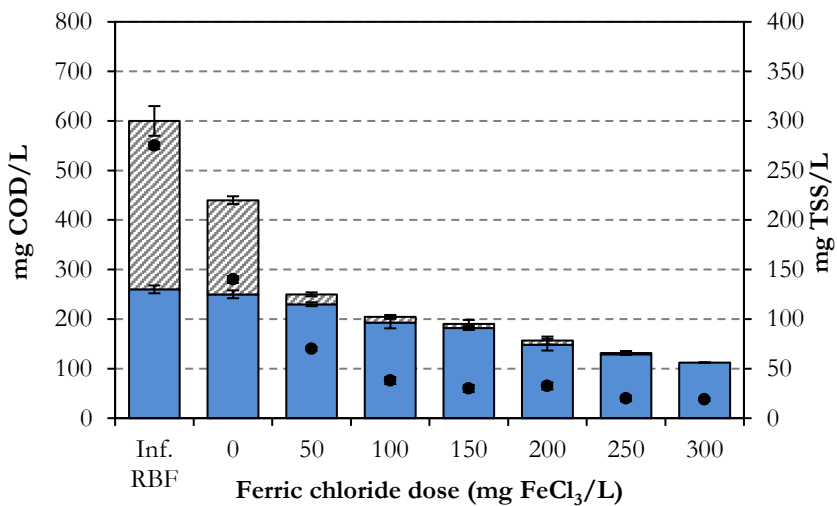
Figure 2.1. Influence of ferric chloride dose on the removal of soluble (■) and particulate (▨) COD and TSS (●) on raw wastewater of Aarle-Rixtel STP. 0 mg $FeCl_3$/L refers to conventional settling without chemicals.

2.3.3. Technical performance of combined rotating belt filter and chemically enhanced settling technologies

RBFs are suitable for partial removal of COD_{part} from wastewater but they are unable to remove COD_{sol}. CES enables complete removal of COD_{part} and partial removal of COD_{sol} with a requirement of high chemical doses. Thus, the combination of RBF and CES was analysed (Figure 2.2) to attempt to overcome the limitation of both technologies and compare with the CES system (Figure 2.1).

The combination of RBF followed by settling without chemicals addition produced a removal of almost 100% of the COD_{part} of wastewater, whereas 50% of removal was achieved when the test was carried out for the RBF influent (Figure 2.1), which may indicate that the presence of cellulose in wastewater limits the settlement of other suspended solids due to its tendency to float.

Contrary, more than 50% of COD_{sol} was removed (Figure 2.2), which accounts for COD_{tot} removal of 84%. To obtain comparable results without an RBF system, a considerably higher dose of $FeCl_3$ (approximately 300 mg/L) was needed (Figure 2.1).
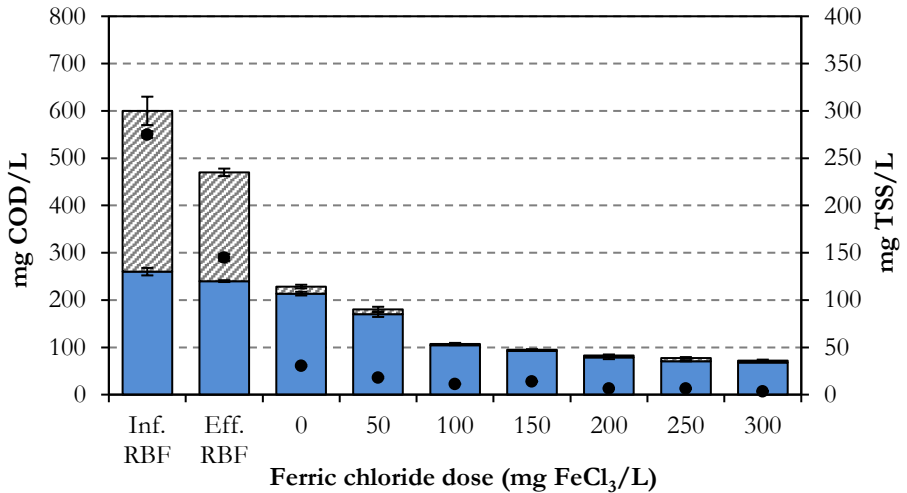

Figure 2.2. Influence of ferric chloride dose on the removal of soluble (■) and particulate (▨) COD and TSS (●) on the RBF effluent of wastewater of Aarle-Rixtel STP. 0 mg $FeCl_3$/L refers to conventional settling without chemicals.

Note that a side effect exists of the addition of the coagulant on the alkalinity, with a consumption of 22 mg IC for each 100 mg of $FeCl_3$ (Metcalf & Eddy, 2003). Taking into account that the further PN-AMX step requires a minimum alkalinity-to-ammonium ratio of 1-1.25 g IC per g NH_4^+-N (Pedrouso et al., 2017), the need for an external bicarbonate addition to avoid acidification in the PN-anammox unit, which considers an ammonium concentration of 67 mg NH_4^+-N/L (Table 2.2), would be much higher if the RBF system is not present.

2.3.4. Biochemical methane potential of the sludges

Figure 2.3 shows the results of the BMP tests of RBF sludge, which comprise the sludges generated after RBFs (settling without chemicals and settling with the addition of 100 mg/L of $FeCl_3$). Three of the sludges showed similar methane production rates and needed 26 days to complete the test, following the criteria proposed by Holliger et al. (2016). The neutral pH values (7.3-7.7) and the absence of VFA (<2.5 ppm acetic acid) at the end of the tests (data not shown) indicated that the performance of the tests was adequate and acidification did not occur.

Dewatered RBF sludge showed the highest BMP value (386 L(N) CH$_4$/kg VS), which is consistent with other results in the literature(Paulsrud et al., 2014). However, the AB (80%) was higher than that the obtained by Ghasimi et al. (2015) (64%), which is explained by its lower COD$_{tot}$/VS ratio. The sludges generated during conventional settling and CES after RBF showed similar BMP values (327 L(N) CH$_4$/kg VS and 310 L(N) CH$_4$/kg VS, which corresponds to 60% and 58% of AB, respectively), but values lower than those for dewatered RBF sludge. These values are comparable to those reported for conventional primary sludge (259-325 L (N) CH$_4$/kg VS) (Paulsrud et al., 2014). Thus, the installation of RBFs seems to not affect the BMP of sludge obtained by conventional settling, which may be explained by the low proportion of cellulose recovered in the latter system (Ruiken et al., 2013). The similar results obtained for both sludges do not agree with those obtained by Kooijman et al. (2017) who reported an important increase in the BMP of the sludge generated during CES compared with conventional settling due to the higher readily degradable biomass removed by flocculation. However, Romero-Güiza et al. (2016) reported that Fe^{3+} reduction can limit the conversion of organics to methane as Fe^{3+} reduction is more thermodynamically favourable than methanogenesis.
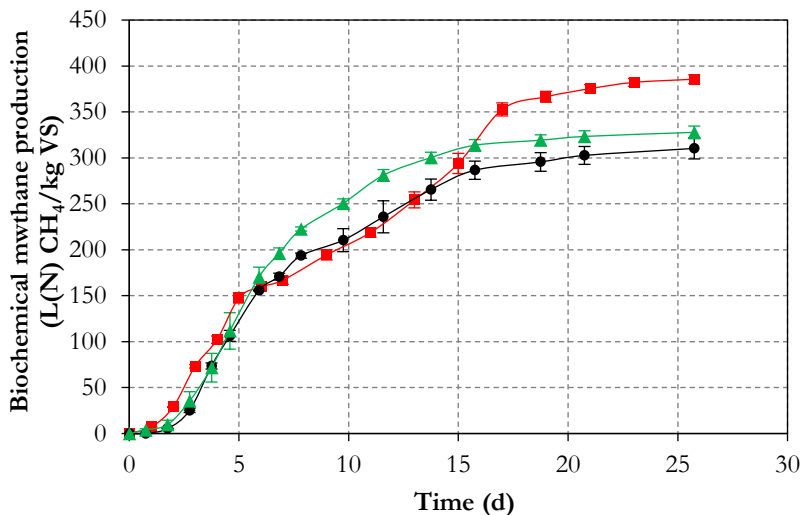
Fig. 2.3. Average BMP results of dewatered sieved sludge (■), conventional settling sludge after RBF (▲) and chemically enhanced settling sludge after RBF (●).

The data from the BMP test and the results of the CES tests enabled calculation of the methane production of each sludge in relation to the COD recovery in each treatment step. RBF enables a very limited energy recovery (62 L(N)

CH$_4$/kg COD of wastewater), which is explained by lower COD$_{tot}$ recovery compared with that of other tested technologies (Figure 2.2). The system RBF followed by settlement without chemicals enabled an increase in the energy recovery to 85 L(N) CH$_4$/kg COD of wastewater). However, the highest energy recovery was achieved with the combination RBF and CES with 100 mg/L of FeCl$_3$, which boosted it to 122 L(N) CH$_4$/kg COD of wastewater due to the higher COD capture determined with the addition of chemicals (Figure 2.1).

2.3.5. Fate of organic micropollutants in the rotating belt filters and chemically enhanced settling systems

The concentrations of the 18 selected OMPs in the influent of both RBF systems are reported in Table 2.4.

Table 2.4. Total concentration of OMPs in the influent of RBFs systems of Blaricum and Aarle-Rixtel.

OMP	Blaricum STP	Aarle-Rixtel STP
HHCB (µg/L)	2.16	1.23
AHTN (µg/L)	1.33	0.95
ADBI (µg/L)	1.09	1.38
IBP (µg/L)	3.47	4.02
NPX (µg/L)	4.84	4.89
SMX (ng/L)	8.9	<LOQ
TMP (ng/L)	48	41
ERY (ng/L)	7.9	4.6
ROX (ng/L)	2.9	<LOQ
FLX (ng/L)	42	38
CBZ (ng/L)	235	32
DZP (ng/L)	33	1.7
CTL (ng/L)	97	96
TCS (µg/L)	1.21	<LOQ
E1 (ng/L)	<LOQ	<LOQ
E2 (ng/L)	57	55
EE2 (ng/L)	11	<LOQ

LOQ: limit of quantification

The highest concentrations of OMPs in both STPs were observed for the anti-inflammatories IBP and NPX (3.47-4.89 µg/L), although the other anti-inflammatory, DCF, was not detected in either of the two STPs. These concentrations are consistent with other concentrations in the literature. (Carballa et al., 2004; Santos et al., 2009; Terzić et al., 2008) Musk fragrances (HHCB, AHTN and ADBI) and the endocrine-disrupting compound TCS were detected in the range 0.95-2.16 µg/L, in accordance with other authors (Clara et al., 2011; Luo et al., 2014; Terzić et al., 2008).

The four antibiotics (SMX, TMP, ERY, and ROX) and the four neurodrugs (FLX, CBZ, DZP and CTL) were detected in the influent of Blaricum STP, whereas SMX and ROX were not detected in the Aarle-Rixtel STP. In general, the measured concentrations (LOQ-235 ng/L) were in the lower range of the literature (Luo et al., 2014; Santos et al., 2009; Terzić et al., 2008; Verlicchi et al., 2012). This fact can be explained by the fact that the Netherlands has the lowest human antibiotic consumption rate of Europe (European Centre for Disease Prevention and Control, 2014).

The concentrations of hormones ranged between LOQ and 57 ng/L, which is the same range of those reported in the literature) (Luo et al., 2014).

The OMP removal efficiencies achieved in the different evaluated systems (RBF, CPT, RBF+CES using 100 mg/L of $FeCl_3$ and CES using 300 mg/L of $FeCl_3$) are shown in Figure 2.4.

Only fragrances and TCS were removed in a significant percentage in the evaluated scenarios. In the RBFs of the Blaricum STP, the removal efficiencies of HHCB, AHTN and ADBI were 39%, 46% and 34%, respectively, and 45% for TCS. In the RBFs of the Aarle-Rixtel STP, the determined removal efficiencies of HHCB, AHTN and ADBI were slightly higher (53%, 54% and 44%, respectively). TCS was not detected in this STP. In conventional settling of the Aarle-Rixtel STP, the elimination of HHCB, AHTN and ADBI were 54%, 56% and 45%, respectively, compared with those obtained during CPT of hospital wastewater (Suarez et al., 2009). In the Aarle-Rixtel STP, the combination of RBF and CES enabled improvement in the removal efficiencies of HHCB and AHTN to 96% an improvement in the elimination efficiency of ADBI to 75%, which is similar to those achieved in the CES. For the remaining OMPs, the elimination of different RBF systems ranged from -8 to 14% (Figure 2.4). The increase in concentration of some OMPs was likely attributed to the analytical deviation caused by the distinctive characteristics of the wastewaters. These results show agreement with the literature (Behera et al., 2011; Carballa et al., 2004; Suarez et al., 2009).
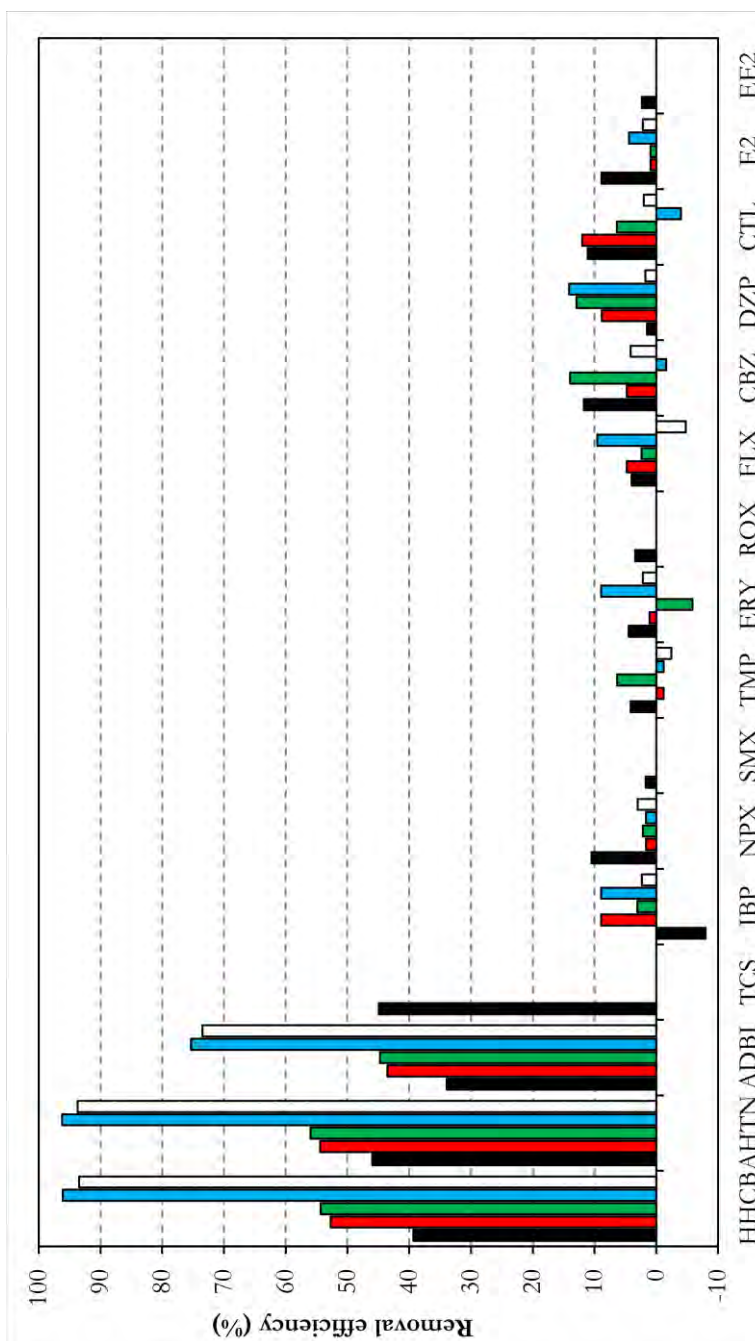
Figure 2.4. Removal efficiencies of the organic micropollutants in RBF system in Blaricum STP (■), in RBF in Aarle-Rixtel STP (■), in CPT in Aarle-Rixtel STP (■), RBF + CES in Aarle-Rixtel STP (■), and CES in Aarle-Rixtel STP (□).

It seems to be a consensus in the literature that most OMPs are poorly removed during coagulation–flocculation processes, however, some exceptions such as musks, a few pharmaceuticals (e.g. DCF) and nonylphenol were found (Luo et al., 2014). Moreover, some authors reported that the different composition of wastewater can play a major role on OMPs removal during CEPT. For example, high fat content in wastewater was reported to improve the removal of hydrophobic compounds (Suarez et al., 2009). Dissolved humic acid could also enhance the elimination of some pharmaceutical compounds, such as DCF or IBP (Vieno et al., 2006). On the contrary, the presence of COD_{sol}, especially low-molecular-weight fractions, can possibly inhibit the OMPs removal due to the preferential removal of COD_{sol} through coagulation. Negatively charged COD_{sol} could react with positively charged coagulants, leading to a less amount of coagulant available for elimination of OMPs (Choi et al., 2008). Thus, no difference was found between RBF and CPT. These results can be explained by the similar removal efficiencies of TSS that are achieved in both systems and the similar affinity of these OMPs to the solid phase of conventional primary and RBF sludges, which is confirmed by the results of the solid-liquid distribution coefficients (Figure 2.5).

In the K_D tests, OMPs of Group I (Figure 2.5) were only detected in the solid phase, so the limit of quantification (LOQ) in the liquid phase was used to calculate the K_D values for these compounds. They showed the highest sorption affinity, which is agreement with literature. The OMPs included in Group II showed K_D coefficients slightly lower than those reported in the literature for primary sludge regardless IBP (Figure 2.5). The higher values obtained in this study for IBP (log K_D: 1.8-2.1) compared with those reported in literature for primary sludge could be explained by the pK_a of IBP (pK_a: 4.5–5.2) and the pH of RBF sludge (5.5), since for acidic compounds, higher K_D values are expected under acidic conditions (Carballa et al., 2008). The compounds of Group III showed K_D values in general one order of magnitude lower than those reported in literature.

Although the system RBF+CES of the proposed alternative did not enable extra removal of hydrophilic OMPs compared with conventional settling, it enabled an increase in the removal efficiency of hydrophobic compounds, which achieved results that were as good as those obtained in the CES with higher doses of $FeCl_3$.
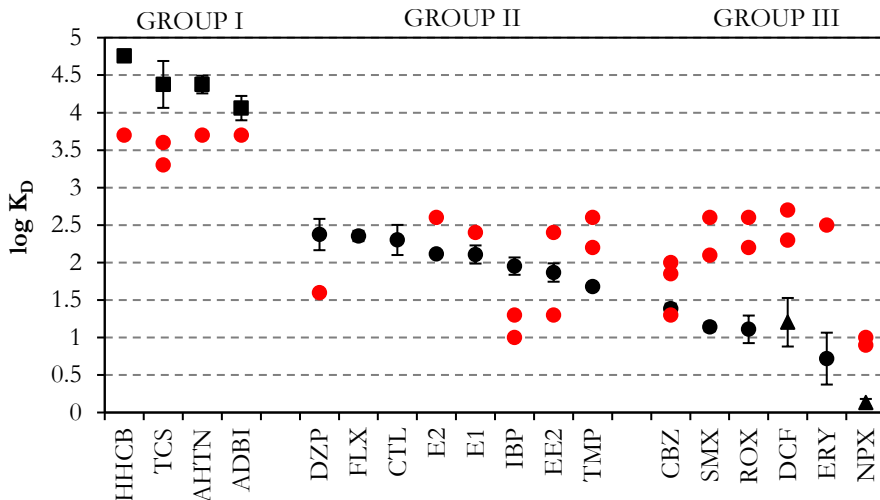
Figure 2.5. OMPs partition (log K_D) between solid and liquid phase in sieved sludge. (■) minimum values calculated with the limit of quantification in the liquid phase (HHCB, AHTN, ADBI and TCS were only quantified in solid phase); (▲) maximum values calculated with the limit of quantification in the solid phase (NPX and DCF were only quantified in the liquid phase); and (●) average values for compounds quantified in the liquid and solid phases. (●) Refers to literature values for primary sludge (Carballa et al., 2008; Narumiya et al., 2013; Stasinakis et al., 2013; Suárez et al., 2008; Ternes et al., 2004). Group I includes the most hydrophobic OMPs, with log K_D >4, Group II, those with medium log K_d values (1.5> log K_d > 2.5) and Group III the most hydrophilic compounds (log K_d >1.5).

2.3.6. Energetic assessment of the proposed sewage treatment plant

Among the evaluated alternatives, the combination of RBF and CES drove the maximum energy production with the lowest ferric chloride and alkalinity consumption and to the highest OMPs removal. Figure 2.6 shows a comparison of this alternative (A) with the conventional STP scheme (B) in terms of energy production/consumption.

In conventional STPs, aeration usually consumes the largest energy fraction (maximum of 70%) (Rosso et al., 2008; Siegrist et al., 2008), which causes a total energy consumption of wastewater in the range 0.6-1.2 kWh/kg COD of wastewater, with an average value of 0.9 kWh/kg COD of wastewater (Zhou et al., 2013). Therefore, 0.54 kWh/m³ wastewater is needed for the treatment, considering 0.6 kg COD_{tot}/m³ of wastewater for the Aarle-Rixtel STP (Table 2.2), in accordance with other reported values in the literature (Cano et al., 2015). As approximately 0.40 kWh per kg of COD of wastewater are commonly

recovered, a maximum of 45% of self-produced energy can be achieved (Figure 5B).
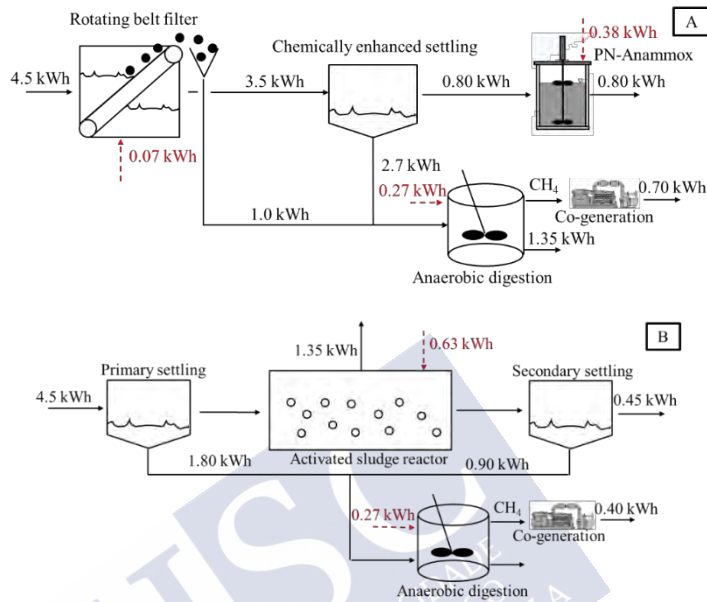
Figure 2.6. COD balance (in relation to 1 kg in the influent) and energy flows for the proposed STP (A) and the conventional STP (adapted from Wan et al. (2016))(B). * Represents the energy required for sludge management and pumping, ---Refers to energy inputs for the wastewater treatment.

In the proposed scenario (Figure 5A), the electricity demand of the PN-AMX unit was considered to be 60% of the nitrification-denitrification electricity demand (Schaubroeck et al., 2015) which yielded 0.23 kWh/m³ of wastewater. The maximum electricity consumption of RBF was reported to be approximately 0.04 kWh/m³ of wastewater (Salsnes, 2016), and the costs due to pumping and sludge treatment were assumed to be 0.17 kWh/m³ of wastewater, which is equivalent to those in conventional configurations (Zhou et al., 2013). Thus, the electricity demand was 0.44 kWh/m³ of wastewater, which is 19% lower than that in the conventional configuration (0.54 kWh/m³ of wastewater). The combination of RBF followed by CEPT enabled 84% recovery of the COD_{tot} of the influent as sludge (Figure 2.2). During AD, 52% of the COD of wastewater was transformed into methane and yielded electricity generation of 0.70 kWh per kg of COD of wastewater (0.42 kWh/m³ of wastewater), which almost doubles the electricity generation in the conventional STP. This fact and the lower

electrical requirements of this configuration enable an electrical self-production of approximately 95-100% of the STP electricity demand.

2.3.7. *Economic assessment of the proposed sewage treatment plants*

Two different scenarios for the proposed configuration were evaluated (Figure 2.7). In the first scenario, the alkalinity of wastewater was assumed to be sufficiently high to bear the consumption produced in CES. Thus, the influent to the PN-anammox would have an appropriate alkalinity-to-ammonium ratio. In the second scenario, an external alkalinity addition as sodium bicarbonate was considered to compensate its consumption in the CES stage. The first scenario yielded an energy and coagulant cost that was 40% lower than in the conventional STP (2.4 *vs* 4.0 c€/m³ of wastewater, Figure 2.7). In the second scenario, the calculated coagulant and energy costs increased to 5.5 c€/m³ of wastewater (Figure 2.7); thus, it was distinctly uncompetitive compared with the conventional STP.
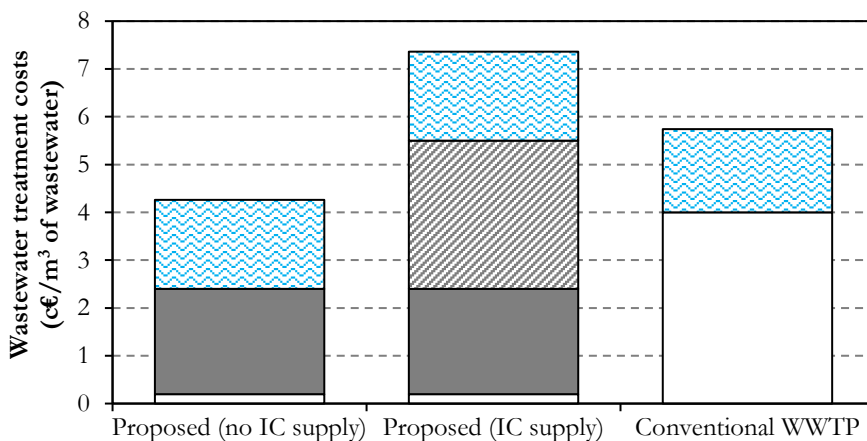
Figure 2.7. Contribution of electricity (▫), coagulant (▪), sodium bicarbonate (▨) and sludge management (▧) to the STP operational costs.

However, depending on specific legislations, it might not be possible to dispose digested sludge without a further hygienization treatment. Although in the proposed alternative a considerably higher COD recovery as sludge is achieved (0.82 versus 0.60 kg COD/kg COD of wastewater, Figure 2.6), the recovered sludge was more anaerobically biodegradable (63 versus 50% of AB). Thereby, in both scenarios approximately 0.30 kg COD/kg COD of wastewater ends up as digested sludge (Figure 2.6). A typical ratio of approximately 1.2 g TSS/g COD_{tot} in digested sludge (Carballa et al., 2007b) for the conventional STP and of 1.3 g TSS/g COD_{tot} for the proposed scenario (the higher value is attributed

to the precipitation of inorganic compounds after the addition of $FeCl_3$) were assumed. Therefore, the sludge management cost for the conventional STP and the proposed scenario was 1.7 and 1.9 c€/m³ of wastewater, respectively (Figure 2.7). Globally, the proposed scenario led to an operational cost of 4.3 c€/m³ of wastewater, 26% lower than for the conventional STP.

2.4. CONCLUSIONS

The implementation of RBFs before CEPT was proven effective for generating suitable effluents for a nutrient removal stage, maximising the energy recovery via the AD of the generated sludges, attaining almost 100% of the electrical autarky and achieving OMP removal that is as substantial as that obtained in CEPT, and decreasing the required dose 3-fold. However, a minimum alkalinity level in wastewaters was shown mandatory to consider this configuration as more economically favourable with respect to the conventional STP
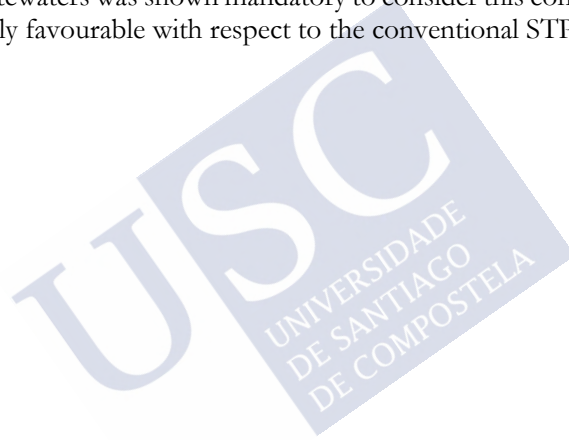
CHAPTER 3

COMPARISON BETWEEN CHEMICALLY
ENHANCED PRIMARY TREATMENT AND
HIGH-RATE ACTIVATED SLUDGE IN
NOVEL SEWAGE TREATMENT PLANTS
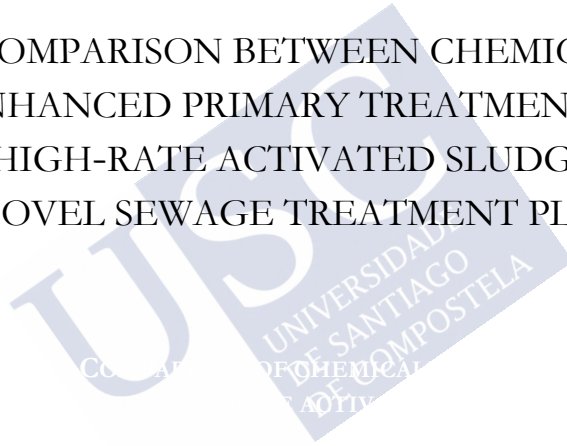
SUMMARY

In this chapter, two different alternatives, such as chemically enhanced primary treatment (CEPT) and high-rate activated sludge (HRAS) are compared in terms of energy demand, operational costs and organic micropollutants (OMPs) and viruses removal in novel sewage treatment plants (STPs). For this purpose, a CEPT pilot-scale plant operated at a hydraulic retention time (HRT) of 30 min and a lab-scale HRAS reactor working at a HRT of 2h and a solid retention time (SRT) of 1 d were operated in continuous mode. A minimum dose of 150 mg/L of ferric chloride ($FeCl_3$) was needed to achieve a threshold chemical oxygen demand (COD)-to-ammonium (NH_4^+) ratio below 2 g COD to g of NH_4^+-N , aiming at fulfilling the requirement for a partial nitritation-anammox (PN-AMX) reactor, reaching high phosphate (PO_4^{3-}) removal efficiency (>99%). A slightly lower (70 vs 84%) COD recovery as biomass was attained in HRAS reactors, due to the partial oxidation of influent COD (15%). The lower PO_4^{3-} removal efficiency achieved in the HRAS alternative (13%) was enhanced to a comparable value of that achieved in CEPT by the addition of 30 mg/L of $FeCl_3$ at the clarifier. The alternative based on CEPT was identified less energetically demanding (0.07 vs 0.13 kWh/m³ of wastewater) but with significantly higher operational costs than the HRAS-based STP (6.0 *vs* 3.8 c€/m³ of wastewater). Regarding OMPs, for those presenting kbiol > 10 L/g$_{VSS}$·d in the biological unit, considerably higher removal efficiencies were achieved in HRAS (80-90%) than in CEPT (4 -55%). For the rest of OMPs removal efficiencies were in general higher in HRAS than in CEPT, but in both configurations below 55%. Finally, CEPT was also less efficient than HRAS for viral removal regardless the virus studied. The comprehensive analysis of all results allows to conclude that HRAS followed by $FeCl_3$ post-treatment appears as a better alternative than CEPT for COD recovery in novel STPs.

3.1. INTRODUCTION

In novel sewage treatment plants (STPs) organic carbon is proposed to be recovered in a first stage, followed by a partial nitritation-anammox (PN-AMX) unit, and subsequently used to produce biogas in anaerobic digesters (AD). For that purpose, different preconcentration alternatives for chemical oxygen demand (COD) recovery such as chemically enhanced primary treatment (CEPT) (Jang et al., 2017; Li et al., 2017) or high-rate activated sludge (HRAS) (Ge et al., 2017; Jimenez et al., 2015) can be applied.

However, not only energetical and economic reasons but also environmental and health aspects must be considered in the design of novel STPs. New challenges in wastewater policy concerning organic micropollutants (OMPs) have promoted that some countries such as Switzerland, have already established OMPs discharge thresholds in STP effluents (GSchVSchweiz, 2016). Likewise, other countries such as Austria, Germany and The Netherlands are considering some initiatives to enhance the removal of OMPs during wastewater treatment, to achieve an overall elimination of 80% (Benstoem et al., 2017).

Many papers studying the removal of OMPs under aerobic conditions identified factors such as the hydraulic retention time (HRT) and the solid retention time (SRT) as key factors governing their removal efficiency (Clara et al., 2005; Fernandez-Fontaina et al., 2016; Radjenović et al., 2009; Santos et al., 2009). The HRAS technology is characterized by much lower HRT (0.25-4 h) and SRT (0.5-2 d), (Ge et al., 2017; Jimenez et al., 2015) than those applied in conventional activated sludge (CAS) reactors (12-24 hours of HRT and more than 10 days of SRT) (Santos et al., 2009; Suarez et al., 2010), what is expected to lead to significantly lower OMPs removal efficiency. Regarding CEPT, the reported OMPs removal efficiencies are quite controversial; whereas some authors found that CEPT contributes to the removal of some compounds which are precipitated in the flocs formed in the process (Asakura and Matsuto, 2009; Carballa et al., 2005; Suarez et al., 2009) others reported no significant removal for most of them (Westerhoff et al., 2005). The causes of the discrepancies are still under discussion, but wastewater physico-chemical characteristics such as pH, alkalinity, temperature, fats or dissolved organic matter might have either positive or negative effects on OMPs removal (Luo et al., 2014; Suarez et al., 2009).

Another emerging aspect of growing interest is related to the presence of viruses in STPs effluents, since conventional STPs fail to ensure the complete removal of viral pathogens (Da Silva et al., 2007). Norovirus (NoV) (family Caliciviridae) is considered one of the major etiological agents of acute sporadic and epidemic gastroenteritis worldwide (Atmar and Estes, 2006; Koopmans and Duizer, 2004;

Rodríguez-Lázaro et al., 2012). Likewise, viruses such as Sapovirus (family Caliciviridae) have also emerged as important enteric pathogens (Oka et al., 2015). Hepatitis A virus (HAV) (family Picornaviridae) is less common in countries with a high standard of hygiene, although it risks leading to more severe disease outcomes (Hollinger and Emerson, 2007). As pathogens with fecal-oral route of transmission, HAV, NoV and Sav are shed in high numbers in the feces of infected individuals (Atmar and Estes, 2006) and are common in sewage also at high numbers (Sassi et al., 2018). Removing or inactivating viruses in STPs is still challenging, despite the developments in secondary and tertiary processes (Schmitz et al., 2016).

The goal of this chapter is to holistically determine the most favourable alternative between two novel configurations of STPs based on CEPT and HRAS for organic matter recovery considering energy demand, operational costs and OMPs and viruses removal.

3.2. MATERIALS AND METHODS

3.2.1. Wastewater and sludge samples

The wastewater used in this work was collected from a urban STP located in Santiago de Compostela (NW of Spain). The STP is designed for 184,000 population equivalent with an average wastewater flowrate of approximately 55,000 m^3/d. Wastewaters were characterised in terms of pH, total suspended solids (TSS, g TSS/kg) and volatile suspended solids (VSS, g VSS/kg), total chemical oxygen demand (COD$_{tot}$, g O$_2$/L) and soluble (COD$_{sol}$, g O$_2$/L), ammonium (g NH$_4^+$-N/L), phosphate (g PO$_4^{3-}$-P/L) according to Standard Methods (APHA, 2005). Inorganic carbon (IC) was determined by a Shimadzu analyser (TOC-5000).

3.2.2. Chemically enhanced primary treatment

3.2.2.1. Jar-test experiments

CEPT tests assays were carried out in a Jar-Test device with vessels of 1 L of liquid volume following the protocol described by Carballa et al. (2005), but in this case without pH neutralization.

Two coagulants widely used for coagulation processes such as ferric chloride (FeCl$_3$) and ferric sulphate (Fe$_2$(SO$_4$)$_3$) (Jang et al., 2017; Liang et al., 2019) were evaluated. The test include an initial 3 min period of rapid stirring (150 rpm) after the addition of the coagulant, followed by 5 min of slow mixing (50 rpm) for emulsion breaking and floc formation, and finally 30 minutes period without mixing for floc separation, after which 500 mL of supernatant were collected for the characterisation. The influence of coagulants dose (0-300 mg/L) on pH and

on the removal of TSS, VSS, COD_{tot}, COD_{sol}, IC, NH_4^+-N and PO_4^{3-}-P was studied at 25°C.

3.2.2.2. *Continuous pilot plant*

The pilot plant used, described by Suarez et al. (2009), consists of three main sections; (i) a 4.4 L coagulation tank with a fixed-speed stirrer; (ii) a 15 L flocculation tank provided with a speed-regulated stirrer; and (iii) a 35-L lamellar settler with 10 stainless steel (AISI-304) plates. The operational conditions were selected from the results obtained in batch experiments to optimise the coagulant selection and dose. The wastewater flowrate was fixed at 70 L/min to achieve a HRT of 30 min in the lamellar settler section, with continuous addition of $FeCl_3$ (selected from the Jar-test results). After 90 min of steady operation of the pilot plant (corresponding to 3 HRT), the effluent was sampled and characterized in terms of pH, COD_{tot}, COD_{sol}, TSS, VSS, NH_4^+-N, PO_4^{3-}-P, IC, OMPs and viruses concentrations.

3.2.3. *High-rate activated sludge reactor*

A 2-L continuous stirred-tank reactor coupled to a 1-L settler was inoculated with biomass collected from a heterotrophic activated sludge reactor from a STP in Madrid, Spain, working at a SRT of 2.5-3 d. It was operated at a HRT of 2 h (plus 1 h in the settling tank). Target SRT was 1 d, this being controlled by wasting sludge from the bottom of the settler (10 times per day). Dissolved oxygen (DO) concentration was maintained between 3 and 3.5 mg O_2/L, without neither temperature nor pH control (Ge et al., 2017). After inoculation, the reactor was operated for 80 days (15 days of biomass adaptation + 65 days of steady-state operation). Biomass target concentration in the reactor was 2 g VSS/L, although it ranged between 2 and 3 g VSS/L due to some operational difficulties to control it. Reactor walls were scratched every day to remove biofilm formation which could eventually increase the effective SRT.

Influent and effluent of the reactor was sampled every day and characterized in terms of pH, COD_{tot}, COD_{sol}, TSS, VSS, NH_4^+-N, PO_4^{3-}-P and IC. Four sampling campaigns for OMPs measurement in the influent and effluent were carried out on days 18, 33, 48 and 63 of operation. Two sampling campaigns for viruses measurement were carried out, on days 18 and 48. On day 18 the effluent of the HRAS reactor was collected and treated with $FeCl_3$ (0-30 mg/L) in Jar-test devices as explained in section 2.4.1 to assess the influence on PO_4^{3-}, OMPs and viruses removal efficiency.

Sludge was also sampled every day and characterized in terms of COD_{tot}, TSS and VSS. The fraction of COD oxidized to CO_2 was calculated from the COD

balance as considering the COD fed to the reactor, the COD recovered in the sludge and the COD in the effluent.

3.2.4. Energetic evaluation

As calculation basis, a typical medium-strength urban wastewater with a COD_{tot} of 500 mg/L and an ammonium concentration of 25 mg NH_4^+-N/L was considered (Metcalf & Eddy, 2003; Wan et al., 2016). In the biogas line, a methane heat combustion of 11 kWh/m^3 (N) CH_4 (Perry, 1984) and electrical efficiency (η) of 0.35 in the co-generation motor (Mills et al., 2014) were assumed. The energy consumption considered in the different technologies studied in this work is gathered in Table 3.1.

In order to determine the expected methane production in each configuration, biomethane potential (BMP) tests of the different sludges (sludge from the continuous operation of the CEPT pilot plant and from the purge of the HRAS reactor) were carried out in an AMPTS II equipment (Bioprocess Control), The tests were conducted in 2 L bottles (1.9 L of working volume) in triplicate and with an ISR (inoculum to substrate ratio in terms of VSS) of 2, following the protocol described by Holliger et al. (2016).

The inoculum was anaerobic flocculant biomass (15-20 g VS/L) from a mesophilic sewage sludge anaerobic digester. After flushing the head space of the reactors with nitrogen, they were incubated at 37ºC. The assays lasted till CH_4 production during three consecutive days was less than 1% of the total production. CH_4 production by each sludge was calculated as the difference between the average production in the bottles with substrate minus the average production in the blank (residual production of the inoculums). BMP was calculated as the experimental ultimate methane production, expressed in L(N)/kg VS fed, where N means normal conditions (1 atm, 0ºC). Anaerobic biodegradability (AB) was expressed as the percentage of the initial COD of the substrate converted to methane. At the end of the test, bottles were opened and pH and volatile fatty acids (VFAs) concentrations were measured to confirm that no acidification occurred.

3.2.5. Economic evaluation

A $FeCl_3$ and electricity costs of 220 €/ton and 0.12 €/kWh, respectively, were considered for the evaluation (De Feo et al., 2008; STOWA, 2012) and a hygienization cost for composting of digested sludge of 80 €/ton TS was assumed (Management Company, 2019). Eq. 2.1-2.3 from Chapter 2 were applied to assess digested sludge production.

Table 3.1. Literature data considered for the STP energetic evaluation.

Technology	Energy demand
Wastewater pumping	0.03 kWh/m^3 wastewater (Longo et al., 2016)
Chemically enhanced primary treatment	0.03 kWh/m^3 wastewater (Longo et al., 2017)
High-rate activated sludge reactor	0.07 kWh/m^3 wastewater (Smith et al., 2014)
Sludge recirculation	0.03 kWh/m^3 wastewater (Longo et al., 2016)
Sludge thickening	0.02 kWh/m^3 wastewater (Longo et al., 2016)
Chemicals addition (tertiary treatment)	0.01 kWh/m^3 wastewater (Longo et al., 2016)
Partial nitritation-anammox reactor	*0.20-0.25 kWh/m^3 wastewater (Schaubroeck et al., 2015)
Sludge dewatering	0.03 kWh/m^3 wastewater (Longo et al., 2016)

* Calculated as 60% of those of a conventional activated sludge reactor (0.42 kWh/m^3 of wastewater according to Gikas (2017))

3.2.6. Organic micropollutants

18 compounds commonly used in daily life were considered in this study: three musk fragrances: galaxolide (HHCB), tonalide (AHTN) and celestolide (ADBI); three anti-inflammatories: ibuprofen (IBP), naproxen (NPX) and diclofenac (DCF); four anti-biotics: sulfamethoxazole (SMX), trimethoprim (TMP), erythromycin (ERY) and roxithromycin (ROX); four neurodrugs: fluoxetine (FLX), carbamazepine (CBZ), diazepam (DZP) and citalopram (CTL); one endocrine disrupting compound, triclosan (TCS); and three hormones: estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2). To ensure their presence in wastewater, OMPs were spiked at the influent stream, according to in the range of the values reported by Luo et al. (2014) and Verlicchi et al. (2012) 20 ppb for musk fragrances, 1 ppb for hormones and 10 ppb for the others).

The protocol described in Chapter 2 was used to characterize the dissolved and sorbed OMPs concentrations. The volume concentrated was 250 mL and the final volume of extract was 3 mL, leading to an enrichment factor of 83 $L_{supernatant}/L_{extract}$. For the solid phase the enrichment factor was 500 $g_{sludge}/L_{extract}$.

Total OMPs concentration was considered in the analysis of influent (Eq.3.1), whereas for effluent only soluble concentration was measured due to its very low TSS concentration.

$$C_{j,total} = C_{j,dissolved} + TSS \cdot C_{j,solid} \qquad \qquad \textit{Equation 3.1}$$

where, $C_{j,total}$ is the total concentration of compound j (μg/L), $C_{j,dissolved}$ is the soluble concentration of compound j (μg/L), $C_{j,solid}$ is the concentration in the solid phase (μg/g) and TSS the suspended solids content (g/L) of the stream.

Mass balances of OMPs in the biological unit were calculated by Eq. 3.2, after achieving steady-state conditions, assuming a continuous stirred tank reactor (CSTR) model.

$$F_{biod} = F_{inf} - F_{eff} - F_{sorb} \qquad \qquad \textit{Equation 3.2}$$

where F_{inf}, F_{eff}, F_{sor} represent mass flows (in μg/d) corresponding to the influent, effluent and sorbed onto solids. Biotransformation kinetic constants (k_{biol}, in L/gVSS day) were obtained considering pseudo-first order kinetics (Eq. 3.3).

$$F_{biod} = k_{biol} \cdot VSS \cdot C_{eff} \cdot V \qquad \qquad \textit{Equation 3.3}$$

where C_{eff} is the OMP concentration in the effluent (μg/L), VSS is the biomass concentration in the reactor (g VSS/L) and V is the reactor volume (L).

3.2.7. *Viruses*

Viral particles were concentrated using the skimmed milk flocculation (SMF) method described by Fernandez-Cassi et al. (2018). Briefly, wastewater (5 L) was preconditioned to a pH of 3.5, and 50 mL of a pre-flocculated skim milk solution at pH 3.5 and a conductivity superior to 1.5 mS/cm^2 was added to each sample. After 8 h of stirring, flocks were centrifuged at 8,000 × *g* for 40 min, and the pellet was suspended in 15 mL of PO$_4^{3-}$ buffer [v/v] (0.2 M Na$_2$HPO$_4$ and 0.2 M NaH$_2$PO$_4$). The viral concentrates were kept at − 80 °C until further use.

The viral RNA from each sample was extracted in duplicate using the commercial kit NucleoSpin® RNA Virus kit (Macherey-Nagel, Dürem, Germany) according to the manufacturer's protocols. Following the ISO 15216-1:2017 standard method (ISO, 2017), mengovirus clone (vMC0) and external controls were employed to determine the extraction and amplification efficiencies respectively, as previously described (Varela et al., (2018). According to this standard procedure, samples with <5% extraction efficiency or <25% RT-qPCR efficiency were re-extracted and tested again.

RT-qPCR for HAV, NoV (GI and GII) and SaV was performed on an Mx3005p QPCR System (Stratagene; USA) thermocycler. Platinum® Quantitative RT-PCR ThermoscriptTM One-step System kit (Invitrogen; France). Primers and probes used for virus detection and quantification were described elsewhere (Costafreda et al., 2006; Da Silva et al., 2007; Svraka et al., 2007; Kageyama et al., 2003; Loisy et al., 2005; Oka et al., 2006; Varela et al., 2018). Amplification conditions were reverse transcription at 55 °C for 30 min, denaturation at 95 °C for 5 min, followed by 45 cycles of amplification with a denaturation at 95 °C for 15 s, annealing at 60 °C (50ºC for SaV) for 1 min and extension at 65 °C for 1 min.

Viral RNA was tested undiluted and at ten-fold dilution to reduce the effect of potential RT-PCR inhibitors. Negative controls containing no nucleic acid as well as positive controls were introduced in each run. Quantification was estimated by standard curves constructed with serial dilutions of RNA in the case of HAV and RNA transcripts for NoV GI, GII and SaV plotting the number of genome copies against the Ct. Results were expressed as number of RNA viral genome copies per litre of wastewater sample.

3.3. RESULTS AND DISCUSSION

3.3.1. *Wastewater physico-chemical characterization*

The physico-chemical characteristics of wastewater, in the typical range for urban STPs influents (Metcalf & Eddy, 2003), are shown in Table 3.2. The important

fluctuations of the measured parameters are mainly due to the dilution caused by rainfalls, since the city has not a separated sewer system (Carballa et al., 2005).

Table 3.2 Wastewater physico-chemical characterization.

Parameter	Value
pH	7.2-7.8
COD_{tot} (mg/L)	375-750
COD_{sol} (mg/L)	80-150
TSS (mg/L)	330-780
VSS (mg/L)	300-540
NH_4^+-N (mg/L)	30-60
PO_4^{3-}-P (mg/L)	1.9-2.6
IC (mg /L)	30-65

3.3.2. Chemically enhanced primary treatment

3.3.2.1. Coagulants selection

$FeCl_3$ and $Fe_2(SO_4)_3$ were selected as potential coagulants and tried and compared in Jar-Test in terms of COD_{sol} and COD_{part} removal efficiency (Figure 3.1). $FeCl_3$ led to slightly higher pH drop and higher removal efficiencies than $Fe_2(SO_4)_3$ when the same coagulant dose was added.

However, when the comparison was carried out in terms of mg of Fe_3^+ added rather than coagulant dose (Figure 3.2A), it can be observed that very comparable results were obtained, indicating that the coagulant anion has no influence in the CEPT. Moreover, very similar inorganic carbon (IC) consumption (46 mg IC per 100 mg Fe_3^+) was obtained with both coagulants (Figure 3.2B). Therefore, $FeCl_3$ was selected as the best coagulant since it led to a higher removal efficiency under the same coagulant dose.

3.3.2.2. Jar-test results

After the addition of $FeCl_3$, COD_{part} was completely removed with a dose of 150 mg/L (Figure 3.1A), similar concentration to those used by other authors in urban STPs (Mbamba et al., 2019). Under these conditions a COD_{tot} removal efficiency of 88% was achieved, and higher doses barely enhanced COD_{tot}. A noticeable pH dropped from 7.8 to 6.8 was observed under these conditions, which was even higher with higher $FeCl_3$ doses.
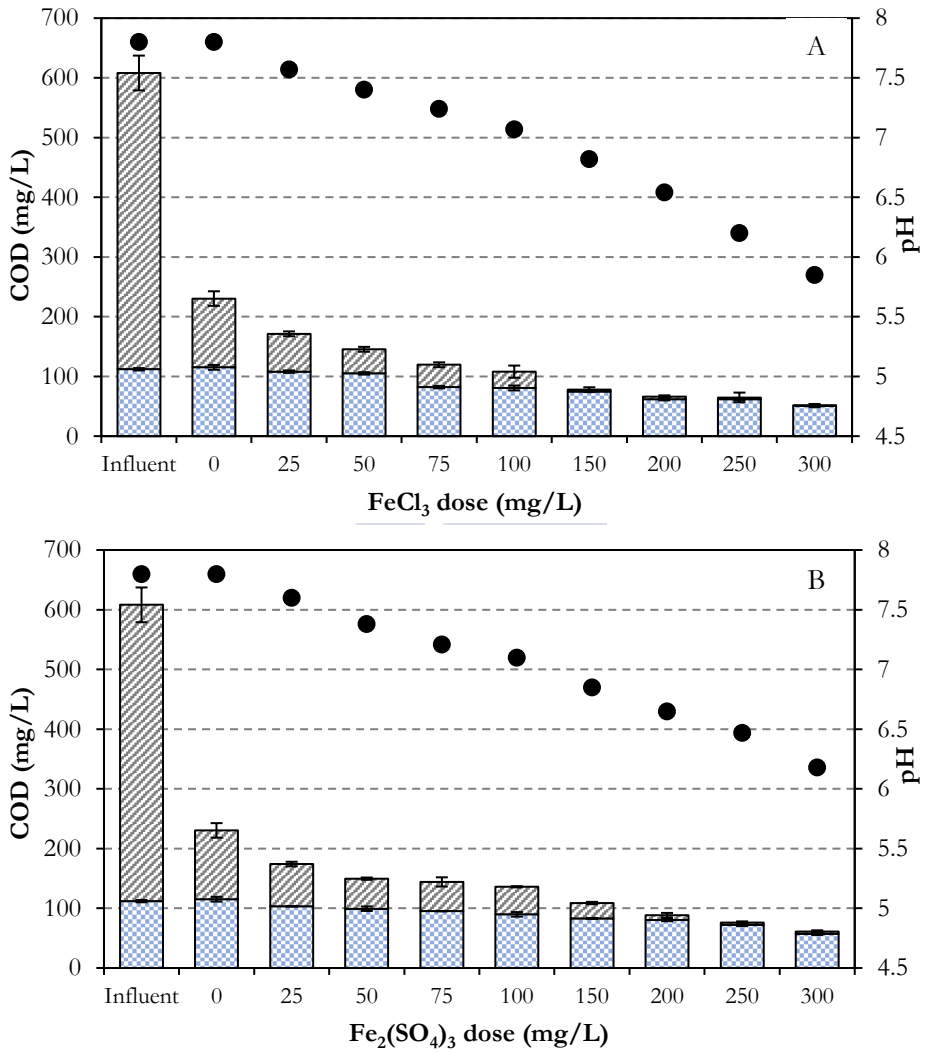
Figure 3.1. Influence of (A) FeCl₃ dose and (B) Fe₂(SO₄)₃ dose on: pH decrease (●) and on the removal of soluble (▨) and particulate (▨) COD. * 0 mg /L refers to settling without coagulant addition.
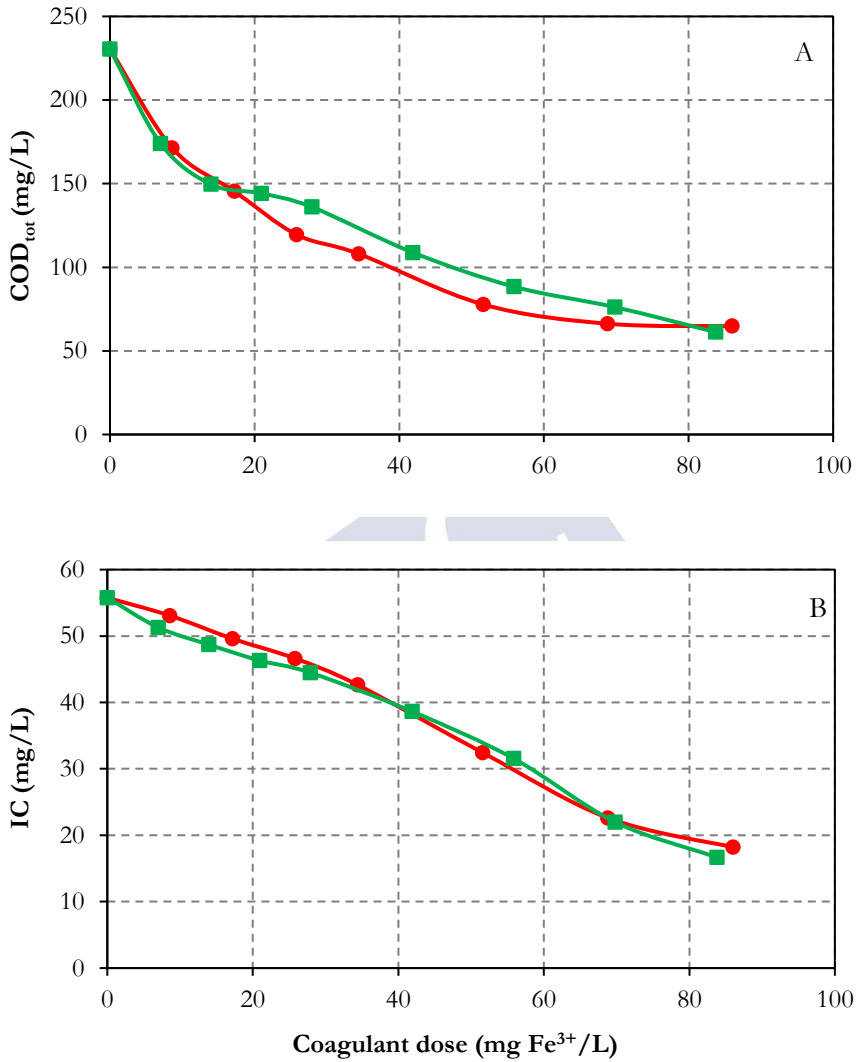
Figure 3.2. (A) Influence of FeCl$_3$ dose (⬤)and Fe$_2$(SO$_4$)$_3$ dose (■) on: (A) effluent COD$_{tot}$ and (B) effluent alkalinity .

Figure 3.3 displays the influence of $FeCl_3$ on IC, PO_4^{3-}-P and NH_4^+-N concentration. Whereas PO_4^3 removal efficiency was above 99% with doses from 100 mg/L of $FeCl_3$, in accordance with Diamantis et al. (2013), reaching a discharge limit of 0.2 mg PO_4^{3-}-P/L (Mbamba et al., 2019). IC showed a total concentration decrease of 22 mg/L, and NH_4^+ concentration stayed unaffected.
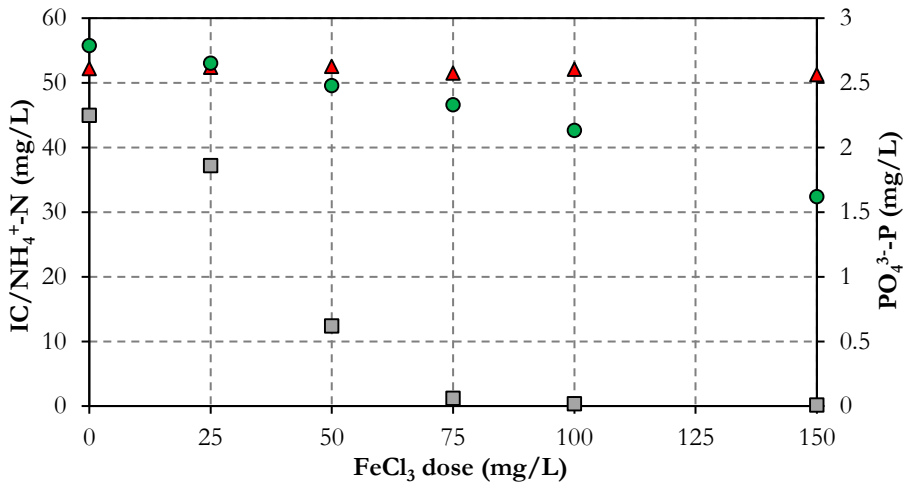
Figure 3.3. Influence of $FeCl_3$ dose on the removal of PO_4^3-P (▢), NH_4^+-N (▲) and alkalinity (●). * 0 mg /L refers to settling without coagulant addition.

3.3.2.3. Pilot plant operation

The results from the Jar-tests experiments were validated in a continuous pilot plant under different wastewater characteristics but maintaining a $FeCl_3$ dose of 125-150 mg/L, achieving very comparable results to those of the batch tests regardless wastewater characteristics (Figure 3.4A and 3.4B); COD_{part} removal was almost completely removed, whereas for COD_{sol} a partial elimination was achieved.

Under these conditions, a COD_{tot} to NH_4^+-N ratio close to 1 was achieved, this being suitable for a PN-AMX unit according to Jin et al. (2012), who reported system failure with a COD_{tot} to NH_4^+-N ratio above 2 due to the growth of heterotrophic denitrifiers which compete for nitrite. However, a minimum alkalinity-to-ammonium ratio of 1-1.25 g IC to g NH_4^+-N was reported as threshold to prevent the PN-AMX unit from acidification (Pedrouso et al., 2017) and subsequent inhibition due to the formation of free nitrous acid (Jin et al., 2012), so depending on the alkalinity and NH_4^+ concentration in wastewater an external alkalinity dose could be required, substantially increasing the treatment costs.
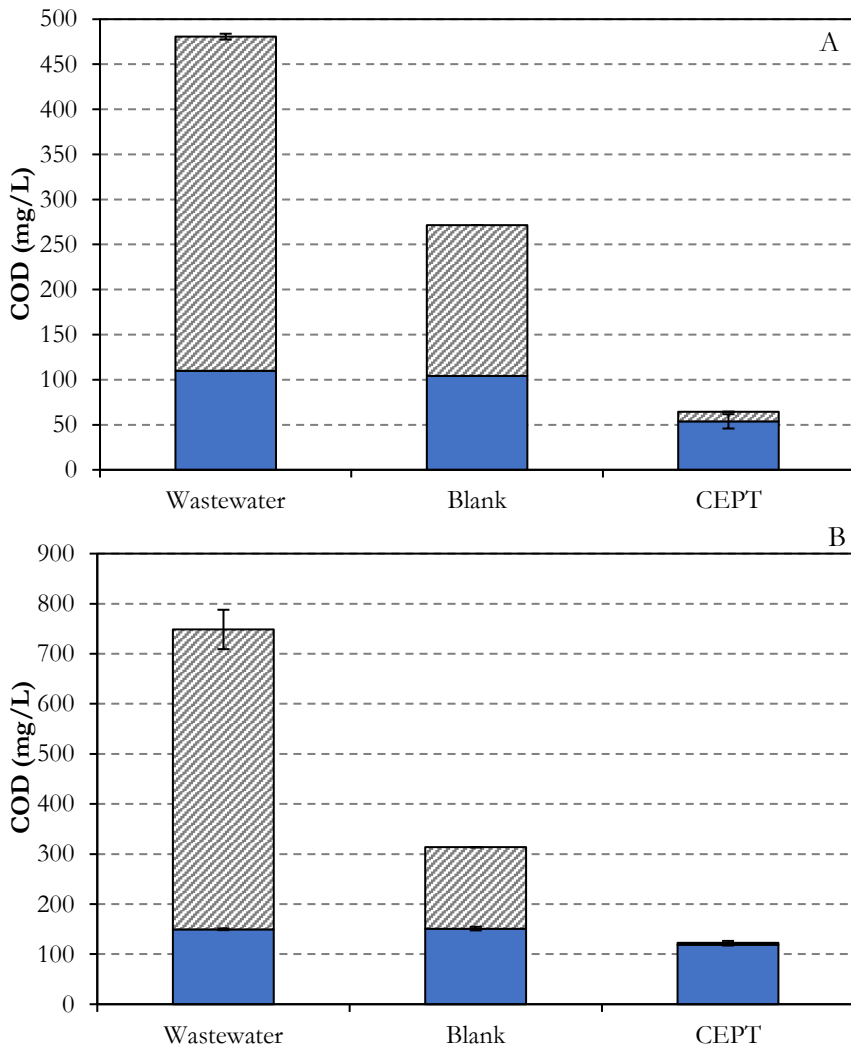
Figure 3.4. Influence of FeCl$_3$ dose on the removal of soluble (■) and particulate (▨) COD during the continuous operation of the pilot plant. Blank refers to settling without chemicals and CEPT to the treatment with 125-150 mg/L of FeCl$_3$.

3.3.3. High-rate activated sludge

The results of the operation of the HRAS reactor are summarised in Table 3.3. COD removal efficiency was approximately 90%. However, COD recovery as sludge was slightly lower than in CEPT(71%), due to the partial oxidation of

wastewater COD (averaged at 16% , which might be reduced working at lower HRT and/or SRT to maximize COD capture (Ge et al., 2017; Jimenez et al., 2015).

Table 3.3. Summary of the operation of the HRAS reactor.

Parameter	Value
pH	7.4 ± 0.3
SRT (d)	0.9 ± 0.1
VSS (mg VSS/L)	2.3 ± 0.4
$COD_{removal}$ (%)	87 ± 4
$COD_{recovery}$ (%)	71 ± 5
$COD_{oxidation}$ (%)	16 ± 10
$NH_4^+{}_{removal}$ (%)	19 ± 4
$PO_4^{3-}{}_{removal}$ (%)	13 ± 4
$IC_{removal}$ (mg IC/L)	5 ± 1

NH_4^+ and PO_4^{3-} removal efficiencies resulted on 19% and 13%, respectively, and attributed to biomass growth. These results are in the range of those found elsewhere (Ge et al., 2017; Laureni et al., 2016), and also in accordance with Chan et al. (2017), who found that a minimum SRT of 3.6-4 days is needed to obtain a proper PO_4^{3-} removal. An average decrease of approximately 5 mg IC/L was observed, much lower than in the CEPT- based STP. Therefore, the effluent of the HRAS reactor would satisfy the requirements for a PN-AMX unit (Jin et al., 2012; Pedrouso et al., 2017) not only in terms of both IC-to- NH_4^+ ratio but also on COD-to-NH_4^+ ratio. However, the effluent does not fulfil discharge limit of 0.2 mg PO_4^{3-}-P/L (Mbamba et al., 2019) so a further removal through chemical precipitation in the clarifier was studied, according to the recommendations of Longo et al. (2017). By the addition of 10, 20 and 30 mg/L of $FeCl_3$, PO_4^{3-}-P concentration in the effluent decreased to 1.1 mg PO_4^{3-}-P/L, 0.5 mg PO_4^{3-}-P/L and 0.2 mg PO_4^{3-}-P/L, respectively. Thus, 30 mg/L was selected as the required $FeCl_3$ dose to carry out the economic evaluation and to assess the OMPs and viruses removal efficiency.

3.3.4. Sludges characterization and biochemical methane potential tests

Table 3.4 presents the physico-chemical characterisation of the sludges generated in CEPT and in both HRAS reactors. CEPT sludge presented a slightly higher COD_{tot}-to volatile solids (VS) ratio (1.68) than the sludge from HRAS reactor (1.59), explained by a higher fat recovery. In terms of VS-to-total solids (TS) ratio, CEPT sludge displayed a lower value (0.69) than that from the HRAS scenario (0.75), mainly due to the precipitation of inorganic compounds after

FeCl$_3$ addition (De Feo et al., 2008). These values were in accordance with other results in the literature for primary and mixed sludge (Astals et al., 2012; Carballa et al., 2007b; Paulsrud et al., 2014).

Table 3.4 Sludges physico-chemical characterisation. CEPT: chemically enhanced primary treatment sludge, HRAS: high-rate activated sludge.

Parameter	CEPT	HRAS
TS	34.2 ± 0.1	20.1 ± 0.1
VS	23.4 ± 0.1	19.3 ± 0.1
COD$_{tot}$	39.3 ± 4.5	24.0 ± 0.3
COD$_{tot}$/VS	1.68 ± 0.19	1.59 ± 0.04
VS/TS	0.69 ± 0.1	0.75 ± 0.01

Figure 3.5 displays the results of the BMP test of the sludges considered in this work. The results for CEPT sludge (301 L(N) CH$_4$/ kg VS, 51 % of AB) are in the range of those reported by Paulsrud et al. (2014) for sludges from conventional primary treatment, indicating that although Fe^{3+} reduction is thermodynamically more favourable, it did not limit the conversion of organics to methane (Romero-Güiza et al., 2016; Zhang et al., 2009). Regarding HRAS, although there is extensive research focused on AD of long SRT (>10 d) sludges, the evaluation of those sludges produced at short SRT it is still quite limited (especially below 5 d). HRAS sludge showed a BMP of 295 L(N) CH$_4$/ kg VS (corresponding to 53 % of AB). These values are a bit lower than those found by Ge et al. (2013), who reported a 60% of AB for HRAS sludges working at SRT of 2 d.
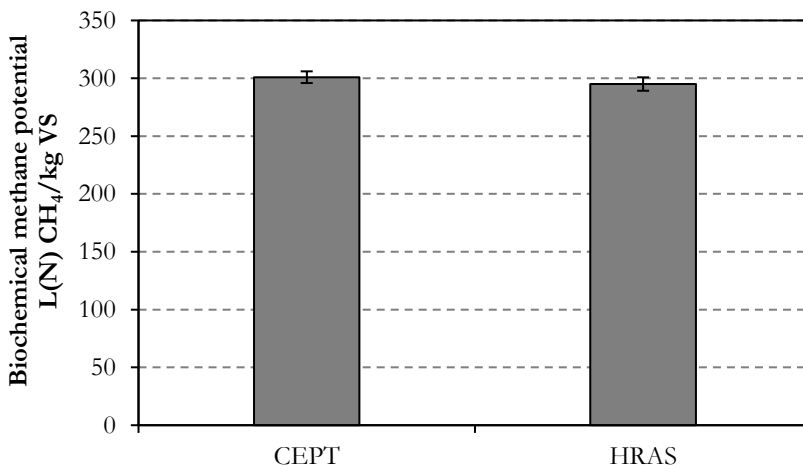
Figure 3.5. Average and standard deviation of the biomethane potential of each sludge.

The neutral pH values (7.3-7.5) and the absence of VFA (<2.5 ppm acetic acid) at the end of the tests (data not shown) indicate that the performance of the tests was adequate and no acidification occurred.

3.3.5. Energetic evaluation

Figure 3.6 represents the energy flow in the STP based on: CEPT (A) and HRAS (B). The HRAS-based STP presents a higher energy demand for COD removal (0.1 kWh/m³ wastewater) due to aeration (0.07 kWh/m³ wastewater), and sludge recirculation (0.03 kWh/m³ wastewater). Moreover, considering that a partial ammonium removal is achieved in this unit, the energy demand of the PN-AMX unit resulted on 0.20 kWh/m³ wastewater, whereas the energy consumption in the PN-AMX unit of the CEPT-based STP reached a higher value of 0.25 kWh/m³ wastewater. For the HRAS-based STP, additional 0.01 kWh/m³ wastewater are required to dose the coagulant to enhance PO_4^{3-} removal. Finally, in both alternatives 0.05 kWh/m³ of wastewater are needed for i) sludge thickening before AD (0.02 kWh/m³ of wastewater) and ii) further sludge dewatering (0.03 kWh/m³ of wastewater). Therefore, considering all the energy inputs, both configurations present a comparable energy demand; CEPT approximately 0.36 kWh/m³ wastewater (Figure 3.6A) and HRAS 0.39 kWh/m³ wastewater (Figure 3.6B).
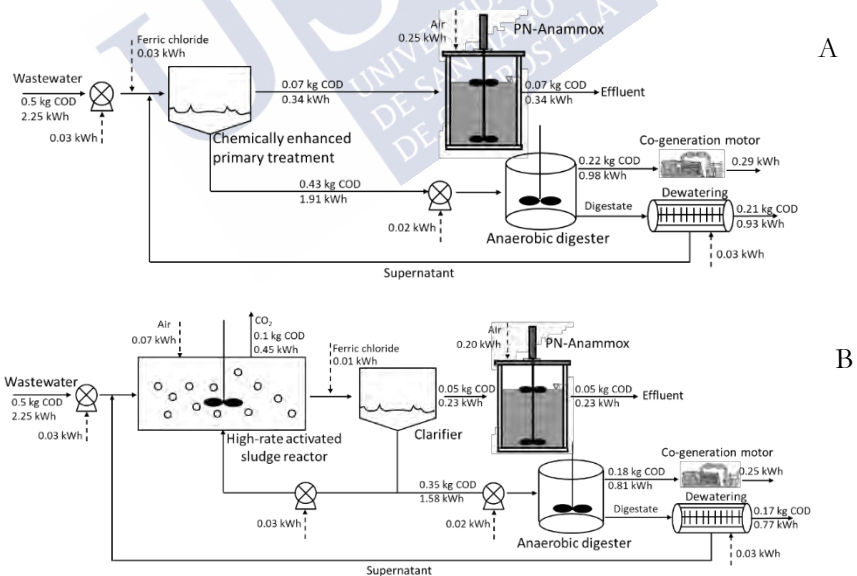
Figure 3.6. STP configurations studied in this work based on: A) CEPT and B) HRAS:

Higher COD recovery from wastewater is obtained in the CEPT-based STP, so higher methane production is achieved (0.29 kWh/m³ of wastewater) in comparison with the HRAS-based one (0.25 kWh/m³ of wastewater). The overall STP balance shows that the CEPT-based STP presents a lower energy demand (0.07 kWh/m³ of wastewater) than the HRAS-based one (0.13 kWh/m³ of wastewater).

3.3.6. Economic evaluation

The operational costs include electricity, chemicals and sludge management. As explained in the previous section, the CEPT-based STP demands up to 0.8 c€/m³ of wastewater while the HRAS-based STP consumes 1.7 c€/m³ of wastewater (Figure 3.7). Besides, a 20% higher digested solids production was achieved in the CEPT alternative (0.23 kg TSS/m³ of wastewater) than in the HRAS-based STP (0.18 kg TSS/m³ of wastewater), due to the higher COD recovery attained in this alternative and also to the higher presence of inorganics in CEPT sludge, this meaning 1.9 and 1.4 c€/m³ of wastewater for CEPT and HRAS-based STPs, respectively (Figure 3.7). Finally, the coagulant represents in the CEPT and HRAS-based STPs 3.3 and 0.7 c€/m³ of wastewater, respectively.

Considering jointly all costs, the alternative based on CEPT leads to significantly higher operational costs (6.0 c€/m³ of wastewater) in comparison with the HRAS-based STP (3.8 c€/m³ of wastewater). Moreover, it must be highlighted that for the CEPT-based STP the most optimistic situation was evaluated, considering that these operational costs would be higher if an external alkalinity supply was needed.
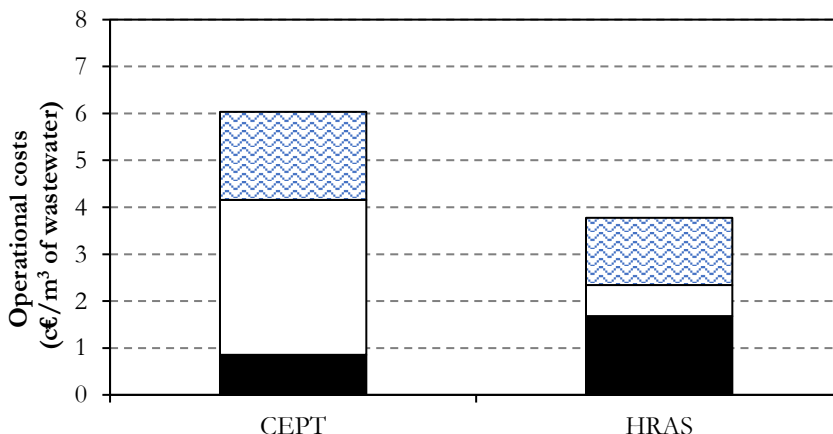
Figure 3.7. STP operational costs due to energy (■), coagulant (□) and sludge management (▨).

3.3.7. Fate of organic micropollutants

3.3.7.1. Chemically enhanced primary treatment

Even though it seems to be a consensus in the literature that most OMPs are poorly removed during CEPT, some authors reported that the different compositions of wastewater can play a major role in OMPs elimination. For example, a high fat content in wastewater was reported to improve the removal of hydrophobic compounds (log solid-liquid equilibrium constant $(K_D)>3.5$, Table 3.5). In contrast, the presence of COD_{sol}, might inhibit the OMPs removal efficiency due to the preference of the coagulant for COD_{sol} (Choi et al., 2008; Vieno et al., 2006). A medium-low removal efficiency (38%-55%) of hydrophobic OMPs (ADBI, AHTN, HHCB and TCS) was obtained (Figure 3.8). This removal is attributed to the corresponding to the sorbed fraction of these OMPs into TSS, in accordance with Suarez et al. (2009).

Table 3.5 Relative amount of OMPs sorbed onto CEPT and HRAS sludges (K_D).

OMP	K_D (L/kg TSS)		
	Influent	CEPT	HRAS
ADBI	3,856 ± 845	2,461 ± 411	4,574 ± 832
HHCB	5,927 ± 2,168	3,412 ± 679	6,853 ± 1,945
AHTN	8,857 ± 2,148	5286 ± 1,066	9,969 ± 2,557
TCS	10,439 ± 2,170	5,918 ± 225	8,748 ± 1,635
IBP	8 ± 8	15 ± 2	16 ± 16
NPX	9 ± 9	0	18 ± 12
DCF	13 ± 3	7 ± 5	21 ± 2
ERY	25 ± 10	87 ± 18	40 ± 11
ROX	54 ± 13	200 ± 25	69 ± 12
SMX	35 ± 11	45 ± 15	52 ± 20
TMP	156 ± 47	108 ± 18	188 ± 28
FLX	1,355 ± 174	1,518 ± 219	1,750 ± 575
CTL	446 ± 67	547 ± 132	667 ± 53
CBZ	50 ± 15	101 ± 21	76 ± 15
DZP	91 ± 17	141 ± 22	166 ± 14
E1	399 ± 49	322 ± 22	346 ± 150
E2	359 ± 53	265 ± 23	599 ± 19
EE2	529 ± 44	407 ± 26	464 ± 6
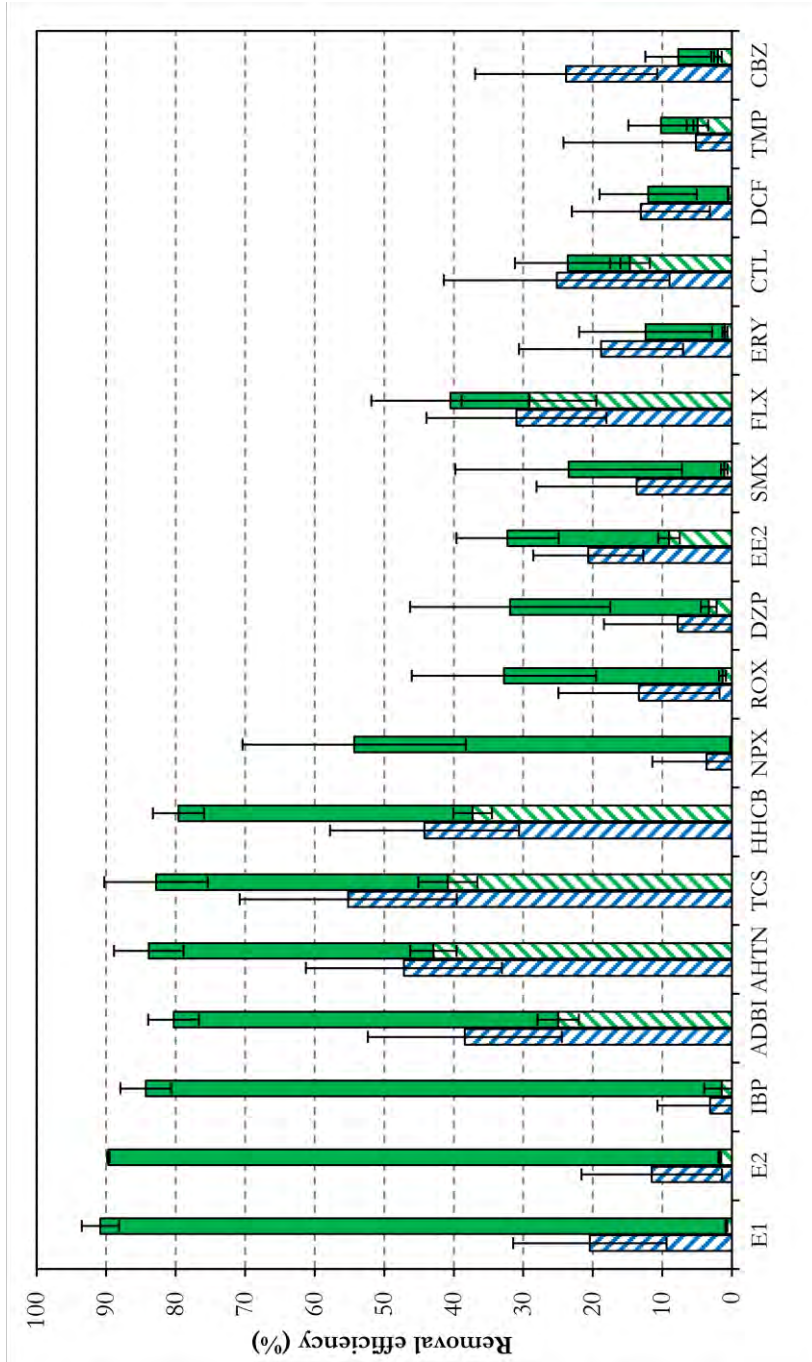
Figure 3.8. OMPs removal efficiencies in CEPT due to sorption (▨) and in HRAS due to sorption (▨) and biotransformation (■).

For hydrophilic compounds, including anti-inflammatories, antibiotics, neurodrugs and hormones, the removal efficiencies were below 31%, in accordance with other authors (Bodzek and Dudziak, 2006; Suarez et al., 2009; Westerhoff et al., 2005), but in disagreement with others who suggested that OMPs with pKa close to 7 such as IBP, SMX or NPX are well removed in CEPT process by precipitating when adding metal salts to wastewater (Carballa et al., 2005; Luo et al., 2014; Suarez et al., 2009)

3.3.7.2. High-rate activated sludge reactor

Figure 3.8 compares the removal efficiency of OMPs achieved in the HRAS reactor with that found in the CEPT process. OMPs were classified into three groups according to their behaviour in this biological unit.

Those OMPs presenting k_{biol} values >10 L/kg $_{VSS}$·d (Table 3.5) such as E1, E2, IBP, ADBI, AHTN, HHCB and TCS (Group I) are much better removed in the HRAS (>80%) unit than in the CEPT one. For musk fragrances and TCS, not only biotransformation but also sorption onto sludge significantly contributed to their removal, explained by their high K_D values also in this biological sludge (Table 3.4). Even though the applied HRT in this work is much lower than in CAS reactors and that the k_{biol} for this group of OMPs are in general lower than those reported by other authors under nitrifying conditions (Table 3.6), they are well removed under these operational conditions as well.

Group II includes OMPs such as NPX, ROX, DZP, EE2, SMX, and FLX, presenting kinetic constants in the range 1-10 L/g_{VSS}·d and biotransformation efficiencies between 20 and 55% (Figure 4). These removal efficiencies were in general lower than those found in CAS reactors and attributed to two reasons; i) the lower k_{biol} values found in this work in comparison with those reported in CAS reactors for OMPs such as ROX, EE2 and FLX (Table 3.6), proving the major role of nitrifiers on the biotransformation of most of the OMPs (Fernandez-Fontaina et al., 2016; Men et al., 2017)and ii) the low HRT applied in this reactor that kinetically limits the biotransformation of OMPs such as NPX or DZP, which present comparable or higher k_{biol} values under heterotrophic than under nitrifying conditions.

Finally, in Group III are included OMPs such as ERY, CTL, DCF, TMP and CBZ, which present k_{biol} values lower than 1 L/g_{VSS}·d (Table 3.6) and subsequent biotransformation efficiencies below 25% (Figure 4). In the case of ERY and CTL, the k_{biol} values found in this work are again much lower than those reported in CAS systems (Table 3.6). Contrary, DCF, TMP and CBZ are not removed neither in HRAS nor CAS reactors.

Table 3.6. Kinetic pseudo first-order degradation constants (kbiol) measured in the HRAS reactor.

OMP	k_{biol} (L/g$_{VSS}$·d)		
	HRAS	**Alvarino et al. (2014)**	**Suarez et al. (2010)**
E1	57 ± 20	43	170
E2	46 ± 10	40	170
IBP	29 ± 9	24	20
ADBI	16 ± 4	63	75
AHTN	15 ± 5	38	115
TCS	13 ± 5	-	-
HHCB	11 ± 4	41	170
NPX	7 ± 3	9	9
ROX	3.3 ± 2.1	9	9
DZP	2.6 ± 1.6	0.4	<0.4
EE2	1.7 ± 0.9	7	20
SMX	1.5 ± 0.8	9	0.3
FLX	1.3 ± 1.1	10	9
ERY	0.9 ± 0.8	4	6
CTL	0.7 ± 0.6	-	3
DCF	0.5 ± 0.4	2	1.2
TMP	0.4 ± 0.3	0.6	0.15
CBZ	0.4 ± 0.3	0.2	<0.06

Moreover, unnoticeable reduction of OMPs concentration was found (<15%) after treating the effluents of the HRAS reactors with 30 mg/L of FeCl$_3$ (data not shown), being these variations attributed to analytical deviations, proving that the addition of chemicals in secondary clarifiers was neither effective for the removal of OMPs.

The comparative against the CEPT shows that whereas for those OMPs classified in Group I considerably higher biotransformation efficiency was achieved in the HRAS reactor, for those of Group II and III the elimination efficiencies were quite comparable. Although the results of this work indicate that HRAS is a better technology than CEPT in terms of OMPs removal, further research is needed to holistically assess the fate of OMPs in novel STPs.

3.3.8. Viruses removal

Recovery efficiencies were generally high, demonstrating minimal viral genome loss during the extraction−RT-qPCR process. With the exception of HAV which

was not detected, all the other enteric viruses analysed were detected in untreated and treated wastewater (Figure 3.9). GI and GII NoV were found at mean concentrations of 6.70 $\log_{10}$ copies/L and 6.05 $\log_{10}$ copies/L, respectively, whereas SaV was detected at mean concentration of 4.52 $\log_{10}$ copies/L. These values are in the range of those found in wastewaters in different geographic areas, including USA, Japan or Tunisia (Ito et al., 2017; Schmitz et al., 2016; Varela et al., 2018).
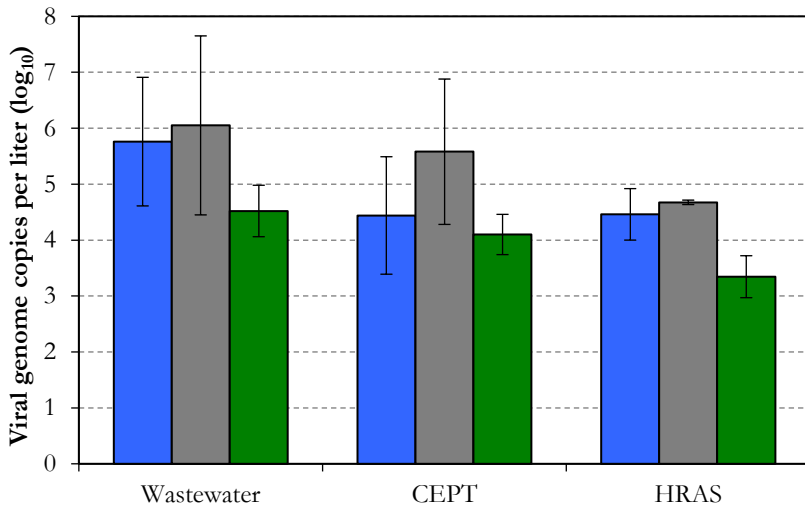
Figure 3.9. Removal of NoV GI (■), NoV GII (□) and SaV (■) in CEPT and HRAS, estimated by the decrease of concentration of viral genome copies/L

3.3.8.1. Chemically enhanced primary treatment

The results show that NoV GI experienced the greatest reduction values (1.3 log units; 94.5%), followed by NoV GII (0.5 log units; 66.5%) and SaV (0.4 log units; 62.2%) (Figure 3.9). Such removal efficiencies were similar to those reported by other authors in a STPs based on CAS reactors or trickling filters for a variety of viruses including NoV, SaV or Aichi virus (Schmitz et al., 2016; Varela et al., 2018).

3.3.8.2. High-rate activated sludge reactor

Viral reductions in the HRAS treatment were, in general, higher than those yielded in the CEPT unit (Figure 3.9). Mean reductions for NoV GI, NOV GII and SaV were of 1.3 log units, 1.4 log units and 1.2 log units, respectively. These values are more in line with those reported elsewhere in STPs based on advanced processes, such as five-stage Bardenpho treatment (Schmitz et al., 2016). This system was originally designed to enhance nutrient removal, and viral reduction

could be related with a greater virus adsorption to suspended particles than in other treatments.

Some differences in the removal efficiencies of viruses in the HRAS reactor were observed between the sampling campaigns, indicating that slight variations in the physico-chemical parameters (pH, TSS, COD, divalent cations, SRT, etc) may differentially affect the removal of the diverse viral types. Likewise, for OMPs, reduction of virus concentration was unnoticeable after treating the effluents of the HRAS reactors with 30 mg/L of $FeCl_3$ (data not shown). The influence of STP configurations and conditions on the efficiency of viral removal has been previously indicated by different authors (Li et al., 2011; Schmitz et al., 2016), who also suggested virus aggregation/disaggregation as one of the main reasons explaining the great viral survival and resistance to diverse chemical compounds (Gerba and Betancourt, 2017). Viral aggregation can also be responsible of inaccurate estimations of removal during different treatment processes, such as ultrafiltration and reverse osmosis, usually considered as more efficient than CAS.

It is important to point out that the procedures employed in this study cannot differentiate whether the virus detected are infective or if the reductions observed are due to physical removal or damage to the nucleic acid, making it no longer detectable by qPCR. Further studies are needed in order to clarify these aspects.

3.4. CONCLUSIONS

Similar COD removal efficiencies are achieved in HRAS and CEPT, although the former reaches lower recovery due to the partial oxidation of the wastewater COD. Whereas in CEPT a high PO_4^{3-} removal efficiency (>99%) is obtained, in HRAS it is quite limited (13%), although it can be enhanced to 99% after a post-treatment with 30 mg/L of $FeCl_3$. Under these conditions, the HRAS-based STP leads to higher energy demand than that based on CEPT, however, the former results in lower operational costs. In general, higher OMPs removal efficiencies were achieved in the HRAS system, although for those recalcitrant they were in both systems quite comparable and low (<25%). HRAS presents higher potential for viral removal than CEPT, but significant variations of performance against the different viruses were observed. All in all, HRAS appears as a better technology than CEPT in novel STP configurations.

CHAPTER 4

FATE OF ORGANIC MICROPOLLUTANTS
IN THERMAL HYDROLYSIS AND
ANAEROBIC DIGESTION

SUMMARY

In sewage treatment plants (STPs) sludge, which is commonly used as fertilizer in agriculture, is the end point of many organic micropollutants (OMPs) fact that was proved to lead to important environmental and human risks. The objective of this chapter is to determine the fate OMPs in thermal hydrolysis (TH) and subsequent anaerobic digestion (AD). Sewage sludge was pretreated in a TH pilot plant at 170ºC for 20 minutes. Afterwards, two anaerobic digesters with a working volume of 14 L fed with fresh and pretreated sludge were operated in parallel in mesophilic conditions. TH proved to be an effective technology to partially or totally remove the dissolved fraction of OMPs as well as the fraction sorbed into those suspended solids that are solubilised by this pretreatment. Contrary, it did not affect the OMPs sorbed concentration into solids that are not solubilised. Globally, the OMPs removal efficiency during TH appears to be linked to the solids solubilisation during this process. Afterwards, the OMPs biotransformation efficiency in fresh and pretreated sludge AD was assessed. Noticeable differences between the microbiome of both reactors was determined, but the anaerobic biotransformation was not substantially different for most of the OMPs. However, it affected musk fragrances, which presented considerably lower biotransformation efficiency in the reactor fed with pretreated sludge. Therefore, TH was proved effective in partially removing OMPs but not in enhancing their bioavailability and subsequent anaerobic biotransformation.

4.1. INTRODUCTION

In sewage treatment plants (STPs) sludge is the end point of not only lipophilic organic micropollutants (OMPs) but also of a considerable fraction of those hydrophilic which are not degraded during biological treatment (Carballa et al., 2008). The fate of OMPs during AD has been extensively studied over the last years (Carballa et al., 2007b; des Mes et al., 2008; Gonzalez-Gil et al., 2016; Malmborg and Magnér, 2015; Narumiya et al., 2013; Samaras et al., 2014). The reported removal efficiencies are sometimes contradictory and the causes of these discrepancies are not completely clear, although previous works suggest that the biotransformation of OMPs during AD might depend on the availability of the specific compounds and therefore on the equilibrium between the particulate and soluble phases (Barret et al., 2010; Delgadillo-Mirquez et al., 2011), suggesting that sludge pretreatment (PT) can be used as an strategy to improve OMP biotransformation through their transfer to the more accessible phase of sludge (Aemig et al., 2016; Gonzalez-Gil et al., 2018a).

However, the number of works studying the influence of sludge PT (specifically TH) on the fate of OMPs is not extensive. Reyes-Contreras et al. (2018) observed no major changes in sorbed concentration of OMPs in sludge after a thermal PT, although they carried out it at a low temperature of 55ºC. Moreover, they did only report the OMPs sorbed concentrations. McNamara et al. (2012) suggested that those OMPs with hydrocarbon chains such as nonylphenol or nonylphenol ethoxylates can be fragmented in TH processes, although they concluded that the removal of these OMPs was attributed to their volatilisation rather than thermal fragmentation/degradation. Contrary, Zhang and Li (2018) found that a PT at 130ºC was effective to achieve a high solubilisation efficiency of some antibiotics and to thermally degrade them. However, for other antibiotics they reported an increase of the total concentration after TH without a clear explanation of the results. Other authors compared the removal efficiency of OMPs in AD against the combination of PT + AD, but they did not specifically report the influence of the PT and the AD stages on the fate of OMPs. , Carballa et al. (2007a) found that ozonation + AD increased carbamazepine and tonalide removal efficiencies and Yang et al. (2017a) that TH + AD enhanced the removal of some OMPs with respect to conventional AD. Moreover, some works in the literature reported important changes in the microbial communities in the AD process after sludge TH (Ennouri et al., 2016; Gagliano et al., 2015), what might also influence the anaerobic biotransformation of OMPs.

A point of consensus in the literature is that most of the OMPs are likely to be mainly found into the solid phase of digested sludge (Carballa et al., 2008; Gonzalez-Gil et al., 2016; Narumiya et al., 2013), regardless the removal

efficiency. This fact is especially important in those countries in which sludge use in agriculture as a fertilizer is the preferable disposal alternative. In Europe, the Directive 86/278/ECC does not consider the presence of OMPs in sludge, although European Commission recently tried to implement a more restrictive legislation, which finally could not be done due to the lack of consensus among the Member States. However, many countries have already set limit values for several organic compounds (Kelessidis and Stasinakis, 2012) as a response to the environmental and human risks already reported due to the accumulation of OMPs in sludge (Barron et al., 2010; Thomaidi et al., 2016), what is becoming a major issue for STPs administrators.

The objective of this work is i) to assess the effect of TH on the fate of OMPs and ii) to determine the influence of TH on the biotransformation efficiency of OMPs during AD, comparing the microbial populations involved in each reactor.

4.2. MATERIALS AND METHODS

4.2.1. Sludge samples

4.2.1.1. Physico-chemical characterization

Sewage sludge was a mixture of primary and secondary sludge (80/20, %v/v), from the thickener and the activated sludge flotator of a STP in the centre of Spain, designed for 255,000 equivalent population, with a flowrate of 24,000 m^3/d. It was kept at 4ºC and characterised every week in terms of pH, total (TS, g TS/L) and volatile (VS, g VS/L) solids, total (TSS, g TSS/L) and volatile (VSS, g VSS/L) suspended solids, total (COD_{tot}, g O_2/L) and soluble (COD_{sol}, g O_2/L) chemical oxygen demand, total Kjeldahl (TKN, g N-TKN/L) and total ammonium nitrogen (g N-TAN/L) concentration, according to Standard Methods (APHA, 2005) and in terms of VFAs (g/L), which were measured by gas chromatograph (HP 5890A) with a Flame Ionization Detector (HP 7637A).

4.2.1.2. Organic micropollutants

18 compounds commonly used in daily life were considered in this study: three musk fragrances, galaxolide (HHCB), tonalide (AHTN) and celestolide (ADBI); three anti-inflammatories, ibuprofen (IBP), naproxen (NPX) and diclofenac (DCF); four antibiotics, sulfamethoxazole (SMX), trimethoprim (TMP), erythromycin (ERY) and roxithromycin (ROX); four neurodrugs, fluoxetine (FLX), carbamazepine (CBZ), diazepam (DZP) and citalopram (CTL); one endocrine disrupting compound, triclosan (TCS); and three hormones, estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2).

The protocol described in Chapter 2 was used to characterize the dissolved and sorbed OMPs concentrations. For the liquid phase, the volume analysed was 250

mL and the final volume of extract was 1 mL, leading to an enrichment factor of 250 $L_{supernatant}/L_{extract}$. The limits of quantification (LOQs) ranged from 3 to 25 ng/L for all the OMPs except DCF, for which it was considerably higher (100 ng/L). For the solid phase, the LOQs were between 1.2 and 20 ng/g except for DCF, for which it was 40 ng/g. The specific data for each OMP is shown in Table 4.1.

Table 4.1. Limits of quantification of dissolved and sorbed OMPs.

OMP	Liquid (ng/L)	Solid (ng/g)
CTL, ERY, FLX, ROX	3	1.2
DZP, CBZ, SMX, TMP	15	6
E1, E2, EE2	15	6
ADBI, AHTN, HHCB, TCS	5	20
IBP	20	8
NPX	25	15
DCF	100	40

To quantify the recoveries in the liquid and solid phase, the procedure detailed by Gonzalez-Gil et al. (2016) was followed. This procedure enables the calculation of the total or absolute recovery of the method, including losses during sample preparation and measurement deviations during the chromatographic analysis. The recovery results are shown in Table 4.2. In general, the recoveries in the solid phase were quite similar regardless the matrix so the average values were used for the calculations. For those OMPs measured by gas chromatography, the recoveries were in the range 80-170% due to the presence of interfering substances in the chromatogram. Contrary, for those measured by liquid chromatography they were in the range 35-75%. Regarding the liquid phase, some OMPs such as FLX, CTL, ADBI or TCS presented very low recoveries (below 40%). This fact was also seen by other authors (Bivins and Novak, 2001; Gonzalez-Gil et al., 2016), who related it to the presence of colloids in the liquid phase, which hiders enormously the filtration process.

4.2.2. Thermal hydrolysis pilot plant

The experiment was carried out in an automatic pilot-scale thermal system as the one described by Sapkaite et al. (2017). The pilot plant consists of a feeding tank, a progressive cavity pump (P_{max} = 12 bar), a steam boiler, a 20 L total volume hydrolysis reactor (V_{utile} = 10 L) connected to a flash tank (V = 100 L) with outlet pipes for steam and hydrolysed sludge. The pilot plant is equipped with automatic valves that control the steam entrance from the boiler and the sludge exit from the reactor to the flash. The pilot plant is equipped with automatic valves that control the steam entrance from the boiler and the sludge exit from the reactor

to the flash. A data acquisition and control system were used to measure pressure and temperature and automatically controls the steam inlet and the hydrolysed sludge exit to the flash.

Table 4.2. Absolute recoveries in the liquid and solid phase of unpretreated and pretreated sludge (SS), and mesophilic digestates (MD).

	OMP	Sludge matrix	Recovery (%)	
			Liquid	Solid
LC/MS-MS	ERY	SS-MD	55-65	45-55
	ROX	SS	45-50	55-60
		MD	15-20	
	SMX	SS	85-90	50-60
		MD	70-75	
	TMP	SS	70-75	50-60
		MD	60-65	40-45
	FLX	SS	30-35	40-45
		MD	5-10	
	CTL	SS	15-20	50-55
		MD	10-12	35-40
	CBZ	SS	80-85	60-65
		MD	75-80	
	DZP	SS	20-25	65-75
		MD	10-12	
	E1	SS	20-25	65-75
		MD	10-15	
	E2	SS	55-60	60-70
		MD	10-20	
	EE2	SS	55-60	65-75
		MD	30-35	
GC/MS	ADBI	SS-MD	10-15	150-170
	HHCB	SS-MD	15-30	150-170
	AHTN	SS-MD	20-40	185-195
	IBP	SS-MD	155-175	170-190
	NPX	SS	190-200	130-135
		MD		80-95
	DCF	SS-MD	130-150	130-140
	TCS	SS-MD	10-15	140-160

The pump introduces 10 L of sludge into the reactor and then the steam valve is opened until pressure and temperature reach the set-point values. TH was carried out at 170 ºC during 20 minutes, since some authors reported that at higher temperatures non-biodegradable compounds begin to be produced due to the called Maillard reactions (Bougrier et al., 2008). At the end of the reaction time, the decompression valve is automatically opened and the hydrolysed sludge flows to the flash tank.

To determine specifically the influence of TH on soluble OMPs, the experiments were performed not only on sludge but also on distilled water due to the complexity of the sludge matrix and the difficulty to filtrate sludge samples (especially after TH), what dramatically hinders their quantification (Bivins and Novak, 2001). However, for this specific purpose distilled wastewater was spiked with OMPs (20 ppb for musk fragrances and TCS, 1 ppb for hormones and 10 ppb for the others).

4.2.3. Lab-scale anaerobic reactors and monitoring campaigns

Two continuous stirred tank reactor (CSTR) (IKA Eurostar 60 digital, 150 rpm) made of stainless steel with a working volume of 14 L were operated in mesophilic range (37 ± 1ºC). After inoculation with anaerobic flocculant biomass (15.3 g VS/L) from the anaerobic digester of a STP in the northwest of Spain treating a mix of primary and biological sludge (70:30 % v/v). The two digesters were operated semi-continuously (once a day draw-off and feeding), R1 fed with fresh sludge and R2 with pretreated sludge. The operation of each anaerobic digester comprised two different periods, according to the organic loading rate (OLR). During the first 37 days of operation the OLR was maintained at 1.5 g COD/L·d. From day 38 till the end of the operation (day 115), the OLR increased to 2.0 g COD/L·d. However, the SRT was slightly different in both digesters caused by a partial condensation of steam after TH, which increased the volume of pretreated sludge around 30%. Although fresh sludge could be also diluted to equalize the SRT, this option would not be representative of a real scenario.

Temperature, stirring speed and biogas flow (μflow flowmeters, Bioprocess Control) were monitored online. pH, partial (PA) and total (TA) alkalinity, COD, TS, VS, TKN, TAN and VFAs in the digestate were measured once per week. Biogas composition was determined by gas chromatography (HP 5890 Series II) (Gonzalez-Gil et al., 2016).

In order to evaluate the fate of OMPs during AD of fresh and pretreated sludge, three samples of both sludges were taken on days 70, 80 and 90 of operation. For digestates, three samples of each reactor were taken with approximately one

HRT of difference (on days 100, 106 and 112 of operation). The samples were immediately centrifuged at 3,500 rpm for 30 min to separate solid and liquid phases (the supernatant and the solid phase were treated as explained in section 4.2.1.2.). For each sample, liquid phase was analysed once and solid phase was analysed in duplicate, and among the six values obtained the one with the highest difference to the average value was discarded.

To characterize the microbiome of the two digesters, homogeneous biomass samples were periodically taken and immediately frozen at -20 ℃ until further processing as explained in section 4.2.4.

4.2.4. *DNA extraction, sequencing, computational and statistical analysis*

Total genomic DNA extractions, library preparation and sequencing and sequences analysis were carried out as previously describe in Braz et al. (2018), although in this work, universal primers were used to amplify the V5V6 region the of 16S rRNA gene with the conditions described in Bohorquez et al. (2012).

A total of 1.5 M high-quality sequences were clustered into 6546 Operational Taxonomic Units (OTUs). Richness was determined as the number of observed species. The analysis of similarity (ANOSIM) using Bray-Curtis distances, was used to test the degree of similarity of the microbiomes of both reactors (Clarke, 1993). ANOSIM analysis ranged between 0 (random grouping) and 1 (completely different groups). The influence of operational parameters and community structure were analysed by transform-based principal component analysis (tb-PCA), based in Hellinger transformed data and Bray-Curtis dissimilarities. ANOSIM and tbPCA were performed using R environment (R Core Team, 2016) with Vegan package (Oksanen et al., 2016).

4.3. RESULTS AND DISCUSSION

4.3.1. *Influence of thermal hydrolysis on physico-chemical characteristics of sludge*

Physicochemical characteristics of fresh and pretreated sludge are shown in Table 4.3. Although the reported range in the literature is wide and very dependent on many factors, the results generally agree with other reported values elsewhere (Astals et al., 2012; Carballa et al., 2008). Physico-chemical properties of pretreated sludge are shown in Table 4.3. It must be noted that after TH, sludge volume increased 30%, attributed to a partial condensation of steam, leading to a dilution factor of 1.3. The main differences were the noticeable COD_{sol} increase (from 5.0 g/L to 16.3 g/L) and the TSS and VSS decrease from 50.1 g/L and 42.3 g/L to 33.1 g/L and 27.5 g/L, respectively. VFAs and NH_4^+ concentration were similar in both scenarios, in agreement with Donoso-Bravo et al. (2011) and Wilson and Novak (2009).

Table 4.3. Physico-chemical characterisation of fresh and pretreated sludge.

	Fresh sludge	**Pretreated sludge**
pH	5.60 ± 0.01	5.62 ± 0.02
TS (g/L)	52.7 ± 0.2	39.6 ± 0.1
VS (g/L)	44.9 ± 0.2	34.0 ± 0.1
TSS (g/L)	50.1 ± 0.2	33.1 ± 0.3
VSS (g/L)	42.3 ± 0.3	27.5 ± 0. 2
COD_{tot} (g/L)	86.7 ± 0.3	66.8 ± 0.6
COD_{sol} (g/L)	5.0 ± 0.1	16.3 ± 0.0
TKN-N (g/L)	3.22 ± 0.05	2.81 ± 0.01
NH_4^+-N (g/L)	0.45 ± 0.05	0.42 ± 0.02
Acetic acid (mg/L)	1,249 ± 137	1,103 ± 23
Propionic acid (mg/L)	529 ± 22	327 ± 11
Butyric acid (mg/L)	516 ± 32	535 ± 116
Valeric acid (mg/L)	258 ± 15	137 ± 3

4.3.2. Occurrence of organic micropollutants in sewage sludge

Table 4.4 shows total concentration of OMPs together with the specific concentration in the liquid and solid phases. Since most of the studies report OMPs concentration in the solid phase, the comparison of results is mainly focused on sorbed concentrations.

The presence of ADBI, DCF, ERY, SMX, TCS and EE2 could not be confirmed since their concentration was below the LOQ in all the analysed samples. Musk fragrances AHTN and HHCB were the compounds that showed the highest concentration in sludge (11.5 and 1.6 μg/g, respectively), in the same range as those reported by Clara et al. (2011) and Reyes-Contreras et al. (2018). The former reported that ADBI is usually present in much lower concentration, what was also seen in this study.

Regarding anti-inflammatories, IBP was detected in both phases but mainly sorbed (1.17 μg/g), resulting in a higher total concentration (63 μg/L) than that reported by Gonzalez-Gil et al. (2016) and Radjenović et al. (2009) (11.8-31.3 μg/L). NPX was only detected in the liquid phase (1.8 μg/L). This concentration was lower than the one found by Carballa et al. (2007b) (11 μg/L), but higher than those found by Gonzalez-Gil et al. (2016) and Radjenović et al. (2009) (maximum concentration of 0.67 μg/L). DCF was not detected in this work, and neither by Carballa et al. (2007a) and Gonzalez-Gil et al. (2016), even though Radjenović et al. (2009) found it up to 1.6 μg/L.

ROX and TMP were detected in this work, whereas ERY and SMX concentration was below the LOQ. ROX concentration (9.6 ng/g) was in the range of those measured by Narumiya et al. (2013) (14-18 ng/g) and Gonzalez-Gil et al. (2016) (1.8-65 ng/g). Moreover, the former reported TMP concentration in the range 13-27 ng/g, slightly higher than the one obtained in this work (11.9 ng/g). The latter did neither detect ERY. Regarding SMX, Mailler et al. (2017) only detected it in five sludge samples of fourteen, with a maximum concentration of 388 ng/g whereas Gonzalez-Gil et al. (2016) found it ranging from <LOQ to 626 ng/g.

The four neurodrugs (FLX, CTL, CBZ and DZP) were detected in sewage sludge. CBZ concentration (12.3 ng/g) was higher than those reported by Narumiya et al. (2013) (1-3 ng/g), but considerably lower than those measured by Radjenović et al. (2009) (up to 160 ng/g) and Mailler et al. (2017) (13.7-421 ng/g). Gonzalez-Gil et al. (2016) found a wide range of concentration of DZP (<LOQ-131 ng/g), CTL (55-122) and FLX (74-423 ng/g). The concentration found in this work for DZP (19.2 ng/g), CTL (183 ng/g) and FLX (79 ng/g) are in the same range.

Endocrine disrupting compound TCS was not detected in this study, neither by Gonzalez-Gil et al. (2016), although other authors reported concentration of TCS up to 15 µg/g (Bolz et al., 2001; Stasinakis, 2012).

Regarding hormones, E1 was the one detected in the highest concentration (37.3 ng/g), followed by E2 (12.9 ng/g) and EE2 (<LOQ). These results are in the low range compared with those reported by Nieto et al. (2010) and Gonzalez-Gil et al. (2016) for E1 (<LOQ-230 ng/g), E2 (2-40 ng/g) and EE2 (<LOQ-313 ng/g). However, Mailler et al. (2017) found very comparable concentration of E1 (21-100 ng/g) and E2 (15-93 ng/g) although they detected EE2 in higher concentrations (17-64 ng/g) as well.

4.3.3. Influence of thermal hydrolysis on the fate of organic micropollutants

Sorbed concentration of OMPs before and after TH (Table 4.4) were very similar and only CTL showed significantly different concentration ($p < 0.05$) after TH. These results indicate that the fraction of OMPs sorbed into solids remains unaffected by TH. In contrast, the soluble concentration of some OMPs such as IBP, NPX, ROX, CBZ, DZP, E1 and E2 decreased (Table 4.4), whereas soluble concentration TMP, FLX and CTL was higher after TH. It must be highlighted that there is an important risk of underestimation of the soluble concentration of OMPs due to the complexity of the matrix and the difficulty to filtrate the samples.

Table 4.4. Average concentration and standard deviation of OMPs in fresh and pretreated sewage sludge.

	Raw sludge			Pretreated sludge*		
	C_w (µg/L)	C_s (µg/g)	C_t (µg/L)	C_w (µg/L)	C_s (µg/g)	C_t (µg/L)
AHTN	<LOQ	21.1 ± 2.7	1,057 ± 135	<LOQ	20.6 ± 5.2	857 ± 193
HHCB	<LOQ	2.1 ± 0.4	103 ± 18	<LOQ	2.0 ± 0.5	85 ± 18
IBP	4.84 ± 1.32	1.17 ± 0.05	63 ± 1	3.49 ± 0.15	1.16 ± 0.03	52 ± 1
NPX	1.91 ± 0.07	<LOQ	1.91 ± 0.07	1.71 ± 0.24	<LOQ	1.71 ± 0.24
	C_w (ng/L)	C_s (ng/g)	C_t (ng/L)	C_w (ng/L)	C_s (ng/g)	C_t (ng/L)
ROX	11.0 ± 1.2	9.6 ± 3.5	490 ± 175	6.19 ± 3.53	9.2 ± 3.5	387 ± 132
TMP	7.54 ± 0.82	11.9 ± 2.0	604 ± 100	10.1 ± 2.8	12.8 ± 2.7	586 ± 63
FLX	13.4 ± 5.3	79 ± 12	3,939 ± 612	37 ± 20	80 ± 4	3,369 ± 157
CTL	8.06 ± 2.79	183 ± 14	9,150 ± 691	59 ± 15	212 ± 15	8,875 ± 570
CBZ	49 ± 14	12.3 ± 1.0	662 ± 51	17.6 ± 7.5	14.8 ± 1.4	634 ± 53
DZP	11.5 ± 7.5	19.2 ± 3.1	971 ± 155	4.39 ± 0.21	20.8 ± 7.8	869 ± 294
E1	173 ± 46	38.3 ± 8.1	2,090 ± 484	129 ± 56	36.3 ± 3.8	1,639 ± 357
E2	59 ± 6	14.2 ± 3.2	767 ± 86	15.0 ± 3.6	15.5 ± 2.6	662 ± 154

*Soluble and total concentration of OMPs in pretreated sludge were corrected by the dilution factor (1.3

Therefore, to have clearer evidences about the removal of the soluble fraction of OMPs during TH, distilled water previously spiked with OMPs was thermally pretreated in the same conditions as sludge. All the OMPs showed significantly different soluble concentration ($p < 0.05$) after TH. HHCB, AHTN, DCF, ERY, ROX, ADBI, TCS and FLX were completely or almost completely removed (85-100%) (Figure 1), whereas CTL, TMP, EE2, E2, SMX, NPX, DZP, E1, CBZ and IBP showed a removal efficiency between 30% and 60%. Therefore, these results prove that whereas the soluble and solubilised fraction of OMPs is partially or totally removed during TH, sorption of OMPs into solids that are not solubilised seems to act as a protective barrier, preventing them from being removed. Regardless NPX, which was entirely found dissolved, the relative presence of the OMPs in the liquid phase of sludge represented less than 8% of the total concentration, so the influence of TH on the removal efficiency of OMPs in TH can be linked to the solubilisation of TSS. Therefore, although TH does not result effective to increase the bioavailability of OMPs before AD, it produces a partial removal by itself. A limitation of this work was that it was not possible to distinguish if OMPs were thermally degraded or volatilized, since due to the pilot plant configuration the excess steam was released to the atmosphere.

Information in the literature about the fate of OMPs in sludge TH is scarce. Reyes-Contreras et al. (2018) found that whereas musk fragrances and TCS sorbed concentration increased after ultrasound PT, after a thermal PT at 50ºC no significant variations were observed. However, they did not measure the soluble concentration of OMPs.. McNamara et al. (2012) found that TH partially removes OMPs such as nonylphenol or nonylphenol ethoxylates, identifying volatilisation rather than thermal fragmentation as the mechanism responsible of the removal of OMPs. Contrary, Zhang and Li (2018) found that after a pretreatment at 130ºC for 60 minutes the total concentration of some antibiotics decreased by 58%-90% (attributed to their poor thermal stability), whereas ERY and ROX concentration increased by 38%-88% (attributed to the extraction of the intracellular or other parts of sludge cells that are not extracted in conventional extraction process). They also reported that the sorbed concentration of some compounds was barely affected, in agreement with the results of this work, although the sorbed concentration of other antibiotics dramatically decreased below the LOQ. The higher temperature (170ºC *vs* 120ºC) and the lower reaction time (20 min *vs* 60 min) that they applied might be a feasible explanation for the substantially different results achieved.
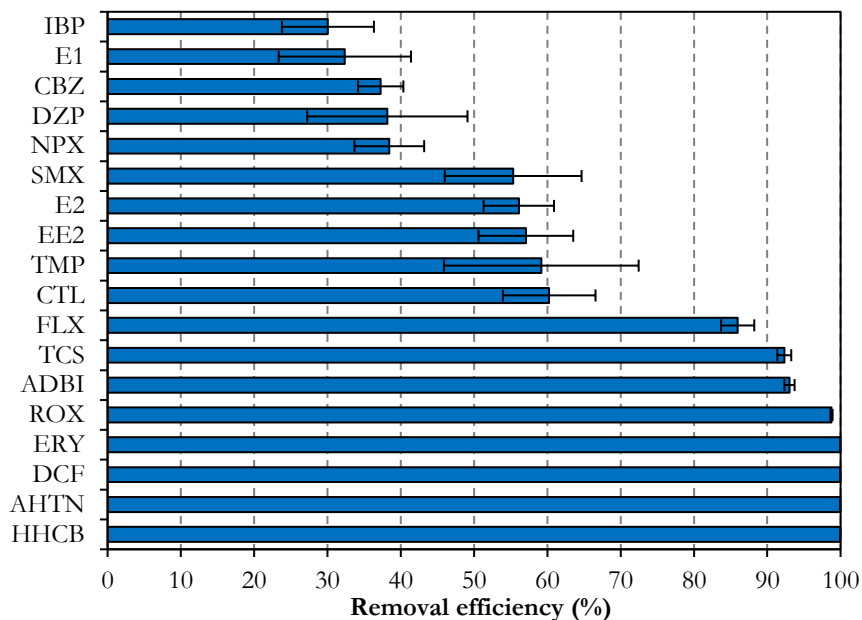
Figure 4.1. Removal efficiencies of the soluble fraction of OMPs during TH (n=3).

4.3.4. Influence of thermal hydrolysis on anaerobic digestion

4.3.4.1. Physico-chemical characterization

Both digesters were operated under the same OLR although with different SRT due to the dilution effect caused by TH. Table 4.5 displays the average operational parameters during the second operational period.

Slightly higher VS reduction and average methane production were obtained in the reactor fed with pretreated sludge (R2) (357 $\pm$ 24 L(N) CH_4/kg VS) in comparison with the one treating fresh sludge (R1) (319 $\pm$ 12 L(N) CH_4/kg VS). No major differences were observed in terms of pH, alkalinity, TAN and biogas composition. TS, VS and COD_{tot} concentration were higher in R1 than in R2, due to the dilution caused by TH and the higher biodegradability achieved in R2. However, higher COD_{sol} was obtained in R2, indicating that part of the COD that is solubilised during TH is not biodegradable, in accordance with Sapkaite et al. (2017).

Table 4.5. Average operational and performance parameters of the mesophilic anaerobic digesters (operation lasted 120 d).

	Reactor 1	Reactor 2
OLR (g COD/L·d)	2.1 ± 0.1	2.1 ± 0.1
SRT (d)	40 ± 1	31 ± 1
pH	7.6 ± 0.1	7.7 ± 0.1
VFA (mg/L)	41 ± 27	21 ± 8
Total alkalinity (g CaCO$_3$/L)	6.7 ± 0.2	6.2 ± 0.1
TS (g/L)	28.9 ± 1.7	22.1 ± 1.9
VS (g/L)	21.5 ± 1.7	15.2 ± 1.4
VS removal (%)	48 ± 5	53 ± 3
COD$_{tot}$ (g/L)	35.1 ± 2.4	25.0 ± 0.9
COD$_{sol}$ (g/L)	1.2 ± 0.1	1.9 ± 0.2
TAN (g N/L)	1.4 ± 0.1	1.3 ± 0.1
Biogas production (L(N)/L$_{reactor}$·d)	0.51 ± 0.03	0.56 ± 0.04
Specific methane production L(N)/kg VS	319 ± 12	357 ± 25
Methane composition (%)	64 ± 1	65 ± 1

4.3.4.2. Anaerobic digestion microbial communities

TH of feedstock did not significantly affect the richness values of the diversity (Figure 4.2). However, the structure of the microbial communities was significantly different, as indicated by the ANOSIM analysis (R = 0.866) and shown by the tbPCA (Figure 4.3). The tbPCA analysis also indicated that communities became more different overtime and that these differences were correlated with feedstock characteristics (COD$_{sol}$ in the feedstock was 58% higher in R2 than R1). Similar results were obtained by Ennouri et al. (2016), who observed important shifts in the microbial community structure in digesters fed with fresh and pretreated sludge.

Both reactors shared the most relative abundant microorganisms; 30% of communities were attributed to unknown genera of the *Bacteroidetes* and *Clostridiales* orders (Figure 4.4(A)). The latter was more abundant in R2 reactor; probably due to the larger presence of particulate COD in fresh sludge, since *Clostridiales* order is related to the hydrolysis step in AD (Cirne et al., 2007).
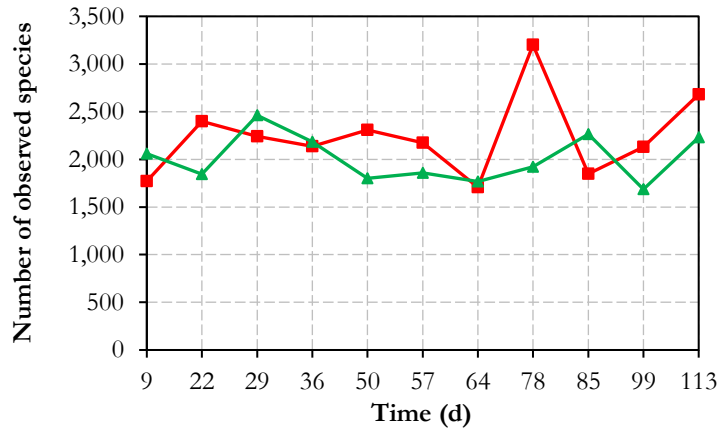
Figure 4.2. Richness values (number of observed species) in R1 (■) and R2 (▲) throughout the experiment.
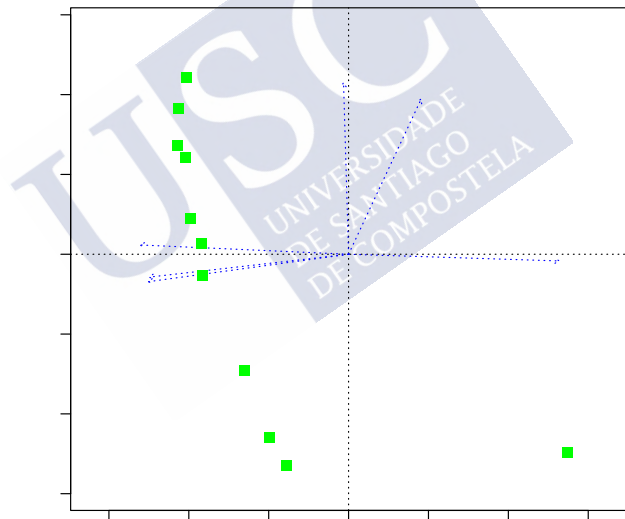
Figure 4.3. PCA analysis of microbial community structure at OTU level. Labels indicate the time in days. Blue vectors indicate incrementing values of the operational variables that are significantly correlated with community structure (ϱ value < 0.01).
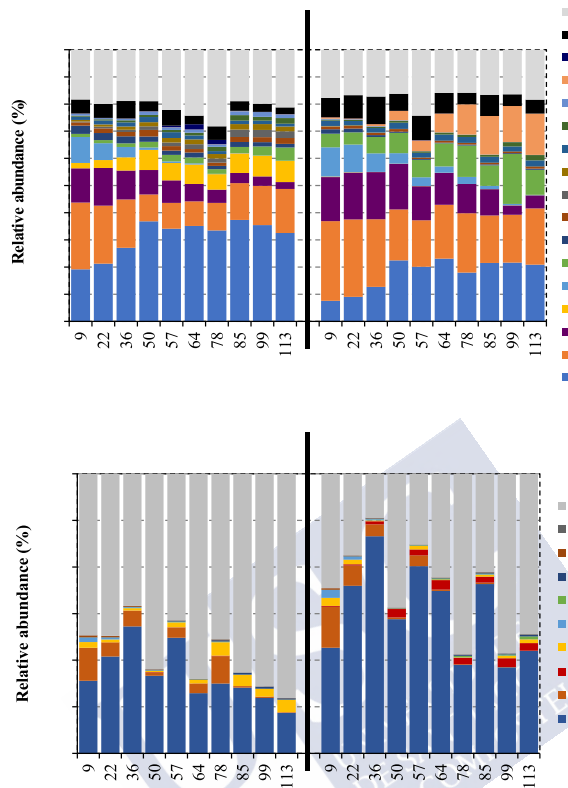
Figure 4.4. Community composition profile at the most detailed taxonomic level available. Relative abundance of the most prevalent taxa in the bacterial (A) and archaeal (B) fractions of the microbial communities in R1 and R2.

Both reactors showed some differences in terms of the fermentative microorganisms. Microorganisms belonging to *Erysipelotrichaceae* and *Comamonadaceae* families, related with fermentation and acetate consumption (Adav et al., 2010; Ziganshina et al., 2015), were approximately 10 times more abundant in R1 than in R2. *Paracoccus*, a genus that comprises two known anaerobic species that are correlated with denitrification and mixotrophic metabolism (Kelly et al., 2006), was also more abundant in R1. In contrast, R2 presented different fermentative microorganisms, such as *Peptostreptococcaceae*, *Mogibacteriaceae* and *Porphyromonadaceae* families (Figure 4.4 (A)). Members of *Porphyromonadaceae* family are known to produce different types of VFA from carbohydrate and protein sources (Ziganshin et al., 2011).

On average, *Archaea* represented the 4% of the community in R1 and the 8% in R2 (Figure 4.4 (B)), which could be related with the higher methane production in R2 (10% higher than in R1). A higher abundance of *Archaea* in digesters in which TH was applied before AD in comparison with reactors fed with fresh feedstock was previously reported by Gagliano et al. (2015). *Methanosaeta* sp., which is the most common acetoclastic methanogen, clearly dominated archaeal communities in both reactors (>80% of *Archaea*). Among other methanogens, *Methanospirilum* displaced *Methanolinea* through time in R1, while *Methanomethylovorans* replaced both genera in R2 (Figure 4.4 (B)). Overall, sludge TH affected bacterial and archaeal community structure and composition but due the high functional redundancy, both reactors operated similarly. However, the different microbial communities present in the reactors could play a major role for OMPs biotransformation in the AD process.

4.3.5. *Fate of organic micropollutants during anaerobic digestion*

4.3.5.1. *Biotransformation efficiency of organic micropollutants during anaerobic digestion*

The average biotransformation efficiency of the 12 detected OMPs in both digesters is summarized in Figure 4.5. Although the two anaerobic digesters were operated under slightly different SRT, previous works in the literature found that SRT does not impact their anaerobic biotransformation (Carballa et al., 2006).

OMPs were classified in three groups according to their biotransformation efficiency. The first group contains only NPX, which was totally removed in both reactors, matching the results of other authors (Alvarino et al., 2014; Gonzalez-Gil et al., 2016; Yang et al., 2017b).

The second group includes those OMPs partially biotransformed (30%-80%) (IBP, DZP, ROX, CTL, TMP, HHCB and AHTN). Among them, IBP was the compound more largely removed in both reactors (73% and 79% in R1 and R2, respectively). The results of IBP biotransformation efficiency during AD in the literature are quite controversial; whereas Phan et al. (2018) and Gonzalez-Gil et al. (2016) found poor removal efficiency (<25%), Carballa et al. (2007b) and Samaras et al. (2014) reported 60% and almost complete removal, respectively, during both mesophilic and thermophilic AD. Regarding ROX, the biotransformation efficiency determined in this work (64% and 72% for R1 and R2, respectively) were in accordance with Narumiya et al. (2013) (≈60%), but slightly lower than those reported by Carballa et al. (2006) and Gonzalez-Gil et al. (2016) (higher than 80%). CTL biotransformation efficiency in this study (60% in R1 and 57% in R2) matches the results of Gonzalez-Gil et al. (2016). The results found for DZP (74% in R1 and 68% in R2) are close to those reported by Carballa et al. (2006) (60 ± 18%) but slightly higher than those reported by

Carballa et al. (2007a) and Gonzalez-Gil et al. (2016) (≈50 %). TMP biotransformation efficiency was 51% and 43% in R1 and R2, respectively, lower than those reported elsewhere (75%-99%) (Alvarino et al., 2014; Gonzalez-Gil et al., 2016; Narumiya et al., 2013; Phan et al., 2018). However, Yang et al. (2017a) reported a very wide range of TMP biotransformation efficiency (5%-95%), being the causes of this variation unclear. Musk fragrances HHCB and AHTN showed noticeable different biotransformation efficiency in both reactors. HHCB (70% and 49%) and AHTN (59% and 32%) biotransformation efficiency in R1 and R2, respectively, was considerably lower in the reactor fed with pretreated sludge. Results in the literature are wide, ranging from negligible removal (Clara et al., 2011; Gonzalez-Gil et al., 2016) up to 60-70% (Carballa et al., 2006). Carballa et al. (2007a) found that after an ozonation PT+AD the removal efficiency of HHCB and AHTN increased, although they did not detail whether the removal occurred in the PT stage or during AD. The causes of this behaviour remain unclear, a possible reason could be that musk fragrances are biotransformed by some specific microorganisms with higher presence in R1 than in R2 such as those from *Erysipelotrichaceae* or *Comamonadaceae* families, although further research is needed to obtain stronger evidences of this fact.
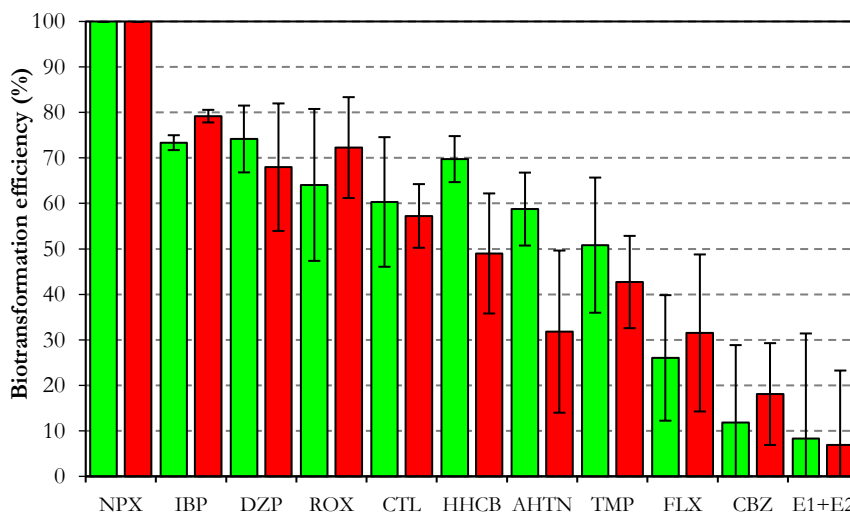
Figure 4.5. Average OMPs biotransformation efficiency in the mesophilic digesters fed with fresh (█) and pretreated sludge (█).

The third group (FLX, E1, E2 and CBZ) comprises those compounds that were not biotransformed (<30%), without significant differences between both scenarios (p<0.05). Malmborg and Magnér (2015) and Bergersen et al. (2012)

reported poor FLX biotransformation efficiency (0-32%), what matches the results of this study, even though higher biotransformation efficiencies were found by Gonzalez-Gil et al. (2016) (up to 70%). Regarding CBZ, it seems to be consensus that it stays almost unaffected during AD (Gonzalez-Gil et al., 2016; Malmborg and Magnér, 2015; Narumiya et al., 2013; Phan et al., 2018). Likewise, the negligible removal of hormones observed in both reactors is in accordance with Gonzalez-Gil et al. (2016), Malmborg and Magnér (2015), Paterakis et al. (2012) and Muller et al. (2010) (the fate of hormones E1 and E2 is usually evaluated as their sum, since under anaerobic conditions E1 can be reduced to E2 until the equilibrium is achieved (des Mes et al., 2008)).

More specific information about the fate of OMPs in the liquid and solid phase of the digestates is gathered in Table 4.6. Although some studies suggested that hydrophobicity would enhance the biotransformation of some OMPs during AD (Delgadillo-Mirquez et al., 2011; Wijekoon et al., 2015), the results of this work show that OMPs biotransformation is not influenced by their partitioning, agreeing with previously reported results (Gonzalez-Gil et al., 2016; Yang et al., 2016).

Despite the risk of finding some OMPs below the LOQ, the use of unspiked sludge is a strong point of this article, since other studies reported that in spiked sludge the OMPs are weakly linked to the matrix becoming more bioavailable and biodegradable (Dictor et al., 2003), this affecting substantially the conclusions.

4.3.6. Overall comparative of the removal of organic micropollutants between both scenarios

A global comparative of the OMPs removal efficiency between AD and the combination of TH and AD is shown in Figure 4.6. The comparison of the whole process evidences that only for IBP significant differences (p≤0.05) were obtained between both scenarios. This is attributed to the low impact of TH on solubilising TSS and therefore on removing OMPs in the pretreatment stage as well as to the comparable removal efficiencies determined during AD in both scenarios. However, the influence of TH on the removal of OMPs in sludge with higher biological proportion is expected to be considerably more relevant, since the TSS solubilisation achieved for biological sludge in TH is known to be much higher than that found in this work (Bougrier et al., 2008; Fdz-Polanco et al., 2008), Therefore, further work should be carried out in this field.

Table 4.6. Average concentration and standard deviation of OMPs in digested sludge of both reactors.

	Digestate R1			Digestate R2		
	C_w (µg/L)	C_s (µg/g)	C_t (µg/L)	C_w (µg/L)	C_s (µg/g)	C_t (µg/L)
AHTN	<LOQ	11.0 ± 0.9	320 ± 29	<LOQ	16.4 ± 1.3	362 ± 30
HHCB	<LOQ	1.45 ± 0.07	42 ± 2	<LOQ	2.16 ± 0.24	48 ± 5
IBP	10.9 ± 0.2	0.21 ± 0.03	16.9 ± 1.1	6.6 ± 0.4	0.08 ± 0.02	8.4 ± 0.7
NPX	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	C_w (ng/L)	C_s (ng/g)	C_t (ng/L)	C_w (ng/L)	C_s (ng/g)	C_t (ng/L)
ROX	4.79 ± 1.19	5.92 ± 1.60	176 ± 52	6.23 ± 3.95	3.72 ± 0.74	89 ± 20
TMP	79.7 ± 30.6	9.47 ± 4.91	353 ± 188	66.2 ± 21.1	9.37 ± 1.15	273 ± 47
FLX	145 ± 81	96 ± 8	2,913 ± 321	61 ± 20	84 ± 20	1,908 ± 461
CTL	49 ± 12	124 ± 39	3,631 ± 1,269	48 ± 8	140 ± 17	3,143 ± 385
CBZ	69.4 ± 5.4	17.8 ± 5.6	582 ± 185	31 ± 15	18.0 ± 1.0	428 ± 39
DZP	23.2 ± 1.2	7.9 ± 1.8	251 ± 59	40.5 ± 3.0	8.5 ± 2.8	228 ± 65
E1	205 ± 78	55.4 ± 6.6	1,805 ± 290	155 ± 27	50 ± 5 *	1,180 ± 142
E2	179 ± 49	18.1 ± 2.9	702 ± 141	62 ± 19	19.7 ± 3.5	498 ± 97
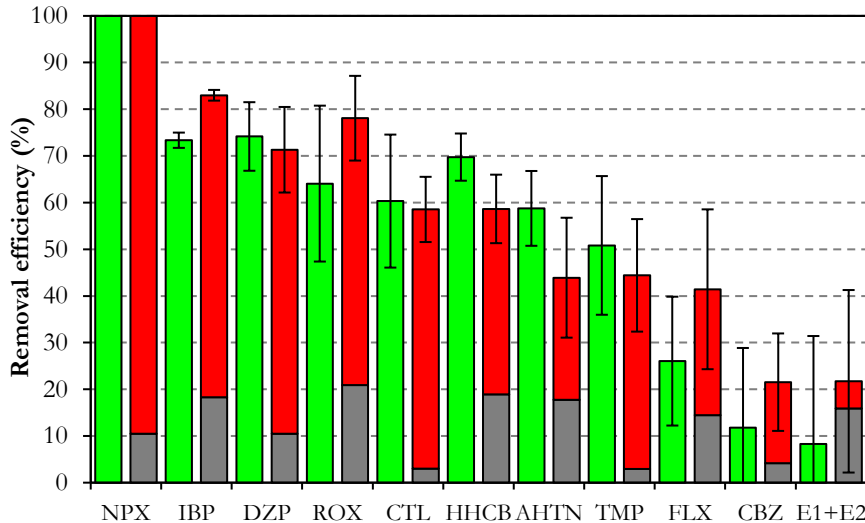
Figure 4.6. Overall comparative of OMPs average removal efficiency between the AD of fresh sludge (▪) and the combined effect of TH (▪) + AD of pretreated sludge (▪).

4.4. CONCLUSIONS

TH proved to be an effective technology to partially or totally remove the dissolved fraction of OMPs as well as the fraction sorbed into suspended solids that are solubilised in the process. Contrary, it does not affect the fraction of OMPs sorbed into solids that are not solubilised by this type of PT. Therefore, the removal efficiency of OMPs achieved in this process appears to depend on the suspended solids solubilisation efficiency. Moreover, TH does not substantially increase the biotransformation efficiency of OMPs during AD, proving that it is ineffective to increase their bioavailability.

CHAPTER 5

INTEGRATION OF THERMAL HYDROLYSIS
IN NOVEL AND CONVENTIONAL
SEWAGE TREATMENT PLANTS
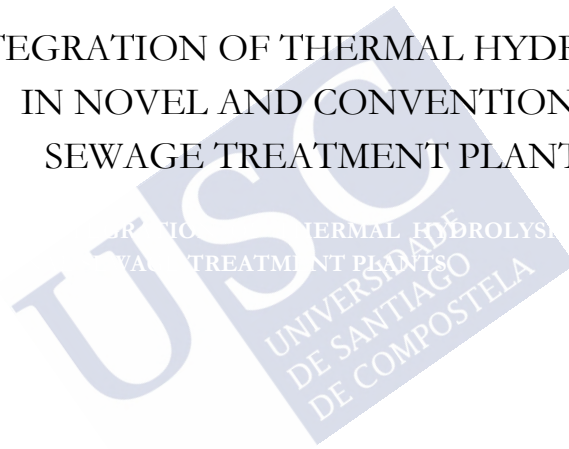
SUMMARY

In conventional STPs, sludge anaerobic biodegradability can be significantly enhanced by applying sludge pretreatment methods, such as thermal hydrolysis (TH), before anaerobic digestion (AD). However, considering that novel-sludges are more anaerobically biodegradable than conventional ones, the impact of TH on their methane production increase is expected to result significantly lower. In this chapter, an energetic and economic assessment of applying TH in novel STPs was performed and results were compared with those from a conventional STP. A threshold of 7-9% TS in sludge is required to obtain energetic profit from TH plants. However, TH is justified to reduce the operational costs as long as sludge TS concentration in the feeding to the TH unit is above 1-2%. This is attributed to the fact that the main impact of TH is on sludge disposal savings (300,000-430,000 €/year for a 500,000 inhabitants STP) rather than on the increase of energy production (achieves maximum savings of 40,000-60,000 €/year). The CEPT-based STP leads to the lowest electricity consumption (approximately 0.05 kWh/m³ of wastewater if sludge is thickened up to 20%), but even in the most favourable conditions the energy autarky is not achievable. However, the HRAS-based STP leads to the lowest treatment costs (below 1.4 c€/m³ wastewater if sludge is thickened over 10% of TS). Payback time is very dependent on the STP size, ranging from 12 to 24 years for a 100,000 inhabitants STP and from 2 to 4 years for a 1,000,000 inhabitants STP.

5.1. INTRODUCTION

In recent years, the application of different pretreatment techniques for sewage sludge before anaerobic digestion (AD), such as ultrasounds, high pressure homogenizer, pulse electric fields or thermal hydrolysis (TH), have gained importance in order to increase biogas yield and reduce the final volume of sludge (Carrère et al., 2010; Zhen et al., 2017). Among them, TH is the most attractive since it leads to a more efficient energy integration in the sewage treatment plant (STP) (Cano et al., 2015). Besides, this technology increases dewaterability, reduces odour emissions and viscosity and removes pathogens, obtaining a sterilized sludge that meets EPA Class A biosolids standards (Barber, 2016; Higgins et al., 2017; Wang et al., 2018).

TH in conventional STPs has been widely studied mainly focusing on increasing methane productivity. There is a consensus in the literature that, whereas biomethane potential (BMP) of primary sludge is barely affected by TH (<20%), BMP of waste activated sludge (WAS) can be increased up to 76% (Bougrier et al., 2006a, 2006b; Carrère et al., 2010; Fdz-Polanco et al., 2008; Perez-Elvira et al., 2008). However, considering the noticeable higher BMP for sludges from RBF, CEPT and HRAS reported in the literature (Ge et al., 2017; Ju et al., 2016; Paulsrud et al., 2014) in comparison with conventional ones, the impact of TH on increasing methane yield is expected to be lower.

The second advantage is the obtention of a sterilized sludge. European Directive 86/278/CEE promotes the use of sewage sludge in agriculture and up to 4-4.5 million ton of TS of sewage sludge were used in Europe in years 2010-2012 as a fertilizer (http://epp. eurostat.ec.europa.eu). Although this Directive does not consider the presence of pathogens, 11 out of 27 EU countries have adopted more restrictive legislation (Kacprzak et al., 2017; Kelessidis and Stasinakis, 2012), establishing thresholds not achievable during mesophilic AD (Astals et al., 2012). Therefore, mesophilic digested sludge usually needs further treatment before its agricultural use, this representing up to 50% of the STP costs (Vázquez-Padín et al., 2011), which can be avoided when TH is included before AD.

The goal of this chapter is to study how the energetic and economic balance in a novel STP can be affected by the installation of a TH unit, assessing the differences with a conventional STP configuration.

5.2. MATERIALS AND METHODS

5.2.1. *Wastewater treatment and sludge production*

RBF sludge was taken from a RBF placed in Blaricum STP (The Netherlands), with a typical mesh size of 350 μm (Behera et al., 2018) treating around 1,600 m^3/h of wastewater. CEPT sludge was generated in a pilot plant located in a STP in the north-west of Spain. The pilot plant, described by Suarez et al. (2009), was fed with 100 L/h of wastewater and operated at a hydraulic retention time (HRT) of 30 minutes with the addition of 125-150 mg/L of FeCl3. Two types of HRAS sludge were considered: HRAS I, from a STP in the centre of Spain, which treats an average flow of 2,200 m^3/h of wastewater. The plant consists on a heterotrophic HRAS reactor working with a HRT of 6-7 hours and a solid retention time (SRT) of 2.5-3 days followed by a secondary settling tank with an HRT of 30 minutes. HRAS II was generated in a pilot plant of 50 L located in the same STP, working at the same conditions as the full-scale HRAS reactor, but with previous primary settling.

Chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS), total solids (TS), volatile solids (VS) and pH were characterised according to Standard Methods (APHA, 2005). Volatile fatty acids (VFAs) were measured by gas chromatography with flame ionization detection (FIC, HP 5890A).

5.2.2. *Thermal hydrolysis pilot plant*

The experiments were carried out in an automatic pilot-scale thermal system described by Sapkaite et al. (2017). The pilot plant consists on a feeding tank, a progressive cavity pump (P_{max} = 12 bar), a steam boiler, a 20 L total volume hydrolysis reactor ($V_{working}$ = 10 L) connected to a flash tank (V = 100 L) with outlet pipes for steam and hydrolysed sludge. It is equipped with automatic valves to control the steam entrance from the boiler and the sludge exit from the reactor to the flash tank. A data acquisition and control system is used to measure pressure and temperature and to control the operation. The pump introduces 10 L of sludge into the reactor and then the steam valve is opened until pressure and temperature reach the set-point values. TH was carried out at 170 ºC during 20 minutes, since some authors reported that non-biodegradable compounds begin to form at higher temperatures (Dwyer et al., 2008). At the end of the reaction time, the decompression valve is automatically opened and the hydrolysed sludge flows to the flash tank.

5.2.3. Biochemical methane potential tests

Biochemical methane potential (BMP) tests of the different sludges (RBF, CEPT, HRAS I and HRAS II sludges) before and after TH were carried out in an AMPTS II equipment (Bioprocess Control) following the protocol described by Holliger et al. (2016). The tests were conducted in 2 L bottles (1.9 L of working volume) in triplicate and with an ISR (inoculum to substrate ratio in terms of VS) of 2. The inoculum was anaerobic flocculant biomass (15-20 g VS/L) from a mesophilic sewage sludge anaerobic digester.

The reactors were dosed with macro- and micro-nutrients, and pH was adjusted to 7.2-7.5 with NaOH or HCl. After flushing the head space with nitrogen, they were incubated at 37ºC. The assays lasted till methane production during three consecutive days was less than 1% of the total production. Methane production by each sludge was calculated as the difference between the average production in the bottles with substrate minus the average production in the blank (residual production of the inoculums). BMP was calculated as the experimental ultimate methane production, expressed in L(N)/kg VS fed, where N means normal conditions (1 atm, 0ºC). Anaerobic biodegradability (AB) was expressed as the percentage of the initial COD of the substrate converted to methane. At the end of the test, bottles were opened and pH and VFAs concentration were measured to confirm that no acidification occurred.

5.3. ENERGETIC AND ECONOMIC ASSESSMENT: CASE STUDY

5.3.1. Novel sewage treatment plant configurations and energy demand inventory

The influence of TH on the energetic and economic balance in four different STPs configurations, depending on the mainstream COD recovery technology, was evaluated; three of them referring to novel configurations based on CEPT (Figure 5.1A), HRAS (Figure 5.1B) and a combination of RBF and HRAS (Figure 5.1C) and one conventional activated sludge (CAS) process (Figure 5.1D). A 500,000 inhabitants equivalent STP, with a flow rate of 125 L/inhabitant·d and a COD of 500 mg/L (Wan et al., 2016) was considered for all the STP configurations. The energy consumption of the different units is gathered in Table 5.1.

5.3.2. Thermal hydrolysis unit and sludge anaerobic digestion

A combined heat and power (CHP) full integration plant was considered for all the STP schemes. Therefore, heat requirements of the TH unit and digester are satisfied by the exhaust gases and hot water from CHP, respectively, and electrical requirements are satisfied by the CHP electricity co-generation. For other scenarios (no heat integration, heat recovery from flash, etc.), it is known

that the increase in energy production is clearly insufficient to cover the operational energy demand of the pretreatment process (Cano et al., 2015; Carrère et al., 2010). Total energy production (E_T, kWh/m³ sludge) in an anaerobic process depends on the volatile solids load (VSL, kg VS/m³ sludge) fed into the digester and on its biomethane production (BMP, m³(N) CH₄/kg VS) (Equation 5.1).

$$E_T = VSL \cdot BMP \cdot \Delta H_c$$ *Equation 5.1*

Considering a methane heat combustion (ΔH_c) of 11 kWh/m³ (N) CH₄ (Perry, 1984), and an electrical efficiency (η) of 0.35 in the co-generation motor (Mills et al., 2014), the net electrical energy produced (ΔE_{elec}) expressed as the difference between the energy produced by pretreated sludge minus the energy produced by fresh sludge can be obtained by Equation 5.2:

$$\Delta E_{elec} = VSL \cdot \left(SMP_{pret} - SMP_{fresh}\right) \cdot \Delta H_c \cdot \eta$$ *Equation 5.2*

TH demands around 10 kWh/m³ sludge of electrical energy (Cano et al., 2015), so it results feasible when the increase in electricity generation (Eq. 2) exceeds this requirement. A maximum TS concentration of 20% was considered for the sludges, since higher values are not attainable with conventional centrifuges (Cano et al., 2015; Zhang et al., 2018), except for RBF sludge, which can be easily dewatered till 30% of TS (Paulsrud et al., 2014; Ruiken et al., 2013). Finally, Equations 2.1-2.3 were applied to calculate total digested solids production:

5.3.3. Data for economic evaluation

Ferric chloride and electricity costs of 220 €/ton and 0.12 €/kWh, respectively, were considered (De Feo et al., 2008; STOWA, 2012). When TH is not included, a hygienization cost for composting of digested sludge of 80 €/ton TS was assumed (Management Company, 2019) In order to evaluate the possible fluctuations in electricity and sludge management costs, a sensitivity analysis was performed varying their costs in the range 0.10-0.14 €/kWh and 60-100 €/ton TS, respectively.

There is an important economy of scale in TH full-scale plants. Hence, to evaluate the importance of the STP size on the payback time for a new installation, four different plant size were considered; 100,000, 250,000, 500,000 and 1,000,000 of population equivalent STPs, with investment costs of 1,000,000 €, 1,250,000 €, 1,500,000 € and 2,000,000 €, respectively. The estimation of the payback time (PBT) for TH plants was done according to Equation 5.3.

$$PBT = \frac{Sludge\ prod \cdot Manag.cost + \Delta E_{elec} \cdot Elec.cost - Maint.}{Investment\ cost}$$ *Equation 5.3*

Table 5.1. Literature data considered for the STP energetic evaluation.

Technology	Energy demand
Wastewater pumping	0.03 kWh/m³ wastewater (Longo et al., 2016).
Chemically enhanced primary treatment	0.03 kWh/m³ wastewater (Longo et al., 2017).
Rotating belt filter	0.03 kWh/m³ wastewater (Salsnes, 2016).
High-rate activated sludge reactor	0.07 kWh/m³ wastewater (Smith et al., 2014).
Sludge recirculation	0.03 kWh/m³ wastewater (Longo et al., 2016).
Sludge thickening	0.02 kWh/m³ wastewater (Longo et al., 2016).
Chemicals addition (tertiary treatment)	0.01 kWh/m³ wastewater (Longo et al., 2016).
Partial nitritation-anammox reactor	0.20–0.25 kWh/m³ wastewater *(Schaubroeck et al., 2015).
Sludge dewatering	0.03 kWh/m³ wastewater (Longo et al., 2016).
Conventional primary treatment	0.03 kWh/m³ wastewater (Longo et al., 2016).
Conventional activated sludge	0.45 kWh/m³ wastewater (Gikas, 2017).

* Calculated as 60% of those of a conventional activated sludge reactor (0.45 kWh/m³ of wastewater according to Gikas (2017)) .
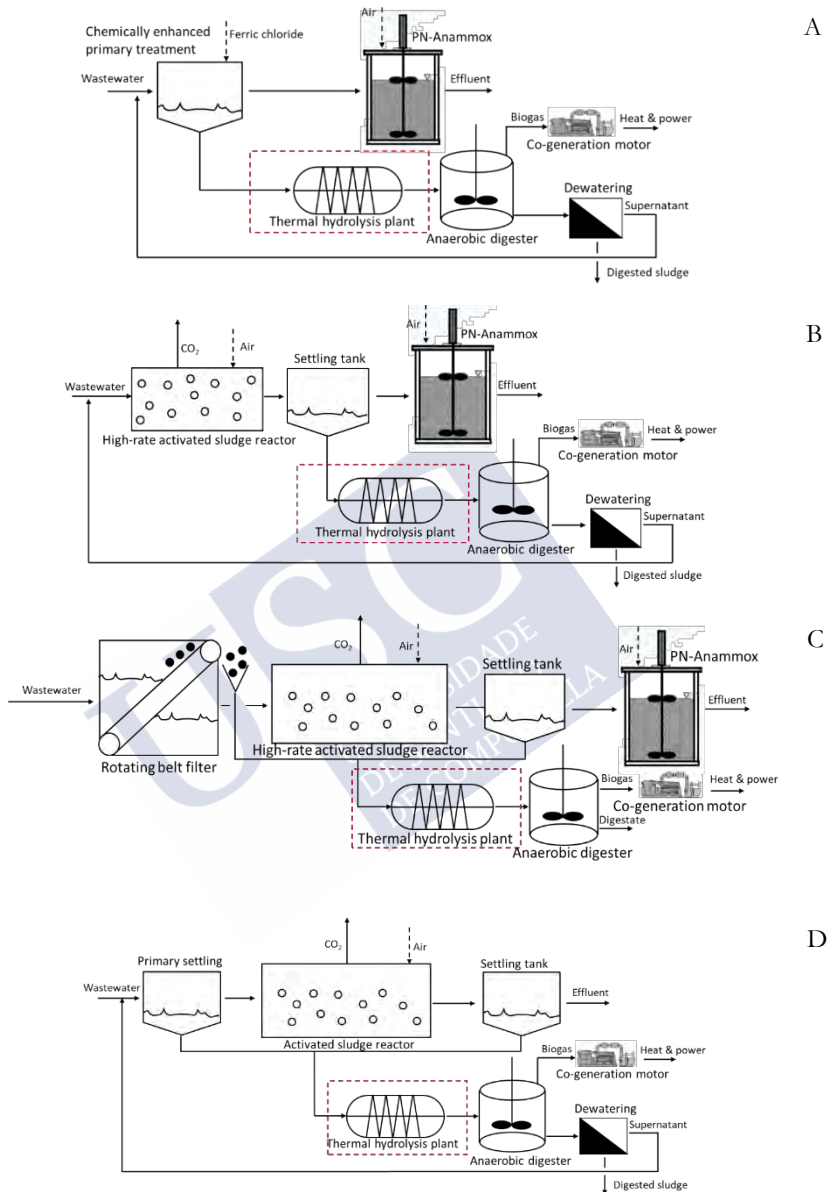
Figure 5.1. Studied STP configurations based on: A) chemically enhanced primary treatment; B) High-rate activated sludge; C) Rotating belt filter + high-rate activated sludge; D) Conventional primary settling + conventional activated sludge.

Where:

Sludge prod.: digested sludge production (ton TS/year).

Manag. cost: hygienization cost for composting of digested sludge (€/ton TS).

ΔE_{elec}: electricity generation (+) or demand (-) of the TH plant (kWh/year).

Elec. cost: electricity cost (€/kWh).

Maint.: maintenance cost of the TH plant (assumed as 10.000 €/year).

5.3.4. *Data for economic evaluation*

Ferric chloride and electricity costs of 220 €/ton and 0.12 €/kWh, respectively, were considered (De Feo et al., 2008; STOWA, 2012). When TH is not included, a hygienization cost for composting of digested sludge of 80 €/ton TS was assumed (Management Company, 2019) In order to evaluate the possible fluctuations in electricity and sludge management costs, a sensitivity analysis was performed varying their costs in the range 0.10-0.14 €/kWh and 60-100 €/ton TS, respectively.

There is an important economy of scale in TH full-scale plants. Hence, to evaluate the importance of the STP size on the payback time for a new installation, four different plant size were considered; 100,000, 250,000, 500,000 and 1,000,000 of population equivalent STPs, with investment costs of 1,000,000 €, 1,250,000 €, 1,500,000 € and 2,000,000 €, respectively. The estimation of the payback time (PBT) for TH plants was done according to Equation 5.4.

$$PBT = \frac{Sludge\ prod \cdot Manag.cost + \Delta E_{elec} \cdot Elec.cost - Maint.}{Investment\ cost} \qquad Equation\ 5.4$$

Where:

Sludge prod.: digested sludge production (ton TS/year).

Manag. cost: hygienization cost for composting of digested sludge (€/ton TS).

ΔE_{elec}: electricity generation (+) or demand (-) of the TH plant (kWh/year).

Elec. cost: electricity cost (€/kWh).

Maint.: maintenance cost of the TH plant (assumed as 10.000 €/year).

5.4. RESULTS AND DISCUSSION

5.4.1. *Organic matter recovery in the different alternatives*

CEPT with the addition of 125-150 mg/L of ferric chloride was the technology leading to the highest COD recovery (84%). It removes almost completely

particulate COD (>95%) and up to 55% of COD_{sol}, values in accordance with other authors (De Feo et al., 2008; Wang et al., 2009).

Similar COD_{tot} removal was achieved in HRAS I reactor. However, it must be pointed out that around 5% of the influent COD_{tot} was oxidized to CO_2 (calculated form the COD balance) and subsequently not recovered as sludge, in accordance with other authors (Ge et al., 2017), resulting in a final COD_{tot} recovery of approximately 80%

RBF was the technology achieving the lowest removal efficiencies (COD_{tot} (35%) and COD_{sol} (0%)), which is in accordance with other reported values (Ruiken et al., 2013; Rusten et al., 2017). As the COD removal is not enough, their effluents need further treatment before a partial nitritation-anammox (PN-AMX) unit, so a HRAS reactor after RBF has been considered in this study. In this HRAS reactor, a COD_{tot} removal of 86% was obtained, which are equivalent to those commonly assumed in CAS reactors. However, COD_{tot} mineralization was much lower (25%) than those obtained in nitrifying-denitrifying reactors, in which it can be up to 50% (Garrido et al., 2013; Wan et al., 2016), explained by the much lower SRT (3 *vs* 15-20 days). Hence, the combination of RBF and HRAS reactor led to a COD_{tot} recovery of 75%, slightly lower than in CEPT and HRAS I configurations.

5.4.2. Novel sludges characterization and influence of thermal hydrolysis on their biomethane potential

RBF sludge showed the highest VS/TS ratio (0.89) and the lowest COD/VS ratio (1.20) (Table 5.2), in agreement with Paulsrud et al. (2014). This fact is explained by the high percentage of cellulose in the sludge (up to 79% of TS) (Ruiken et al., 2013). Both fresh and pretreated RBF sludge displayed similar BMP (315 and 323 L(N) CH_4/kg VS, respectively) (Figure 5.2), with the highest AB (76.8% and 78.0%, respectively) among the four sludges, in accordance with other values from the literature (Ghasimi et al., 2016, 2015; Paulsrud et al., 2014).

CEPT sludge displayed the highest COD/VS ratio (1.68), explained by a higher fat proportion, close to those reported by other authors for primary sludge (Carballa et al., 2007b; Paulsrud et al., 2014). Moreover, it showed the lowest VS/TS ratio (0.69), characteristic from a CEPT process using metal salts, which increase the proportion of inorganic solids (De Feo et al., 2008). Contrary to RBF sludge, TH affected its BMP (Figure 5.2), i.e. 300 and 340 L(N) CH_4/kg VS for fresh and pretreated sludge, respectively, corresponding to AB of 51.2% and 56.8%, similar to the BMP obtained for conventional primary sludge (CPS) from the same STP (303 L(N) CH_4/kg VS, data not shown). This indicates that Fe^{3+} reduction, which is thermodynamically more favourable, did not limit the

conversion of organics to methane (Romero-Güiza et al., 2016; Zhang et al., 2009). On the contrary, Kooijman et al. (2017) found that the BMP of CEPT sludges were considerably higher than those of CPS and attributed to the fact that additional small particles with a higher biodegradability are removed during CEPT, which was not seen in this study.

Table 5.2. Novel sludges physico-chemical characterization. CEPT: chemically enhanced primary treatment sludge, HRAS: high-rate activated sludge, RBF: rotating belt filters sludge.

	CEPT	**HRAS I**	**RBF**	**HRAS II**
TS (g/kg)	34.2 ± 0.1	59.2 ± 0.1	57.7 ± 2.4	44.3 ± 0.3
VS (g/kg)	23.4 ± 0.1	42.7 ± 0.2	51.6 ± 2.4	33.6 ± 0.2
COD_{tot} (g/kg)	39.3 ± 4.5	73.0 ± 2.5	61.9 ± 2.0	51.0 ± 0.6
COD_{sol} (g kg)	1.02 ± 0.01	2.06 ± 0.05	1.64 ± 0.02	0.65 ± 0.01
VS/TS	0.69 ± 0.1	0.72 ± 0.04	0.89 ± 0.08	0.76 ± 0.01
COD/VS	1.68 ± 0.19	1.71 ± 0.07	1.20 ± 0.06	1.52 ± 0.03

HRAS I characteristics (VS/TS ratio of 0.72 and COD/VS ratio of 1.71) are similar to conventional mixed sludge (MS) (Astals et al., 2012; Carballa et al., 2007b), since particulate matter entering the HRAS reactor is removed through adsorption or particulate enmeshment rather than biotransformation (Jimenez et al., 2005). Regarding its BMP, it must be pointed that although there is extensive research focused on AD of long SRT (>10 days) sludges, the evaluation of those sludges produced at short SRT, especially below 5 days, has been limited so far (Ge et al., 2013). Fresh HRAS I sludge showed a BMP of 323 L(N) CH_4/ kg VS (corresponding to 53.9% of AB), which increased around 13% (363 L(N) CH_4/kg VS, 62.0% of AB) after TH (Figure 5.2). Ge et al. (2013) reported an AB of 60% for HRAS sludges working at SRT of 2 days and found that it decreased nearly 10% with every additional day of SRT, which can explain our results (SRT of 3 days). The BMP increase after TH was in the range of other reported values for MS (5-40%), which is very sensitive to the proportion of primary and biological sludge (Higgins et al., 2017; Kepp et al., 2000; Perez-Elvira et al., 2008).

Finally, the characteristics of HRAS II (VS/TS ratio (0.76) and COD/VS ratio (1.52)) are comparable to those of conventional waste activated sludge (WAS) (Cano et al., 2015; Mahdy et al., 2014; Perez-Elvira et al., 2008; Thorin et al., 2017). BMP of fresh and pretreated HRAS II sludge were 257 (N) CH_4/kg VS (47.9% of AB) and 309 L(N) CH_4/kg VS (58.8% of AB), respectively (Figure 5.2). Despite HRAS II displayed the lowest BMP among the fresh novel sludges, it resulted 20% more biodegradable than WAS (~40% of AB) (Garrido et al., 2013; Wan et al., 2016). However, after TH similar BMP values were achieved.

The neutral pH values (7.3-7.7) and the absence of VFA (<2.5 ppm acetic acid) at the end of the tests (data not shown) indicate that the performance of the tests was adequate and no acidification occurred.
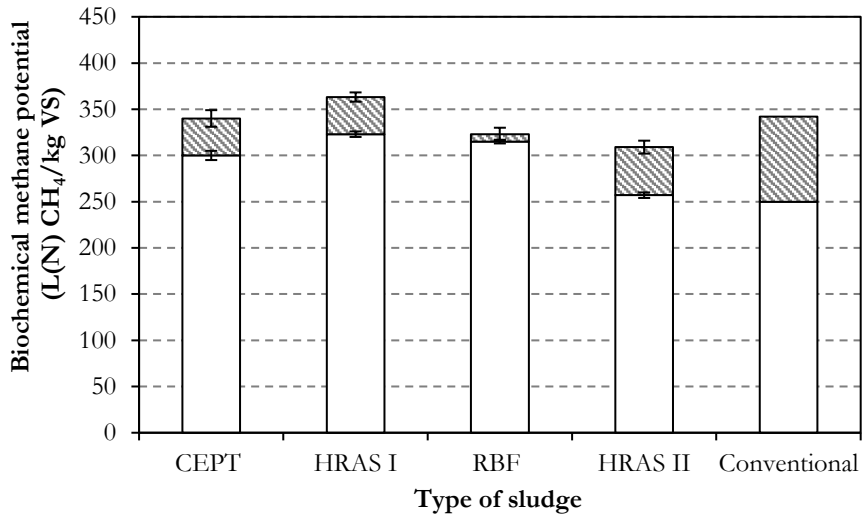
Figure.5.2. BMP for fresh (☐) and pretreated sludges (▨) (For the conventional configuration data was considered from Perez-Elvira et al. (2008).

5.4.3. Influence of thermal hydrolysis on methane and sludge production

In Figure 5.3 the expected average methane production in the four configurations with and without TH, for a 500,000 inhabitants STP, is shown. STPs based on RBF+HRAS II produce the highest methane flow (5,000 m³ (N)/d), which increases to 5,500 m³ (N)/d after TH. On the contrary, STPs based on HRAS show a lower methane production (around 4,700 m³(N)/d) increasing to 5,300 m³(N)/d after TH. For the conventional configuration, methane production only attained 2,900 m³ (N)/d, much lower than in novel configurations, explained by the lower COD recovery and the lower BMP of the sludge without TH. However, the effect of TH was much more relevant, as methane production raises up to 4,000 m³ (N)/d, an increase 2-fold higher than in novel STPs.

Regarding solids production (Equations 5.3-5.6), CEPT leads to the highest digested sludge flow (14.7 tons TS/d, Figure 5.4), explained by the solids increase due to the inorganic compounds precipitated. Even after TH (13.9 tons TS/d), it is higher than that obtained in other configurations without TH. HRAS I and the combination RBF+HRAS II produce around 12.4 and 10.2 tons TS/d, respectively, achieving in both configurations a reduction of around 1 ton TS/d

when sludge is pretreated. Digested sludge flow in conventional configuration is 11.1 tons TS/d, achieving a noticeable higher reduction in comparison with other configurations when TH is applied (2.1 tons TS/d).
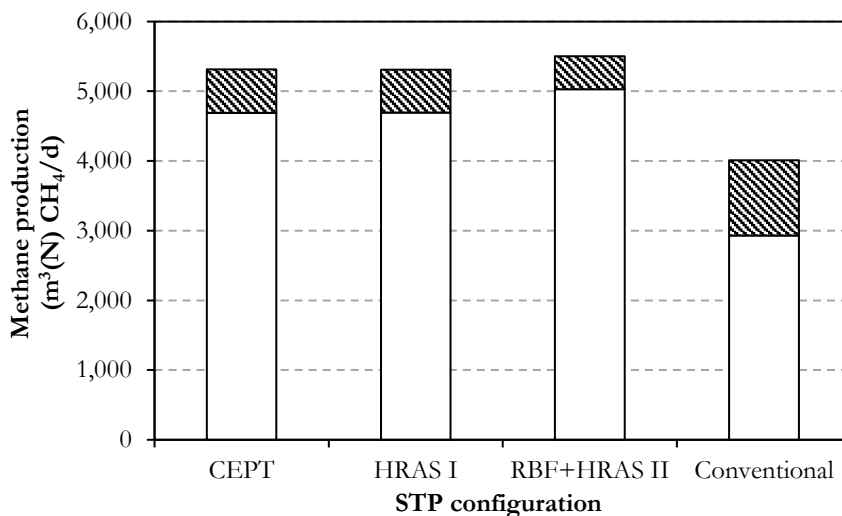
Figure 5.3. Methane production in the different STP configurations (□) and additional production caused by sludge TH (▨).
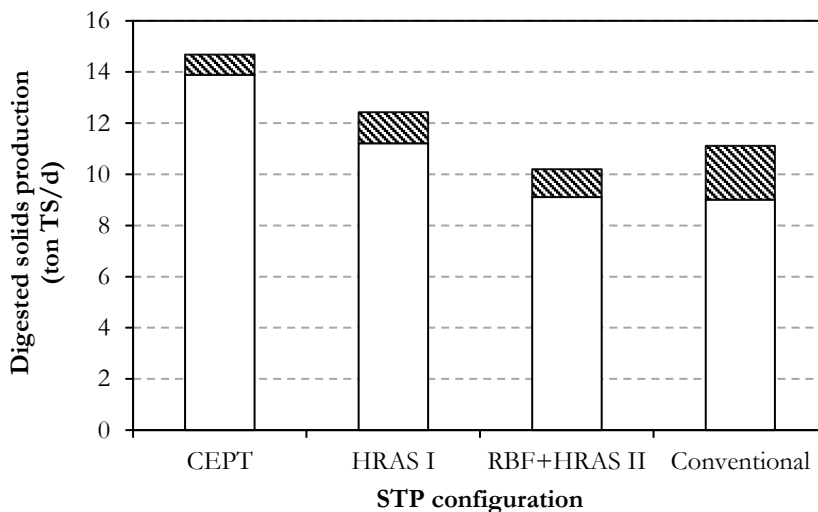
Figure 5.4. Digested solids production in each STP configuration with (□) and without (▨) TH.

5.4.4. Energetic integration of thermal hydrolysis in sewage treatment plants

In this section, an energetic balance in the TH unit in the three different novel STP configurations was performed and compared with the conventional one. The TH unit demands an electrical energy of around 10 kWh/m³ sludge in the feeding. Thickening the sludge and increasing the TS concentration reduces its volume and subsequently the energy consumption, so the feasibility of the TH unit is increased. For novel configurations, the threshold sludge concentration in the TH unit to become energetically self-sufficient (Equation 5.2) was between 7% and 9% (it must be noted that for RBF a concentration of 30% was considered since it is easily attainable, so the threshold sludge concentration of the mix RBF+HRAS sludges was 12%), being this value around 2-fold higher than in conventional configurations (4%). The impact of sludge TS concentration in the feeding to the TH unit on the energy demand of the STP is represented in Figure 5.5.
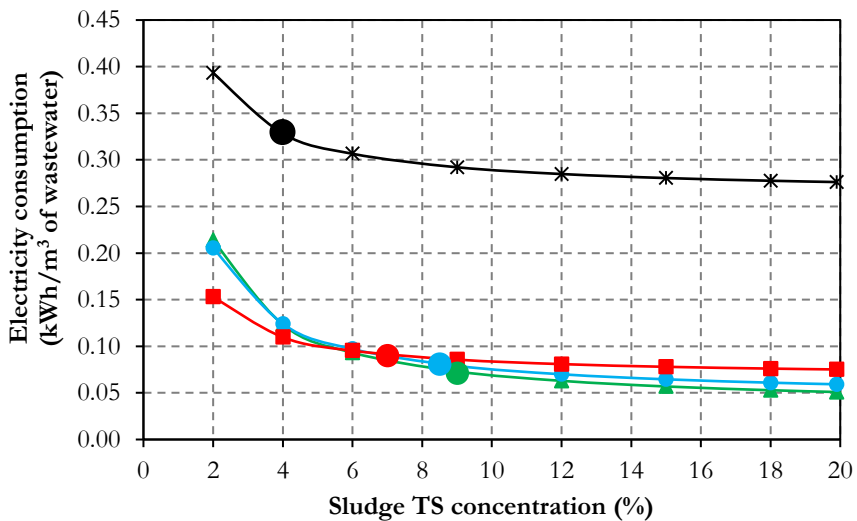
Figure 5.5. Influence of sludge TS concentration in the feeding to the TH unit on the STP energy consumption: CEPT (▲), HRAS (●), RBF (30% TS) + HRAS (■) and conventional (*) configurations. (●) represent the STP energy consumption when sludge is not pretreated before AD.

The optimised scenario consists on thickening sludges up to 20% of TS. The three novel configurations lead to a much lower energy consumption in comparison with the conventional one when TH is not applied. However, in the conventional STP TH has a more relevant effect since it can reduce almost 0.05 kWh/m³ wastewater, whereas for novel configurations a maximum energy

reduction of 0.02-0.03 kWh/m³ wastewater can be achieved. Even so, in any of the evaluated configurations the STP energy autarky can be reached. Among them, CEPT is the one that allow to obtain the lowest energy demand regardless sludge TS concentration. However, this does not necessary mean that this technology achieves the lowest operational costs, since other treatment costs need to be considered.

5.4.5. Impact of thermal hydrolysis on operational costs

The contribution of each electricity, coagulant and sludge management on STP operational costs without TH is shown in Figure 5.6. Although the alternative based on CEPT was the one with the lowest energy requirements, it achieves the highest operational costs (mainly due to the addition of ferric chloride), which are very comparable with the conventional configuration. STP based on HRAS and on the combination of RBF+HRAS resulted on 2- to 3-fold lower operational costs.
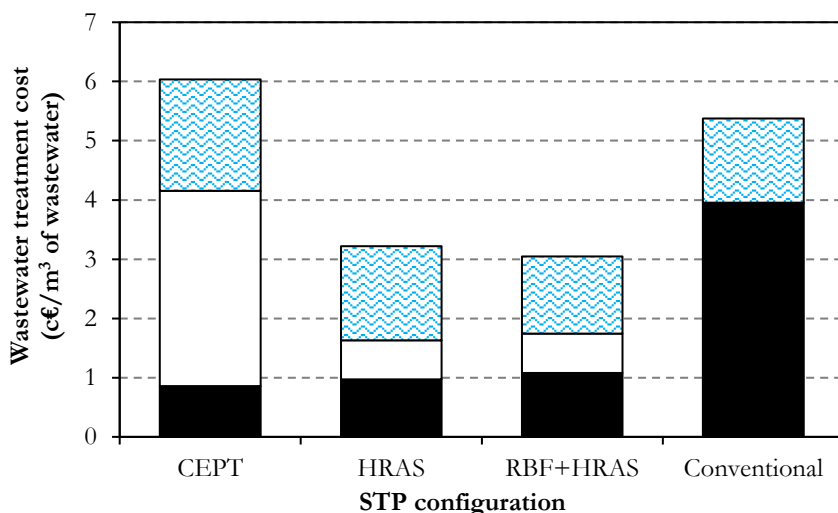
Figure 5.6. Contribution of electricity (■), coagulant (□) and sludge management (▨) to the STP operational costs.

The influence of TH on these operational costs is displayed in Figure 5.7. TH has a beneficial impact on STP operational costs even when sludge TS concentration is 1-2% for novel and also conventional configurations. These minimum values are lower than those found in the previous section for the TH unit to be energetically profitable since sludge management costs are greatly reduced. Therefore, even if the TH unit becomes electricity demanding it can

result economically favourable. The former drives to the lowest operational costs which can result even below 2 c€/m³ of wastewater (Figure 5.7) when sludge is thickened till more than 10% of TS. Moreover, the operational costs in these novel configurations would be very low affected by a fluctuation of the electricity cost since they present a considerably lower energy demand.
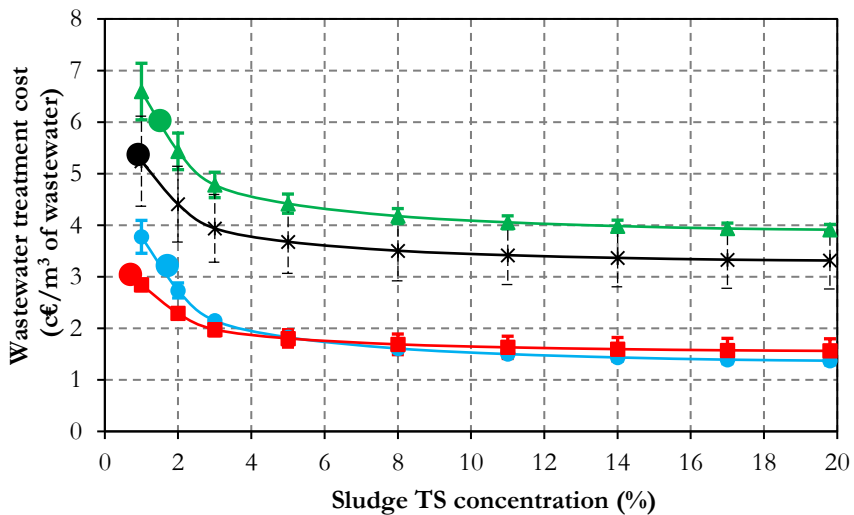
Figure 5.7. Influence of sludge TS concentration in the feeding to the TH unit on the STP operational costs: CEPT (▲), HRAS (●), RBF (30% TS) + HRAS (■) and conventional (*) configurations. (●) represent the STP energy consumption when sludge is not pretreated before AD. Error bars represent the impact of the potential fluctuations of electricity cost.

The economic impact of additional self-produced electricity and sludge disposal savings are specifically shown in Figure 5.8. In novel configurations, for a TS concentration of 10%, almost no benefit from electricity production in novel schemes is obtained, being sludge disposal savings 300,000 €/year for RBF+HRAS configuration, 360,000 €/year for HRAS alternative and 430,000 €/year for CEPT configuration (Figure 5.8). In conventional STPs, the economic benefits of TH due to extra self-produced electricity are much higher (110,000-145,000 €/year, Figure 5.8), being sludge disposal comparable to those of the HRAS configuration (320,000 €/year, Figure 5.8).

In the optimised scenario, TH in novel STPs drives to an additional economic benefit of 41,000-58,000 €/year due to extra self-produced electricity. As a conclusion, it appears that the impact of TH on reducing wastewater treatment costs is mainly due to sludge disposal savings rather than other energetic factors.
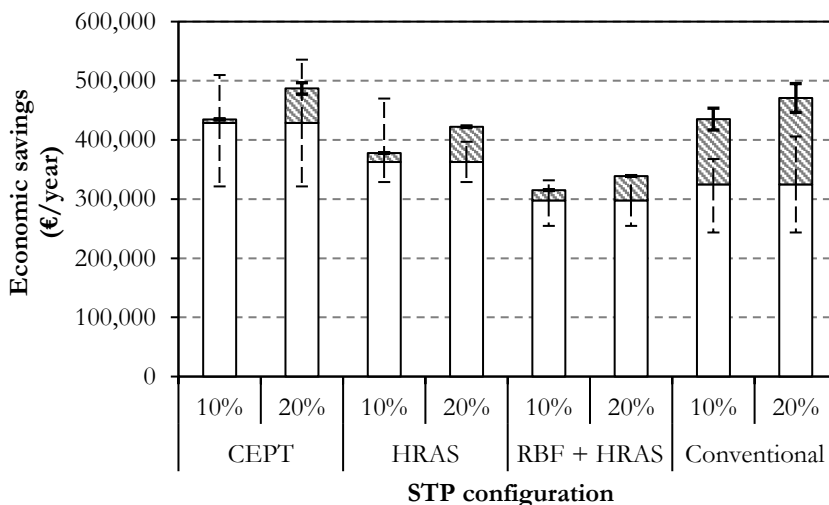
Figure 5.8. Economic benefit of sludge TH due to electricity generation (▨) and sludge disposal savings (□). 10% and 20% refer to sludge TS concentration. Continuous bar errors represent the impact of the potential fluctuations of electricity cost between 0.10 and 0.14 €/kWh and discontinuous bar errors of sludge management cost between 60 and 100 €/ton TS.

5.4.6. Economy of scale: influence of size on the payback time of thermal hydrolysis units

Figure 5.9 shows the influence of sludge TS concentration on the payback times for the TH unit in the different STP sizes considered in this work. The comparison of the different STP configurations for a specific size shows that the conventional STPs is the one that achieves the lowest payback times, whereas the alternative based on RBF+HRAS is the one achieving the highest ones. The effect of TS concentration on the payback time is much more relevant in the 100,000 inhabitants STP (Figure 5.9A), and more specifically in the range 5-11% of TS. The minimum payback times for this STP size are 18 years for the configuration based on RBF+HRAS and 12-14 for the others, including the conventional alternative, what might result too high. For the 250,000 inhabitants STP (Figure 5.9B) payback times are 2-fold decreased compared to the 100,000 inhabitants STP, achieving minimum values of 8 years for the RBF+HRAS alternative and around 6 for the others.

For the 500,000 inhabitants STPs (Figure 5.9C), considerably lower payback periods were determined. Sludge concentration has a much lower influence on payback time than in smaller STPs. Minimum values of 5 years for RBF+HRAS configuration and of 3-4 years for the other alternatives were calculated for the 500,000 inhabitants STP.
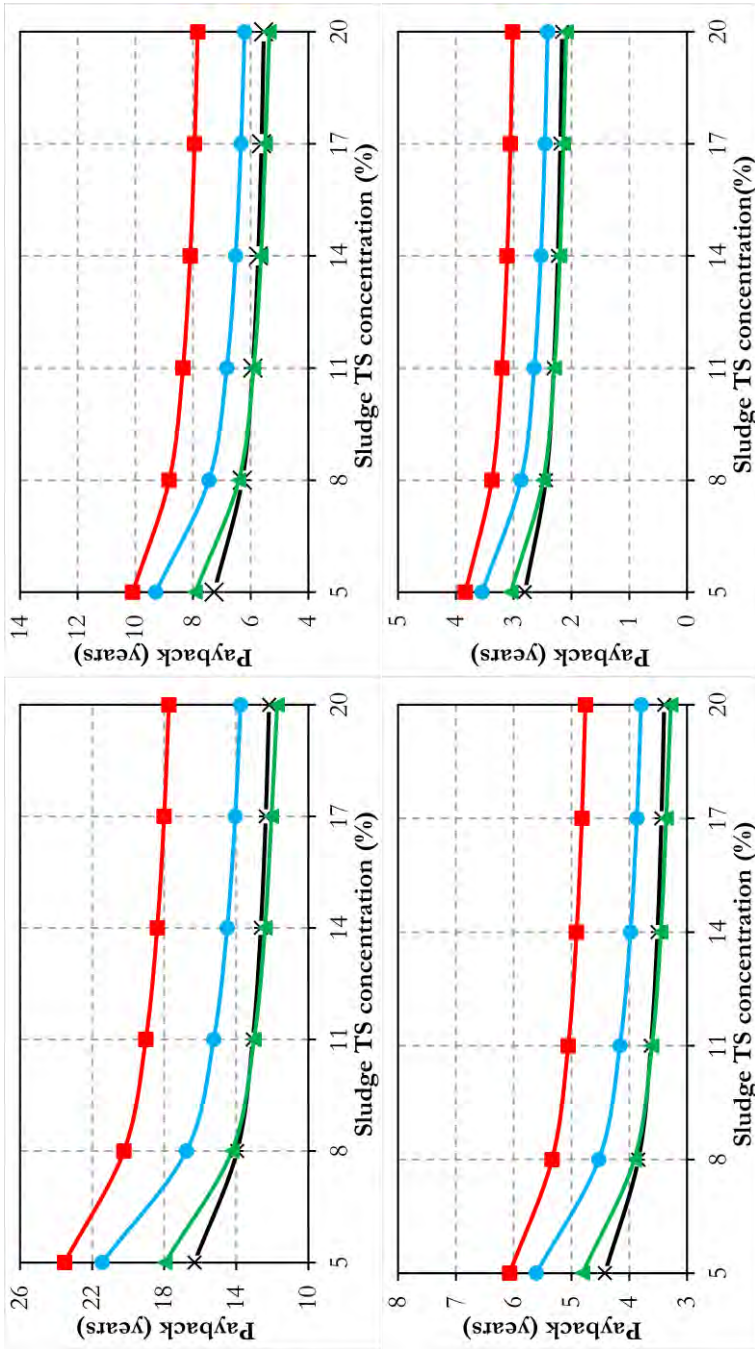
Figure 5.9. Influence of sludge concentration on the payback time for a TH plant in CEPT (▲), HRAS (●), RBF+HRAS (II) (■) and conventional (*) STP configuration for a wastewater treatment plant for A) 100,000 B) 250,000 C)500,000 and D) 1,000,000 inhabitants equivalent.

Very similar payback periods were achieved for the 1,000, 000 inhabitants STP, which range from 2 to 4 years, without important differences among the different configurations, being the influence of TS concentration almost negligible for all of them.

Moreover, a sensitivity analysis was performed in order assess the influence of a potential fluctuation of: i) the electricity cost between 0.10 €/kWh and 0.14 €/kWh and ii) of sludge management cost between 60 €/ton TS and 100 €/ton TS on the payback time of the TH plants (Figures A5.1-A5.4 in Annex) . The results show that the fluctuation of sludge disposal cost is much more relevant than a fluctuation of electricity cost, which barely impacts the payback time for all the analysed STP configurations and its sizes. Whereas for the STPs for 100,000 and 250,000 inhabitants equivalents a hypothetical decrease in sludge management cost would substantially increase the payback time for a TH plant for not only the three novel configurations but also for the conventional one, for the two biggest STP (500,000 and 1,000,000 inhabitants equivalents STPs) the payback time would be barely affected by this potential fluctuation.

5.5. CONCLUSIONS

Sludge TH approaches novel STPs to the energy self-sufficiency, which is not reachable in any of the analysed configurations. In novel STP schemes, the impact of TH on the STP economy is mainly due to sludge disposal savings rather than other energetic factors. A minimum total solids concentration in the sludge of approximately 1-2% to achieve a reduction in operational costs was found. Payback times for a new TH unit are greatly dependent on the STP size, showing that their profitability is considerably higher in huge STPs.

5.6. ANNEXES
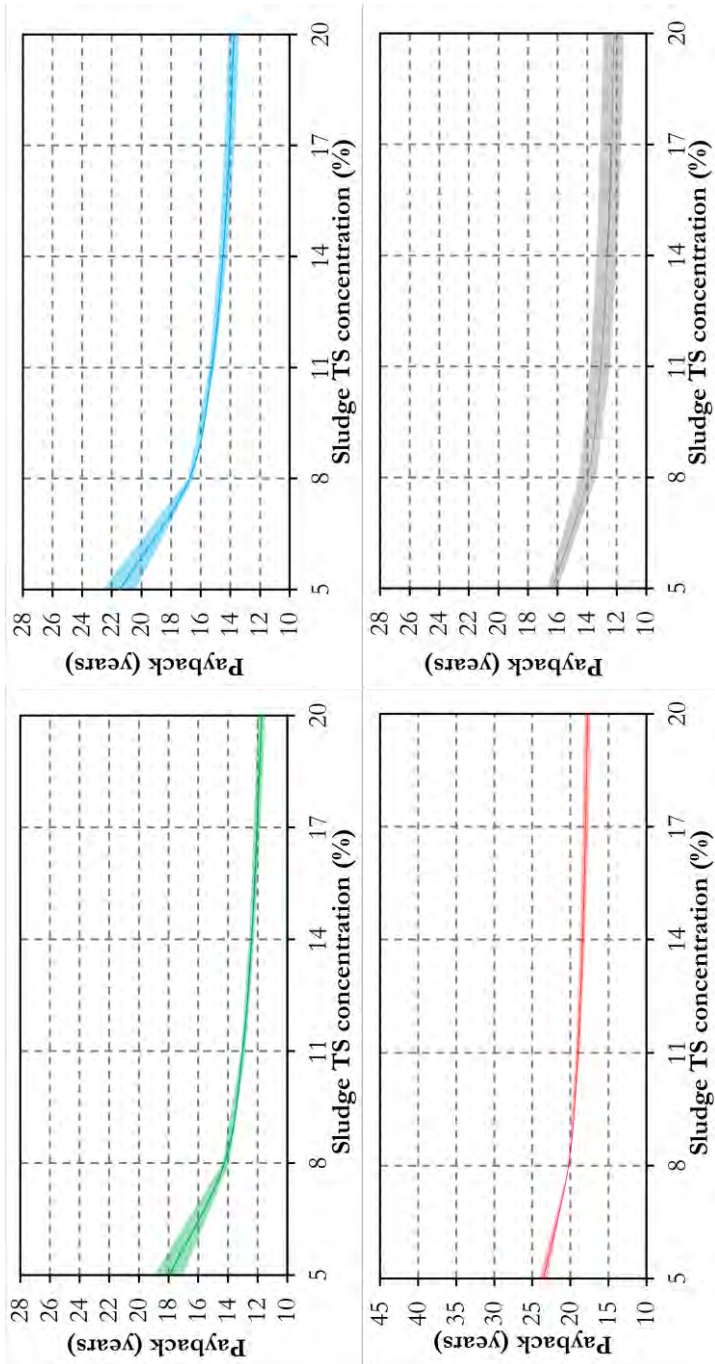
Figure A5.1a. Influence of electricity cost between 0.10 €/kWh and 0.14 €/kWh on the payback time for a thermal hydrolysis plant in (A) CEPT, (B) HRAS, (C) RBF+HRAS II and (D) conventional STP configuration for a wastewater treatment plant for 100,000 inhabitants equivalents.
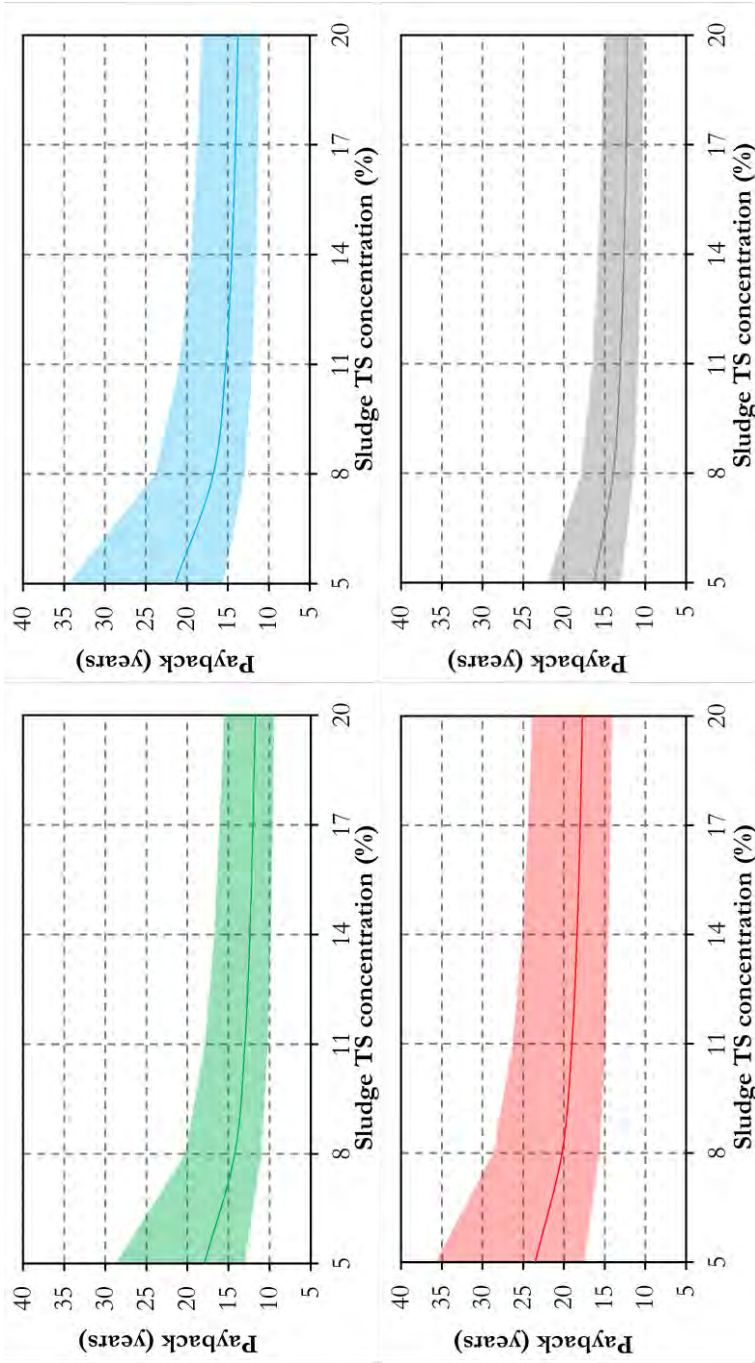
Figure A5.1b. Influence of sludge disposal cost between 60 €/ton TS and 100 €/ton TS on the payback time for a thermal hydrolysis plant in (A) CEPT, (B) HRAS, (C) RBF+HRAS II and (D) conventional STP configuration for a wastewater treatment plant for 100,000 inhabitants equivalents.
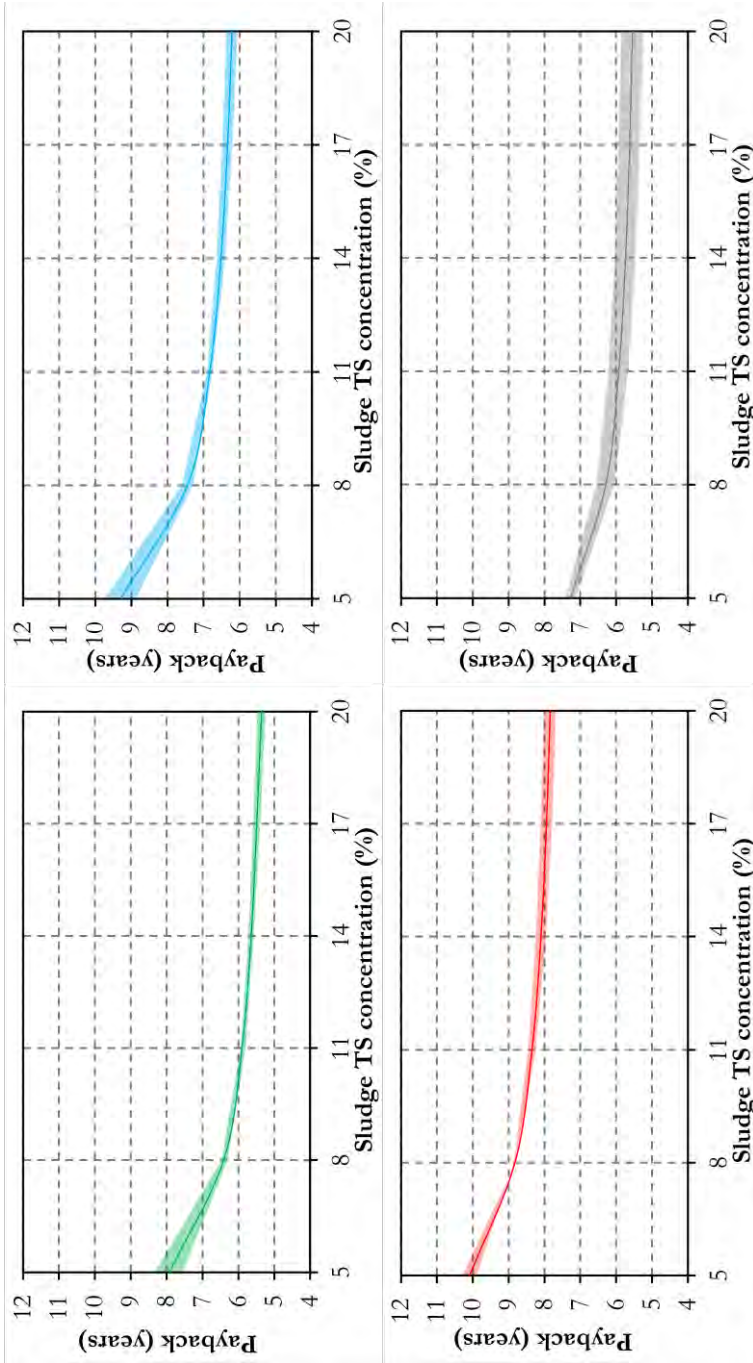
Figure A.5.2a. Influence of electricity cost between 0.10 €/kWh and 0.14 €/kWh on the payback time for a thermal hydrolysis plant in (A) CEPT, (B) HRAS, (C) RBF+HRAS II and (D) conventional STP configuration for a wastewater treatment plant for 250,000 inhabitants equivalents.
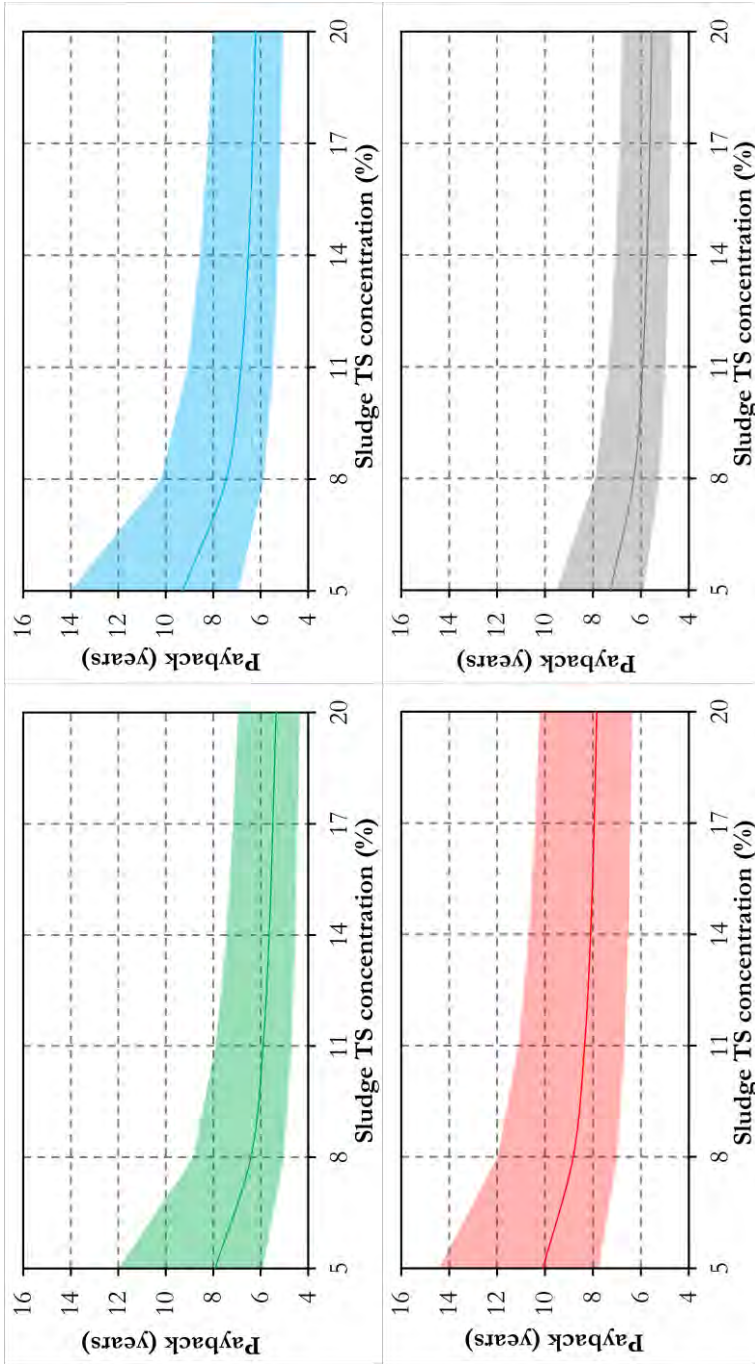
Figure A5.2b. Influence of sludge disposal cost between 60 €/ton TS and 100 €/ton TS on the payback time for a thermal hydrolysis plant in (A) CEPT, (B) HRAS, (C) RBF+HRAS II and (D) conventional STP configuration for a wastewater treatment plant for 250,000 inhabitants equivalents.
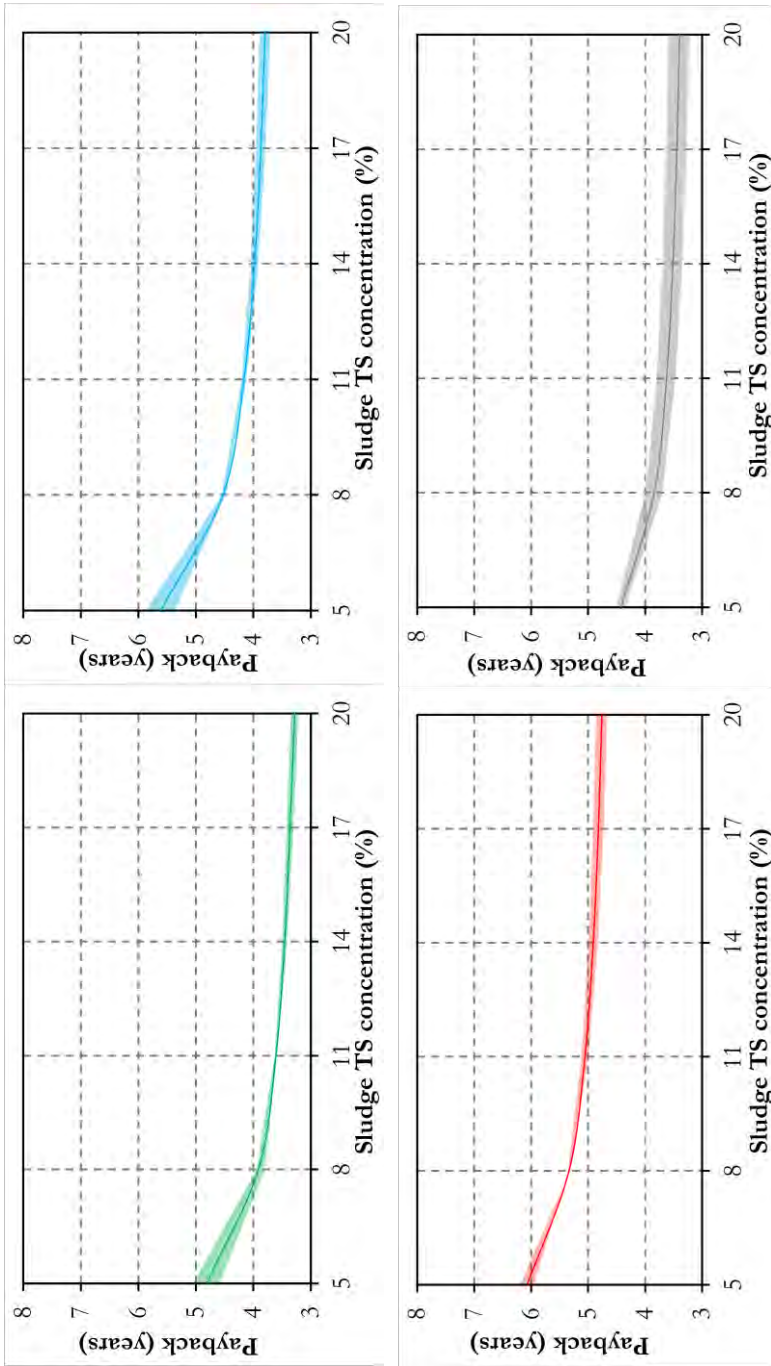
Figure A5.3a. Influence of electricity cost between 0.10 €/kWh and 0.14 €/kWh on the payback time for a thermal hydrolysis plant in (A) CEPT, (B) HRAS, (C) RBF+HRAS II and (D) conventional STP configuration for a wastewater treatment plant for 500,000 inhabitants equivalents.
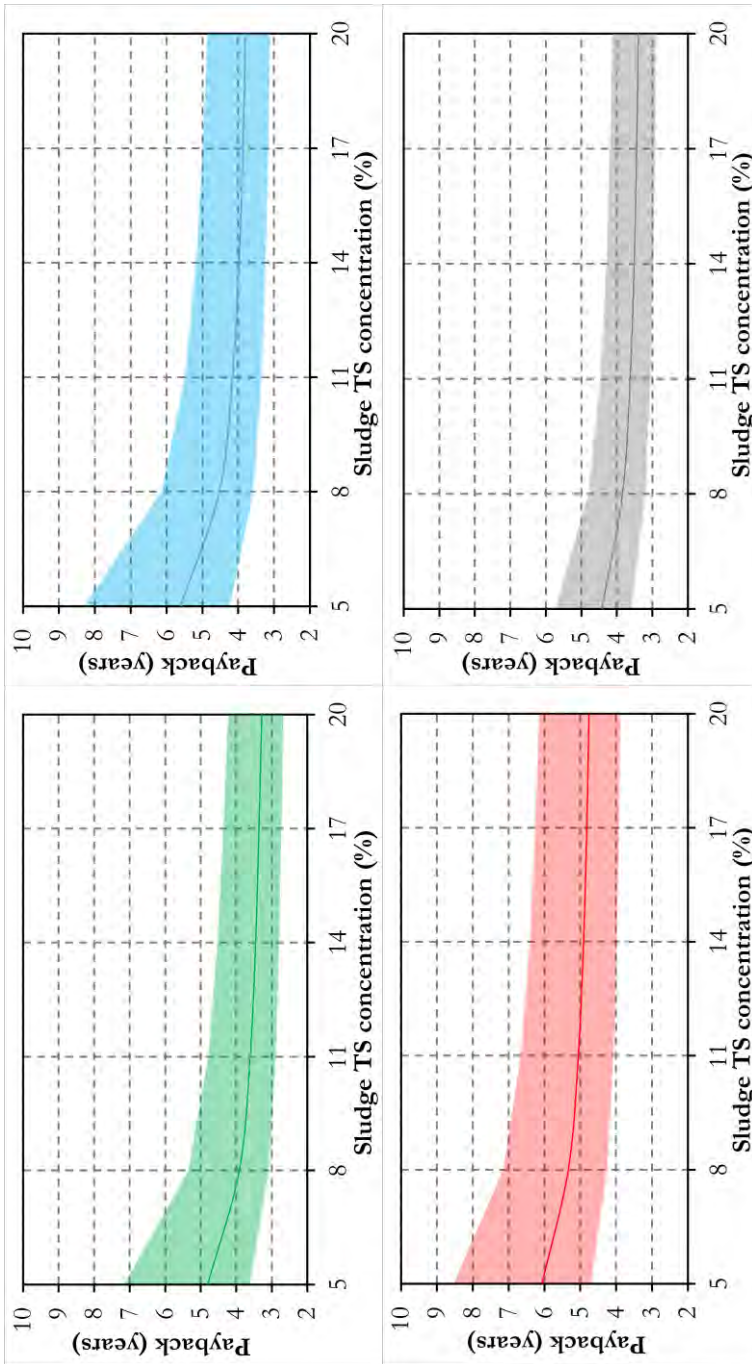
Figure A5.3b. Influence of sludge disposal cost between 60 €/ton TS and 100 €/ton TS on the payback time for a thermal hydrolysis plant in (A) CEPT, (B) HRAS, (C) RBF+HRAS II and (D) conventional STP configuration for a wastewater treatment plant for 500,000 inhabitants equivalents.
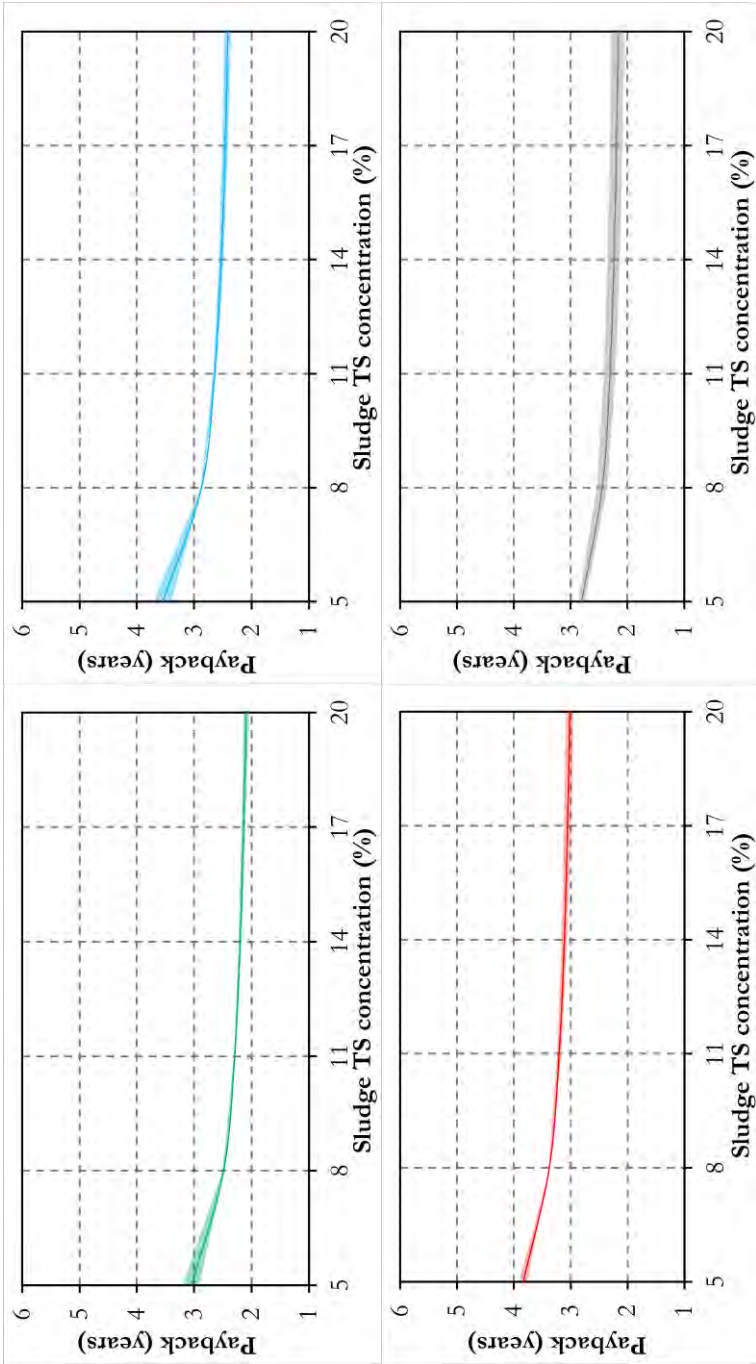
Figure A5.4a. Influence of electricity cost between 0.10 €/kWh and 0.14 €/kWh on the payback time for a thermal hydrolysis plant in (A) CEPT, (B) HRAS, (C) RBF+HRAS II and (D) conventional STP configuration for a wastewater treatment plant for 1,000,000 inhabitants equivalents.
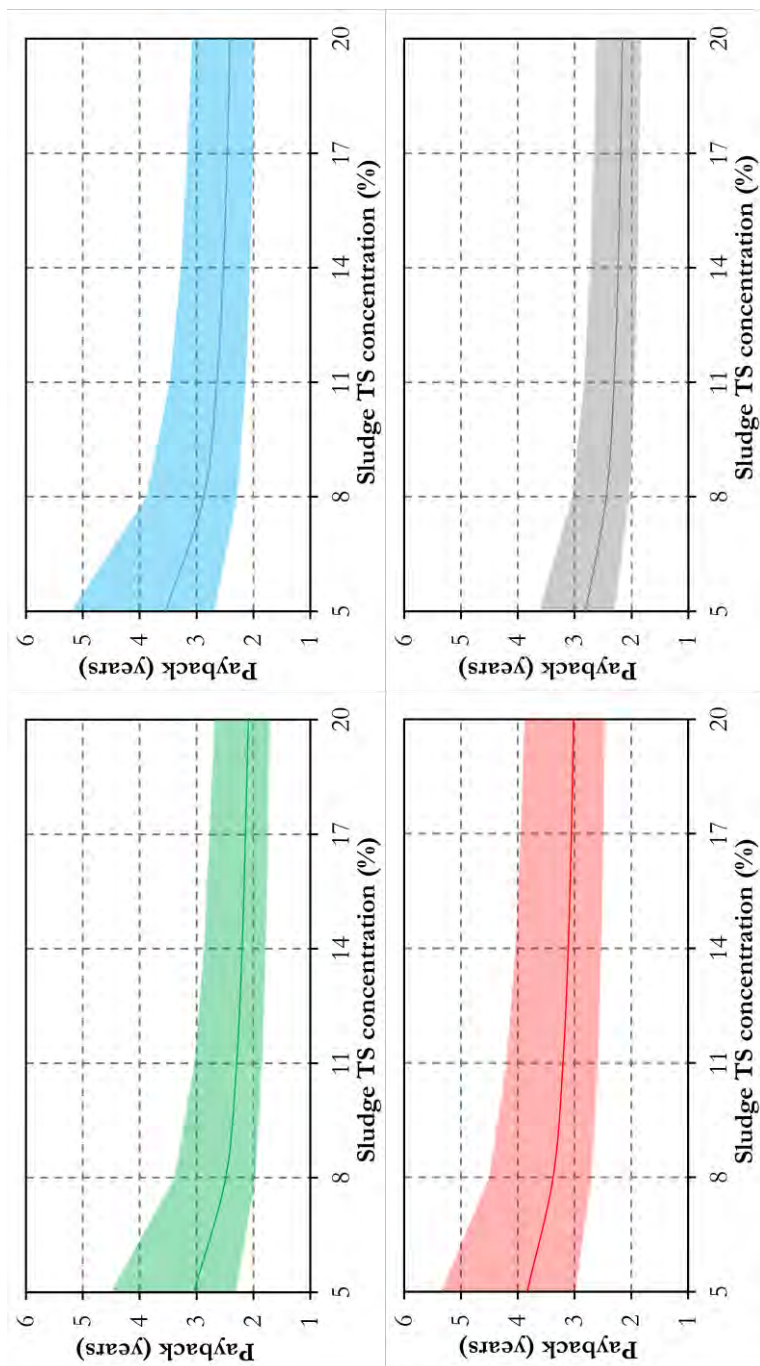
Figure A5.4b. Influence of sludge disposal cost between 60 €/ton TS and 100 €/ton TS on the payback time for a thermal hydrolysis plant in (A) CEPT, (B) HRAS, (C) RBF+HRAS II and (D) conventional STP configuration for a wastewater treatment plant for 1,000,000 inhabitants equivalents

CHAPTER 6

FATE OF ORGANIC MICROPOLLUTANTS IN NOVEL AND CONVENTIONAL SEWAGE TREATMENT PLANTS

SUMMARY

Scarce information is available about the fate of organic micropollutants (OMPs) in novel sewage treatment plants (STPs). Therefore, the objective of this work is to assess the fate of OMPs in three novel STP configurations by using a plant-wide simulation that integrates multiple units. The difference among the three configurations is the organic carbon preconcentration technology: chemically enhanced primary treatment (CEPT), high-rate activated sludge (HRAS) and a rotating belt filter (RBF) followed by a partial-nitritation anammox (PN-AMX) unit. The results show that the three selected novel configurations lead to comparable OMPs removal efficiencies from wastewater, which were similar or lower, depending on the OMP, than those obtained in conventional STPs. However, the presence of hydrophobic OMPs in the digested sludge noticeably differes among the three configurations. Whereas the HRAS-based configuration leads to a lower presence of OMPs in digested sludge than the conventional STP, in the other two novel configurations this presence is noticeable higher. In conclusion, novel STP configurations do not improve OMPs elimination, being the HRAS-based STP configuration the most efficient alternative.
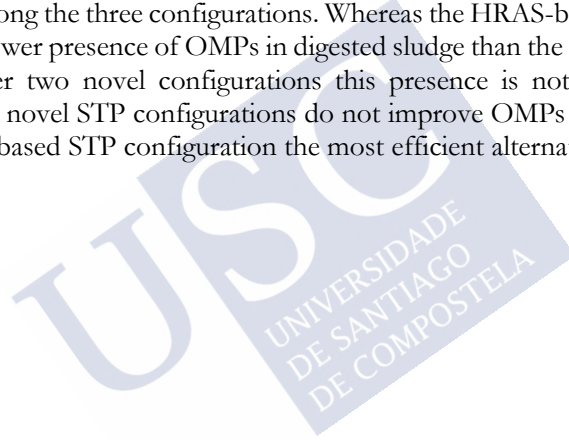
6.1. INTRODUCTION

A great effort has been made over the last two decades to determine the occurrence of organic micropollutants (OMPs) in wastewater and their fate in the different units that conform conventional sewage treatment plants (STPs), such as primary clarifiers (Behera et al., 2011; Carballa et al., 2004), activated sludge reactors (Alvarino et al., 2014; Radjenović et al., 2009; Santos et al., 2009; Suarez et al., 2010) or anaerobic digesters (Gonzalez-Gil et al., 2016; Narumiya et al., 2013; Yang et al., 2016). However, these novel technologies are yet at their early stages of industrial implementation, although preliminary works studying the fate of OMPs in rotating belt filters (RBFs) systems (Chapter 2) high-rate activated sludge (HRAS) reactors and chemically enhanced primary treatment (CEPT) (Chapter 3), partial nitritation-anammox (PN-AMX) reactors (Alvarino et al., 2015; Kassotaki et al., 2018; Laureni et al., 2016) or sludge thermal hydrolysis (TH) (Reyes-Contreras et al., 2018; Zhang et al., 2018, Chapter 4) can already be found in the literature. However, these units are commonly studied individually, so it is essential to integrate multiple units to holistically assess the fate of OMPs in novel STPs. Plant-wide simulation can be an appropriate approach since it has been successfully applied in wastewater treatment, mainly focused on energetic and/or economic aspects (Behera et al., 2018; Flores-Alsina et al., 2014, 2011; Mbamba et al., 2019). Few full-scale modelling studies are also available on OMPs removal in conventional STPs (Lautz et al., 2017; Polesel et al., 2016; Pomiès et al., 2013; Snip et al., 2014; Struijs et al., 2016; Xue et al., 2010). However, to the best of the author's knowledge, there are not works available on the fate of in novel configurations of STPs.

The goal of this work is to evaluate the fate of OMPs in novel STP configurations by using an empirical mechanistical model. The results obtained were compared with the fate of OMPs in conventional STPs.

6.2. MATERIALS AND METHODS

6.2.1. *Novel technologies for sewage treatment*

Three novel STP configurations based on HRAS (Figure 6.1A), a combination of RBF and HRAS (Figure 6.1B) and CEPT (Figure 6.1C) for COD capture, followed by a mainstream PN-AMX were considered. The sludge line was common for the three configurations: a sludge thickener, a TH unit, an anaerobic digester and a dewatering unit.

A fourth configuration, representing a conventional STP based on conventional primary treatment (CPT) + conventional activated sludge (CAS) in the water line and thickener + anaerobic digester + dewatering in the sludge line was also included (Figure 6.1D).
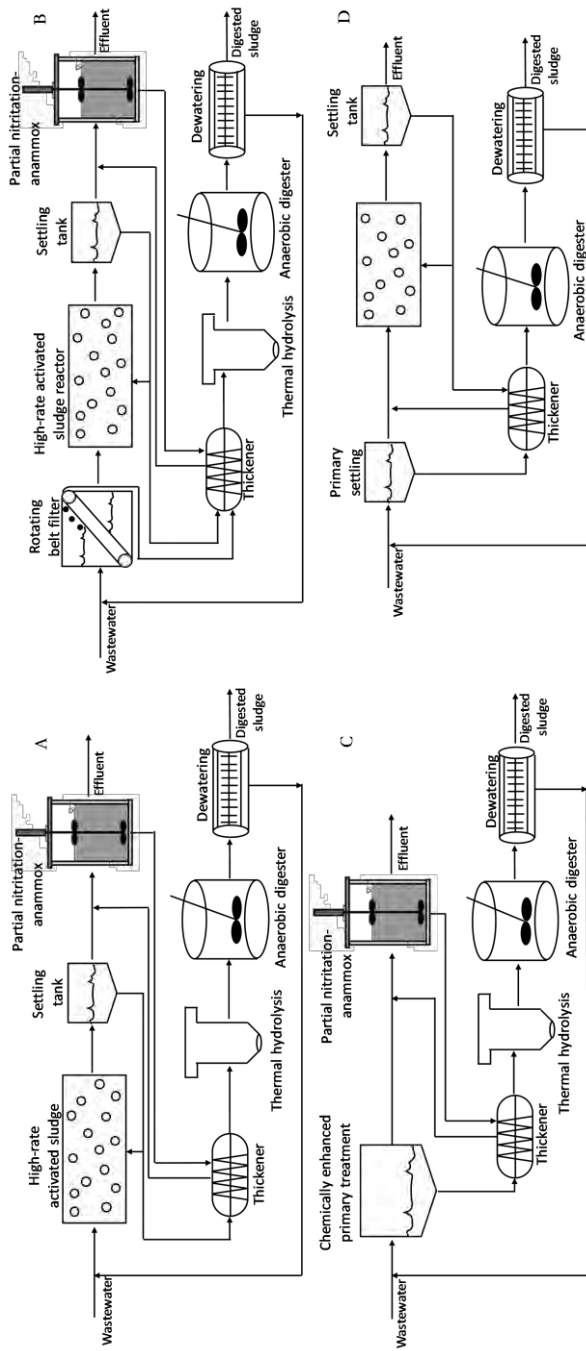
Figure 6.1. Novel and conventional STPs considered for assessing the fate of OMPs

6.2.2. Plant-wide modelling

The STP considered for the plant-wide analysis was for 100,000 inhabitants equivalents capacity with an average flowrate of 20,800 m³/d (Gernaey et al., 2011).

6.2.2.1. Conventional and chemically enhanced primary treatment and rotating belt filters systems

The CPT was modelled based on the gravity settling principle by which heavier solids settle down faster. The performance of primary clarifiers can be enhanced by the addition of chemicals or polymers, known as CEPT, which boost not only the particulate matter but also the soluble matter removal. The CEPT unit was modelled as an ideal separator where, by the addition of 125-150 mg/L of ferric chloride, particulate COD matter removal was set to 99% and the soluble COD fraction was set to 50-60% (Taboada-Santos et al., 2019b).The RBF unit works based on cake filtration and sieving. It was modelled as described elsewhere (Behera et al., 2018; Boiocchi et al., 2019).

6.2.2.2. Conventional and high-rate activated sludge reactors

The HRAS which works on bio-sorption principle was modelled as a continuous stirred-tank reactor CSTR followed by a settler (Smitshuijzen et al., 2016). The hydraulic retention time (HRT) and solid retention time (SRT) were set to 30 min and 0.3 d, respectively. The dissolved oxygen (DO) concentration inside the reactor was set to 0.2 mg/L to avoid unnecessary oxidation of biodegradable COD.

Likewise, the CAS unit was modelled as a Modified Ludzack-Ettinger (MLE) system with two anoxic tanks (for pre-denitrification) and three aerobic tanks (for nitrification) (Gernaey et al., 2014), followed by a settler. The activated sludge model ASMG1 (Guo and Vanrolleghem, 2014) was used to model both tanks. The DO in the aerobic tanks was maintained at 1 mg/L and a constant addition of external carbon (800 kg/d) to anoxic tanks was assumed for complete denitrification. A HRT of 21 hours and a SRT of 14 days were maintained in CAS system to ensure efficient nitrification.

The settler of both CAS and HRAS was modelled as a 10 layers non-reactive settling tank using the exponential settling velocity function proposed by Takács et al. (1991).

6.2.2.3. Partial nitritation-anammox reactor

The PN-AMX unit was considered as integrated fixed film activated sludge system (IFAS), a promising technology for mainstream nitrogen removal

application (Malovanyy et al., 2015). The IFAS system was modelled using a multiscale approach where the carrier geometry was assumed to be a flat sheet. The biofilm growth was simplified to one dimensional, a commonly used approach in other studies (Eberl et al., 2006; Lindblom et al., 2016; Vangsgaard et al., 2013). A relatively low DO (0.1 mg/L) compared to CAS system was maintained to suppress the nitrite oxidizing bacteria growth (Cao et al., 2017; Malovanyy et al., 2015).

6.2.2.4. *Thermal hydrolysis and anaerobic digestion units*

The TH unit was modelled by converting inert and slowly biodegradable particulate COD to soluble biodegradable COD (Bougrier et al., 2008) in the same percentage as anaerobic biodegradability increased after TH, according to Chapter 5.

The anaerobic digester was modelled using ADM1 (Batstone et al., 2002), assuming a SRT of 19 days in all configurations (Gernaey et al., 2014).

6.2.2.5. *Thickening and dewatering units*

The thickening and the dewatering units were modelled using a constant thickening and dewatering factor (Gernaey et al., 2014).

6.2.3. *Incorporation of organic micropollutants to the sewage treatment plant model*

6.2.3.1. *Raw wastewater*

Most of the authors in the literature disregard the solid phase when they determine the occurrence of OMPs in the influents of STPs. However, in this work, both liquid and solid phases were considered in order to perform a more sensitive analysis. Total OMPs concentration in a stream (C_t, mg/m³) is normally expressed as the sum of its soluble concentration (C_w, mg/m³) and its sorbed concentration (C_s, mg/m³) (Eq. 6.1).

$$C_t = C_w + C_s$$
Equation 6.1

A common approach to determine the fraction of OMPs sorbed onto suspended solids is the use of the solid–water distribution coefficient (K_D, m³/kg TSS), defined as the ratio between the concentrations in the solid and liquid phases at equilibrium conditions (Eq. 6.2).

$$K_D = \frac{C_s}{C_w \cdot TSS}$$
Equation 6.2

Where (TSS, kg/m³) is the total suspended solids concentration in that stream. Combining Eq.6.1 and Eq. 6.2, C_t, can be obtained by Eq. 6.3.

$$C_t = C_w + TSS \cdot K_D \cdot C_w \qquad\qquad Equation\ 6.3$$

6.2.3.2. Conventional and chemically enhanced primary treatment and rotating belt filters systems

The fate of OMPs in the physico-chemical separation units was modelled assuming that no biodegradation occurred, so the removal of OMPs in these units is attributed to TSS separation (Carballa et al., 2004). As sorption depends on several factors, such as the physico-chemical properties of TSS, the chemicals involved or the ambient conditions (pH, ion strength, temperature, etc) (Carballa et al., 2008), different K_D values in CPT, RBF an CEPT sludges were considered, and soluble and particulate concentrations were calculated by Eq. 6.1-6.3.

6.2.3.3. Conventional and high-rate activated sludge and partial-nitritation reactors

Considering pseudo steady-state conditions and assuming a CSTR and negligible volatilisation as previously stated (Alvarino et al., 2014), the following mass balance can be established (Eq. 6.4) in any biological reactor (CAS, HRAS and PN-AMX):

$$F_{biod} = F_{inf} - F_{eff} - F_s \qquad\qquad Equation\ 6.4$$

where F_{inf}, F_{eff}, and F_s represent the mass flows (in mg/d) corresponding to the influent, effluent and the purged sludge. F_{inf} F_{eff} and F_s can be expressed as the product of the flowrate ($F_{R,inf}$, $F_{R,eff}$, $F_{R,s}$, m³/d) by the total OMP concentration in that stream ($C_{t,inf}$, $C_{t,eff}$, $C_{t,s}$, mg/m³), respectively (Eq. 6.5).

$$F_{biod} = F_{R,inf} \cdot C_{t,inf} - F_{R,eff} \cdot C_{t,eff} - F_{R,s} \cdot C_{t,s} \qquad\qquad Equation\ 6.5$$

Assuming a pseudo-first kinetic biotransformation, the flux of biotransformed OMP (F_{biod}, mg/d) can be expressed as shown in Eq.6.6.

$$F_{biod} = k_{biol} \cdot VSS \cdot C_{t,eff} \cdot V \qquad\qquad Equation\ 6.6$$

where k_{biol} (m³/kg$_{VSS}$·d) represents the pseudo-first order kinetic constant, VSS is the biomass concentration in the reactor (kg VSS/m³) and V is the reactor volume (m³). Assuming that soluble OMP concentration in the effluent ($C_{w,eff}$, mg/m³) and in sludge ($C_{w,sl}$, mg/m³) is exactly the same and that the liquid and solid phase of each stream are in equilibrium, the $C_{w,eff}$ can be calculated by Eq. 6.7.

$$C_{w,eff} = \frac{C_{t,inf} \cdot F_{R,inf}}{k_{biol} \cdot VSS \cdot V \cdot \left(1 + TSS_{eff} \cdot K_D\right) + F_{R,eff} \cdot \left(1 + TSS_{eff} \cdot K_D\right) + F_{R,sl} \cdot (1 + TSS_s \cdot K_D)}$$

$$Equation\ 6.7$$

where K_D (m³/kg TSS) is the OMP solid-liquid equilibrium constant in the biological sludge, TSS_{eff} and TSS_s (kg/m³) the TSS concentration in the effluent and in waste sludge, respectively. From $C_{w,eff}$, sorbed concentration in the effluent and in the sludge can be calculated by Eq. 6.2.

6.2.3.4. Sludge thickener

The fate of OMPs during sludge thickening was modelled assuming that there is no variation in soluble neither specific sorbed OMPs concentration (μg/g of TSS). Therefore, the total OMP concentration in thickened sludge ($C_{t,thick}$, mg/m³) was calculated by Eq. 6.1.

6.2.3.5. Thermal hydrolysis unit

It is well known that TH causes a partial solubilisation of particulate solids and organic matter; however, the information in the literature assessing the fate of OMPs in TH plants is quite scarce. In Chapter 5 it was found that after TH the sorbed OMPs concentration in sludge ($C_{s,pt}$, mg/m³) was reduced with respect to that in the influent ($C_{s,fresh}$, mg/m³) in the same percentage as TSS were solubilised, and can be calculated by Eq. 6.8.

$$C_{s,pt} = C_{s,fresh} \cdot \frac{TSS_{pt}}{TSS_{fresh}} \qquad \textit{Equation 6.8}$$

Being TSS_{fresh} (kg SST/m³) the TSS of sludge before TH and TSS_{pt} (kg SST/m³) the TSS of pretreated sludge. They also found that the soluble (and solubilised) concentrations of some OMPs decreased during TH. Therefore, OMPs soluble concentration in pretreated sludge can be calculated by Eq. 6.9.

$$C_{w,pt} = \left(C_{w,fresh} + C_{s,fresh} \cdot \frac{TSS_{fresh} - TSS_{pt}}{TSS_{fresh}} \right) \cdot (1 - R) \qquad \textit{Equation 6.9}$$

Being R (0-1) the removal of soluble and solubilised OMPs achieved during TH. Total OMPs concentration in pretreated sludge ($C_{t,pt}$, mg/m³) is subsequently calculated as the sum of its soluble and particulate concentration (Eq. 6.10).

$$C_{t,pt} = C_{s,fresh} \cdot \frac{TSS_{pt}}{TSS_{fresh}} + \left(C_{w,fresh} + C_{s,fresh} \cdot \frac{TSS_{fresh} - TSS_{pt}}{TSS_{fresh}} \right) \cdot (1 - R)$$

$$\textit{Equation 6.10}$$

6.2.3.6. Anaerobic digestion unit

Contrary to the mainstream biological units, the fate of OMPs during sludge AD was not modelled as a pseudo-first kinetics, since in a recent study Gonzalez-Gil et al. (2018) found that OMPs biotransformation during AD is likely limited by

thermodynamic rather than kinetic constraints, and using pseudo-first order kinetics could lead to an overestimation of the biotransformation capacity. Therefore, for modelling this unit, a fixed OMPs biodegradability (B_t) was considered, and the total OMPs concentrations in digested sludge ($C_{t,dig}$, mg/m³) was calculated by Eq. 6.11.

$$C_{t,dig} = C_{t,feed} \cdot (1 - \frac{B_t}{100})$$

Equation 6.11

Being $C_{t,feed}$ the total OMPs concentration (mg/m³). The soluble and sorbed OMPs concentration in digested sludge can be calculated by Eq. 6.1-6.3.

6.2.3.7. Sludge dewatering unit

The fate of OMPs in the digested sludge dewatering unit was modelled as previously explained for the sludge thickener.

6.2.4. Selection of organic micropollutants and data input for the model

Seventeen compounds commonly used in daily life were considered in this study: three musk fragrances, galaxolide (HHCB), tonalide (AHTN) and celestolide (ADBI); three anti-inflammatories, ibuprofen (IBP), naproxen (NPX) and diclofenac (DCF); four anti-biotics, sulfamethoxazole (SMX), trimethoprim (TMP), erythromycin (ERY) and roxithromycin (ROX); three neurodrugs, fluoxetine (FLX), carbamazepine (CBZ), diazepam (DZP); one endocrine disrupting compound, triclosan (TCS); and three hormones, estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2).

The occurrence of OMPs in urban wastewater is quite wide, and OMPs concentrations in the influent were selected in the range of the values reported by Luo et al. (2014) and Verlicchi et al. (2012); 1 ppb for estrogens and 10 ppb for the rest of compounds. As previously indicated, both soluble and sorbed fractions of OMPs in the influent were considered. Figure 6.2 shows the relative presence in the liquid and solid phase of the 17 selected OMPs for this study for an influent with 380 mg/L of TSS.

Table 6.1 shows, for the different sludges considered in this work, the K_D values found in the literature together with those chosen as the most representative ones, which were assumed to carry out this work.

Table 6.1. Solid-liquid distribution constants (K_D) values (in bold) considered in this study and range of the values found in the literature.

OMP	Influent	CEPT sludge	HRAS sludge	Cellulosic sludge	Primary sludge	CAS sludge	Anaerobic sludge
				K_D (L/kg SS)			
AHTN	**8,857** 8,857 ± 2,148 [1]	**5,286** 5,286 ± 1,066 [1]	**10,150** 9,969 ± 2,557 [1] 10,332 ± 1,094 [1]	**24,247** 24,247 ± 6,069 [2]	**5,300** 5,300 ± 1,900 [3] 5,010 [4]	**4,200** 2,400 ± 960 [3] 6000 ± 300 [5] 2,714 ± 1,313 [6] 2,571-2,838 [7] 3,347 ± 1,900 [8]	**14,050** 3,000 ± 2,000 [5] 11,375 [9] 15,200 ± 7,800 [10] 16,500 - 72,000 [11]
ABDI	**3,856** 8,857 ± 845 [1]	**2,461** 2,461 ± 411 [1]	**4,936** 4,574 ± 832 [1] 5,298 ± 889 [1]	**12,000** 12,003 ± 4,037 [2]	**5,010** 5,010 [4]	**5,142** 5,142 ± 2,531 [6]	**1,200** 1,200 ± 500 [5]
HHCB	**5,927** 5,927 ± 2,168 [1]	**3,412** 3,412 ± 679 [1]	**6,823** 6,853 ± 1,945 [1] 6,792 ± 1,151 [1]	**57,450** 57,450 ± 9,770 [2]	**4,920** 4,920 ± 2,080 [3] 5,010 [4]	**2,110** 1,616 ± 772 [6] 2,214-2,478 [7] 2428 ± 1297 [8]	**9,700** 3,700 ± 1,200 [5] 12,000 [9] 13,300 ± 5,500 [10]
TCS	**10,439** 10,439 ± 2,170 [1]	**5,918** 5,918 ± 225 [1]	**8,510** 8,748 ± 1,635 [1] 8,272 ± 978 [1]	**27,947** 27,947 ± 18,228 [2]	**3,650** 1,000-6,310*[12] Mixed sludge	**5,725** 1,905-9,549 [13]	**7,020** 3,630-22,390 [11] 794-1,259 [12]
IBP	**8** 8 ± 8 [1]	**15** 15 ± 2 [1]	**14** 12 ± 10 [1] 16 ± 16 [1]	**92** 92 ± 25 [2]	**225** <20 [3] 9.5 ± 3.1 [14] 453 [15] <30 [16]	**210** 7 ± 2 [3] 240 ± 10 [5] 24 ± 5 [6] 33-80 [7] <30 [16] 144-417 [13] 6 ± 4 [17]	**60** 100 ± 100 [5] 31 [9] 38 ± 14 [10] 11-58 [11] 20-40 [12]

Table 6.1. (cont.) Solid-liquid distribution constants (K_D) values (in bold) considered in this study and range of the values found in the literature.

OMP	Influent	CEPT sludge	HRAS sludge	Cellulosic sludge	Primary sludge	CAS sludge	Anaerobic sludge
				K_D (L/kg SS)			
NPX	**9**	**0**	**20**	**1**	**125**	**125**	**10**
	9 ± 9 [1]	0 [1]	18 ± 12 [1]	1 ± 1 [2]	217 [15]	100 ± 10 [5]	0 [5]
			23 ± 12 [1]		<30 [16]	17 ± 6 [6]	<50 [9]
						36-58 [7]	11 [10]
						217 [15]	0 [11]
						<30 [16]	
						79-245 [13]	
						10 ± 1 [17]	
DCF	**13**	**7**	**25**	**10**	**245**	**155**	**79**
	13 ± 3 [1]	7 ± 5 [1]	26 ± 8 [1]	10 ± 8 [2]	459 ± 32 [3]	16 ± 3 [3]	0 [5]
			23 ± 6 [1]		500 [10]	0 [5]	600 [9]
					194 ± 134 [14]	32 ± 14 [6]	66 ± 23 [10]
					459 ± 210 [18]	<6 [7]	79-158 [12]
					<30 [16]	120 [14]	
						232 ± 139 [18]	
						<30 [16]	
						81-309 [13]	
ERY	**25**	**87**	**37**	**6**	**235**	**50**	**630**
	25 ± 10 [1]	87 ± 18 [1]	40 ± 11 [1]	6 ± 4 [2]	309 ± 272 [14]	50 ± 10 [5]	30 ± 15 [5]
			34 ± 6 [1]		165 [15]	28 ± 10 [6]	40-1,260 [12]
						49-70 [7]	
						74 ± 26 [8]	

Table 6.1. (cont.) Solid-liquid distribution constants (K_D) values (in bold) considered in this study and range of the values found in the literature.

OMP		Influent	CEPT sludge	HRAS sludge	Cellulosic sludge	Primary sludge	CAS sludge	Anaerobic sludge
					K_D **(L/kg SS)**			
ROX		**54** 54 ± 13 [1]	**200** 200 ± 25 [1]	**68** 69 ± 12 [1] 67 ± 15 [1]	**14** 14 ± 5 [2]	**400** 400 [19]	**296** 100 ± 10 [5] 51 ± 11 [6] 80-99 [7] 75 ± 48 [8] 170 [19] 570 ± 60 [17]	**1,000** 40 ± 30 [5] 2,000 [9] 83 [10] 80-2,000 [12]
SMX		**35** 35 ± 11 [1]	**45** 45 ± 15 [1]	**49** 52 ± 20 [1] 46 ± 16 [1]	**14** 14 ± 2 [2]	**15** 3.2 ± 4.5 [14] <30 [16]	**50** 80 ± 10 [5] 11 ± 7 [6] 33-63 [7] <30 [16] 50 ± 13 [17] 87-851 [13]	**250** 45 ± 30 [5] 500 [9] 23 [10] 16-25 [12]
TMP		**162** 162 ± 42 [1]	**108** 108 ± 18 [1]	**172** 188 ± 28 [1] 155 ± 20 [1]	**48** 48 ± 2 [2]	**339** 427 ± 238 [14] 251 ± 99 [16]	**212** 80 ± 5 [5] 25 ± 8 [6] 61-90 [7] 45 ± 30 [8] 119 ± 49 [16] 193 ± 104 [16] 178-398 [13] 330 ± 25 [17]	**368** 12 ± 7 [5] 83 - 724 [11]

Table 6.1. (cont.) Solid-liquid distribution constants (K_D) values (in bold) considered in this study and range of the values found in the literature.

OMP	Influent	CEPT sludge	HRAS sludge	Cellulosic sludge	Primary sludge	CAS sludge	Anaerobic sludge
				K_D (L/kg SS)			
FLX	**1,420**	**1,518**	**1,628**	**228**	**639**	**1,430**	**1,515**
	1,420 ± 124 [1]	1,518 ± 219 [1]	1,750 ± 575 [1]	228 ± 37 [2]	590-687 [11]	2,500 ± 200 [5]	700 ± 200 [5]
			1,506 ± 542 [1]			355 ± 145 [6]	275-2,754 [11]
						762-1,043 [7]	
						1,603 ± 905 [8]	
						851-1,820 [13]	
CBZ	**53**	**101**	**76**	**17**	**167**	**117**	**300**
	53 ± 15 [1]	101 ± 21 [1]	76 ± 15 [1]	17 ± 13 [2]	<20 [3]	1.2 ± 0.5 [3]	0 [5]
			75 ± 18 [1]		314 ± 205 [14]	0 [5]	20 [9]
					178 [15]	<1.0 [6]	35 [10]
					65 ± 5 [16]	15-20 [7]	40 - 186 [11]
						135 [14]	
						36 ± 2 [16]	
						50 ± 1 [16]	
						47-234 [13]	
						<75 [17]	
						17 ± 1 [20]	
DZP	**1,420**	**1,518**	**1,628**	**228**	**639**	**1,430**	**1,515**
	1,420 ± 124 [1]	1,518 ± 219 [1]	1,750 ± 575 [1]	228 ± 37 [2]	590-687 [11]	2,500 ± 200 [5]	700 ± 200 [5]
			1,506 ± 542 [1]			355 ± 145 [6]	275-2,754 [11]
						762-1,043 [7]	
						1,603 ± 905 [8]	
						851-1,820 [13]	

Table 6.1. (cont.) Solid-liquid distribution constants (K$_D$) values (in bold) considered in this study and range of the values found in the literature.

OMP	Influent	CEPT sludge	HRAS sludge	Cellulosic sludge	Primary sludge	CAS sludge	Anaerobic sludge
	K$_D$ (L/kg SS)						
E1	**399** 399 ± 49 [1]	**322** 322 ± 22 [1]	**396** 346 ± 150 [1] 446 ± 217 [1]	**131** 131 ± 8 [2]	**636** 636 ± 104 [16]	**373** 150 ± 30 [5] 607 ± 48 [16] 645 ± 87 [16] <100 [17]	**235** 300 ± 250 [5] <250 [9] 303 ± 59 [10] 58 - 813 [11]
E2	**359** 359 ± 53 [1]	**265** 265 ± 23 [1]	**656** 599 ± 19 [1] 711 ± 15 [1]	**132** 132 ± 39 [2]	**560** 560 ± 67 [16]	**667** 800 ± 100 [5] 771 ± 108 [16] 533 ± 34 [16]	**436** 250 ± 150 [5] <1,000 [9] 461 ± 212 [10] 166 - 2,188 [11]
EE2	**529** 529 ± 44 [1]	**407** 407 ± 26 [1]	**448** 464 ± 6 [1] 431 ± 67 [1]	**76** 76 ± 23 [2]	**634** 278 ± 3 [3] 251 [10] 1,017 ± 105 [16]	**875** 349 ± 4.7 [3] 200 ± 100 [5] 1,103 ± 76 [16] 1,550 ± 223 [16] 300-500 [17]	**224** 300 ± 250 [5] <1,000 [9] 432 ± 168 [10] 16-25 [11]

1. Chapter 3, 2. Chapter 2, 3. Ternes et al. (2004), 4. Suárez et al. (2008), 5. Alvarino et al. (2014), 6. Fernandez-Fontaina et al. (2013), 7. Fernandez-Fontaina et al. (2014), 8. Fernandez-Fontaina et al. (2012), 9. Carballa et al. (2007), 10. Carballa et al. (2008), 11. Gonzalez-Gil et al. (2016), 12. Narumiya et al. (2013), 13. Hyland et al. (2012), 14. Radjenović et al. (2009), 15. Jones et al. (2002), 16. Stevens-Garmon et al. (2011), 17. Abegglen et al. (2009), 18. Wick et al. (2009), 19. Joss et al. (2005), 20. Wick et al. (2009).
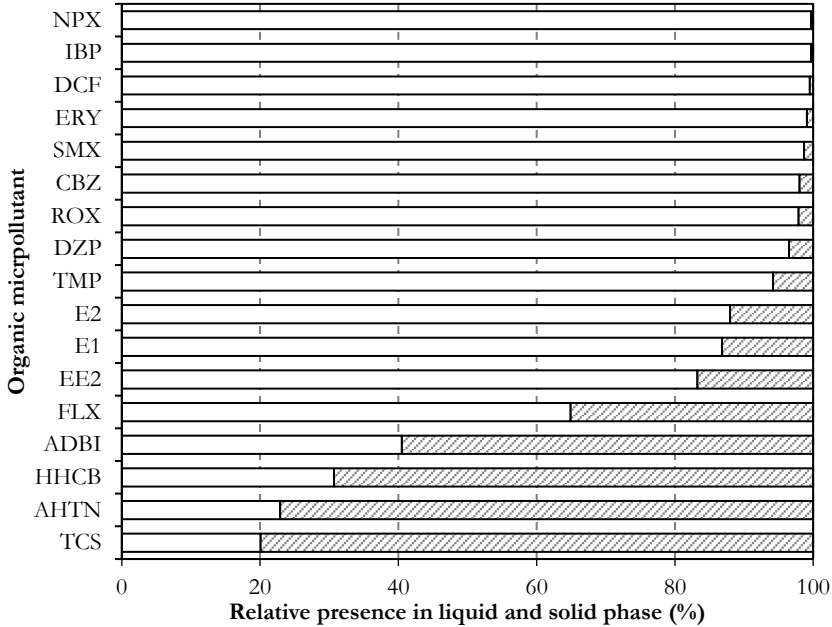
Figure 6.2 Relative presence of OMPs in the liquid (□) and solid (▨) phases of urban wastewater. Sorbed concentrations were calculates from the K_D values reported in Table 6.1.

2.4.2. Pseudo-first order biotransformation constants (k_{biol}) of organic micropollutants in the different main-stream biological reactors

Table 6.2 displays the values of k_{biol} found in the literature for the different biological units considered in this work.

The number of studies in CAS based on the nitrification-denitrification process is huge; however, for HRAS and PN-AMX reactors, the information is still scarce (Table 6.2). For the latter, only one study was found (Alvarino et al. (2015), although they studied a PN-AMX reactor treating the sludge supernatant rather than in mainstream conditions. However, a recent study from Laureni et al. (2016) reported, for some OMPs, very comparable removal efficiency in a CAS and a mainstream PN-AMX reactor, and considering that the k_{biol} values reported by Alvarino et al. (2015) were in the same range of those found for CAS, they were taken as representative for mainstream PN-AMX unit.

Table 6.2. Pseudo first-order transformation constants (k_{biol}) (in bold) considered in this study and range of the values found in the literature.

OMP	HRAS sludge	PN-AMX sludge	CAS sludge
AHTN	**15**	**0.5**	**60**
	15 ± 5 [1]	0.5 ± 0.3 [21]	38 ± 16 [5]
			2 ± 2 [5]
			3.9 [6]
			14.2 [7]
			15.7 [7]
			115 [22]
			0.02 [23]
ADBI	**16**	**1.3**	**40**
	16 ± 4 [1]	1.3 ± 0.6 [21]	6 ± 1 [5]
			63 ± 25 [5]
			9.1 [6]
			75 [22]
HHCB	**11**	**0.8**	**30**
	11 ± 4 [1]	0.8 ± 0.3 [21]	7 ± 1 [5]
			41 ± 42 [5]
			1.7 [6]
			20.9 [7]
			32.9 [7]
			170 [22]
TCS	**13**	**0.7**	**0.7**
	13 ± 5 [1]	0.7 ± 0.3 [21]	
IBP	**29**	**38**	**20**
	29 ± 9 [1]	38 ± 7 [21]	2 ± 1 [5]
			24 ± 7 [5]
			6 [6]
			2.4 [7]
			4.3 [7]
			1.3-3 [17]
			20 [22]
			21-35 [23]
NPX	**7**	**17**	**5**
	7 ± 3 [1]	17 ± 0 [21]	1 ± 0 [5]
			9 ± 2 [5]
			0.5 [6]
			1.4 [7]
			2.6 [7]
			0.1 [17]
			9 [22]
			1-1.9 [23]

Table 6.2 (cont.). Pseudo first-order transformation constants (k_{biol}) (in bold) considered in this study and range of the values found in the literature.

OMP	k_{biol} (L/g $_{VSS}$ ·d)		
	HRAS sludge	**PN-AMX sludge**	**CAS sludge**
DCF	**0.5**	**0.9**	**0.05**
	0.5 ± 0.4 [1]	0.9 ± 0.1 [21]	2 ± 1 [5]
			0.1 ± 0.1 [5]
			0.02 [6]
			0 [7]
			<0.02 [17]
			1.2 [22]
			0.03-0.05 [23]
ERY	**0.9**	**0.5**	**3**
	0.9 ± 0.8 [1]	0.5 ± 0.3 [21]	1 ± 1 [5]
			3 ± 0 [5]
			0.5 [6]
			0.8 [7]
			3 [7]
			6 [22]
			0.1 [23]
ROX	**3.3**	**0.3**	**5**
	3.3 ± 2.1 [1]	0.3 ± 0.1 [21]	8 ± 3 [5]
			2.2 ± 1.5 [5]
			1.2 [6]
			2.3-3.4 [7]
			0.023 ± 0.018 [17]
			9 [22]
			0.1 [23]
SMX	**1.5**	**0.3**	**4.5**
	1.5 ± 0.8 [1]	0.3 ± 0.1 [21]	0.7 ± 0.9 [5]
			9 ± 1 [5]
			0.1 [6]
			1 [7]
			0.3 [7]
			0.2 [17]
			0.3 [22]
			5.9-7.6 [23]
TMP	**0.4**	**0.2**	**0.3**
	0.4 ± 0.3 [1]	0.2 ± 0.1 [21]	0.6 ± 0.3 [5]
			0 [5]
			0.09 [6]
			0 [7]
			0.9 [7]
			0.22 ± 0.02 [17]
			0.15 [22]

Table 6.2 (cont.). Pseudo first-order transformation constants (kbiol) (in bold) considered in this study and range of the values found in the literature.

OMP	k_{biol} (L/g $_{VSS}$ ·d)		
	HRAS sludge	**PN-AMX sludge**	**CAS sludge**
FLX	**1.3** 1.3 ± 1.1 [1]	**0.1** 0.10 ± 0.05 [21]	**6** 10 ± 1 [5] 0.8 ± 0.5 [5] 1.98 [6] 1.3 [7] 9 [22]
CBZ	**0.4** 0.4 ± 0.3 [1]	**0** 0 [21]	**0.1** 0.2 ± 0.1 [5] 0 [5] 0.01 [6] 0 [7] <0.008 [17] <0.1 [20] 0.1 [22] <0.01 [23]
DZP	**2.6** 2.6 ± 1.6 [1]	**0** 0 [21]	**0.2** 0.4 ± 0.1 [5] 0.02 ± 0.00 [5] 0.19 [6] 0 [7] <0.16 [20] 0.4 [22] 0.02-0.04 [23]
E1	**57** 57 ± 20 [1]	**53** 53 ± 14 [21]	**85** 2 ± 4 [5] 14 ± 13 [5] 170 [22] >100 [23] 162 ± 25 [24]
E2	**46** 46 ± 10 [1]	**27** 27 ± 12 [21]	**180** 19 ± 14 [5] 11 ± 13 [5] 170 [22] >100 [23] 350 ± 42 [24]
EE2	**1.7** 1.7 ± 0.9 [1]	**2** 2 ± 1 [21]	**10** 7 ± 4 [5] 2 ± 1 [5] 20 [22] 5-10 [23] 8 ± 2 [24]

1.Chapter 3, 5. Alvarino et al. (2014), 6. Fernandez-Fontaina et al. (2013), 7. Fernandez-Fontaina et al. (2014), 17. Abegglen et al. (2009), 20. Wick et al. (2009), 21. Alvarino et al. (2015), 22. Suarez et al. (2010), 23. Joss et al. (2006), 24. Joss et al. (2004).

The range of removal efficiencies of OMPs during AD in the literature is quite wide, and sometimes controversial. Table 6.3 summarises the results found in the literature for the selected OMPs and the representative values considered in this work.

Table 6.3. OMP removal efficiency in AD (in bold) and range of the values found in the literature.

OMP	Removal during AD	OMP	Removal during AD
AHTN	**30** 60 [9] 0 [11] 0/45 [25] 40 [26] 30/60 [27]	NPX	**90** 85 [9] 100 [11] 60 [26] 100 [27] 85 [28] 90 [29] 85 [30]
ABDI	**30** *	DCF	**50** 0/80 [9] 25 [12] 20 [26] 95 [28] 25 [30]
HHCB	**30** 60 [9] 10 [11] 40 [26] 50/70 [27]	ERY	**45** 45 [12] 35 [26]
TCS	**40** 20 [11] 30 [12] 50 [26] 65 [28] 50 [29]	ROX	**50** 95 [9] 85 [11] 65 [12] 25 [26] 65/70 [27] 0 [29]
IBP	**45** 45 [9] 30 [11] 25 [26] 70-75 [27] 95 [28] 10 [29] 30 [30]	SMX	**95** 100 [9] 80 [11] 100 [12] 100 [26]

Table 6.3 (cont.). OMP removal efficiency in AD (in bold) and range of the values found in the literature.

OMP	Removal during AD	OMP	Removal during AD
TMP	**70** 75 [11] 100 [12] 75 [26] 35/40 [27] 90 [29] 100 [30]	DZP	**55** 30 [9] 50 [11] 35 [26] 70/75 [27]
FLX	**35** 70 [11] 35 [26] 25-30 [27] 30 [29] 0 [30] 30 [31]	E1+E2	**40** 80 [9] 0 [11] 35 [26] 0/10 [27] 0 [30] 50 [32]
CBZ	**20** 5 [9] 30 [11] 0 [12] 10 [26] 10/20 [27] 15 [30] 0 [29]	EE2	**50** 40/95 [9] 75 [11] 45 [26] 0 [30] 20 [32]

9. Carballa et al. (2007), 11. Gonzalez-Gil et al. (2016), 12. Narumiya et al. (2013), 25. Clara et al. (2011), 26. Gonzalez-Gil et al. (2018), 27. Chapter 4, 28. Samaras et al. (2014), 29. Yang et al. (2016), 30. Malmborg and Magnér (2015), 31. Bergersen et al. (2012), 32. Paterakis et al. (2012). * Considered as for the other musk fragrances.

6.3. RESULTS AND DISCUSSION

6.3.1. Influence of novel sewage treatment plants on aeration demand, methane production and effluent quality

As expected, novel configurations lead to considerably lower aeration demand than the conventional configuration (Table 6.4). This is primarily because of the implementation of the mainstream PN-AMX which greatly reduces the energy consumption compared to the CAS reactor, supporting other studies findings (Cao et al., 2017; Malovanyy et al., 2015). Moreover, lower TN concentrations in the effluent are achieved in the novel configurations, since nitrate removal is only partial in the conventional configuration due to insufficient COD.

Novel STPs also achieve considerable higher methane production than the conventional alternative, not only due to the higher COD recovery from wastewater but also due to the increase of methane productivity after sludge

pretreatment. Moreover, sludge production also results higher in novel STPs, as explained in Chapter 5.

Table 6.4. Comparison of energy requirements, digested sludge production, methane production and effluent quality in novel and conventional STP configurations

Parameters	HRAS	RBF+HRAS	CEPT	Convent.
Aeration demand (kWh/d)	1,997	1,881	1,311	4,216
CH_4 production (Nm^3/d)	2,161	2,295	2,351	1,719
Digested sludge (ton TS/d)	2.7	2.6	3.6	2.3
Effluent COD (g COD/m^3)	46	45	28	47
Effluent TN (g N/m^3)	4.4	3.8	4.2	17.6

6.3.2. Comparison of the removal efficiency of organic micropollutants from the water line in novel and conventional sewage treatment plants

Figure 6.2 shows the removal efficiency of the selected OMPs from wastewater (attributed to biotransformation and sorption into sludge) in the three novel STPs configurations and also in the conventional one. For compounds such as AHTN, HHCB, ADBI, TCS, E1+E2, IBP and NPX, high removal efficiencies (>70%) were found in both novel and conventional configurations. Other OMPs, such as TMP, DZP, CBZ and DCF also presented similar removal efficiencies in novel and conventional STPs configurations, but in this case with lower values (< 40%). Finally, E2, FLX, ROX, SMX and ERY displayed much lower removal efficiencies in novel STPs (between 13% and 61%) than in the conventional ones (between 84% and 95%).

The lower removal efficiencies obtained in novel configurations can be attributed to two reasons. First, the low HRT applied in HRAS reactors to minimize COD mineralization, since for most of them medium or high k_{biol} values were obtained in Chapter 3, indicating that their biotransformation is limited by the low HRT applied. Furthermore, according to Jimenez et al. (2005), particulate and colloidal COD is removed from wastewater by biological flocculation and subsequent settling, whereas the soluble fraction is eliminated by intracellular storage, biosynthesis or biological oxidation. Therefore, less COD is metabolized in this unit than in CAS reactors, producing a reduction of co-metabolism activity, which is thought to be the main mechanism for OMPs biotransformation (Gauthier et al., 2010; Kassotaki et al., 2016).

Second, because in CAS units it is desired that 100% of the ammonia is converted to nitrite and afterwards to nitrate, but in PN-AMX units only the 50% of ammonia is oxidized to nitrite. Considering again a co-metabolic approach, this lower ammonia oxidation could result on a lower biotransformation efficiency of OMPs. Moreover, the lack of nitrite oxidizing microorganisms in PN-AMX

reactors might limit OMPs biotransformation. Even though some works in the literature indicate that the removal of OMPs in CAS is linked to nitrifying activities (Fernandez-Fontaina et al., 2016), other works suggest that there is a potential overestimation of the contribution of ammonia oxidizers to OMP biotransformation to the detriment of nitrite oxidizers (Men et al., 2017).

6.3.3. Fate of organic micropollutants is in novel sewage treatment plants

According to the fate of selected OMPs in novel STP configurations, they were classified into four groups.

Group I: Hydrophobic OMPs (log $K_D \geq 3.5$)

Hydrophobic OMPs, such as AHTN, HHCB, ADBI and TCS, are well eliminated from wastewater, attaining removal efficiencies between 73% and 88% (Figure 6.2). Although the removal efficiencies were quite comparable in the three configurations, important differences were found regarding their fate (TCS, was selected as representative of this group of OMPs in Table 6.5). The HRAS-based configuration is the alternative that leads to the lowest flux in both the final effluent and in the digested sludge (Table 6.5). This is due to the high biotransformation efficiency of TCS (up to 43%) achieved in the HRAS reactor (Figure 6.3), even with the very low HRT (30 min) applied, attributed to its very high k_{biol} value under heterotrophic conditions (Table 6.2). In contrast, the PN-AMX unit did barely contribute to biotransform TCS (<4%, Figure 6.3) Additionally, 41% of TCS is removed from wastewater sorbed into sludge (Figure 6.3), attributed to its high hydrophobic behaviour, but its presence in the digested sludge (Table 6.5) is reduced due to its medium biotransformation during AD.

The partial TSS removal achieved in the RBF causes that approximately 33% of TCS in the influent is diverted to the sludge line before reaching the biological units (Figure 6.4). As a consequence, biotransformation efficiency decreases to 25%, although not affecting the mass flux in the final effluent (Table 6.5), whereas removal by sorption into sludge increases up to 60% (Figure 6.5). Therefore, a slightly higher mass flux in digested sludge is obtained in this configuration (Table 6.5).

A slightly higher effluent mass flux is obtained in the CEPT-based configuration (Table 6.5) attributed to the lack of a HRAS reactor. The high TSS elimination achieved in the CEPT unit produces a removal efficiency due to sorption of almost 80% (Figure 6.5). Subsequently, its mass flux in digested sludge is the highest one (Table 6.5).
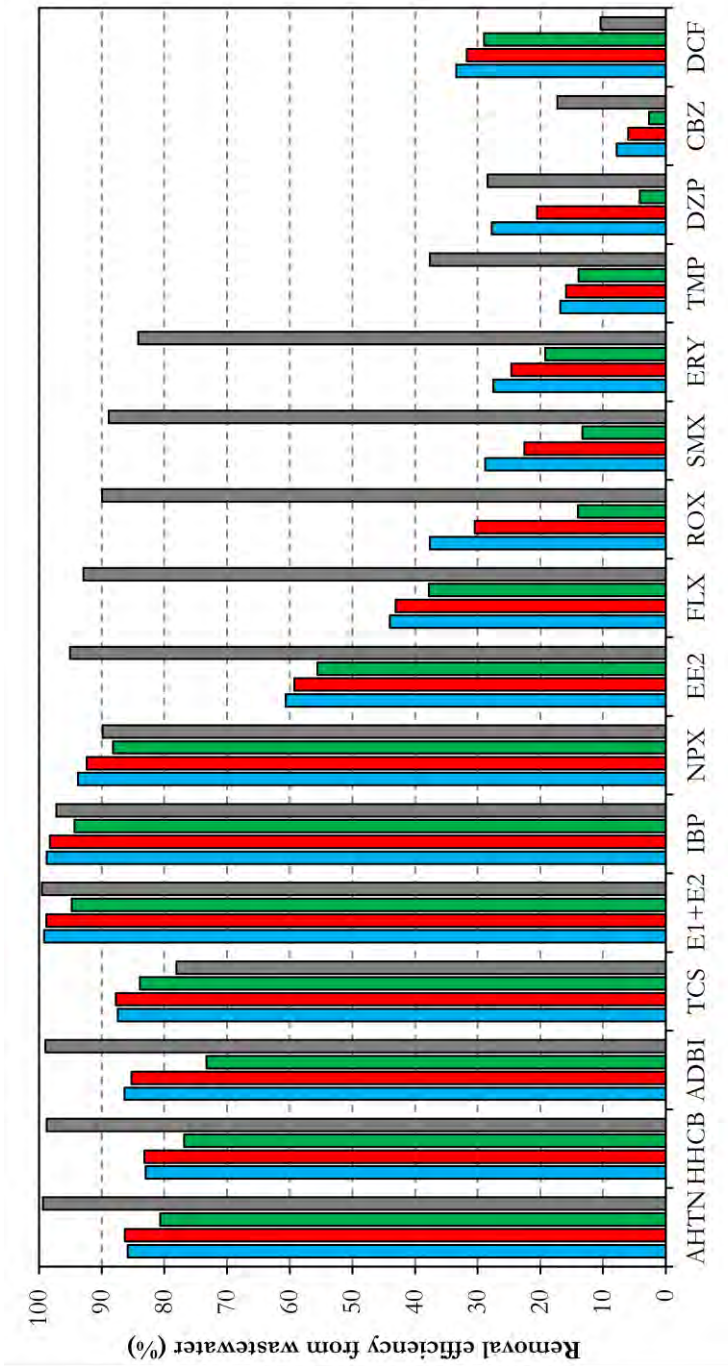
Figure 6.2. Overall comparative of the OMPs removal efficiency from wastewater achieved in the HRAS-based STP (■) the RBF+HRAS-based STP (■) the CEPT-based STP (■) and the conventional STP (■).

Table 6.5. Presence of the representative OMPs of each group in the STPs effluents and in digested sludge.

Stream	TCS	IBP	EE2	CBZ
Influent STP (mg/d)	206	206	20.6	206
Effluent HRAS (mg/d)	26	2.5	8.2	191
Effluent RBF+HRAS (mg/d)	25	3.6	8.6	195
Effluent CEPT (mg/d)	34	12	9.3	202
Effluent conventional (mg/d)	46	6	1.0	172
Digested sludge HRAS (mg/d)	36	0.1	0.8	3.5
Digested sludge RBF+HRAS (mg/d)	48	0.2	0.8	3.1
Digested sludge CEPT (mg/d)	78	0.4	1.1	3.0
Digested sludge conventional (mg/d)	74	0.5	0.7	3.7

Group II: Hydrophilic OMPs (log $K_D \leq 3.2$) with $k_{biol} \geq 10$ L/g $_{VSS}$·d in the HRAS reactor and/or ≥ 5 L/g $_{VSS}$·d in the PN-AMX reactors.

This group includes those hydrophilic OMPs that present high k_{biol} values in the HRAS and/or in the PN-AMX reactors, such as E1, E2, IBP and NPX. These compounds are well biotransformed in both biological units reaching removal efficiencies from wastewater above 95% in the three configurations. IBP was selected as representative of this group in Table 6.5.

The mass fluxes in the final effluent (Table 6.5) are very comparable in the three configurations, which is explained by the high biotransformation efficiencies in both biological systems, 69-79% in the HRAS unit and 93-94% in the PN-AMX one. In the HRAS- and RBF+HRAS-based configurations, approximately 70-80% of IBP is biotransformed under heterotrophic conditions, noticeably reducing the mass flux that reaches the PN-AMX reactor, in which just 20-30% of the OMP in the influent is biotransformed (Figure 6.3 and 6.4).

Contrary, in the CEPT-based configuration the PN-AMX reactor biotransforms 94% of the IBP in the influent (Figure 6.5), fact might be important since different transformation products (TP) are formed due to the different mechanisms involved (heterotrophic or ammonium oxidizer biomass) in the different STP configurations, and these TP might present different k_{biol} values and/or toxicity (Collado et al., 2012).

The presence of these OMPs in the digested sludge is very low in all configurations (Table 6.5) since sorption into sludge hardly contributes to their removal from wastewater (Figures 6.3-6.5).

Group III: Hydrophilic OMPs with k_{biol}<10 L/g $_{VSS}$·d in the HRAS reactor and (1≤ k_{biol} <5 L/g $_{VSS}$·d) in the PN-AMX reactor.

This group includes those hydrophilic OMPs which are partially or not removed in the HRAS reactor but show a medium-high removal efficiency in the PN-AMX one, such as EE2, which was selected as representative of this group in Table 6.5.

Similarly to the previous group, the presence of these OMPs in digested sludge is very low in all configurations (Table 6.5) since sorption into sludge barely contributes to their removal from wastewater. Regarding the water line, no major differences in their removal were found among the different novel STP configurations (Table 6.5), achieving removal efficiencies of approximately 50-60%, mainly due to the PN-AMX reactor, since the biotransformation in the HRAS reactors results below 15% (Figure 6.3-6.5).

Group IV: Hydrophilic OMPs with k_{biol} <10 L/g_{VSS}·d in the HRAS and k_{biol} <1 L/g_{VSS}·d in the PN-AMX reactors.

This group contains those hydrophilic OMPs that are not removed neither in the HRAS nor in the PN-AMX reactor (Figure 6.3-6.5) such as ROX, SMX, ERY, TMP DZP, CBZ and DCF, showing a recalcitrant behaviour. CBZ was selected as the compound representative of this group. Due to their hydrophilic behaviour, sorption does not contribute to their removal (Figures 6.3-6.5), so their presence in digested sludge is very low in all configurations (Table 6.5). Medium-low biotransformation efficiencies from wastewater (between 0 and 40%) are obtained, so they achieve a noticeable presence in the STPs effluents (Table 6.5). It must be highlighted that for part of the OMPs of this group including ROX, SMX or DZP, their biotransformation efficiency in the HRAS- and RBF+HRAS-based STPs could be enhanced to comparable values to those obtained in the CAS in the conventional configuration (Figure 6.6) by increasing the HRT, since they present medium k_{biol} values in the HRAS reactor, demonstrating that their biotransformation is limited by the low HRT. However, this would lead to a lower methane production and therefore energy recovery due to a higher COD oxidation, as reported by Jimenez et al. (2015).

6.3.4. Fate of organic micropollutants is in the sludge line of novel sewage treatment plants

Not only the removal from wastewater but also the presence of OMPs in sludge is an important issue, particularly when sludge is used as fertilizer in agriculture. Important differences were found among the novel scenarios, being the CEPT-based configuration the alternative reaching the highest OMP load in the sludge line (Figure 6.5) and the HRAS-based configuration the lowest one (Figures 6.3).
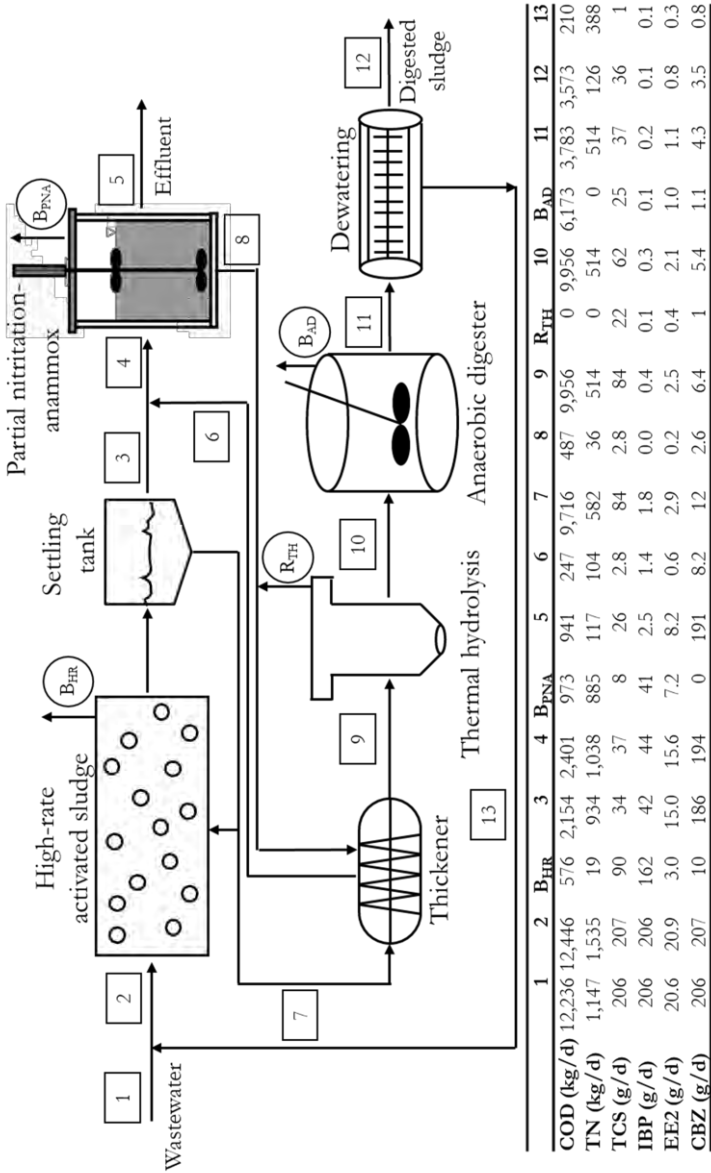
Figure 6.3 Mass balance of COD, TN and example of OMP of each type in the HRAS-based STP.

	1	2	B_{HR}	3	4	B_{PNA}	5	6	7	8	9	R_{TH}	10	B_{AD}	11	12	13
COD (kg/d)	12,236	12,446	576	2,154	2,401	973	941	247	9,716	487	9,956	0	9,956	6,173	3,783	3,573	210
TN (kg/d)	1,147	1,535	19	934	1,038	885	117	104	582	36	514	0	514	0	514	126	388
TCS (g/d)	206	207	90	34	37	8	26	2.8	84	2.8	84	22	62	25	37	36	1
IBP (g/d)	206	206	162	42	44	41	2.5	1.4	1.8	0.0	0.4	0.1	0.3	0.1	0.2	0.1	0.1
EE2 (g/d)	20.6	20.9	3.0	15.0	15.6	7.2	8.2	0.6	2.9	0.2	2.5	0.4	2.1	1.0	1.1	0.8	0.3
CBZ (g/d)	206	207	10	186	194	0	191	8.2	12	2.6	6.4	1	5.4	1.1	4.3	3.5	0.8

	1	2	3	B_HR	4	5	B_PNA	6	7	8	9	10	11	R_TH	12	B_AD	13	14	15
COD (kg/d)	12,236	12,472	8,415	743	1,667	1,674	564	919	7	4,057	6,005	191	10,246	0	10,246	6,557	3,689	3,453	236
TN (kg/d)	1,147	1,584	1,383	13	975	1,036	939	83	61	201	395	14	549	0	549	0	549	112	437
TCS (g/d)	206	208	140	53	32	34	8	25	2.2	68	54	1.4	122	39	83	33	50	48	1.7
IBP (g/d)	206	206	206	143	61	63	59	3.6	2.1	0.9	2.4	0.0	1.3	0.3	1.0	0.5	0.5	0.2	0.4
EE2 (g/d)	20.6	21.0	19.5	1.9	15.5	16.1	7.4	8.6	0.6	1.5	2.1	0.1	3.1	0.6	2.5	1.3	1.2	0.8	0.4
CBZ (g/d)	206	207	205	6	189	197	0	195	7.5	2.3	10	1.4	6.3	1.0	5.3	1.0	4.3	3.1	1.1

Figure 6.4 Mass balance of COD, TN and example of OMP of each type in the RBF+HRAS-based STP
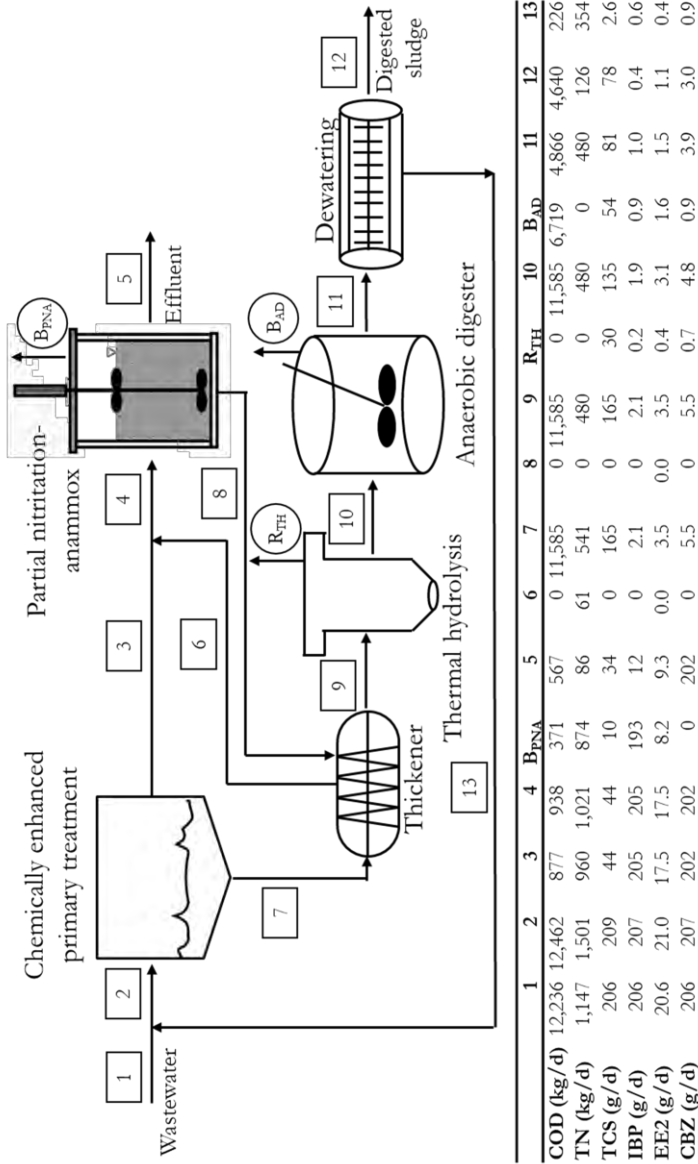
Figure 6.5 Mass balance of COD, TN and example of OMP of each type in the CEPT-based STP

	1	2	3	4	B_PNA	5	6	7	8	9	R_TH	10	B_AD	11	12	13
COD (kg/d)	12,236	12,462	877	938	371	567	0	11,585	11,585	11,585	0	11,585	6,719	4,866	4,640	226
TN (kg/d)	1,147	1,501	960	1,021	874	86	61	541	0	480	0	480	0	480	126	354
TCS (g/d)	206	209	44	44	10	34	0	165	0	165	30	135	54	81	78	2.6
IBP (g/d)	206	207	205	205	193	12	0	2.1	0	2.1	0.2	1.9	0.9	1.0	0.4	0.6
EE2 (g/d)	20.6	21.0	17.5	17.5	8.2	9.3	0.0	3.5	0.0	3.5	0.4	3.1	1.6	1.5	1.1	0.4
CBZ (g/d)	206	207	202	202	0	202	0.0	5.5	0	5.5	0.7	4.8	0.9	3.9	3.0	0.9

	1	2	3	4	B_AS	5	6	7	8	9	B_AD	10	11	12
COD (kg/d)	12,236	12,373	7,280	7,351	3,351	942	71	5,093	3,059	8,081	4,912	3,269	3,132	137
TN (kg/d)	1,147	1,443	1,176	1,186	592	363	10	267	231	488	0	488	192	296
TCS (g/d)	206	208	128	129	56	46	1.3	80	28	107	30	77	74	2.3
IBP (g/d)	206	207	205	205	199	6	0.1	1.8	0.2	1.9	0.9	1.0	0.5	0.5
EE2 (g/d)	20.6	20.8	19.0	19.0	18.0	1.0	0.0	1.8	0.1	1.9	1.0	0.9	0.7	0.2
CBZ (g/d)	206	207	204	207	30	172	3.0	3.4	5.4	5.9	1.2	4.7	3.7	1.0

Figure 6.6 Mass balance of COD, TN and example of OMP of each type in the conventional STP

Besides increasing biogas production in AD, TH contributes to a partial removal of OMPs, linked to TSS solubilisation (Chapter 4). This is especially relevant for hydrophobic compounds (Group I), attaining mass fluxes reduction of 26% in the HRAS-based configuration (Figure 6.3), 32% in the RBF+HRAS-based configuration (Figure 6.4) and 18% in the CEPT- based alternative (Figure 6.5). However, the low-medium anaerobic biodegradability reported in the literature for this group of compounds (Table 6.3) causes that AD only contributes to a partial removal from sludge. Consequently, most OMPs are present in the digested sludge (Figure 6.7), but this presence of course depends on the characteristics of each specific compound, mainly hydrophobicity and anaerobic biotransformability. For hydrophilic compounds, less than 6% of the influent mass flow is present in digested sludge, whereas for hydrophobic compounds, this number can increase up to 40% (Table 6.5).
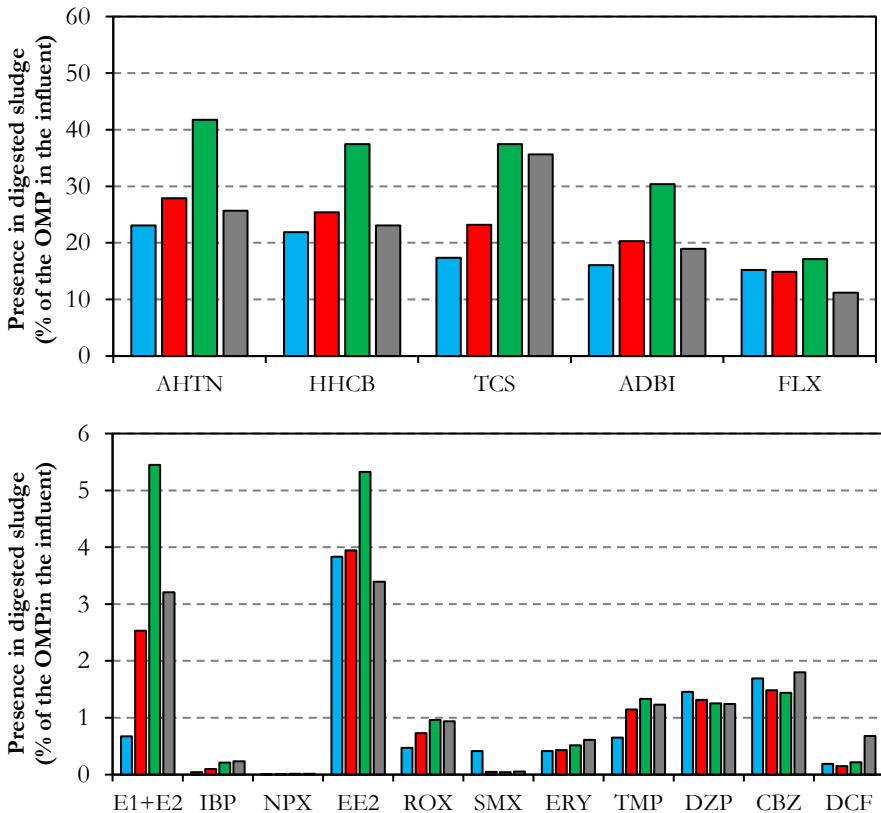
Figure 6.7. Relative presence of OMPs in digested sludge in the HRAS-based STP (■), the RBF+HRAS STP (■), the CEPT-based STP (■) and the conventional STP (■).

6.4. CONCLUSIONS

In general, the technology selected for organic matter recovery in novel STP configurations does not influence the removal efficiency of OMPs from wastewater, which was found comparable for most of them. Moreover, these novel configurations achieve, depending on the OMP, comparable or lower removal efficiency than a conventional STP configuration. However, the organic matter recovery technology determines the presence of hydrophobic OMPs in the sludge line, and subsequently, in the digested sludge. Whereas the HRAS-based STP achieves comparable or even lower OMPs presence in digested sludge than the conventional configuration, in the HRAS+RBF and mainly CEPT-based alternatives, their presence is expected to be considerably higher. Therefore, the HRAS-based STP configuration is the preferable option in terms of OMPs elimination.

CHAPTER 7

GENERAL DISCUSSION AND CONCLUSIONS

7.1. MAIN OUTCOMES OF THE THESIS

The replacement of the conventional activated sludge (CAS) process by the partial nitritation-anammox (PN-AMX) one for the autotrophic removal of nitrogen from municipal wastewater opens new possibilities for significantly reducing the sewage treatment plants (STPs) aeration requirements (Laureni et al., 2016). In contrast to CAS, the PN-AMX system permits that the organic matter contained in wastewater can be concentrated through physical, chemical or biological treatments and further valorised into biogas via anaerobic digestion (AD). This biogas can be burned in combined heat and power systems to produce electricity, bringing STPs close to energy autarky.

At same time, the increasingly use of pharmaceuticals, personal care products, pesticides, hormones and other kind of organic compounds has resulted in the release of these OMPs into the environment via diverse pathways (Barbosa et al., 2016), with important negative effects on human and ecosystem health (Santos et al., 2010). Not only the presence of OMPs in the waterline but also in sludge is important, since agricultural reuse of sewage sludge is the main practice in many countries of the EU-27, and some OMPs reach higher concentrations in sludge than in water line.

This Thesis tries to bring some insights to respond the main open questions concerning the implementation of novel STP configurations.

7.1.1. Technical viability of the different technologies for organic matter recovery in novel sewage treatment plants

The implementation of novel configurations of STPs, based on a first stage for maximum organic matter recovery followed by a PN-AMX reactor, allows to significantly reduce the energy consumption in STPs. In this Thesis, several technologies or combination of technologies such as rotating belt filters (RBFs), chemically enhanced primary treatment plant (CEPT) and high-rate activated sludge (HRAS) for chemical oxygen demand (COD) capture have been studied. First, in Chapter 2 it was proved that RBFs allow a very limited recovery of the influent COD (22-35%) that appears as clearly insufficient for a further PN-AMX unit and for maximizing COD recovery. Although some authors reported that particulate COD recovery in RBFs systems can be substantially increased by decreasing the mesh size up to 10-20 μm (Razafimanantsoa et al., 2014) or by allowing a thick mat formation, soluble COD, ammonium (NH_4^+) or phosphate (PO_4^{3-}) are not affected, so these effluents are still not appropriate for PN-AMX reactors due to their high COD-to-NH_4^+ ratio.

On the contrary, HRAS reactors were proved effective to reach the required threshold value of 2 g COD per g of NH_4^+-N (Jin et al., 2012), although a partial

oxidation of the influent COD is produced, reducing its recovery (Chapter 3). Additionally, by using this technology, a partial NH_4^+ removal, attributed to biomass growth, is attained. Unfortunately, HRAS system does not fulfil the required PO_4^{3-} removal in STPs (it is barely affected in PN-AMX reactors so it must be removed in the previous stages), so its removal through chemical precipitation appears as mandatory in these novel STPs.

Finally, the CEPT process also allows to produce effluents that fulfil the COD-to- NH_4^+ threshold, although the required chemical dose for its achievement was found very dependent of the wastewater characteristics, specially of the soluble-to-particulate COD ratio. Additionally, these processes lead to a very high PO_4^{3-} removal efficiency. However, the addition of metal salts decreases the wastewater alkalinity, what can cause that the CEPT effluents are not suitable for a PN-AMX process due to the low alkalinity-to-NH_4^+ ratio (below than 1-1.25 g inorganic carbon per g NH_4^+-N). Thus, the viability of this process is very much dependent on wastewater alkalinity, which varies significantly from one to another region.

7.1.2. Comparison of the energy requirements and operational costs of novel and conventional sewage treatment plants

The different STP configurations evaluated in this Thesis were proved effective to significantly decrease the energy requirements in comparison with conventional STPs (Chapters 2 and 3). This is due to two reasons; first, the lower aeration demand to drive the process and second the higher self-produced electricity obtained from biogas combustion, as it is shown in Figure 7.1.
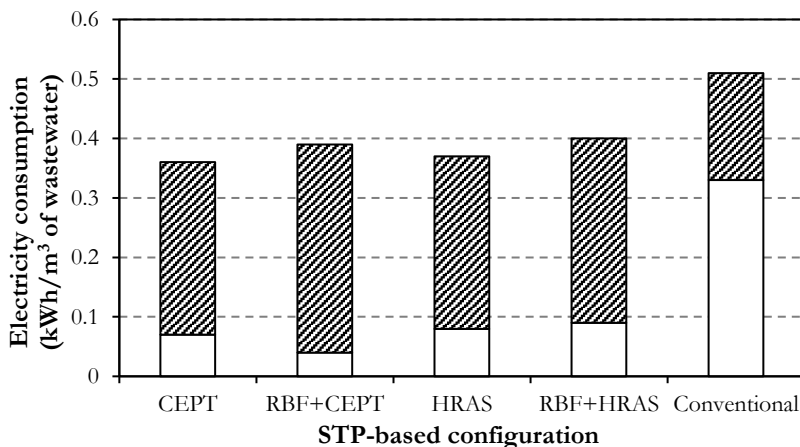
Figure 7.1. Electricity requirements (□) and self-produced electricity (▨) in each STP configuration (considering an influent with 500 mg/L of COD and 25 mg/L of NH_4^+-N.

Moreover, in Chapter 5 was proved that energy requirements can also be reduced in approximately 0.02-0.03 kWh/m³ of wastewater the STP if sludge is properly managed in thermal hydrolysis (TH) plants. However, this reduction appears as significantly lower than in conventional STPs, in which the energy demand can decrease up to 0.05 kWh/m³ of wastewater.

As discussed in the different chapters, all the evaluated novel STP configurations are noticeably less energetically demanding that conventional ones, although the energy autarky is hardly reachable in any of the studied configurations. However, this does not necessarily mean that these novel strategies can reduce the operational costs of wastewater treatment. Processes based on the addition of chemicals to wastewater were proved to lead to significantly higher operational costs than those based on biological principles and even higher than those attributed to conventional STPs. Although RBFs appear to be very useful to greatly decrease the required chemical dose (Chapter 2), this configuration still results on higher operational costs than HRAS processes. Therefore, although there are several works in the literature claiming for "energy autarky" or "energy positive" STPs (Gikas, 2017; Gude, 2015; Siegrist et al., 2008), the energetic evaluations must always be accompanied by economic assessments. In this approach, it was discussed that TH plays a crucial role to decrease operational costs since it allows to the obtention of a high-quality sludge that can be used for agriculture purposes avoiding the high costs associated to sludge disposal when it is not sterilized (Chapter 5). This fact becomes more important in novel than in conventional STPs, since in novel configurations higher sludge production is achieved. By the installation of TH plants before AD, operational costs in novel STPs can be reduced around 31-49%, whereas in conventional STPs this reduction is significantly lower.

7.1.3. Comparison of the fate of organic micropollutants in novel and conventional sewage treatment plants

Although novel STPs greatly reduce energy requirements and can also decrease, depending on the STP configuration, operational costs, they appear to be less efficient than conventional ones to remove OMPs, as discussed in Chapter 6. According to these finds, some OMPs are noticeably worse removed in HRAS and PN-AMX units than in CAS reactors. In HRAS reactors, these results could be initially expected due to the low hydraulic retention time (HRT) applied in these reactors to minimize COD mineralization. Actually, for most of them, medium or high k_{biol} values were obtained, indicating that their biotransformation is limited by the low HRT applied. Furthermore, according to Jimenez et al. (2005), particulate and colloidal organic matter is removed from wastewater by biological flocculation and subsequent settling, whereas the soluble fraction is

eliminated by intracellular storage, biosynthesis or biological oxidation. Therefore, less COD is metabolized in this unit than in CAS reactors, producing a reduction of co-metabolism activity, which is thought to be the main mechanism for OMPs biotransformation (Gauthier et al., 2010; Kassotaki et al., 2016). According to this hypothesis, the more efficient novel STPs become in terms of energy requirements (by reducing COD mineralization), the less efficient they result for OMPs biotransformation.

Regarding the PN-AMX reactor, considerably lower OMPs removal efficiencies were determined in novel STPs than in conventional configurations (Chapter 6). The removal efficiency of OMPs in novel configurations could be even lower, since these conclusions were obtained in Chapter 6 applying the only data available for PN-AMX units, reported by Alvarino et al. (2015) for sidestream conditions that operate at higher temperature and biomass activity. On the other hand, they worked with granular rather than flocculent sludge which might be an additional limitation to OMPs mass transfer inside the cells. The causes for this lower biotransformation efficiencies cannot be totally clarified in this Thesis, although some hypothesis can be considered. First, in PN-AMX units only the 50% of ammonia is oxidized to nitrite, while in CAS units the 100% of the ammonia is converted. Considering again a co-metabolic approach, this could result on a lower biotransformation efficiency. A second feasible explanation is the lack of nitrite oxidizing microorganisms in PN-AMX reactors. Although some works in the literature indicate that the removal of OMPs in CAS is linked to nitrifying activities (Fernandez-Fontaina et al., 2016), other works suggest that there is a potential overestimation of the contribution of ammonia oxidizers to OMP biotransformation to the detriment of nitrite oxidizers (Men et al., 2017). Therefore, further experimental work should be carried out to clarify these open questions.

7.2. RESEARCH GAPS AND FUTURE PERSPECTIVES

Although this Thesis contributes to find answers for some research issues dealing with the implementation of novel configurations of STPs, there are still many information gaps that need to be addressed to have a complete and detailed overview of this novel generation of STPs.

The HRAS-based configuration was proved the best alternative not only in terms of operational costs but also on OMPs removal. However, the HRAS technology should be further assessed to determine the operational conditions such as temperature, DO, HRT or SRT that minimize COD oxidation (and therefore maximize COD capture and subsequent biogas production), always ensuring an appropriate effluent quality to be treated in the PN-AMX reactor. Furthermore,

the impact of these operational parameters on OMPs removal still remains unexplored and should be further assessed.

Although the CEPT process leads to higher operational costs than the HRAS (and even than the conventional STP configuration), the addition of coagulants and/or flocculants to wastewater before the RBF accompanied by a reduction of the RBF mesh size could be a feasible option to generate effluents suitable for a PN-AMX unit while reducing the operational costs, making them more competitive against the HRAS-based alternative.

In order to promote the use of sludge in agriculture, future investigations determining the influence of TH on the fate of OMPs should be carried with different kind of sludges to validate the results discussed in Chapter 4. Additionally, it should be also evaluated the potential of anaerobic co-digestion on promoting the biotransformation of OMPs since it could be a win-win strategy; boosting electricity production in STPs and, simultaneously, obtaining a higher-quality digested sludge.

Finally, the comparative analysis of the fate of OMPs between conventional and novel STP configurations indicates that the latter leads to lower OMPs removal efficiencies. However, as previously stated an important limitation of this Thesis is the lack of works in the literature studying the fate of OMPs in HRAS and PN-AMX reactors. Therefore, future experimental works should be carried out to obtain further biotransformation rate constants (k_{biol}) to feed properly the model developed in Chapter 6, this producing more reliable results. Additionally, the transformation products of OMPs in these novel configurations should be determined as well as toxicity tests that allow to compare the toxicity of the effluents of novel and conventional STPs.

7.3. GENERAL CONCLUSIONS

The general conclusions drawn from this Thesis are listed below.

o Among the three technologies compared to recover organic matter from wastewater, it was proved that CEPT processes and HRAS reactors allow to produce suitable effluents for a PN-AMX treatment. However, the effluents from RBFs require the implementation of additional steps due to the low COD recovery attained with this technology.

o Whereas a very high PO_4^{3-} removal efficiency is achieved in novel STP configurations that apply CEPT for COD recovery, in those based on HRAS reactors this removal is limited and their effluents do not fulfil PO_4^{3-} discharge limit, therefore being mandatory a further removal through chemical precipitation in the clarifier.

o CEPT for COD capture leads to lower electricity demand than those based on HRAS reactors + chemical precipitation. On the contrary, the latter requires lower operational costs and achieves higher OMPs removal efficiency.

o The implementation of RBFs before CEPT allows to decrease up to 3-fold, the required chemical dose for generating suitable effluents for a PN-AMX reactor maintaining comparable OMPs removal efficiency. This combination of technologies still lead to higher operational costs than the HRAS-based STP configuration. Moreover, a minimum alkalinity level in wastewaters is mandatory to consider the CEPT-based STP configuration as more economically favourable with respect to the conventional one.

o Novel STP configurations produce sludges with higher anaerobic biodegradability than those characteristic from conventional configurations. This fact together with the higher COD recovery achieved from wastewater results in a considerably higher electricity production.

o Biogas production increase after TH in novel STP configurations is approximately half of that obtained in conventional STP configurations. As a consequence, in novel STP configurations a threshold of 7-9% TS concentration in sludge in TH plant is required to reach the energy self-sufficient in the unit.

o The impact of TH on the STP economy is mainly due to sludge disposal savings rather than energetic factors. A minimum sludge TS concentration of approximately 1-2% to achieve a reduction in operational costs was found.

o TH plants present are seriously affected by the economy of scale factor. Payback times for a new plant are greatly dependent on the STP size, showing that their profitability is considerably higher in huge ones.

o TH proved to be an effective technology to partially or totally remove the dissolved fraction of OMPs as well as the fraction sorbed into suspended solids that are solubilised in the process, but it does not affect the fraction of OMPs sorbed into solids that are not solubilised by this type of pretreatment.

o TH does not substantially increase the biotransformation efficiency of OMPs during AD, proving that it is ineffective to increase their bioavailability.

o In general, novel STP configurations achieve comparable or lower OMPs removal efficiencies from wastewater than conventional ones.

o The removal efficiency from wastewater for most of the OMPs is very comparable in all the studied novel STP configurations, regardless the

technology selected for organic matter recovery. However, it affects to the presence of hydrophobic OMPs in the sludge line and subsequently in digested sludge. Among the studied alternatives, the novel STP configuration based on HRAS for COD recovery is the preferable one, since it achieves comparable OMPs removal efficiency from wastewater to the other novel configurations but it reaches the lowest presence of hydrophobic OMPs in digested sludge.

o Novel STP configuration consisting on HRAS for COD capture + PO_4^{3-} precipitation in the mainstream with TH+AD in the sidestream was holistically found the best alternative amongst the studied configurations.

REFERENCES

Abegglen, C., Joss, A., Mcardell, C.S., Fink, G., Schlu, M.P., Ternes, T.A., Siegrist, H., 2009. The fate of selected micropollutants in a single-house MBR. Water Res. 43, 2036–2046. doi:10.1016/j.watres.2009.02.005

Adav, S.S., Lee, D.J., Lai, J.Y., 2010. Microbial community of acetate utilizing denitrifiers in aerobic granules. Appl. Microbiol. Biotechnol. 85, 753–762. doi:10.1007/s00253-009-2263-6

Aemig, Q., Chéron, C., Delgenès, N., Jimenez, J., Houot, S., Steyer, J.P., Patureau, D., 2016. Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in sludge organic matter pools as a driving force of their fate during anaerobic digestion. Waste Manag. 48, 389–396. doi:10.1016/j.wasman.2015.11.045

Aiyuk, S., Forrez, I., Lieven, D.K., van Haandel, A., Verstraete, W., 2006. Anaerobic and complementary treatment of domestic sewage in regions with hot climates-A review. Bioresour. Technol. 97, 2225–2241. doi:10.1016/j.biortech.2005.05.015

Aiyuk, S., Xu, H., van Haandel, A., 2004. Removal of Ammonium Nitrogen from Pretreated Domestic Sewage Using a Natural Ion Exchanger. Environ. Technol. 25, 1321–1330. doi:10.1080/09593332508618377

Alvarino, T., Suarez, S., Katsou, E., Vazquez-Padin, J., Lema, J.M., Omil, F., 2015. Removal of PPCPs from the sludge supernatant in a one stage nitritation/anammox process. Water Res. 68, 701–709. doi:10.1016/j.watres.2014.10.055

Alvarino, T., Suarez, S., Lema, J.M., Omil, F., 2014. Understanding the removal mechanisms of PPCPs and the influence of main technological parameters in anaerobic UASB and aerobic CAS reactors. J. Hazard. Mater. 278, 506–513. doi:10.1016/j.jhazmat.2014.06.031

APHA, 2005. Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA. American Public Health Association, Washington DC.

Asakura, H., Matsuto, T., 2009. Experimental study of behavior of endocrine-disrupting chemicals in leachate treatment process and evaluation of removal efficiency. Waste Manag. 29, 1852–1859. doi:10.1016/j.wasman.2008.11.030

Astals, S., Venegas, C., Peces, M., Jofre, J., Lucena, F., Mata-Alvarez, J., 2012. Balancing hygienization and anaerobic digestion of raw sewage sludge.

Water Res. 46, 6218–6227. doi:10.1016/j.watres.2012.07.035

Atmar, R.L., Estes, M.K., 2006. The Epidemiologic and Clinical Importance of Norovirus Infection. Gastroenterol. Clin. North Am. 35, 275–290. doi:10.1016/j.gtc.2006.03.001

Barber, W.P.F., 2016. Thermal hydrolysis for sewage treatment: A critical review. Water Res. 104, 53–71. doi:10.1016/j.watres.2016.07.069

Barbosa, M.O., Moreira, N.F.F., Ribeiro, A.R., Pereira, M.F.R., Silva, A.M.T., 2016. Occurrence and removal of organic micropollutants: An overview of the watch list of EU Decision 2015/495. Water Res. 94, 257–279. doi:10.1016/j.watres.2016.02.047

Barret, M., Patureau, D., Latrille, E., Carrère, H., 2010. A three-compartment model for micropollutants sorption in sludge: Methodological approach and insights. Water Res. 44, 616–624. doi:10.1016/j.watres.2009.08.029

Barron, L., Nesterenko, E., Hart, K., Power, E., Quinn, B., Kelleher, B., Paull, B., 2010. Holistic visualisation of the multimodal transport and fate of twelve pharmaceuticals in biosolid enriched topsoils. Anal. Bioanal. Chem. 397, 287–296. doi:10.1007/s00216-010-3494-1

Batstone, D.J., Keller, J., Angelidaki, I., Kalyuzhnyi, S. V, Pavlostathis, S.G., Rozzi, A., Sanders, W.T.M., Siegrist, H., Vavilin, V.A., 2002. The IWA Anaerobic Digestion Model No 1 (ADM1). Water Sci. Technol. 45, 65–73.

Behera, C.R., Santoro, D., Gernaey, K. V., Sin, G., 2018. Organic carbon recovery modeling for a rotating belt filter and its impact assessment on a plant-wide scale. Chem. Eng. J. 334, 1965–1976. doi:10.1016/j.cej.2017.11.091

Behera, S.K., Kim, H.W., Oh, J.E., Park, H.S., 2011. Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. Sci. Total Environ. 409, 4351–4360. doi:10.1016/j.scitotenv.2011.07.015

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

Bergersen, O., Hanssen, K.Ø., Vasskog, T., 2012. Anaerobic treatment of sewage sludge containing selective serotonin reuptake inhibitors. Bioresour. Technol. 117, 325–332. doi:10.1016/j.biortech.2012.04.086

Bivins, J.L., Novak, J.T., 2001. Changes in Dewatering Properties between the Thermophilic and Mesophilic Stages in Temperature-Phased Anaerobic Digestion Systems. Water Environ. Res. 73, 444–449. doi:10.2307/25045520

Bodzek, M., Dudziak, M., 2006. Elimination of steroidal sex hormones by conventional water treatment and membrane processes. Desalination 198, 24–32. doi:10.1016/j.desal.2006.09.005

Bohorquez, L.C., Delgado-Serrano, L., López, G., Osorio-Forero, C., Klepac-Ceraj, V., Kolter, R., Junca, H., Baena, S., Zambrano, M.M., 2012. In-depth Characterization via Complementing Culture-Independent Approaches of the Microbial Community in an Acidic Hot Spring of the Colombian Andes. Microb. Ecol. 63, 103–115. doi:10.1007/s00248-011-9943-3

Boiocchi, R., Behera, C.R., Sherrat, A., DeGroot, C.T., Gernaey, K. V., Sin, G., Santoro, D., 2019. Dynamic model validation and plant-wide assessment of rotating belt filtration as primary treatment of domestic wastewaters. Submitt. to Chem. Eng. J.

Bolz, U., Hagenmaier, H., Körner, W., 2001. Phenolic xenoestrogens in surface water, sediments, and sewage sludge from Baden-Württemberg, south-west Germany. Environ. Pollut. 115, 291–301. doi:10.1016/S0269-7491(01)00100-2

Bougrier, C., Albasi, C., Delgenès, J.P., Carrère, H., 2006a. Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability. Chem. Eng. Process. Process Intensif. 45, 711–718. doi:10.1016/j.cep.2006.02.005

Bougrier, C., Delgenès, J.P., Carrère, H., 2008. Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties and anaerobic digestion. Chem. Eng. J. 139, 236–244. doi:10.1016/j.cej.2007.07.099

Bougrier, C., Delgenès, J.P., Carrère, H., 2006b. Combination of thermal treatments and anaerobic digestion to reduce sewage sludge quantity and improve biogas yield. Process Saf. Environ. Prot. 84, 280–284. doi:10.1205/psep.05162

Braz, G.H.R., Fernandez-Gonzalez, N., Lema, J.M., Carballa, M., 2018. The time response of anaerobic digestion microbiome during an organic loading rate shock. Appl. Microbiol. Biotechnol. 102, 10285–10297. doi:10.1007/s00253-018-9383-9

Cano, R., Pérez-Elvira, S.I., Fdz-Polanco, F., 2015. Energy feasibility study of sludge pretreatments: A review. Appl. Energy 149, 176–185. doi:10.1016/j.apenergy.2015.03.132

Cao, Y., van Loosdrecht, M.C.M., Daigger, G.T., 2017. Mainstream partial nitritation–anammox in municipal wastewater treatment: status, bottlenecks, and further studies. Appl. Microbiol. Biotechnol. 101, 1365–1383. doi:10.1007/s00253-016-8058-7

Carballa, M., Fink, G., Omil, F., Lema, J.M., Ternes, T., 2008. Determination of the solid-water distribution coefficient (Kd) for pharmaceuticals, estrogens and musk fragrances in digested sludge. Water Res. 42, 287–295. doi:10.1016/j.watres.2007.07.012

Carballa, M., Manterola, G., Larrea, L., Ternes, T., Omil, F., Lema, J.M., 2007a. Influence of ozone pre-treatment on sludge anaerobic digestion: Removal of pharmaceutical and personal care products. Chemosphere 67, 1444–1452. doi:10.1016/j.chemosphere.2006.10.004

Carballa, M., Omil, F., Alder, A.C., Lema, J.M., 2006. Comparison between the conventional anaerobic digestion of sewage sludge and its combination with a chemical or thermal pre-treatment concerning the removal of pharmaceuticals and personal care products. Water Sci. Technol. 53, 109–117. doi:10.2166/wst.2006.241

Carballa, M., Omil, F., Lema, J.M., 2005. Removal of cosmetic ingredients and pharmaceuticals in sewage primary treatment. Water Res. 39, 4790–4796. doi:10.1016/j.watres.2005.09.018

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

Carballa, M., Omil, F., Ternes, T., Lema, J.M., 2007b. Fate of pharmaceutical and personal care products (PPCPs) during anaerobic digestion of sewage sludge. Water Res. 41, 2139–2150. doi:10.1016/j.watres.2007.02.012

Carrère, H., Dumas, C., Battimelli, A., Batstone, D.J., Delgenès, J.P., Steyer, J.P., Ferrer, I., 2010. Pretreatment methods to improve sludge anaerobic degradability: A review. J. Hazard. Mater. 183, 1–15. doi:10.1016/j.jhazmat.2010.06.129

Chan, C., Guisasola, A., Baeza, J.A., 2017. Enhanced Biological Phosphorus Removal at low Sludge Retention Time in view of its integration in A-stage

systems. Water Res. 118, 217–226. doi:10.1016/j.watres.2017.04.010

Chen, F., Ying, G.G., Ma, Y.B., Chen, Z.F., Lai, H.J., Peng, F.J., 2014. Field dissipation and risk assessment of typical personal care products TCC, TCS, AHTN and HHCB in biosolid-amended soils. Sci. Total Environ. 470–471, 1078–1086. doi:10.1016/j.scitotenv.2013.10.080

Choi, K.J., Kim, S.G., Kim, S.H., 2008. Removal of antibiotics by coagulation and granular activated carbon filtration. J. Hazard. Mater. 151, 38–43. doi:10.1016/j.jhazmat.2007.05.059

Cirne, D.G., Lehtomäki, A., Björnsson, L., Blackall, L.L., 2007. Hydrolysis and microbial community analyses in two-stage anaerobic digestion of energy crops. J. Appl. Microbiol. 103, 516–527. doi:10.1111/j.1365-2672.2006.03270.x

Clara, M., Gans, O., Windhofer, G., Krenn, U., Hartl, W., Braun, K., Scharf, S., Scheffknecht, C., 2011. Occurrence of polycyclic musks in wastewater and receiving water bodies and fate during wastewater treatment. Chemosphere 82, 1116–1123. doi:10.1016/j.chemosphere.2010.11.041

Clara, M., Kreuzinger, N., Strenn, B., Gans, O., Kroiss, H., 2005. The solids retention time - A suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. Water Res. 39, 97–106. doi:10.1016/j.watres.2004.08.036

Clarke, K.R., 1993. Non-parametric multivariate analyses of changes in community structure. Aust. J. Ecol. 18, 117–143. doi:10.1111/j.1442-9993.1993.tb00438.x

Collado, N., Buttiglieri, G., Ferrando-climent, L., Rodriguez-mozaz, S., Barceló, D., 2012. Removal of ibuprofen and its transformation products : Experimental and simulation studies. Sci. Total Environ. 433, 296–301. doi:10.1016/j.scitotenv.2012.06.060

Costafreda, M.I., Bosch, A., Pintó, R.M., 2006. Development, evaluation, and standardization of a real-time TaqMan reverse transcription-PCR assay for quantification of hepatitis A virus in clinical and shellfish samples. Appl. Environ. Microbiol. 72, 3846–3855. doi:10.1128/AEM.02660-05

Crutchik, D., Frison, N., Eusebi, A.L., Fatone, F., 2018. Biorefinery of cellulosic primary sludge towards targeted Short Chain Fatty Acids, phosphorus and methane recovery. Water Res. 136, 112–119. doi:10.1016/j.watres.2018.02.047

Da Silva, A.K., Le Saux, J.C., Parnaudeau, S., Pommepuy, M., Elimelech, M., Le

Guyader, F.S., 2007. Evaluation of removal of noroviruses during wastewater treatment, using real-time reverse transcription-PCR: Different behaviors of genogroups I and II. Appl. Environ. Microbiol. 73, 7891–7897. doi:10.1128/AEM.01428-07

De Feo, G., De Gisi, S., Galasso, M., 2008. Definition of a practical multi-criteria procedure for selecting the best coagulant in a chemically assisted primary sedimentation process for the treatment of urban wastewater. Desalination 230, 229–238. doi:10.1016/j.desal.2007.12.003

Delgadillo-Mirquez, L., Lardon, L., Steyer, J.P., Patureau, D., 2011. A new dynamic model for bioavailability and cometabolism of micropollutants during anaerobic digestion. Water Res. 45, 4511–4521. doi:10.1016/j.watres.2011.05.047

des Mes, T.Z.D., Kujawa-Roeleveld, K., Zeeman, G., Lettinga, G., 2008. Anaerobic biodegradation of estrogens - Hard to digest. Water Sci. Technol. 57, 1177–1182. doi:10.2166/wst.2008.102

Diamantis, V., Verstraete, W., Eftaxias, A., Bundervoet, B., Vlaeminck, S.E., Melidis, P., Aivasidis, A., 2013. Sewage pre-concentration for maximum recovery and reuse at decentralized level. Water Sci. Technol. 67, 1188–1193. doi:10.2166/wst.2013.639

Dictor, M.C., Berne, N., Mathieu, O., Moussay, a., Saada, a., 2003. Influence of Ageing of Polluted Soils on Bioavailability of Phenanthrene. Oil Gas Sci. Technol. 58, 481–488. doi:10.2516/ogst:2003031

Donoso-Bravo, A., Pérez-Elvira, S., Aymerich, E., Fdz-Polanco, F., 2011. Assessment of the influence of thermal pre-treatment time on the macromolecular composition and anaerobic biodegradability of sewage sludge. Bioresour. Technol. 102, 660–666. doi:10.1016/j.biortech.2010.08.035

DrugBank database [WWW Document], n.d. . http://www.drugbank.ca.

Dwyer, J., Starrenburg, D., Tait, S., Barr, K., Batstone, D.J., Lant, P., 2008. Decreasing activated sludge thermal hydrolysis temperature reduces product colour, without decreasing degradability. Water Res. 42, 4699–4709. doi:10.1016/j.watres.2008.08.019

Eberl, H., Morgenroth, E., Noguera, D., Picioreanu, C., Rittmann, B., van Loosdrecht, M., Wanner, O., 2006. Mathematical modeling of biofilms. IWA publishing London.

EC, 2015. Commission Implementing Decision (EU) 2015/495 establishing a

watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council. Official Journal of the European.

EC, 2013. Council Directive 2013/39/EU amending directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Official Journal of the European Union L 226.

Ennouri, H., Miladi, B., Diaz, S.Z., Güelfo, L.A.F., Solera, R., Hamdi, M., Bouallagui, H., 2016. Effect of thermal pretreatment on the biogas production and microbial communities balance during anaerobic digestion of urban and industrial waste activated sludge. Bioresour. Technol. 214, 184–191. doi:10.1016/j.biortech.2016.04.076

Escher, B.I., Allinson, M., Altenburger, R., Bain, P.A., Balaguer, P., Busch, W., Crago, J., Denslow, N.D., Dopp, E., Hilscherova, K., Humpage, A.R., Kumar, A., Grimaldi, M., Jayasinghe, B.S., Jarosova, B., Jia, A., Makarov, S., Maruya, K.A., Medvedev, A., Mehinto, A.C., Mendez, J.E., Poulsen, A., Prochazka, E., Richard, J., Schifferli, A., Schlenk, D., Scholz, S., Shiraishi, F., Snyder, S., Su, G., Tang, J.Y.M., Burg, B. Van Der, Linden, S.C.V. Der, Werner, I., Westerheide, S.D., Wong, C.K.C., Yang, M., Yeung, B.H.Y., Zhang, X., Leusch, F.D.L., 2014. Benchmarking organic micropollutants in wastewater, recycled water and drinking water with in vitro bioassays. Environ. Sci. Technol. 48, 1940–1956. doi:10.1021/es403899t

European Centre for Disease Prevention and Control, 2014. Surveillance of antimicrobial consumption in Europe.

Fdz-Polanco, F., Velazquez, R., Perez-Elvira, S.I., Casas, C., del Barrio, D., Cantero, F.J., Fdz-Polanco, M., Rodriguez, P., Panizo, L., Serrat, J., Rouge, P., 2008. Continuous thermal hydrolysis and energy integration in sludge anaerobic digestion plants. Water Sci. Technol. 57, 1221–1226. doi:10.2166/wst.2008.072

Fent, K., Weston, A.A., Caminada, D., 2006. Ecotoxicology of human pharmaceuticals. Aquat. Toxicol. 76, 122–159. doi:10.1016/j.aquatox.2005.09.009

Fernandez-Cassi, X., Timoneda, N., Martínez-Puchol, S., Rusiñol, M., Rodriguez-Manzano, J., Figuerola, N., Bofill-Mas, S., Abril, J.F., Girones, R., 2018. Metagenomics for the study of viruses in urban sewage as a tool for public health surveillance. Sci. Total Environ. 618, 870–880. doi:10.1016/j.scitotenv.2017.08.249

Fernadez-Fontaina, E., Omil, F., Lema, J.M., Carballa, M., 2012. Influence of

nitrifying conditions on the biodegradation and sorption of emerging micropollutants. Water Res. 46, 5434–5444. doi:10.1016/j.watres.2012.07.037

Fernandez-Fontaina, E., Carballa, M., Omil, F., Lema, J.M., 2014. Modelling cometabolic biotransformation of organic micropollutants in nitrifying reactors. Water Res. 65, 371–383. doi:10.1016/j.watres.2014.07.048

Fernandez-Fontaina, E., Gomes, I.B., Aga, D.S., Omil, F., Lema, J.M., Carballa, M., 2016. Biotransformation of pharmaceuticals under nitrification, nitratation and heterotrophic conditions. Sci. Total Environ. 541, 1439–1447. doi:10.1016/j.scitotenv.2015.10.010

Fernandez-Fontaina, E., Pinho, I., Carballa, M., Omil, F., Lema, J.M., 2013. Biodegradation kinetic constants and sorption coefficients of micropollutants in membrane bioreactors. Biodegradation 24, 165–177. doi:10.1007/s10532-012-9568-3

Flores-Alsina, X., Arnell, M., Amerlinck, Y., Corominas, L., Gernaey, K. V., Guo, L., Lindblom, E., Nopens, I., Porro, J., Shaw, A., Snip, L., Vanrolleghem, P.A., Jeppsson, U., 2014. Balancing effluent quality, economic cost and greenhouse gas emissions during the evaluation of (plant-wide) control/operational strategies in WWTPs. Sci. Total Environ. 466–467, 616–624. doi:10.1016/j.scitotenv.2013.07.046

Flores-Alsina, X., Corominas, L., Snip, L., Vanrolleghem, P.A., 2011. Including greenhouse gas emissions during benchmarking of wastewater treatment plant control strategies. Water Res. 45, 4700–4710. doi:10.1016/j.watres.2011.04.040

Franchi, A., Santoro, D., 2015. Current status of the rotating belt filtration (RBF) technology for municipal wastewater treatment. Water Pract. Technol. 10, 319 LP – 327.

Gagliano, M.C., Braguglia, C.M., Gianico, A., Mininni, G., Nakamura, K., Rossetti, S., 2015. Thermophilic anaerobic digestion of thermal pretreated sludge: Role of microbial community structure and correlation with process performances. Water Res. 68, 498–509. doi:10.1016/j.watres.2014.10.031

Gao, B., Liu, B., Chen, T., Yue, Q., 2011. Effect of aging period on the characteristics and coagulation behavior of polyferric chloride and polyferric chloride-polyamine composite coagulant for synthetic dying wastewater treatment. J. Hazard. Mater. 187, 413–420. doi:10.1016/j.jhazmat.2011.01.044

Gao, H., Scherson, Y.D., Wells, G.F., 2014. Towards energy neutral wastewater treatment : methodology and state of the art. Environ. Sci. Process. Impacts 16, 1223–1246. doi:10.1039/c4em00069b

Gao, H., Zhang, L., Lu, Z., He, C., Li, Q., Na, G., 2018. Complex migration of antibiotic resistance in natural aquatic environments. Environ. Pollut. 232, 1–9. doi:10.1016/j.envpol.2017.08.078

Garrido, J.M., Fdz-Polanco, M., Fdz-Polanco, F., 2013. Working with energy and mass balances: A conceptual framework to understand the limits of municipal wastewater treatment. Water Sci. Technol. 67, 2294–2301. doi:10.2166/wst.2013.124

Gauthier, H., Yargeau, V., Cooper, D.G., 2010. Biodegradation of pharmaceuticals by Rhodococcus rhodochrous and Aspergillus niger by co-metabolism. Sci. Total Environ. 408, 1701–1706. doi:10.1016/j.scitotenv.2009.12.012

Ge, H., Batstone, D.J., Keller, J., 2015. Biological phosphorus removal from abattoir wastewater at very short sludge ages mediated bynovel PAO clade Comamonadaceae. Water Res. 69, 173–182. doi:10.1016/j.watres.2014.11.026

Ge, H., Batstone, D.J., Keller, J., 2013. Operating aerobic wastewater treatment at very short sludge ages enables treatment and energy recovery through anaerobic sludge digestion. Water Res. 47, 6546–6557. doi:10.1016/j.watres.2013.08.017

Ge, H., Batstone, D.J., Mouiche, M., Hu, S., Keller, J., 2017. Nutrient removal and energy recovery from high-rate activated sludge processes – Impact of sludge age. Bioresour. Technol. 245, 1155–1161. doi:10.1016/j.biortech.2017.08.115

Gerba, C.P., Betancourt, W.Q., 2017. Viral Aggregation: Impact on Virus Behavior in the Environment. Environ. Sci. Technol. 51, 7318–7325. doi:10.1021/acs.est.6b05835

Gernaey, K.V., Jeppsson, U., Vanrolleghem, P.A., Copp, J.B., 2014. Benchmarking of control strategies for wastewater treatment plants. IWA Scientific and Technical Report no. 23. IWA Publishing. doi:https://doi.org/10.2166/9781780401171

Gernaey, K. V., Flores-Alsina, X., Rosen, C., Benedetti, L., Jeppsson, U., 2011. Dynamic influent pollutant disturbance scenario generation using a phenomenological modelling approach. Environ. Model. Softw. 26, 1255–

1267. doi:10.1016/J.ENVSOFT.2011.06.001

Ghasimi, D.S.M., Tao, Y., de Kreuk, M., Abbas, B., Zandvoort, M.H., van Lier, J.B., 2015. Digester performance and microbial community changes in thermophilic and mesophilic sequencing batch reactors fed with the fine sieved fraction of municipal sewage. Water Res. 87, 483–493. doi:10.1016/j.watres.2015.04.027

Ghasimi, D.S.M., Zandvoort, M.H., Adriaanse, M., Lier, J.B. Van, Kreuk, M. De, 2016. Comparative analysis of the digestibility of sewage fine sieved fraction and hygiene paper produced from virgin fibers and recycled fibers. Waste Manag. 53, 156–164. doi:10.1016/j.wasman.2016.04.034

Gikas, P., 2017. Towards energy positive wastewater treatment plants. J. Environ. Manage. 203, 621–629. doi:10.1016/j.jenvman.2016.05.061

Gonzalez-Gil, L., Mauricio-Iglesias, M., Carballa, M., Lema, J.M., 2018a. Why are organic micropollutants not fully biotransformed? A mechanistic modelling approach to anaerobic systems. Water Res. 142, 115–128. doi:https://doi.org/10.1016/j.watres.2018.05.032

Gonzalez-Gil, L., Mauricio-Iglesias, M., Serrano, D., Lema, J.M., Carballa, M., 2018b. Role of methanogenesis on the biotransformation of organic micropollutants during anaerobic digestion. Sci. Total Environ. 622–623, 459–466. doi:10.1016/j.scitotenv.2017.12.004

Gonzalez-Gil, L., Papa, M., Feretti, D., Ceretti, E., Mazzoleni, G., Steimberg, N., Pedrazzani, R., Bertanza, G., Lema, J.M., Carballa, M., 2016. Is anaerobic digestion effective for the removal of organic micropollutants and biological activities from sewage sludge? Water Res. 102, 211–220. doi:10.1016/j.watres.2016.06.025

GSchVSchweiz, 2016. Swiss Act for the Protection of Receiving Waters.

Gu, Y., Li, Y., Li, X., Luo, P., Wang, H., Robinson, Z.P., Wang, X., Wu, J., Li, F., 2017. The feasibility and challenges of energy self-sufficient wastewater treatment plants. Appl. Energy 204, 1463–1475. doi:10.1016/j.apenergy.2017.02.069

Gude, V.G., 2015. Energy and water autarky of wastewater treatment and power generation systems. Renew. Sustain. Energy Rev. 45, 52–68. doi:10.1016/j.rser.2015.01.055

Guo, L., Vanrolleghem, P.A., 2014. Calibration and validation of an activated sludge model for greenhouse gases no. 1 (ASMG1): Prediction of temperature-dependent N2O emission dynamics. Bioprocess Biosyst. Eng.

37, 151–163. doi:10.1007/s00449-013-0978-3

Heidrich, E.S., Curtis, T.P., Dolfing, J., 2011. Determination of the internal chemical energy of wastewater. Environ. Sci. Technol. 45, 827–832. doi:10.1021/es103058w

Higgins, M.J., Beightol, S., Mandahar, U., Suzuki, R., Xiao, S., Lu, H.W., Le, T., Mah, J., Pathak, B., DeClippeleir, H., Novak, J.T., Al-Omari, A., Murthy, S.N., 2017. Pretreatment of a primary and secondary sludge blend at different thermal hydrolysis temperatures: Impacts on anaerobic digestion, dewatering and filtrate characteristics. Water Res. 122, 557–569. doi:10.1016/j.watres.2017.06.016

Holliger, C., Alves, M., Andrade, D., Angelidaki, I., Astals, S., Baier, U., Bougrier, C., Buffière, P., Carballa, M., De Wilde, V., Ebertseder, F., Fernández, B., Ficara, E., Fotidis, I., Frigon, J.C., De Laclos, H.F., Ghasimi, D.S.M., Hack, G., Hartel, M., Heerenklage, J., Horvath, I.S., Jenicek, P., Koch, K., Krautwald, J., Lizasoain, J., Liu, J., Mosberger, L., Nistor, M., Oechsner, H., Oliveira, J.V., Paterson, M., Pauss, A., Pommier, S., Porqueddu, I., Raposo, F., Ribeiro, T., Pfund, F.R., Strömberg, S., Torrijos, M., Van Eekert, M., Van Lier, J., Wedwitschka, H., Wierinck, I., 2016. Towards a standardization of biomethane potential tests. Water Sci. Technol. 74, 2515–2522. doi:10.2166/wst.2016.336

Hollinger, F.B., Emerson, S.U., 2007. Hepatitis A virus, Fields Vir. ed. Lippincott Williams & Wilkins, Philadelphia.

Hyland, K.C., Dickenson, E.R.V., Drewes, J.E., Higgins, C.P., 2012. Sorption of ionized and neutral emerging trace organic compounds onto activated sludge from different wastewater treatment configurations. Water Res. 46, 1958–1968. doi:10.1016/j.watres.2012.01.012

Ito, T., Kitajima, M., Kato, T., Ishii, S., Segawa, T., Okabe, S., Sano, D., 2017. Target virus log 10 reduction values determined for two reclaimed wastewater irrigation scenarios in Japan based on tolerable annual disease burden. Water Res. 125, 438–448. doi:10.1016/j.watres.2017.08.057

Jang, H.M., Shin, J., Choi, S., Shin, S.G., Park, K.Y., Cho, J., Kim, Y.M., 2017. Fate of antibiotic resistance genes in mesophilic and thermophilic anaerobic digestion of chemically enhanced primary treatment (CEPT) sludge. Bioresour. Technol. 244, 433–444. doi:10.1016/j.biortech.2017.07.153

Jelic, A., Gros, M., Ginebreda, A., Cespedes-Sánchez, R., Ventura, F., Petrovic, M., Barcelo, D., 2011. Occurrence, partition and removal of

pharmaceuticals in sewage water and sludge during wastewater treatment. Water Res. 45, 1165–1176. doi:10.1016/j.watres.2010.11.010

Jia, M., Castro-Barros, C.M., Winkler, M.K.H., Volcke, E.I.P., 2018. Effect of organic matter on the performance and N2O emission of a granular sludge anammox reactor. Environ. Sci. Water Res. Technol. 4. doi:10.1039/c8ew00125a

Jimenez, J. a, La Motta, E.J., Parker, D.S., 2007. Effect of operational parameters on the removal of particulate chemical oxygen demand in the activated sludge process. Water Environ. Res. 79, 984–990. doi:10.2175/106143007X175717

Jimenez, J., Miller, M., Bott, C., Murthy, S., De Clippeleir, H., Wett, B., 2015. High-rate activated sludge system for carbon management - Evaluation of crucial process mechanisms and design parameters. Water Res. 87, 476–482. doi:10.1016/j.watres.2015.07.032

Jimenez, J.A., La Motta, E.J., Parker, D.S., 2005. Kinetics of Removal of Particulate Chemical Oxygen Demand in the Activated-Sludge Process. Water Environ. Res. 77, 437–446. doi:10.2175/106143005X67340

Jin, R.C., Yang, G.F., Yu, J.J., Zheng, P., 2012. The inhibition of the Anammox process: A review. Chem. Eng. J. 197, 67–79. doi:10.1016/j.cej.2012.05.014

Jones, O.A.H., Voulvoulis, N., Lester, J.N., 2002. Aquatic environmental assessment of the top 25 English prescription pharmaceuticals. Water Res. 36, 5013–5022. doi:10.1016/S0043-1354(02)00227-0

Jordao, E.P., Volschan, I., 2004. Cost-effective solutions for sewage treatment in developing countries--the case of Brazil. Water Sci. Technol. 50, 237–242.

Joss, A., Andersen, H., Ternes, T., Richle, P.R., Siegrist, H., 2004. Removal of estrogens in municipal wastewater treatment under aerobic and anaerobic conditions: Consequences for plant optimization. Environ. Sci. Technol. 38, 3047–3055. doi:10.1021/es0351488

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

Joss, A., Zabczynski, S., Go, A., Hoffmann, B., Lo, D., Mcardell, C.S., Ternes, T.A., Thomsen, A., Siegrist, H., 2006. Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme. Water Res. 40, 1686–1696.

doi:10.1016/j.watres.2006.02.014

Ju, F., Wang, Y., Lau, F.T.K., Fung, W.C., Huang, D., Xia, Y., Zhang, T., 2016. Anaerobic digestion of chemically enhanced primary treatment (CEPT) sludge and the microbial community structure. Appl. Microbiol. Biotechnol. 100, 8975–8982. doi:10.1007/s00253-016-7730-2

Kacprzak, M., Neczaj, E., Fijalkowski, K., Grobelak, A., Grosser, A., Worwag, M., Rorat, A., Brattebo, H., Almas, A., Singh, B.R., 2017. Sewage sludge disposal strategies for sustainable development. Environ. Res. 156, 39–46. doi:10.1016/j.envres.2017.03.010

Kageyama, T., Kojima, S., Shinohara, M., Uchida, K., Fukushi, S., Hoshino, F.B., Takeda, N., Katayama, K., 2003. Broadly reactive and highly sensitive assay for Norwalk-like viruses based on real-time quantitative reverse transcription-PCR. J. Clin. Microbiol. 41, 1548–57. doi:10.1128/JCM.41.4.1548

Karen, A.K., Paul, J.B., Kenneth, H.M., Vinc, e P.P., Robert, E.E., James, M.L., Robert, W.F., 2007. Collapse of a fish population after exposure to a synthetic estrogen. Proc. Natl. Acad. Sci. 104, 8897–8901. doi:10.1073/pnas.0609568104

Kassotaki, E., Buttiglieri, G., Ferrando-Climent, L., Rodriguez-Roda, I., Pijuan, M., 2016. Enhanced sulfamethoxazole degradation through ammonia oxidizing bacteria co-metabolism and fate of transformation products. Water Res. 94, 111–119. doi:10.1016/j.watres.2016.02.022

Kassotaki, E., Pijuan, M., Joss, A., Borrego, C.M., Rodriguez-Roda, I., Buttiglieri, G., 2018. Unraveling the potential of a combined nitritation-anammox biomass towards the biodegradation of pharmaceutically active compounds. Sci. Total Environ. 624, 722–731. doi:10.1016/j.scitotenv.2017.12.116

Kelessidis, A., Stasinakis, A.S., 2012. Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. Waste Manag. 32, 1186–1195. doi:10.1016/j.wasman.2012.01.012

Kelly, D.P., Rainey, F. a., Wood, A.P., 2006. The Genus Paracoccus. The Prokaryotes 232–249. doi:10.1007/0-387-30745-1_12

Kepp, U., Machenbach, I., Weisz, N., Solheim, O.E., 2000. Enhanced stabilisation of sewage sludge through thermal hydrolysis-three years of experience with full scale plant. Water Sci. Technol. 42, 89–96.

Kooijman, G., De Kreuk, M.K., van Lier, J.B., 2017. Influence of chemically

enhanced primary treatment on anaerobic digestion and dewaterability of waste sludge. Water Sci. Technol. 76, 2017. doi:10.2166/wst.2017.314

Koopmans, M., Duizer, E., 2004. Foodborne viruses: An emerging problem. Int. J. Food Microbiol. 90, 23–41. doi:10.1016/S0168-1605(03)00169-7

Kümmerer, K., 2010. Pharmaceuticals in the Environment. Annu. Rev. Environ. Resour. 35, 57–75. doi:10.1146/annurev-environ-052809-161223

Lackner, S., Gilbert, E.M., Vlaeminck, S.E., Joss, A., Horn, H., van Loosdrecht, M.C.M., 2014. Full-scale partial nitritation/anammox experiences - An application survey. Water Res. 55, 292–303. doi:10.1016/j.watres.2014.02.032

Laureni, M., Falås, P., Robin, O., Wick, A., Weissbrodt, D.G., Nielsen, J.L., Ternes, T.A., Morgenroth, E., Joss, A., 2016. Mainstream partial nitritation and anammox: Long-term process stability and effluent quality at low temperatures. Water Res. 101, 628–639. doi:10.1016/j.watres.2016.05.005

Lautz, L.S., Struijs, J., Nolte, T.M., Breure, A.M., van der Grinten, E., van de Meent, D., van Zelm, R., 2017. Evaluation of SimpleTreat 4.0: Simulations of pharmaceutical removal in wastewater treatment plant facilities. Chemosphere 168, 870–876. doi:10.1016/j.chemosphere.2016.10.123

Li, D., Gu, A.Z., Zeng, S.Y., Yang, W., He, M., Shi, H.C., 2011. Monitoring and evaluation of infectious rotaviruses in various wastewater effluents and receiving waters revealed correlation and seasonal pattern of occurrences. J. Appl. Microbiol. 110, 1129–1137. doi:10.1111/j.1365-2672.2011.04954.x

Li, N., Sheng, G.P., Lu, Y.Z., Zeng, R.J., Yu, H.Q., 2017. Removal of antibiotic resistance genes from wastewater treatment plant effluent by coagulation. Water Res. 111, 204–212. doi:10.1016/j.watres.2017.01.010

Liang, Y.L., Kraus, T.E.C., Silva, L.C.R., Bachand, P.A.M., Bachand, S.M., Doane, T.A., Horwath, W.R., 2019. Effects of ferric sulfate and polyaluminum chloride coagulation enhanced treatment wetlands on Typha growth, soil and water chemistry. Sci. Total Environ. 648, 116–124. doi:10.1016/j.scitotenv.2018.07.341

Lindblom, E., Arnell, M., Flores-Alsina, X., Stenström, F., Gustavsson, D.J.I., Yang, J., Jeppsson, U., 2016. Dynamic modelling of nitrous oxide emissions from three Swedish sludge liquor treatment systems. Water Sci. Technol. 73, 798–806.

Loisy, F., Atmar, R.L., Guillon, P., Le Cann, P., Pommepuy, M., Le Guyader, F.S., 2005. Real-time RT-PCR for norovirus screening in shellfish. J. Virol.

Methods 123, 1–7. doi:10.1016/j.jviromet.2004.08.023

Longo, S., d'Antoni, B.M., Bongards, M., Chaparro, A., Cronrath, A., Fatone, F., Lema, J.M., Mauricio-Iglesias, M., Soares, A., Hospido, A., 2016. Monitoring and diagnosis of energy consumption in wastewater treatment plants. A state of the art and proposals for improvement. Appl. Energy 179, 1251–1268. doi:10.1016/j.apenergy.2016.07.043

Longo, S., Frison, N., Renzi, D., Fatone, F., Hospido, A., 2017. Is SCENA a good approach for side-stream integrated treatment from an environmental and economic point of view? Water Res. 125, 478–489. doi:10.1016/j.watres.2017.09.006

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

Macova, M., Escher, B.I., Reungoat, J., Carswell, S., Chue, K.L., Keller, J., Mueller, J.F., 2010. Monitoring the biological activity of micropollutants during advanced wastewater treatment with ozonation and activated carbon filtration. Water Res. 44, 477–492. doi:10.1016/j.watres.2009.09.025

Mahdy, A., Mendez, L., Ballesteros, M., González-Fernández, C., 2014. Algaculture integration in conventional wastewater treatment plants: Anaerobic digestion comparison of primary and secondary sludge with microalgae biomass. Bioresour. Technol. 184, 236–244. doi:10.1016/j.biortech.2014.09.145

Mailler, R., Gasperi, J., Patureau, D., Vulliet, E., Delgenes, N., Danel, A., Deshayes, S., Eudes, V., 2017. Fate of emerging and priority micropollutants during the sewage sludge treatment : Case study of Paris conurbation . Part 1 : Contamination of the different types of sewage sludge. Waste Manag. 59, 379–393. doi:10.1016/j.wasman.2016.11.010

Malmborg, J., Magnér, J., 2015. Pharmaceutical residues in sewage sludge: Effect of sanitization and anaerobic digestion. J. Environ. Manage. 153, 1–10. doi:10.1016/j.jenvman.2015.01.041

Malovanyy, A., Trela, J., Plaza, E., 2015. Mainstream wastewater treatment in integrated fixed film activated sludge (IFAS) reactor by partial nitritation/anammox process. Bioresour. Technol. 198, 478–487.

Management Company, 2019. Personal communication with management

company.

Martínez Bueno, M.J., Gomez, M.J., Herrera, S., Hernando, M.D., Agüera, A., Fernández-Alba, A.R., 2012. Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: Two years pilot survey monitoring. Environ. Pollut. 164, 267–273. doi:10.1016/j.envpol.2012.01.038

Mbamba, C.K., Lindblom, E., Flores-Alsina, X., Tait, S., Anderson, S., Saagi, R., Batstone, D.J., Gernaey, K.V., Jeppsson, U., 2019. Plant-wide model-based analysis of iron dosage strategies for chemical phosphorus removal in wastewater treatment systems. Water Res. doi:10.1016/J.WATRES.2019.01.048

McNamara, P.J., Wilson, C.A., Wogen, M.T., Murthy, S.N., Novak, J.T., Novak, P.J., 2012. The effect of thermal hydrolysis pretreatment on the anaerobic degradation of nonylphenol and short-chain nonylphenol ethoxylates in digested biosolids. Water Res. 46, 2937–2946. doi:10.1016/j.watres.2012.03.015

Men, Y., Achermann, S., Helbling, D.E., Johnson, D.R., Fenner, K., 2017. Relative contribution of ammonia oxidizing bacteria and other members of nitrifying activated sludge communities to micropollutant biotransformation. Water Res. 109, 217–226. doi:10.1016/j.watres.2016.11.048

Metcalf & Eddy, 2003. Wastewater Engineering: Treatment and Reuse. New York.

Mills, N., Pearce, P., Farrow, J., Thorpe, R.B., Kirkby, N.F., 2014. Environmental & economic life cycle assessment of current & future sewage sludge to energy technologies. Waste Manag. 34, 185–195. doi:10.1016/j.wasman.2013.08.024

Mohapatra, S., Huang, C.H., Mukherji, S., Padhye, L.P., 2016. Occurrence and fate of pharmaceuticals in WWTPs in India and comparison with a similar study in the United States. Chemosphere 159, 526–535. doi:10.1016/j.chemosphere.2016.06.047

Mulder, A., van de Graaf, A.A., Robertson, L.A., Kuenen, J.G., 1995. Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. FEMS Microbiol. Ecol. 16, 177–183.

Muller, M., Combalbert, S., Delgenès, N., Bergheaud, V., Rocher, V., Benoît, P., Delgenès, J., Patureau, D., Hernandez-raquet, G., 2010. Occurrence of

estrogens in sewage sludge and their fate during plant-scale anaerobic digestion. Chemosphere 81, 65–71. doi:10.1016/j.chemosphere.2010.06.062

Narumiya, M., Nakada, N., Yamashita, N., Tanaka, H., 2013. Phase distribution and removal of pharmaceuticals and personal care products during anaerobic sludge digestion. J. Hazard. Mater. 260, 305–312. doi:10.1016/j.jhazmat.2013.05.032

Nieto, A., Borrull, F., Pocurull, E., Marcé, R.M., 2010. Occurrence of pharmaceuticals and hormones in sewage sludge. Environ. Toxicol. Chem. 29, 1484–1489. doi:10.1002/etc.188

Oka, T., Wang, Q., Katayama, K., Saifb, L.J., 2015. Comprehensive review of human sapoviruses. Clin. Microbiol. Rev. 28, 32–53. doi:10.1128/CMR.00011-14

Oksanen, J., Blanchet, F.G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., Minchin, P.R., O'Hara, R.B., Simpson, G.L., Solymos, P., Stevens, M.H.H., Szoecs, E., Wagner, H., 2016. vegan: Community Ecology Package. R package version 2.4-1.

Osorio, V., Larrañaga, A., Aceña, J., Pérez, S., Barceló, D., 2016. Concentration and risk of pharmaceuticals in freshwater systems are related to the population density and the livestock units in Iberian Rivers. Sci. Total Environ. 540, 267–277. doi:10.1016/j.scitotenv.2015.06.143

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

Paterakis, N., Chiu, T.Y., Koh, Y.K.K., Lester, J.N., McAdam, E.J., Scrimshaw, M.D., Soares, A., Cartmell, E., 2012. The effectiveness of anaerobic digestion in removing estrogens and nonylphenol ethoxylates. J. Hazard. Mater. 199–200, 88–95. doi:10.1016/j.jhazmat.2011.10.075

Paulsrud, B., Rusten, B., Aas, B., 2014. Increasing the sludge energy potential of wastewater treatment plants by introducing fine mesh sieves for primary treatment. Water Sci. Technol. 69, 560–565. doi:10.2166/wst.2013.737

Pedrouso, A., Val del Río, Á., Morales, N., Vázquez-Padín, J.R., Campos, J.L., Méndez, R., Mosquera-Corral, A., 2017. Nitrite oxidizing bacteria suppression based on in-situ free nitrous acid production at mainstream conditions. Sep. Purif. Technol. 186, 55–62.

doi:10.1016/j.seppur.2017.05.043

Pérez-Elvira, S.I., Fdz-Polanco, F., 2012. Continuous thermal hydrolysis and anaerobic digestion of sludge. Energy integration study. Water Sci. Technol. 65, 1839–1846. doi:10.2166/wst.2012.863

Perez-Elvira, S.I., Fernandez-Polanco, F., Fernandez-Polanco, M., Rodrriguez, P., Rouge, P., 2008. Hydrothermal multivariable approach. Full-scale feasibility study. Electron. J. Biotechnol. 11. doi:10.2225/vol11-issue4-fulltext-14

Perry, R.H., 1984. Chemical Engineers' Handbook, 6th ed. McGraw-Hill, New York.

Petrie, B., Barden, R., Kasprzyk-Hordern, B., 2015. A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring. Water Res. 72, 3–27. doi:10.1016/j.watres.2014.08.053

Phan, H. V., Wickham, R., Xie, S., McDonald, J.A., Khan, S.J., Ngo, H.H., Guo, W., Nghiem, L.D., 2018. The fate of trace organic contaminants during anaerobic digestion of primary sludge: A pilot scale study. Bioresour. Technol. 256, 384–390. doi:10.1016/j.biortech.2018.02.040

PhysProp database [WWW Document], n.d.

Polesel, F., Andersen, H.R., Trapp, S., Plosz, B.G., 2016. Removal of Antibiotics in Biological Wastewater Treatment Systems□ A Critical Assessment Using the Activated Sludge Modeling Framework for Xenobiotics (ASM-X). Environ. Sci. Technol. 50, 10316–10334.

Pomiès, M., Choubert, J.M., Wisniewski, C., Coquery, M., 2013. Modelling of micropollutant removal in biological wastewater treatments: A review. Sci. Total Environ. 443, 733–748. doi:10.1016/j.scitotenv.2012.11.037

Puig, S., van Loosdrecht, M.C.M., Flameling, A.G., Colprim, J., Meijer, S.C.F., 2010. The effect of primary sedimentation on full-scale WWTP nutrient removal performance. Water Res. 44, 3375–3384. doi:10.1016/j.watres.2010.03.024

R Core Team, 2016. R: A language and environment for statistical computing. R Foundation for Statistical Comupting, Vienna, Austria, Austria.

Radjenović, J., Petrović, M., Barceló, D., 2009. Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR)

treatment. Water Res. 43, 831–841. doi:10.1016/j.watres.2008.11.043

Rao, K., Li, N., Ma, M., Wang, Z., 2014. In vitro agonistic and antagonistic endocrine disrupting effects of organic extracts from waste water of different treatment processes. Front. Environ. Sci. Eng. 8, 69–78. doi:10.1007/s11783-013-0502-7

Razafimanantsoa, V.A., Ydstebo, L., Bilstad, T., Sahu, A.K., Rusten, B., 2014. Effect of selective organic fractions on denitrification rates using Salsnes Filter as primary treatment. Water Sci. Technol. 69, 1942–1948. doi:10.2166/wst.2014.110

Reyes-Contreras, C., Neumann, P., Barriga, F., Venegas, M., Domínguez, C., Bayona, J.M., Vidal, G., 2018. Organic micropollutants in sewage sludge: influence of thermal and ultrasound hydrolysis processes prior to anaerobic stabilization. Environ. Technol. 1–22. doi:10.1080/09593330.2018.1534892

Rizzo, L., Manaia, C., Merlin, C., Schwartz, T., Dagot, C., Ploy, M.C., Michael, I., Fatta-Kassinos, D., 2013. Urban wastewater treatment plants as hotspots for antibiotic resistant bacteria and genes spread into the environment: A review. Sci. Total Environ. 447, 345–360. doi:10.1016/j.scitotenv.2013.01.032

Rodríguez-Lázaro, D., Cook, N., Ruggeri, F.M., Sellwood, J., Nasser, A., Nascimento, M.S.J., D'Agostino, M., Santos, R., Saiz, J.C., Rzezutka, A., Bosch, A., Gironés, R., Carducci, A., Muscillo, M., Kovač, K., Diez-Valcarce, M., Vantarakis, A., von Bonsdorff, C.H., de Roda Husman, A.M., Hernández, M., van der Poel, W.H.M., 2012. Virus hazards from food, water and other contaminated environments. FEMS Microbiol. Rev. 36, 786–814. doi:10.1111/j.1574-6976.2011.00306.x

Romero-Güiza, M.S., Vila, J., Mata-Alvarez, J., Chimenos, J.M., Astals, S., 2016. The role of additives on anaerobic digestion: A review. Renew. Sustain. Energy Rev. 58, 1486–1499. doi:10.1016/j.rser.2015.12.094

Rosso, D., Larson, L.E., Stenstrom, M.K., 2008. Aeration of large-scale municipal wastewater treatment plants: State of the art. Water Sci. Technol. 57, 973–978. doi:10.2166/wst.2008.218

Ruiken, C.J., Breuer, G., Klaversma, E., Santiago, T., Loosdrecht, M.C.M. Van, 2013. Sieving wastewater e Cellulose recovery, economic and energy evaluation. Water Res. 47, 43–48. doi:10.1016/j.watres.2012.08.023

Rusten, B., Ødegaard, H., 2006. Evaluation and testing of fine mesh sieve

technologies for primary treatment of municipal wastewater. Water Sci. Technol. 54, 31–38. doi:10.2166/wst.2006.710

Rusten, B., Rathnaweera, S.S., Rismyhr, E., Sahu, A.K., Ntiako, J., 2017. Rotating belt sieves for primary treatment , chemically enhanced primary treatment and secondary solids separation. Water Sci. Technol. 75, 1–10. doi:10.2166/wst.2017.145

Salsnes, 2016. Eco-Efficient Solids Separation Benchmarking water solutions.

Samaras, V.G., Stasinakis, A.S., Thomaidis, N.S., Mamais, D., Lekkas, T.D., 2014. Fate of selected emerging micropollutants during mesophilic, thermophilic and temperature co-phased anaerobic digestion of sewage sludge. Bioresour. Technol. 162, 365–372. doi:10.1016/j.biortech.2014.03.154

Santos, J.L., Aparicio, I., Callejón, M., Alonso, E., 2009. Occurrence of pharmaceutically active compounds during 1-year period in wastewaters from four wastewater treatment plants in Seville (Spain). J. Hazard. Mater. 164, 1509–1516. doi:10.1016/j.jhazmat.2008.09.073

Santos, L.H.M.L.M., Araújo, A.N., Fachini, A., Pena, A., Delerue-Matos, C., Montenegro, M.C.B.S.M., 2010. Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment. J. Hazard. Mater. 175, 45–95. doi:10.1016/j.jhazmat.2009.10.100

Sapkaite, I., Barrado, E., Fdz-Polanco, F., Pérez-Elvira, S.I., 2017. Optimization of a thermal hydrolysis process for sludge pre-treatment. J. Environ. Manage. 192, 25–30. doi:10.1016/j.jenvman.2017.01.043

Scallan, E., Hoekstra, R.M., Angulo, F.J., Tauxe, R. V., Widdowson, M.A., Roy, S.L., Jones, J.L., Griffin, P.M., 2011. Foodborne illness acquired in the United States-Major pathogens. Emerg. Infect. Dis. 17, 7–15. doi:10.3201/eid1701.P11101

Schaubroeck, T., De Clippeleir, H., Weissenbacher, N., Dewulf, J., Boeckx, P., Vlaeminck, S.E., Wett, B., 2015. Environmental sustainability of an energy self-sufficient sewage treatment plant: Improvements through DEMON and co-digestion. Water Res. 74, 166–179. doi:10.1016/j.watres.2015.02.013

Schmitz, B.W., Kitajima, M., Campillo, M.E., Gerba, C.P., Pepper, I.L., 2016. Virus reduction during advanced bardenpho and conventional wastewater treatment processes. Environ. Sci. Technol. 50, 9524–9532. doi:10.1021/acs.est.6b01384

Schwindt, A.R., Winkelman, D.L., Keteles, K., Murphy, M., Vajda, A.M., 2014.

An environmental oestrogen disrupts fish population dynamics through direct and transgenerational effects on survival and fecundity. J. Appl. Ecol. 51, 582–591. doi:10.1111/1365-2664.12237

Shizas, I., Bagley, D.M., 2004. Experimental Determination of Energy Content of Unknown Organics in Municipal Wastewater Streams. J. Energy Eng. 130, 45–53. doi:10.1061/(ASCE)0733-9402(2004)130:2(45)

Siegrist, H., Salzgeber, D., Eugster, J., Joss, A., 2008. Anammox brings WWTP closer to energy autarky due to increased biogas production and reduced aeration energy for N-removal. Water Sci. Technol. 57, 383–388. doi:10.2166/wst.2008.048

Smith, A.L., Stadler, L.B., Cao, L., Love, N.G., Raskin, L., Skerlos, S.J., 2014. Navigating wastewater energy recovery strategies: A life cycle comparison of anaerobic membrane bioreactor and conventional treatment systems with anaerobic digestion. Environ. Sci. Technol. 48, 5972–5981. doi:10.1021/es5006169

Smitshuijzen, J., Pérez, J., Duin, O., Loosdrecht, M.C.M. va., 2016. A simple model to describe the performance of highly-loaded aerobic COD removal reactors. Biochem. Eng. J. 112, 94–102. doi:10.1016/J.BEJ.2016.04.004

Snip, L.J.P., Flores-Alsina, X., Plósz, B.G., Jeppsson, U., Gernaey, K. V, 2014. Modelling the occurrence, transport and fate of pharmaceuticals in wastewater systems. Environ. Model. Softw. 62, 112–127.

Stasinakis, A.S., 2012. Review on the fate of emerging contaminants during sludge anaerobic digestion. Bioresour. Technol. 121, 432–440. doi:10.1016/j.biortech.2012.06.074

Stasinakis, A.S., Thomaidis, N.S., Arvaniti, O.S., Asimakopoulos, A.G., Samaras, V.G., Ajibola, A., Mamais, D., Lekkas, T.D., 2013. Contribution of primary and secondary treatment on the removal of benzothiazoles, benzotriazoles, endocrine disruptors, pharmaceuticals and perfluorinated compounds in a sewage treatment plant. Sci. Total Environ. 463–464, 1067–1075. doi:10.1016/j.scitotenv.2013.06.087

Stevens-Garmon, J., Drewes, E., Khan, S.J., Mcdonald, J.A., Dickenson, E.R. V, 2011. Sorption of emerging trace organic compounds onto wastewater sludge solids. Water Res. 45, 3417–3426. doi:10.1016/j.watres.2011.03.056

STOWA, 2012. Verkenning naar mogelijkheden voor verwaarding van zeefgoed.

Struijs, J., van de Meent, D., Schowanek, D., Buchholz, H., Patoux, R., Wolf, T., Austin, T., Tolls, J., van Leeuwen, K., Galay-Burgos, M., 2016. Adapting

SimpleTreat for simulating behaviour of chemical substances during industrial sewage treatment. Chemosphere 159, 619–627. doi:10.1016/j.chemosphere.2016.06.063

Suárez, S., Carballa, M., Omil, F., Lema, J.M., 2008. How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? Rev. Environ. Sci. Biotechnol. 7, 125–138. doi:10.1007/s11157-008-9130-2

Suarez, S., Lema, J.M., Omil, F., 2010. Removal of Pharmaceutical and Personal Care Products (PPCPs) under nitrifying and denitrifying conditions. Water Res. 44, 3214–3224. doi:10.1016/j.watres.2010.02.040

Suarez, S., Lema, J.M., Omil, F., 2009. Pre-treatment of hospital wastewater by coagulation-flocculation and flotation. Bioresour. Technol. 100, 2138–2146. doi:10.1016/j.biortech.2008.11.015

Svraka, S., Duizer, E., Vennema, H., De Bruin, E., Van Der Veer, B., Dorresteijn, B., Koopmans, M., 2007. Etiological role of viruses in outbreaks of acute gastroenteritis in The Netherlands from 1994 through 2005. J. Clin. Microbiol. 45, 1389–1394. doi:10.1128/JCM.02305-06

Takács, I., Patry, G.G., Nolasco, D., 1991. A dynamic model of the clarification-thickening process. Water Res. 25, 1263–1271. doi:10.1016/0043-1354(91)90066-Y

Tan, D.T., Shuai, D., 2015. Research highlights: advances and challenges in developing mainstream anammox treatment. Environ. Sci. Water Res. Technol. 1, 546–549. doi:10.1039/C5EW90020D

Ternes, T., Joss, A., 2006. Human Pharmaceuticals, Hormones and Fragrances - The Challenge of Micropollutants in Urban Water Management. doi:10.2166/9781780402468

Ternes, T.A., Herrmann, N., Bonerz, M., Knacker, T., Siegrist, H., Joss, A., 2004. A rapid method to measure the solid-water distribution coefficient (Kd) for pharmaceuticals and musk fragrances in sewage sludge. Water Res. 38, 4075–4084. doi:10.1016/j.watres.2004.07.015

Terzić, S., Senta, I., Ahel, M., Gros, M., Petrović, M., Barcelo, D., Müller, J., Knepper, T., Martí, I., Ventura, F., Jovančić, P., Jabučar, D., 2008. Occurrence and fate of emerging wastewater contaminants in Western Balkan Region. Sci. Total Environ. 399, 66–77. doi:10.1016/j.scitotenv.2008.03.003

Thomaidi, V.S., Stasinakis, A.S., Borova, V.L., Thomaidis, N.S., 2016. Assessing the risk associated with the presence of emerging organic contaminants in

sludge-amended soil : A country-level analysis. Sci. Total Environ. 548–549, 280–288. doi:10.1016/j.scitotenv.2016.01.043

Thorin, E., Olsson, J., Schwede, S., Nehrenheim, E., 2017. Co-digestion of sewage sludge and microalgae - Biogas production investigations. Appl. Energy 227, 64–72. doi:10.1016/j.apenergy.2017.08.085

Tijani, J.O., Fatoba, O.O., Petrik, L.F., 2013. A review of pharmaceuticals and endocrine-disrupting compounds: Sources, effects, removal, and detections. Water. Air. Soil Pollut. 224. doi:10.1007/s11270-013-1770-3

Tiwari, B., Sellamuthu, B., Ouarda, Y., Drogui, P., Tyagi, R.D., Buelna, G., 2017. Review on fate and mechanism of removal of pharmaceutical pollutants from wastewater using biological approach. Bioresour. Technol. 224, 1–12. doi:10.1016/j.biortech.2016.11.042

Tousova, Z., Oswald, P., Slobodnik, J., Blaha, L., Muz, M., Hu, M., Brack, W., Krauss, M., Di Paolo, C., Tarcai, Z., Seiler, T.B., Hollert, H., Koprivica, S., Ahel, M., Schollée, J.E., Hollender, J., Suter, M.J.F., Hidasi, A.O., Schirmer, K., Sonavane, M., Ait-Aissa, S., Creusot, N., Brion, F., Froment, J., Almeida, A.C., Thomas, K., Tollefsen, K.E., Tufi, S., Ouyang, X., Leonards, P., Lamoree, M., Torrens, V.O., Kolkman, A., Schriks, M., Spirhanzlova, P., Tindall, A., Schulze, T., 2017. European demonstration program on the effect-based and chemical identification and monitoring of organic pollutants in European surface waters. Sci. Total Environ. 601–602, 1849–1868. doi:10.1016/j.scitotenv.2017.06.032

Tran, N.H., Reinhard, M., Gin, K.Y.H., 2018. Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review. Water Res. 133, 182–207. doi:10.1016/j.watres.2017.12.029

van Loosdrecht, M.C.M., Brdjanovic, D., 2014. Anticipating the next century of wastewater treatment. Science (80-.). 344, 1452–1453. doi:10.1126/science.1255819

Vangsgaard, A.K., Mutlu, A.G., Gernaey, K. V, Smets, B.F., Sin, G., 2013. Calibration and validation of a model describing complete autotrophic nitrogen removal in a granular SBR system. J. Chem. Technol. Biotechnol. 88, 2007–2015.

Varela, M.F., Ouardani, I., Kato, T., Kadoya, S., Aouni, M., Sano, D., Romalde, J.L., 2018. Sapovirus in Wastewater Treatment Plants in Tunisia: Prevalence, Removal, and Genetic Characterization. Appl. Environ. Microbiol. 84, 1–11.

Varhanickova, D., Y. Shiu, W., Mackay, D., 1995. Aqueous solubilities of alkylphenols and methoxyphenols at 25 C, Journal of Chemical and Engineering Data.

Vázquez-Padín, J.R., Fernández, I., Morales, N., Campos, J.L., Mosquera-Corral, A., Méndez, R., 2011. Autotrophic nitrogen removal at low temperature. Water Sci. Technol. 63, 1282–1288. doi:10.2166/wst.2011.370

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

Verlicchi, P., Zambello, E., 2015. Pharmaceuticals and personal care products in untreated and treated sewage sludge : Occurrence and environmental risk in the case of application on soil — A critical review. Sci. Total Environ. 538, 750–767. doi:10.1016/j.scitotenv.2015.08.108

Vieno, N., Tuhkanen, T., Kronberg, L., 2006. Removal of pharmaceuticals in drinking water treatment: Effect of chemical coagulation. Environ. Technol. 27, 183–192. doi:10.1080/09593332708618632

Wan, J., Gu, J., Zhao, Q., Liu, Y., 2016. COD capture: A feasible option towards energy self-sufficient domestic wastewater treatment. Sci. Rep. 6, 1–9. doi:10.1038/srep25054

Wang, H., Li, F., Keller, A.A., Xu, R., 2009. Chemically enhanced primary treatment (CEPT) for removal of carbon and nutrients from municipal wastewater treatment plants: A case study of Shanghai. Water Sci. Technol. 60, 1803–1809. doi:10.2166/wst.2009.547

Wang, X., Andrade, N., Shekarchi, J., Fischer, S.J., Torrents, A., Ramirez, M., 2018. Full scale study of Class A biosolids produced by thermal hydrolysis pretreatment and anaerobic digestion. Waste Manag. 78, 43–50. doi:10.1016/j.wasman.2018.05.026

WATER, E., 2015. STRATEGIC IMPLEMENTATION PLAN.

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

WHO/UNICEF, 2017. Progress on Drinking Water, Sanitation and Hygiene: 2017 Update and SDG Baselines.

Wick, A., Fink, G., Joss, A., Siegrist, H., Ternes, T.A., 2009. Fate of beta blockers and psycho-active drugs in conventional wastewater treatment. Water Res. 43, 1060–1074. doi:10.1016/j.watres.2008.11.031

Wijekoon, K.C., McDonald, J.A., Khan, S.J., Hai, F.I., Price, W.E., Nghiem, L.D., 2015. Development of a predictive framework to assess the removal of trace organic chemicals by anaerobic membrane bioreactor. Bioresour. Technol. 189, 391–398. doi:10.1016/j.biortech.2015.04.034

Wilson, C.A., Novak, J.T., 2009. Hydrolysis of macromolecular components of primary and secondary wastewater sludge by thermal hydrolytic pretreatment. Water Res. 43, 4489–4498. doi:10.1016/j.watres.2009.07.022

WWAP, 2017. WASTEWATER, THE UNTAPPED RESOURCE. The United Nations Word Water Development Report 2017. Paris.

Xu, G., Zhou, Y., Yang, Q., Lee, Z.M.P., Gu, J., Lay, W., Cao, Y., Liu, Y., 2015. The challenges of mainstream deammonification process for municipal used water treatment. Appl. Microbiol. Biotechnol. 99, 2485–2490. doi:10.1007/s00253-015-6423-6

Xue, W., Wu, C., Xiao, K., Huang, X., Zhou, H., 2010. Elimination and fate of selected micro-organic pollutants in a full-scale anaerobic / anoxic / aerobic process combined with membrane bioreactor for municipal wastewater reclamation. Water Res. 44, 5999–6010. doi:10.1016/j.watres.2010.07.052

Yang, S., Hai, F.I., Price, W.E., McDonald, J., Khan, S.J., Nghiem, L.D., 2016. Occurrence of trace organic contaminants in wastewater sludge and their removals by anaerobic digestion. Bioresour. Technol. 210, 153–159. doi:10.1016/j.biortech.2015.12.080

Yang, S., McDonald, J., Hai, F.I., Price, W.E., Khan, S.J., Nghiem, L.D., 2017a. Effects of thermal pre-treatment and recuperative thickening on the fate of trace organic contaminants during anaerobic digestion of sewage sludge. Int. Biodeterior. Biodegrad. 124, 146–154. doi:10.1016/j.ibiod.2017.06.002

Yang, S., McDonald, J., Hai, F.I., Price, W.E., Khan, S.J., Nghiem, L.D., 2017b. The fate of trace organic contaminants in sewage sludge during recuperative thickening anaerobic digestion. Bioresour. Technol. 240, 197–206. doi:10.1016/j.biortech.2017.02.020

Zhang, J., Li, N., Dai, X., Tao, W., Jenkinson, I.R., Li, Z., 2018. Enhanced dewaterability of sludge during anaerobic digestion with thermal hydrolysis pretreatment: New insights through structure evolution. Water Res. 131,

177–185. doi:10.1016/j.watres.2017.12.042

Zhang, L., Keller, J., Yuan, Z., 2009. Inhibition of sulfate-reducing and methanogenic activities of anaerobic sewer biofilms by ferric iron dosing. Water Res. 43, 4123–4132. doi:10.1016/j.watres.2009.06.013

Zhang, X., Li, R., 2018. Variation of antibiotics in sludge pretreatment and anaerobic digestion processes: Degradation and solid-liquid distribution. Bioresour. Technol. 255, 266–272. doi:10.1016/j.biortech.2018.01.100

Zhen, G., Lu, X., Kato, H., Zhao, Y., Li, Y.Y., 2017. Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: Current advances, full-scale application and future perspectives. Renew. Sustain. Energy Rev. 69, 559–577. doi:10.1016/j.rser.2016.11.187

Zhou, H., Zhang, Z., Wang, M., Hu, T., Wang, Z., 2017. Enhancement with physicochemical and biological treatments in the removal of pharmaceutically active compounds during sewage sludge anaerobic digestion processes. Chem. Eng. J. 316, 361–369. doi:10.1016/j.cej.2017.01.104

Zhou, Y., Zhang, D.Q., Le, M.T., Puah, A.N., Ng, W.J., 2013. Energy utilization in sewage treatment - A review with comparisons. J. Water Clim. Chang. 4, 1–10. doi:10.2166/wcc.2013.117

Ziganshin, A.M., Schmidt, T., Scholwin, F., Il'Inskaya, O.N., Harms, H., Kleinsteuber, S., 2011. Bacteria and archaea involved in anaerobic digestion of distillers grains with solubles. Appl. Microbiol. Biotechnol. 89, 2039–2052. doi:10.1007/s00253-010-2981-9

Ziganshina, E.E., Belostotskiy, D.E., Ilinskaya, O.N., Boulygina, E.A., Grigoryeva, T. V., Ziganshin, A.M., 2015. Effect of the Organic Loading Rate Increase and the Presence of Zeolite on Microbial Community Composition and Process Stability During Anaerobic Digestion of Chicken Wastes. Microb. Ecol. 70, 948–960. doi:10.1007/s00248-015-0635-2

LIST OF PUBLICATIONS

Scientific journals

➢ Taboada-Santos, A., Braz, G.H.R., Fernandez-Gonzalez, N., Carballa, M., Lema, J.M., 2019. *Thermal hydrolysis of sewage sludge partially removes organic micropollutants but does not enhance their anaerobic biotransformation.* Science of the Total Environment. 690, 534–542. Chapter 4 is based on this publication.

➢ Taboada-Santos, A., Carballa, M., Morales, N., Vázquez-Padín, J.R., Gutierrez, R., Lema, J.M., 2019. *An optimised control system to steer the transition from anaerobic mono- to co-digestion in full-scale plants.* Environmental Science: Water Research and Technology. 5, 1004–1011.

➢ Taboada-Santos, A., Lema, J.M., Carballa, M., 2019. *Energetic and economic assessment of sludge thermal hydrolysis in novel wastewater treatment plant configurations.* Waste Managment. 92, 30–38. Chapter 5 is based on this publication.

➢ Taboada-Santos, A., Lema, J.M., Carballa, M., 2019. *Opportunities for rotating belt filters in novel wastewater treatment plant configurations.* Environmental Science: Water Research and Technology. 5, 704–712. Chapter 2 is based on this publication.

➢ Taboada-Santos, A., Paredes, L., Rivadulla, E., Carballa, M., Romalde, J.L., Lema, J.M., 2019. *Comprehensive comparative between chemically enhanced primary treatment and high-rate activated sludge for preconcentration of organic carbon in novel wastewater treatment plant configurations.* Submitted to Water Research. Chapter 3 is based on this publication.

➢ Taboada-Santos, A., Ranjan *A comparative analysis of the fate of organic micropollutants between novel and conventional wastewater treatment plant configurations through an empirical mechanistic model.* Submitted to Science of the Total Environment. Chapter 6 is based on this publication.

Conference proceedings

- *Oral contributions*

➢ Taboada-Santos A., Omil F., Paredes L., Carballa M. and Lema JM (2019). *Fate of organic micropollutants during the preconcentration step of organic carbon in novel wastewater treatment plant configurations.* (Oral Presentation) 9th IWA Micropol&Ecohazard Conference, IWA, Seul, Korea.

➢ Taboada-Santos, A., Lema, J.M., and Carballa, M. (2019). *Energetic and economic assessment of sludge thermal hydrolysis in novel wastewater treatment plant configurations* (Oral Presentation) 16th IWA Anaerobic Digestion Conference, IWA, Delft, Netherlands.

➢ Taboada-Santos, A., Lema, J.M. and Carballa, M. (2018). *Are Rotating Belts Sieves Comparable To Conventional Primary Treatment In Terms Of Organic Micropollutants Removal?* (Oral Presentation) 4th IWA Specialized International Conference, IWA, Ontario, Canada.

➢ Taboada-Santos, A., Lema, J.M. and Carballa, M. (2018). *Opportunities Of Sieving Filter In Novel Wastewater Treatment Plants.* (Oral Presentation) 4th IWA Specialized International Conference, IWA, Ontario, Canada.

- *Poster presentations*

➢ Taboada-Santos, A., Carballa, M., Lema, J.M. (2019), *Thermal hydrolysis of sewage sludge partially removes organic micropollutants but does not enhance their anaerobic biotransformation* (Oral Presentation) 9th IWA Micropol&Ecohazard Conference, IWA, Seul, Korea.

➢ Braz, G.H.R., Taboada-Santos, A., Fernandez-Gonzalez, N., Carballa, M., Lema, J.M *Thermal hydrolysis affects the microbiome structure and composition in sewage sludge anaerobic reactors* (Short-oral poster Presentation) 16th IWA Anaerobic Digestion Conference, IWA, Delft, Netherlands

➢ Taboada-Santos, A., Carballa, M., Morales, N., Vázquez-Padín, JR, Gutierrez, R., and Lema, JM (2019). *Anaerobic co-digestion approaches traditional WWTPs to electrical self-sufficiency and reduces co-substrates treatment costs.* (Poster Presentation) 16th IWA Anaerobic Digestion Conference, IWA, Delft, Netherlands.

➤ Taboada-Santos, A., Rodriguez-Verde, I., Regueira, A., Sanchez, A., Carballa, M., Lema, JM (2017). *Steering transition from anaerobic mono-digestion of sewage sludge towards co-digestion, at pilot scale.* (Poster Presentation) 15th IWA Anaerobic Digestion Conference, IWA, Pekin, China.