Integration of Membrane Filtration and Photolysis Processes for Drinking Water Treatment

Sandra Sanches

Dissertation presented to obtain the Ph.D degree in Engineering and Technology Sciences, Chemical Engineering

Instituto de Tecnologia Química e Biológica | Universidade Nova de Lisboa

Oeiras,
December, 2013

INSTITUTO
DE TECNOLOGIA
QUÍMICA E BIOLÓGICA
/UNL

Knowledge Creation

Integration of Membrane Filtration and Photolysis Processes for Drinking Water Treatment

Sandra Marisa Lourenço Sanches

Dissertation presented to obtain the Ph.D degree in
Engineering and Technology Sciences, Chemical Engineering
Instituto de Tecnologia Química e Biológica | Universidade Nova de Lisboa

Oeiras, December 2013

INSTITUTO
DE TECNOLOGIA
QUÍMICA E BIOLÓGICA
/UNL

Knowledge Creation

ITQB-UNL and IBET, Microbiology of Man-made Environments Laboratory
Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa and
Instituto de Biologia Experimental e Tecnológica
Apartado 12, 2781-901 Oeiras, Portugal
Fax: +351 21 442 11 61; Phone: +351 21 446 95 52
http://www.itqb.unl.pt
http://www.ibet.pt

Printed in Portugal

SUPERVISORS

Prof. João Crespo: Full Professor at the Chemistry Department of FCT-UNL (supervisor).

Dr. Vanessa Pereira: Post-doctoral researcher at the Microbiology of Man-Made Environments Laboratory, IBET and ITQB-UNL (co-supervisor).

Dr. Teresa Crespo: Researcher and Head of the Microbiology of Man-Made Environments Laboratory of IBET and ITQB-UNL and Director of the Analytical Services Unit of IBET and ITQB-UNL (co-supervisor).

Aos meus pais

ACKNOWLEDGEMENTS

O trabalho conducente à elaboração desta tese teve o apoio financeiro da Fundação para a Ciência e Tecnologia (FCT) e do FSE no âmbito do quadro Comunitário de apoio, BD nº 72244/2010. O trabalho desenvolvido teve também o apoio do IBET e ITQB-UNL.

Muitos são aqueles a quem quero expressar a minha gratidão por me terem encorajado e ajudado, contribuindo para a concretização desta etapa.

À Doutora Vanessa Pereira, minha orientadora, agradeço por me ter guiado ao longo de vários anos e por todo o conhecimento e rigor científico que me transmitiu. Vanessa, amiga, "irmã", muito obrigada por estares sempre disponível para me ouvir e "aturar" os meus desânimos face aos resultados menos bons ou aos altos e baixos da vida. Obrigada por teres estado sempre lá, mesmo que fosse à distância de um "click", por teres sempre uma palavra de conforto e por me mostrares sempre os dois lados da "moeda". O teu bom senso, generosidade com todos os que te rodeiam e rigor em tudo o que fazes caracterizam-te e inspiraram-me durante o meu percurso. Guardo com carinho os teus conselhos e os momentos de cumplicidade!

Ao Professor João, meu orientador, agradeço também por me ter guiado numa viagem repleta de valiosas discussões científicas que tantas vezes me fizeram olhar para os vários assuntos de uma outra perspetiva. Foi um privilégio poder beneficiar da sua experiência e quantidade incrível de conhecimentos que tem para transmitir. Obrigada pelo apoio, confiança e por me fazer acreditar que sou capaz, ajudando-me a crescer não só profissionalmente mas também pessoalmente. Foi um prazer fazer esta viagem consigo!

À Doutora Teresa Crespo, minha orientadora, agradeço todo o carinho com que me recebeu no seu laboratório, mesmo para trabalhar com instalações grandes e ruidosas que não são habituais num laboratório de microbiologia. Obrigada pelos seus "inputs", pela sua boa disposição e por tornar o seu laboratório num local onde nos sentimos em casa e gostamos de trabalhar. O meu muito obrigada também por tornar os meus fins de tarde, a caminho de casa, mais animados com conversas banais sobre cultura, viagens, política e tantas histórias tão bem humoradas que são autênticas lições de vida. Vou guardar esses momentos de descontração comigo!

Aos meus colegas da Microbiologia, especialmente aqueles que estiveram lá desde o primeiro dia e que ainda lá se encontram: Filipa e Paula. Também àqueles que já partiram em busca de novas aventuras – Rusa, Marta, Bárbara, Catarina e Joana Galinha – e àqueles que se juntaram mais tarde: Dulce, Beatriz e Joana Lamego. Muito obrigada pelo vosso companheirismo e momentos de descontração! Gilda, minha companheira de "gym", obrigada também pelas conversas bem-humoradas na passadeira do "holmicos" e pelos momentos de cumplicidade e descontração nas aulas de zumba.

À Cláudia Galinha, agradeço todo o empenho em transmitir-me os seus conhecimentos em modelação e as muitas e valiosas discussões nesta área.

À Paula Chicau e à Cristina Leitão, agradeço o apoio técnico, a disponibilidade sempre demonstrada para ajudar-me e o companheirismo. Agradeço também a colaboração da Doutora Paula Passarinho, da Doutora Clarisse Nunes e do Doutor Frederico Ferreira. Ao Engenheiro Vitor Cardoso, Ana Penetra, Alexandre Rodrigues, Engenheira Maria João Benoliel e Doutora Elisabete Ferreira, da Empresa Portuguesa das Águas Livres, quero expressar a minha sincera gratidão pela excelente colaboração, essencial para a concretização desta tese.

À Doutora Maria João Rosa e à Doutora Cristina Almeida, agradeço as frutíferas discussões científicas.

Ao Doutor Sebastien Logette e à sua equipa da Veolia Environnement Recherche & Innovation, Maisons Laffitte, France, agradeço por me terem recebido e ensinado técnicas e metodologias que contribuíram para o alargamento dos meus conhecimentos e por me permitirem contactar diretamente com problemas reais.

Aos meus amigos, agradeço toda a amizade. O vosso apoio, mesmo que por vezes à distância, foi muito importante! Um obrigado especial à Inês Oliveira e à Inês Veiga. Inês Veiga, a tua amizade ficará para sempre associada à minha tese, através da bonita fotografia gentilmente cedida para a capa.

À minha família, quero agradecer todo o apoio. Um obrigado muito especial àqueles que me acolheram em Paris durante o meu estágio na Veolia; o vosso apoio e carinho foram fundamentais e fizeram-me sentir realmente em casa!

Aos meus pais, dedico esta tese. Obrigada por estarem presentes em todos os momentos da minha vida e por me apoiarem incondicionalmente. Vocês são o meu exemplo de integridade, humildade, dedicação e trabalho. Mostram-me todos os dias que nada se faz sem esforço e que é sempre possível fazer mais, mesmo quando as forças nos querem abandonar e pensamos que já não somos capazes de prosseguir. O orgulho que vejo nos vossos olhos é aquilo que me motiva a continuar e a querer fazer sempre mais e melhor. É um orgulho ser vossa filha!

iBET itqb FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA EDUCAÇÃO E CIÊNCIA

ABSTRACT

Water is a fundamental resource for life. The presence of hazardous micropollutants such as pesticides and hormones in drinking water sources as well as the evidence of their presence in several treated waters raised concerns regarding the quality of the water intended for human consumption. The development of new technologies which are able to cope with these micropollutants and ensure the fulfillment of future more stringent regulations is therefore needed. Low pressure ultraviolet direct and indirect photolysis (using hydrogen peroxide and titanium dioxide) and nanofiltration are extremely promising technologies to effectively remove organic micropollutants from water. Nevertheless, there are some challenges related with their application: namely, the formation of photolysis by-products and the need to remove titanium dioxide particles downstream from the photocatalysis process, as well as the development of membrane fouling and formation of a concentrated retentate during nanofiltration.

In this study, the potential of either low pressure ultraviolet direct photolysis, titanium dioxide photocatalysis or nanofiltration to remove several pesticides (atrazine, isoproturon, diuron, alachlor, pentachloropnenol, and chlorfenvinphos) and hormones (17β-estradiol, 17α-ethinylestradiol, estrone, estriol, and progesterone) from drinking water sources was evaluated. A configuration that combines ultraviolet photolysis and nanofiltration technologies in sequence was assembled to tackle the aforementioned challenges and produce high quality drinking water in terms of these micropollutants, selected due to their persistence, different structures and physico-chemical properties, bioaccumulation potential, and toxicity.

Low pressure ultraviolet direct photolysis demonstrated high potential towards the degradation of all the pesticides addressed except isoproturon as well as the hormones progesterone and estrone. Similar degradations were obtained for the

target compounds when assessed individually or as mixtures. Titanium dioxide photocatalysis was able to improve significantly the degradation attained by direct photolysis for the hormones 17β-estradiol, 17α-ethinylestradiol, and estriol while noteworthy differences were not observed for the other compounds. The main kinetic parameters of the degradation of the target pesticides were determined and applied to predict their degradation under different experimental conditions, allowing further optimisation of the process. The applied model predicted well direct photolysis while overestimating titanium dioxide photocatalysis efficiency.

Ultrafiltered groundwater and surface water were used to address the potential of nanofiltration to treat waters with different compositions and understand the impact of ionic species and natural organic matter, without the interference of particulate and large colloidal organic matter. Using the flat-sheet Desal 5DK membrane, nanofiltration showed high effectiveness towards the removal of the target pesticides and hormones, often independently of the water composition. Similar results were also generally attained during the experiments carried out with pre-adsorption of the compounds on the membrane, suggesting that the removal of the target micropollutants may not be considerably changed after long term operation in water utilities. Even though results suggested that size exclusion and hydrophobic interactions were important rejection mechanisms, multivariate statistical analysis was further conducted to better elucidate the synergies and concurrent effects that impact rejection and adsorption. Multilinear projection to latent structure models with good descriptive capability were developed. Alkalinity, molecular size descriptors, molecular weight, molar volume, and the logarithm of the octanol-water distribution ratio were found to be the most relevant contributors for the rejection of the selected micropollutants, showing the impact of size exclusion and electrostatic interactions. Molecular geometry was found to be very important to determine rejection, when molecules have very different geometry.

When the sequential treatment of titanium dioxide followed by nanofiltration was conducted, the catalyst was completely adsorbed on the membrane, limiting further assessment. However, a combined treatment consisting of direct low pressure ultraviolet photolysis followed by nanofiltration was able to efficiently remove the target pesticides and hormones from surface water collected after the sedimentation process, with removal higher than 85.1% throughout a six hour treatment. Remarkable decreases in the endocrine disrupting activity were also attained in the treated water for the mixture of pesticides (64.4-93.8%) and hormones (95.4-99.6%) throughout the treatment. Generally, photolysis by-products generated with higher endocrine disrupting activity than the parent compounds were successfully retained by the membrane. Furthermore, the concentration of the selected micropollutants in the retentate was highly decreased, reducing the need to further treat/dispose the retentate and lowering the respective costs. Fouling was not significantly observed during the treatment. The combined treatment thus demonstrated the potential to tackle the challenges associated with the individual application of the UV and nanofiltration processes.

The work presented in this thesis provides important knowledge that may be further applied to improve the design and operation of drinking water treatment systems.

RESUMO

A água é fundamental para a vida. A presença de micropoluentes, tais como pesticidas e hormonas, em águas superficiais e águas destinada ao consumo humano constitui um problema. Torna-se, por isso, necessário o desenvolvimento de novas tecnologias de tratamento capazes de remover estes compostos da água e assegurar o cumprimento de futuras legislações mais rígidas do que as atuais. A fotólise direta e indireta (usando peróxido de hidrogénio e dióxido de titânio) promovida por radiação ultravioleta de baixa pressão, assim como a nanofiltração, são tecnologias promissoras para a remoção efetiva de micropoluentes orgânicos da água. No entanto, a aplicação destas tecnologias enfrenta alguns desafios: a formação de subprodutos da fotólise, a necessidade de remover as partículas de dióxido de titânio após fotocatálise, a ocorrência de colmatação de membranas durante a nanofiltração e a formação de um retentado de nanofiltração muito concentrado.

Na presente tese, os processos de fotólise direta de baixa pressão, fotocatálise com dióxido de titânio e nanofiltração são avaliados individualmente em termos do seu potencial para remover vários pesticidas (atrazina, isoproturão, diurão, alacloro, pentaclorofenol e clorofenvinfos) e hormonas (17β-estradiol, 17α-etinilestradiol, estrona, estriol e progesterona) de águas superficiais. Estes pesticidas e hormonas foram selecionados neste estudo devido à sua persistência, diferentes estruturas e propriedades físico-químicas, potencial de bioacumulação e elevada toxicidade. A combinação sequencial de fotólise/fotocatálise com dióxido de titânio e nanofiltração foi depois avaliada em termos da sua capacidade de superar os desafios referidos acima e produzir água com boa qualidade.

A fotólise direta de baixa pressão demonstrou elevado potencial para degradar todos os pesticidas selecionados, exceto o isoproturão, assim como as hormonas estrona e progesterona. As degradações obtidas para os compostos fortificados individualmente ou sob a forma de misturas foram bastante semelhantes. Apesar da fotocatálise com dióxido de titânio ter melhorado significativamente a degradação das hormonas 17β-estradiol, 17α-etinilestradiol e estriol, obtida por fotólise direta, não foram observadas diferenças significativas para os restantes compostos. Este estudo permitiu a determinação de parâmetros cinéticos relacionados com a degradação dos pesticidas alvo, que foram posteriormente usados para prever a sua degradação em diferentes condições experimentais, permitindo a otimização do processo. O modelo matemático usado permitiu prever os resultados experimentais obtidos por fotólise direta, embora sobrestime a eficiência da fotocatálise com dióxido de titânio.

A membrana Desal 5DK foi usada para testar a eficiência da nanofiltração para tratar águas com diferentes composições, tais como água subterrânea e água superficial ultrafiltradas. O impacto de espécies iónicas e da matéria orgânica foram por isso estudados, sem a interferência de matéria particulada e matéria orgânica coloidal de grandes dimensões. O processo de nanofiltração demonstrou elevada eficiência para remover os pesticidas e as hormonas selecionados, de forma geralmente independente da composição da água. A semelhança dos resultados obtidos nas experiências realizadas, com e sem pré-adsorção dos compostos à membrana, sugeriu que a remoção destes micropoluentes não deverá ser significativamente alterada após longa operação em estações de tratamento de água. Apesar dos resultados experimentais obtidos sugerirem que a exclusão molecular e as interações hidrofóbicas são importantes mecanismos de rejeição destes compostos, uma análise estatística multivariada foi também realizada para elucidar as sinergias e efeitos concorrentes que influenciam a sua rejeição e adsorção à membrana. Modelos multilineares, via projeção de estruturas latentes, com boa capacidade descritiva foram desenvolvidos. De acordo com os modelos obtidos, os parâmetros mais relevantes para descrever a rejeição são os seguintes: alcalinidade, descritores de

tamanho molecular, peso molecular, volume molar e o logaritmo do coeficiente de distribuição octanol-água. A importância destes parâmetros evidencia o impacto de mecanismos de exclusão molecular e interações eletrostáticas, demonstrando que a geometria molecular tem um papel muito importante na rejeição.

O catalisador dióxido de titânio foi completamente adsorvido na membrana quando o processo que integra a fotocatálise, seguido de nanofiltração, foi testado, não sendo possível avaliar a eficiência deste processo. No entanto, o processo que integra a fotólise direta com a nanofiltração demonstrou ser extremamente eficiente para remover os pesticidas e as hormonas alvo de água superficial, recolhida após o processo de sedimentação numa estação de tratamento. As remoções obtidas durante 6 horas de tratamento foram superiores a 85.1%. A atividade de disrupção endócrina da água tratada ao longo do tempo também foi consideravelmente reduzida relativamente à água não tratada, fortificada com uma mistura dos pesticidas (64.4%-93.8%) ou uma mistura das hormonas (95.4-99.6%). Os sub-produtos da fotólise gerados durante o tratamento foram retidos pela membrana. A concentração dos micropoluentes alvo no retentado foi também consideravelmente reduzida, atenuando a necessidade de efetuar um tratamento posterior e reduzindo os respetivos custos. A colmatação da membrana durante o tratamento não foi significativa. Estes resultados demonstram que o tratamento integrado permite ultrapassar as limitações associadas à aplicação individual dos processos de fotólise e nanofiltração.

Os estudos realizados no âmbito desta tese fornecem conhecimentos importantes que podem ser aplicados para otimizar as operações dos sistemas de tratamento de águas destinadas ao consumo humano.

THESIS PUBLICATIONS

Sanches S, Barreto Crespo MT, Pereira VJ (2010) Drinking water treatment of priority pesticides using low pressure UV photolysis and advanced oxidation processes. *Water Res* 44(6): 1809-1818.

Sanches S, Penetra A, Rodrigues A, Ferreira E, Cardoso VV, Benoliel MJ, Barreto Crespo MT, Pereira VJ, Crespo JG (2012) Nanofiltration of hormones and pesticides in different real drinking water sources. *Sep Purif Technol* 94: 44-53.

Sanches S, Galinha CF, Barreto Crespo MT, Pereira VJ, Crespo JG (2013) Assessment of phenomena underlying the removal of micropollutants during water treatment by nanofiltration using a multivariate statistical analysis. *Sep Purif Technol* 118: 377-386.

Sanches S, Penetra A, Rodrigues A, Cardoso VV, Ferreira E, Benoliel MJ, Barreto Crespo MT, Crespo JG, Pereira VJ (2013) Removal of pesticides from water combining low pressure UV photolysis with nanofiltration. *Sep Purif Technol* 115: 73-82.

Sanches S, Rodrigues A, Cardoso VV, Ferreira E, Benoliel MJ, Barreto Crespo MT, Crespo JG, Pereira VJ (2013) Combination of UV photolysis and nanofiltration to overcome their drawbacks and remove endocrine disrupting compounds from a drinking water source. Re-submitted after revision to Desalination.

LIST OF ABBREVIATIONS

a	Absorbance
A	Adsorption
ACN	Acetonitrile
ALA	Alachlor
Alk	Alkalinity
AOPs	Advanced oxidation processes
ATR	Atrazine
ByP	By-product
C_f	Concentration of a given compound in the feed
CFVP	Chlorfenvinphos
C_p	Concentration of a given compound in the permeate
CPRG	Chlorophenol red-β-D-galactopyranoside
C_r	Concentration of a given compound in the retentate
DBPs	Disinfection by-products
DC	Direct current
DIU	Diuron
DOC	Dissolved organic carbon
Dyn ads	Mass pre-adsorbed under dynamic conditions
EC_{50}	Concentration of a given compound that induces 50% of the maximum response
EDCs	Endocrine disrupting compounds
EEQ	Estradiol equivalents
E_p°	Incident photon irradiance
EPAL	Empresa Portuguesa das Águas Livres
ERE	Estrogen response elements
exp	Experimental
FL	Fluorescence
GC	Gas chromatography
GW	Groundwater
H_2O_2	Hydrogen peroxide
hER	Human estrogen receptor
HPLC	High performance liquid chromatography
$h\nu$	Radiant energy
ind	Individual
ISO	Isoproturon
k'_d	Pseudo-first order direct photolysis rate constant
k'_f	Fluence-based pseudo-first order photolysis rate constant
k'_i	Pseudo-first order indirect photolysis rate constant

$k_{OH/CO_3^{2-}}$	Pseudo-first-order rate of reaction of hydroxyl radicals with carbonate ions
$k_{OH/DOC}$	Pseudo-first-order rate of reaction of hydroxyl radicals with dissolved organic carbon
k_{OH/H_2O_2}	Pseudo-first-order rate of reaction of hydroxyl radicals with hydrogen peroxide
k_{OH/HCO_3^-}	Pseudo-first-order rate of reaction of hydroxyl radicals with bicarbonate ions
$k_{OH/M}$	Second-order rate constant for reaction of hydroxyl radicals with micropollutants
$k_{OH/pCBA}$	Pseudo-first-order rate of reaction of hydroxyl radicals with *para*-chlorobenzoic acid
K_s	Specific rate of light absorption by a given compound
k'_t	Time-based pseudo-first order photolysis rate constant
LGW	Laboratory grade water
log D	Logarithm of the octanol-water distribution ratio at pH 7.4
log K_{ow}	Logarithm of octanol-water partition coefficient
LP	Low pressure
M_d	Molecular depth
MeOH	Methanol
MF	Microfiltration
mix	Mixture
M_l	Molecular length
MP	Medium pressure
MQ	Milli-Q water
MRM	Multiple reaction monitoring
MS	Mass spectrometry
MW	Molecular weight
MWCO	Molecular weight cut-off
M_{wd}	Molecular width
m/z	Mass to charge ratio
na	Not available
nd	Not determined
NF	Nanofiltration
NOM	Natural organic matter
$^{\bullet}OH$	Hydroxyl radicals
$[^{\bullet}OH]_{ss}$	Steady-state concentration of hydroxyl radicals
P	Polarisability
PAHs	Polycyclic aromatic hydrocarbons
pCBA	*para*-Chlorobenzoic acid

PCP	Pentachlorophenol
pK_a	Inverse of the logarithm of the acid dissociation constant
PLS	Projection to latent structures
Q_f	Feed flow rate
Q_p	Permeate flow rate
R^2	Determination coefficient
R_{app}	Apparent rejection
RMSECV	Root mean square error of cross-validation
RMSEP	Root mean square error of prediction
RO	Reverse osmosis
S	Scavengers
SPE	Solid phase extraction
Stat ads	Mass pre-adsorbed under static conditions
SW	Surface water
t	Time
T	Temperature
t_{filt}	Time of filtration
TiO_2	Titanium dioxide
TOC	Total organic carbon
TOTCO3	Total carbonate
UF	Ultrafiltration
UPLC	Ultra performance liquid chromatography
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
V_f	Volume of feed
V_{filt}	Filtered volume
V_m	Molar volume
V_p	Volume of permeate
V_r	Volume of retentate
Ws	Water solubility
YES	Yeast estrogen screen assay
z	Distance to the UV source
$\alpha_{1,}$ α_2	Distribution coefficients of the carbonate species
ε	Decadic molar absorption coefficient
ϕ	Quantum yield
λ	Wavelength
λ_{em}	Emission wavelength
λ_{ex}	Excitation wavelength
μ	Dipole moment

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

Introduction: state-of-the-art and thesis motivation

CONTENTS

This chapter comprises the state-of-the-art related with the water treatment technologies addressed in the present thesis - ultraviolet (UV) direct photolysis, advanced oxidation processes (AOPs), and nanofiltration (NF) - as well as the motivation for the approach followed and the main objectives of this Thesis.

1.1 WATER AVAILABILITY AND QUALITY

Water covers 70 percent of the earth's surface. Nevertheless, only approximately 2.5 percent is freshwater, and because most of that water is locked up in ice and glaciers, only 0.3 percent of the total freshwater is easily accessible in rivers and lakes, which are the most common sources of drinking water (Oki and Kanae 2006, Shiklomanov 1993).

Moreover, the exponential growth of population has led to an increasing demand of potable water. Since water is a fundamental resource for life, water availability and quality (chemical and microbial) are among the main environmental challenges of the 21st century.

1.2 EMERGING MICROPOLLUTANTS IN WATER

The disposal of several chemicals that are used in several industries, agriculture, medicine, and other activities have raised increasing concern regarding their potential adverse effects for human health and environment in the last decades. Many organic compounds such as pesticides, pharmaceutical and personal care products, endocrine disrupting compounds (EDCs), polychlorinated biphenyls, phthalates, alkylphenols, and polycyclic aromatic hydrocarbons (PAHs) have been detected in water sources all over the world at ng L^{-1} to low μg L^{-1} levels (Cabeza *et al*. 2012, Zheng *et al*. 2012, Velicu and Suri 2009, Rao *et al*. 2013).

Based on their relevance in terms of occurrence levels, hazardous potential as well as the need to comply with current and potentially more stringent future regulations, some pesticides and endocrine disrupting compounds with different chemical structures, properties, and behaviour were selected to be addressed in the studies carried out in the scope of the present thesis.

1.2.1 Pesticides

The widespread and extensive use of pesticides in agriculture and wood preservation to control weeds, insects, and plant diseases has led to their presence in several water sources, mainly through runoffs, spray drift, and drainage (Knauert *et al*. 2008).

A group of pesticides with different structures and properties was targeted in the studies described in this thesis that included: atrazine (ATR), isoproturon (ISO), diuron (DIU), alachlor (ALA), pentachlorophenol (PCP), and chlorfenvinphos (CFVP). Table 1.1 depicts their structures, occurrence concentrations in surface water (SW) and groundwater (GW), toxicity effects, and specific physico-chemical properties such as molecular weight (MW), water solubility (W_s), logarithm of octanol-water partition coefficient (log K_{ow}), inverse of the logarithm of the acid dissociation constant (pK_a), and molar volume (V_m).

Table 1.1 *Characterisation of the pesticides atrazine, isoproturon, diuron, alachlor, pentachlorophenol, and chlorfenvinphos in terms of their physico-chemical properties, occurrence levels in groundwater and surface water, and toxicity effects. The colours of the atoms in the molecular structures of the pesticides have the following meaning: grey – carbon; white – hydrogen; green – chloride; red – oxygen; blue – nitrogen; orange – phosphorus.*

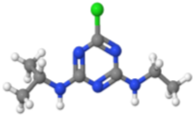
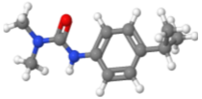
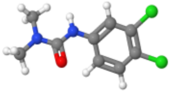
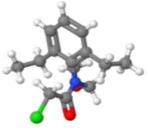
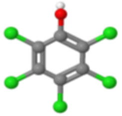
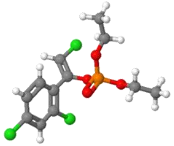
Compound* [CAS number]	**Description**	**Molecular formula**	**MW (Da)**	**W_s at 25 °C ($mg\ L^{-1}$)**	**log K_{ow}**	**pK_a**	**V_m ($cm^3 mol^{-1}$)**	**Occurrence levels ($ng\ L^{-1}$)**	**Toxicity effects**
 Atrazine [1912-24-9]	Herbicide	$C_8H_{14}ClN_5$	215.7	34.7[1]	2.56[2]	1.70[3]	169.9[4]	2[5] – 5200[6]	Decrease of pituitary hormone levels, ovarian and liver histopathology, effects on nervous immune, and cardiovascular systems[7]. Non-Hodgkin's lymphoma, preterm delivery, and intrauterine growth retardation[8,9]. Demasculinisation of male gonads (reduced germ cell numbers in teleost fish, amphibians, reptiles, and mammals), partial and/or complete feminisation of fish, amphibians, and reptiles[10]. Changes in the testosterone metabolism[11].
 Isoproturon [34123-59-6]	Herbicide	$C_{12}H_{18}N_2O$	206.3	14[1]	2.87[12]	na	196.3 [4]	7[13] – 1959[14]	Hepatocellular tumours, preneoplastic, and neoplastic lesions[15].
 Diuron [330-54-1]	Herbicide	$C_9H_{10}Cl_2N_2O$	233.1	42[1]	2.68[12]	na	170.2[4]	0.27[5] – 864[14]	Hemolytic anaemia and compensatory hematopoiesis. Urinary bladder, kidney, and mammary gland carcinomas[16].

Table 1.1 *Characterisation of the pesticides atrazine, isoproturon, diuron, alachlor, pentachlorophenol, and chlorfenvinphos in terms of their physico-chemical properties, occurrence levels in groundwater and surface water, and toxicity effects. The colours of the atoms in the molecular structures of the pesticides have the following meaning: grey – carbon; white – hydrogen; green – chloride; red – oxygen; blue – nitrogen; orange – phosphorus (continuation).*

Compound* [CAS number]	**Description**	**Molecular formula**	**MW (Da)**	**W_s at 25 °C (mg L^{-1})**	**log K_{ow}**	**pK_a**	**V_m (cm^3mol^{-1})**	**Occurrence levels (ng L^{-1})**	**Toxicity effects**
 Alachlor [15972-60-8]	Herbicide	$C_{14}H_{20}ClNO_2$	269.8	240[1]	3.52[17]	0.62[18]	240.9[4]	27[19] – 9950[20]	Lymphomatopoietic cancers, leukaemia, multiple myeloma[21], and thyroid[22]. Anaemia, increased risk of cancer, and problems in the eye, liver, kidney and spleen[23].
 Pentachlorophenol [87-86-5]	Herbicide Insecticide Fungicide	C_6HCl_5O	266.3	14.0[1]	5.12[24]	4.70[25]	147.6[4]	20 – 21620[26]	Trachea, bronchus and lung cancers, non-Hodgkin lymphoma, chronic obstructive pulmonary disease, leukaemia[27], and thyroid[28].
 Chlorfenvinphos [470-90-6]	Insecticide	$C_{12}H_{14}Cl_3O_4P$	359.6	124[1]	3.81[12]	na	261.8[4]	2.48[29] – 145[5]	Changes in the central and peripheral nervous system[30]. Lipid peroxidation, hemolysis, and erythrocyte malformation[31].

*molecular structures depicted were obtained from the Jmol software; na – not available; MW – molecular weight; W_s – water solubility; log K_{ow} – logarithm of octanol-water partition coefficient; pK_a –inverse of the logarithm of the acid dissociation constant; V_m – molar volume; **[1]** Meylan and Howard 1994 **[2]** Schwarzenbach *et al*. 1993 **[3]** Yangali-Quintanilla *et al*. 2009 **[4]** Chemspider **[5]** Cabeza *et al*. 2012 **[6]** Vryzas *et al*. 2012 **[7]** ATSDR 2003 **[8]** Munger *et al*. 1997 **[9]** Villanueva *et al*. 2005 **[10]** Hayes *et al*. 2011 **[11]** Jin *et al*. 2013 **[12]** Ardrey 2003 **[13]** Loos *et al*. 2010a **[14]** Loos *et al*. 2009 **[15]** WHO 1996 **[16]** US EPA 2003 **[17]** Comerton *et al*. 2007 **[18]** Pesticide Properties DataBase **[19]** Loos *et al*. 2010b **[20]** Postigo *et al*. 2010 **[21]** Lee *et al*. 2004 **[22]** Wilson *et al*. 1996 **[23]** US EPA 2009a **[24]** Krieger *et al*. 2001 **[25]** Cessna and Grover 1978 **[26]** Zheng *et al*. 2012 **[27]** Ruder and Yiin 2011 **[28]** Orton *et al*. 2009 **[29]** Teijon *et al*. 2010 **[30]** Vidyasagar *et al*. 2004 **[31]** Sosnowska *et al*. 2013.

The high water solubility of these compounds and their relatively low log K_{ow} values (exception of pentachlorophenol) suggest that these compounds are expected to partition to some extent into the aquatic environment. In fact, these micropollutants have been found in the surface water and groundwater all over the world at concentrations up to 21.62 μg L^{-1} (Zheng *et al*. 2012) (Table 1.1). Based on the toxicity data available, these levels are able to cause severe diseases. Several pathologies have been related with the exposure of humans and animals, namely aquatic organisms, to the aforementioned pesticides: disruption of the endocrine system (e.g. Hayes *et al*. 2011), several types of cancer (e.g. Ruder and Yin 2011), as well as liver pathologies and modifications in the nervous, immune, and cardiovascular system (e.g. Vidyasagar *et al*. 2004, ATSDR 2003) (Table 1.1). Due to their occurrence levels, toxicity, persistence, and bioaccumulation potential, these pesticides were considered priority by the European Water Framework Directive (Decision 2455/2001/EC). This classification constituted an alert for the need to reduce and monitor their presence in drinking water sources and was withdrawn by the amending Directive 2013/39/EU, probably because of their banning or introduction of application restrictions. Even though atrazine, alachlor, and chlorfenvinphos were banned in the European Union before 2007 (Decisions 2004/248/EC and 2006/966/EC, Regulation 2076/2002) and pentachlorophenol and diuron face severe restrictions in terms of application for plant protection (Decisions 2004/248/EC, 2006/966/EC, Regulation 2076/2002), they were still detected in European countries such as Spain and Greece in 2010-2012 at levels up to 10 μg L^{-1} (Postigo *et al*. 2010, Vryzas *et al*. 2012, Cabeza *et al*. 2012).

Furthermore, these compounds are still extensively produced and applied in other countries. As an example, atrazine remains one of the most widely used herbicides in the United States with application of approximately 76.4 million pounds of active ingredient each year (US EPA 2012). Even though PCP is considered priority by the

United States Environmental Protection Agency (US EPA) and regulatory actions were introduced in 1984 to restrict certain non wood-preservation applications (US EPA 2008), its production is still noteworthy in USA (Van der Zande 2010). Maximum contaminant levels in drinking water are established in the US National Primary Drinking Water Regulations for atrazine, alachlor, and pentachlorophenol (3, 2, and 1 μg L^{-1}, respectively). Generally less restrictive guideline values are implemented in Australia (NHMRC and NRMMC 2011) and Canada (Health Canada 2012) although a similar maximum acceptable concentration is set for atrazine in Canada (5 μg L^{-1}).

There is often a gap between legislation and research since banned micropollutants are still present in drinking water sources and despite their proven hazardous effects they are not legislated yet in countries where their occurrences have been reported as maximum.

1.2.2 Endocrine disrupting compounds

Endocrine disrupting compounds are natural or synthetic compounds with the ability to interfere with hormone biosynthesis, metabolism, secretion, binding action, and transport, resulting in a deviation from normal homeostatic control or reproduction, even at very low exposure levels. Endocrine disruptors include plant products such as phytoestrogens, pesticides, plasticisers, phenols, and hormones (Diamanti-Kandarakis *et al*. 2009).

Hormones constitute the most important group of EDCs due to their extremely high estrogenic activity. A woman is able to excrete daily approximately 64 μg of estriol as well as 3-20 μg and 0.5-5 μg of estrone and 17β-estradiol, respectively, as revised by Birkett (2003). Remarkable quantities of progesterone are also excreted by women, particularly during pregnancy, and 17α-ethinylestradiol is one of the most relevant ingredient compounds of oral contraceptive pills. Since they are not fully assimilated by humans, hormones are continuously released to the environment mostly via domestic wastewater effluents either in the original form or partially metabolised. Conventional wastewater treatment processes are often not completely effective to remove these anthropogenic compounds from the effluent. Thus, non eliminated compounds are directly released into the environment (Kolpin *et al*. 2002, Hecker and Hollert 2011). Hormones such as 17β-estradiol, 17α-ethinylestradiol, estrone, estriol, and progesterone became ubiquitous in the environment and are the major contributors of the estrogenic activity observed in water sources (Birkett 2003).

Based on their water solubility and hydrophilicity, these hormones are also expected to partition to some degree in the aquatic environment (Table 1.2). These hormones present very different structures and physico-chemical properties comparatively with the aforementioned pesticides and are therefore expected to behave differently during drinking water treatment.

These hormones have been reported to occur in surface waters and groundwaters in USA (Velicu and Suri 2009), Europe (Aydin and Talinli 2013, Jardim *et al*. 2012), and particularly China (Rao *et al*. 2013, Zhou *et al*. 2011), at concentrations up to 180 ng L^{-1} (Table 1.2). Despite the lower occurrence levels of these hormones comparatively with the pesticides aforementioned, hormones are able to induce severe endocrinologic disorders such as male feminisation (Table 1.2). Purdom *et al*. (1994) reported the production of vitellogenin (the precursor of egg yolk proteins expressed in females for embryos development) by male trout due to exposure to 17α-ethinylestradiol at doses as low as 0.1 ng L^{-1} during 10 days. Furthermore, a 7-year research in a canadian lake demonstrated that chronic exposure of fathead minnow (*Pimephales promelas*) to 5-6 ng L^{-1} of 17α-ethinylestradiol led to feminisation of males and near extinction of this specie (Kidd *et al*. 2007).

Table 1.2 *Characterisation of the hormones 17β-estradiol, 17α-ethinylestradiol, estrone, estriol, and progesterone in terms of their physico-chemical properties, occurrence levels in groundwater and surface water, and toxicity effects. The colours of the atoms in the molecular structures of the hormones have the following meaning: grey – carbon; white – hydrogen; red – oxygen.*

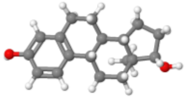
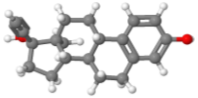
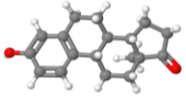
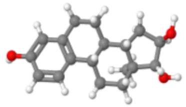
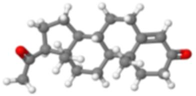
Compound* [CAS number]	**Description**	**Molecular formula**	**MW (Da)**	**W_s at 25 °C (mg L^{-1})**	**log K_{ow}**	**pK_a**	**V_m ($cm^3 mol^{-1}$)**	**Occurrence levels (ng L^{-1})**	**Toxicity effects**
 17β-Estradiol [50-28-2]	Natural steroid hormone	$C_{18}H_{24}O_2$	272.4	3.6[1]	4.01[2]	10.4[2]	232.6[3]	0.09[4] – 134[5]	Feminisation of male species (vitellogenin production by male fish and chorionic proteins production within male or juvenile animals, impact on gonadal development, reductions in sperm count and motility). Altered oogenesis in females and early-stage eggs, ovarian and testicular hispathology[6-10]. Mammary tumors[11].
 17α-Ethinylestradiol [57-63-6]	Synthetic oral contraceptive	$C_{20}H_{24}O_2$	296.4	11.3[1]	3.67[2]	10.4[2]	244.5[3]	1.55[12] – 127.9[13]	Feminisation of male species (see details in the first line of the table). Near extinction of *Pimephales promelas* in canadian lakes[14].
 Estrone [53-16-7]	Natural steroid hormone	$C_{18}H_{22}O_2$	270.4	30.0[1]	3.13[2]	10.4[2]	232.1[3]	0.60[12] – 180[5]	Feminisation of male species (see details in the first line of the table). Abnormal embryogenesis[15].

***Table 1.2** Characterisation of the hormones 17β-estradiol, 17α-ethinylestradiol, estrone, estriol, and progesterone in terms of their physico-chemical properties, occurrence levels in groundwater and surface water, and toxicity effects. The colours of the atoms in the molecular structures of the hormones have the following meaning: white – hydrogen; grey – carbon; red – oxygen (continuation).*

Compound* [CAS number]	**Description**	**Molecular formula**	**MW (Da)**	**W_s at 25 °C (mg^{-1} L)**	**log K_{ow}**	**pK_a**	**V_m (cm^3 mol^{-1})**	**Occurrence levels (ng L^{-1})**	**Toxicity effects**
 Estriol [50-27-1]	Natural steroid hormone	$C_{18}H_{24}O_3$	288.4	441[1]	2.45[2]	10.4[2]	229.6[3]	0.33[4] – 94[5]	Feminisation of male species[10].
 Progesterone [57-83-0]	Natural steroid hormone	$C_{21}H_{30}O_2$	314.5	8.8[1]	3.87[2]	**	288.9[3]	0.07[16] - 11.81[4]	Incidence of postmenopausal cardiovascular diseases[17].

*molecular structures depicted were obtained from the Jmol software; **no dissociation; MW – molecular weight; W_s – water solubility; log K_{ow} – logarithm of octanol-water partition coefficient; pK_a –inverse of the logarithm of the acid dissociation constant; V_m – molar volume; **[1]** Meylan and Howard 1994 **[2]** Snyder *et al*. 2007 **[3]** Chemspider **[4]** Velicu and Suri 2009 **[5]** Zhou *et al*. 2011 **[6]** Harries *et al*. 1997 **[7]** Jobling *et al*. 1998 **[8]** Desbrow *et al*. 1998 **[9]** Vajda *et al*. 2008 **[10]** Vajda *et al*. 2011 **[11]** Turan *et al*. 2004 **[12]** Rao *et al*. 2013 **[13]** Sun *et al*. 2009 **[14]** Kidd *et al*. 2007 **[15]** Saito *et al*. 2012 **[16]** Chang *et al*. 2008 **[17]** Nickenig *et al*. 2000.

Recently, a directive amending Directives 2000/60/EC and 2008/105/EC has been submitted that recommends the inclusion of 17β-estradiol and 17α-ethinylestradiol in the list of priority substances (European Commission 2012). 17β-estradiol, 17α-ethinylestradiol, estrone, and estriol are included in the US EPA Contaminant Candidate List 3, which comprises compounds that are suspected to require regulation under the Safe Drinking Water Act (US EPA 2009b).

1.3 DRINKING WATER TREATMENT: AIM AND CHALLENGES

The main goal of drinking water suppliers is to provide water with high microbial and chemical quality. Conventional surface water treatment often includes coagulation, flocculation, sedimentation, filtration, and final disinfection (chlorination or chloramination). Disinfection is sometimes sufficient to obtain drinking water from groundwater. Although chloramination is also applied, chlorine is the disinfectant most widely used. Disinfection by-products (DBPs), that are produced during chlorination, have been detected in several distribution systems (e.g. Wlodyka-Bergier and Bergier 2011, Jeong *et al*. 2012) and have been related to different types of cancer (Costet *et al*. 2011, Rahman *et al*. 2010) and adverse reproductive outcomes (Grellier *et al*. 2010).

As revised by Brunkard *et al*. (2011), several outbreaks related with the presence of bacteria (e.g. *Legionella*, *Salmonella*, *Campylobacter*), viruses (norovirus, hepatitis A virus), and protozoa (*Giardia intestinalis*, *Cryptosporidium*) have been registered due to failures of sand filtration units, sedimentation contact units and chlorination during drinkng water treatment. In 1993, a serious outbreak was caused by *Cryptosporidium* oocysts that passed through the sand filtration system and were not properly inactivated by chlorination in one of the plants that supplyed the city of Milwaukee, USA. Up to 400,000 cases of serious illness and 100 deaths were registered (Gerba 2000a).

Several pesticides and hormones, namely atrazine (McInnis 2010, Rodriguez-Mozaz *et al*. 2004), pentachlorophenol (McInnis 2010), and estriol (Kuster *et al*. 2008) have also been detected in treated water from drinking water utilities applying conventional treatment processes. The monitoring of the presence of several compounds in Canadian municipal treated drinking water from 1986 to 2006 revealed the presence of several contaminants; atrazine was the most frequently detected pesticide in treated surface water, largely exceeding the legal limits (McInnis 2010).

The development of alternative technologies that enable the efficient removal of both microorganisms and chemicals is therefore required. Moreover, such technologies should allow water utilities to comply with current and future more stringent regulations.

The need to comply with more stringent US regulations regarding drinking water quality led to a shift towards the implementation of UV disinfection, as alternative or in combination with chlorine, due to its proven higher inactivation potential towards bacteria and protozoa relatively to chlorination (Shin *et al*. 2009, Le Goff *et al*. 2010). Another advantage of using UV radiation is the decrease of the chlorine doses needed to achieve final disinfection and the consequent reduction in the production of DBPs. Moreover, many organic compounds may be photochemically degraded by UV direct photolysis and advanced oxidation processes (e.g. Wu and Linden 2008, Shemer and Linden 2007a, Pereira *et al*. 2007a, Marotta *et al*. 2013, De la Cruz *et al*. 2013). UV radiation may, thus, be suitable to considerably improve both microbial and chemical quality of drinking water.

Good microbial and chemical quality of the water is also likely to be achieved by pressure-driven-membrane processes, as alternative to commonly rapid sand filtration, that will act as an effective barrier to organic compounds (e.g. Yangali-Quintanilla *et al*. 2009, Verliefde *et al*. 2009, Salvaterra *et al*. 2011) and natural organic matter (NOM) (Salvaterra *et al*. 2011) as well by constituting an extra barrier for bacteria and viruses (Patterson *et al*. 2012).

1.4 UV BASED PROCESSES

1.4.1 UV direct photolysis

UV direct photolysis is a process that leads to the degradation of organic compounds through the application of radiation at the ultraviolet range (200-400 nm). Molecules in its ground state can absorb a quantum of light energy or photon and transit to a higher-energy state. Such molecules are therefore much more reactive and can undergo different reactions than more stable molecules, following different reaction pathways (Kopecký 1992). These reactions lead to the degradation of molecules that ultimately result in their mineralisation, with the formation of carbon dioxide, water, and inorganic ions.

A wide range of UV lamps may be applied to degrade organic compounds. Nevertheless, a lamp that may simultaneously achieve good microbial inactivation and micropollutants degradation is ideal. Low pressure (LP) and medium pressure (MP) UV mercury lamps are conventional UV sources applied for water disinfection due to their germicidal effect. MP lamps emit radiation at 200 – 500 nm while LP lamps emit predominantly radiation at 254 nm. Although the use of both LP and MP lamps is already well implemented in some drinking water utilities for disinfection, by-product formation and energy demand as well as operating costs are typically lower for LP lamps (IJpelaar *et al*. 2007). Even though UV fluences typically applied for disinfection vary between 40 and 200 mJ cm^{-2} (Wu and Linden 2008), to achieve degradation of micropollutants higher UV fluences need to be used. Despite its high efficiency for disinfection the use of UV radiation for the degradation of organic compounds should be further tested and optimised.

LP lamps have demonstrated effectiveness towards several micropollutants such as the pharmaceuticals clofibric acid, iohexol (Pereira *et al*. 2007b), phenazone, and phenytoin (Yuan *et al*. 2009) or the PAHs anthracene and benzo(a)pyrene (Sanches *et al*. 2011a). Nevertheless, several compounds do not have the capacity to absorb photons at 254 nm. As an example, only 6% of dibenzothiophene and dibenzofuran as well as 15% of fluorine spiked in phosphate buffer solutions were removed by a LP lamp at a UV fluence of 1000 mJ cm^{-2} (Shemer and Linden 2007b). Photolysis of carbamazepine by a LP lamp above 5% was also not observed in another study, even when a UV fluence of 1700 mJ cm^{-2} was applied (Pereira *et al*. 2007b).

1.4.2 Advanced oxidation processes

Advanced oxidation processes combine UV radiation with oxidants or semi-conductors (heterogeneous photocatalysis) and rely on the formation of highly reactive, unselective, and short-lived hydroxyl radicals ($^{\bullet}OH$) (Schwarzenbach *et al*. 1993). These radicals initiate sequential reactions that result in partial or total degradation of organic micropollutants. For some compounds, chemical oxidation processes involved in AOPs have been reported to enhance degradation rates obtained by direct photolysis (Pereira *et al*. 2007b, Pereira *et al*. 2012, Rosenfeldt *et al*. 2007) and/or improve their mineralisation levels (De la Cruz *et al*. 2013).

Hydrogen peroxide (H_2O_2) and ozone have become the most popular oxidants while the most common semiconductors are zinc oxide, cadmium sulphide, and titanium dioxide (TiO_2) (Konstantinou *et al*. 2001).

1.4.2.1 UV combined with hydrogen peroxide

During UV/H_2O_2 oxidation, degradation of micropollutants takes place through the reaction of organic micropollutants with hydroxyl radicals that are generated by the reaction between H_2O_2 and UV photons with certain radiant energy ($h\nu$). This mechanism is described in general by the following equations:

$$H_2O_2 + hv \rightarrow 2\,{}^{\bullet}OH \tag{1.1}$$

$${}^{\bullet}OH + micropollutant \rightarrow by - products \tag{1.2}$$

At very high concentrations, hydrogen peroxide also acts as an hydroxyl radical scavenger producing a much less reactive hydroperoxyl radical, ${}^{\bullet}HO_2$, leading to the production of water (H_2O) and oxygen (O_2) as illustrated by Equations 1.3 and 1.4 (Wu and Linden 2008).

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \tag{1.3}$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \tag{1.4}$$

LP/UV/H_2O_2 has been described for the degradation of several micropollutants. Removals of 90% were attained for estriol, octilphenol, and progesterone in a surface water employing a UV fluence of 1500 mJ cm^{-2} and 100 mg L^{-1} of H_2O_2 while less than 20% removal was achieved by direct photolysis for estriol and octilphenol (Pereira *et al*. 2012). In other studies, the degradation of the pesticides parathion (Wu and Linden 2008) and metaldehyde (Autin *et al*. 2012) in synthetic waters by this AOP was also noteworthy using LP and MP lamps. Hindered effects, attributed to the presence of H_2O_2, were, however, observed during the degradation of fluorene, dibenzofuran, and dibenzothiophene in a natural water (Shemer and Linden 2007a).

1.4.2.2 Titanium dioxide heterogeneous photocatalysis

Heterogeneous photocatalysis is a photoreaction process that is accelerated by the presence of a solid semi-conductor. Among the semiconductors applied, TiO_2 is the reference material in promoting a good level of disinfection, even towards *Cryptosporidium* (Sunnotel *et al*. 2010), as well as an efficient degradation and mineralisation of a multitude of organic compounds (e.g. Maldonado *et al*. 2007, Wang *et al*. 2009, Sousa *et al*. 2013).

The primary step in the photocatalytic process involves the generation of conduction band electrons (e^-) and valence band holes (h^+) through the irradiation/ activation of TiO_2 with energy greater than its band gap energy. The incidence of radiation induces the ejection of an electron of the valence band to the conduction band, producing a positively charged hole in the catalyst and generating an electron-hole pair:

$$TiO_2 + hv \rightarrow e^- + h^+ \tag{1.5}$$

Electron and hole pairs can recombine in the bulk catalyst or diffuse to the catalyst surface and react with adsorbed species, undergoing reductive and oxidative reactions. In the presence of water, hydroxyl radical formation occurs on the semiconductor surface due to the hole trapping by interfacial electron transfer. Photogenerated holes can oxidise organic compounds directly, while the electrons formed can react with the adsorbed molecular oxygen on the Ti(III)-surface, reducing it to superoxide radical anion, $[O_2]^{\bullet -}$ (Balasubramanian *et al*. 2004, Konstantinou *et al*. 2002). These reactions occur as follows:

$$O_2 + e^- \rightarrow [O_2]^{\bullet -} \tag{1.6}$$

$$[O_2]^{\bullet -} + H_2O \rightarrow HO_2 + OH^- \tag{1.7}$$

$$HO_2 + e^- \rightarrow [HO_2]^- \tag{1.8}$$

$$[OH_2]^- + H_2O \rightarrow H_2O_2 + OH^- \tag{1.9}$$

$$OH^- + h^+ \rightarrow {}^{\bullet}OH \tag{1.10}$$

Since OH radicals are generated on the semiconductor surface, photocatalysis is a surface-dependent process. Oxidation may also occur via other oxygen-containing radicals formed in reactions between the positive holes and hydroxyl groups or water adsorbed at the catalyst surface. Hydroxyl radical attack and hole oxidation have been shown to be the primary oxidants responsible for the heterogeneous TiO_2 photodecomposition of organic substrates (Balasubramanian *et al*. 2004, Konstantinou *et al*. 2002).

Anatase, rutile and brokite are the three polymorph TiO_2 phases that can be synthesised and applied as pure phases or as mixtures. Photocatalytic activity has been demonstrated for the three phases. Due to the difficulty of synthesising pure brookite (it is usually a minority phase along with rutile and/or anatase depending on experimental conditions), anatase and rutile are the TiO_2 polymorphs more commonly addressed (Addamo *et al*. 2006). Anatase and rutile present energy band gaps of 3.2 and 3.0 eV, respectively (Balasubramanian *et al*. 2004). Anatase is generally regarded as the most photochemically active phase of titania, presumably due to the combined effect of lower rates of recombination (related with its greater rate of hole trapping) and higher surface adsorptive capacity towards organic compounds. Mixed-phase titania exhibit higher photocatalytic activity than anatase or rutile alone due to three factors: (1) the smaller band gap of rutile extends the useful range of photoactivity into the visible region; (2) the stabilisation of charge separation by electron transfer from rutile to anatase slows recombination; (3) the small size of the rutile crystallites facilitates this transfer, generating catalytic hot spots at the rutile/anatase interface (Hurum *et al*. 2003). Different commercial formulations of TiO_2 are available. The photoactivity of Degussa® P25 TiO_2 was found to be higher than that of Hombikat UV 100 TiO_2 for the treatment of alkylbenzene sulfonate (Mehrvar and Venhuis 2005). Wong and Chu (2003) also reported an almost duplication of alachlor degradation using Degussa® P25 comparatively to anatase TiO_2 from BDH under 300 nm irradiation due to the larger surface area available in Degussa® P25. Degussa® P25, consisting of 70% anatase and 30% rutile with an average particle size of 20-30 nm, and a BET surface area of 50 ± 15 m^2 g^{-1} is therefore the most widely used photocatalyst (Alhakimi *et al*. 2003).

It has been demonstrated that the pesticides and hormones selected for the study described in this thesis as well as other organic compounds can be treated by heterogeneous photocatalysis. Efficient degradations using 200 mg L^{-1} of suspended Degussa® P25 were attained in a solar pilot plant: atrazine completely disappeared in less than 1hour while complete mineralisation of alachlor and chlorfenvinphos was attained within 240 and 320 min, respectively (Maldonado *et al*. 2007). Photomineralisation of diuron in less than 45 min was also achieved using Degussa® P25 TiO_2 when an UV lamp with a maximum of light emission at 365 nm was employed although no degradation was attained by direct photolysis (El Madani *et al*. 2006). 81% of propanolol was degraded after 240 min of irradiation in a solar plant while only 30% mineralisation was reached using 0.4 g L^{-1} of TiO_2 (De la Cruz *et al*. 2013). Total organic carbon (TOC) and bisphenol A were also highly removed (removals of 95 and 97%, respectively) after 6 hours of LP/UV irradiation using immobilised TiO_2 (Wang *et al*. 2009). LP/UV radiation is much more effective to achieve disinfection and degradation of some chemical compounds than solar.

Few studies have been conducted to date that address the potential of LP/UV lamps towards TiO_2 photocatalysis of the selected pesticides and hormones. Furthermore, results are often provided as function of the time needed to achieve certain degradation instead of UV fluence, which makes the comparison between data obtained using different experimental setups impossible (Bolton and Linden 2003).

The use of TiO_2 is already well-established for a number of technological applications: indoor and outdoor self-cleaning materials (tiles, lamps, windows, and spray coatings) and air cleaners, self-sterilising hospital uniforms, and cancer therapy (Fujishima *et al*. 2000). It presents several advantages relatively to other semiconductors related to its chemical and biological inertness over a wide range of pH, photostability, absence of toxicity, recyclability, and low cost (Doll and Frimmel 2005). Another advantage of using this catalyst is the possibility of its application either as powder dispersion or immobilised. Furthermore, several light sources including low pressure UV lamps may be used since TiO_2 is catalytically active at wavelengths lower than 380 nm (Wong and Chu 2003).

1.4.3 Impact of water composition upon UV photolysis

Natural organic matter may accelerate photodegration through the stimulation of the production of hydroxyl radicals. Its presence may also hinder photodegradation, particularly the degradation of more hydrophobic compounds, due to the competition between NOM and organic compounds for radiation absorption (Sanches *et al*. 2011a, Xia *et al*. 2009, Fasnacht and Blough 2002).

Chloride ions were found to accelerate the photodegradation rates of phenicols using UV–visible radiation due to the formation of singlet oxygen (Ge *et al*. 2009). The presence of nitrate has been also reported to increase photodegradation rates of compounds such as phenanthrene (Jacobs *et al*. 2008) or atrazine (Sharpless *et al*. 2003) due to its ability to form hydroxyl radicals. These radicals may also react with scavengers such as bicarbonate, carbonate, and dissolved organic carbon (Buxton *et al*. 1988, Larson and Zepp 1988), reducing photolysis efficiency. Nevertheless, the impact of these components depends on the overall water composition (e.g. Ge *et al*. 2009, Jacobs *et al*. 2008, Ge *et al*. 2010) as well the water components ability to absorb radiation at a certain wavelength range (Zepp *et al*. 1987).

UV photolysis studies have been mainly carried out in pure or synthetic waters. Nevertheless, the efficiency of these processes may be accurately predicted only if representative natural water matrices are addressed, creating conditions as close as possible to those found in water utilities. Further studies using representative natural waters are therefore needed.

1.4.4 Current use and challenges

UV disinfection became a well established technology in the last decades in several USA water treatment plants that supply water to very populated cities such as Seattle, Washington, and New York. UV disinfection has gained acceptance worldwide and it is also already implemented in some European countries (US EPA 2006). In Portugal, UV disinfection has been applied in combination with chlorination by Empresa Portuguesa das Águas Livres (EPAL) to treat spring water from Olhos de Água (EPAL 2010).

A study published some years ago by the (US EPA 1996) estimated an average overall disinfection cost of 0.39-1.09 US$ m^{-3} during water treatment, based on data provided by three disinfection manufacturers for a UV dose of 40 mWs cm^{-2}. More recent data regarding UV costs are not publicly available. Even so, advances in the UV technology are providing lower cost, more efficient lamps, as well as more reliable equipment which has contributed to its widespread application (Gerba 2000b).

While widely used for disinfection, the use of UV for degradation of organic contaminants is still not common practice. Nevertheless, a UV/H_2O_2 oxidation process has been in operation since 2004 in a large drinking water treatment plant in Andijk, The Netherlands, for both primary disinfection and organic contaminants control. An UV fluence of 540 mJ cm^{-2} and a H_2O_2 concentration of 6 mg L^{-1} are applied in this utility where removals of atrazine around 80% are achieved (Baeza 2008). Large scale application of suspended TiO_2 photocatalytic treatment is constrained by technical challenges mainly related with the effective recovery of the catalyst particles in a continuous process. The release of nanoparticles to the environment, which is presently a topic of discussion for implementation of legislation, must be avoided since toxicological effects have recently been associated with their presence in the environment (Wang *et al.* 2013, Battin *et al.* 2009). A subsequent separation step is therefore needed such as filtration, centrifugation or coagulation/flocculation (Van der Bruggen *et al.* 2008).

Even though UV direct and indirect photolysis are extremely promising treatment processes, further work is needed to define the best operating conditions to achieve removal of different contaminants due to the higher UV fluences needed, the impact of the matrix composition in the process performance, and the possible formation of by-products.

The formation of by-products, that may be even more toxic than the parent compounds, has been previously observed during the photodegradation of carbamazepine (Donner *et al*. 2013) and sulfamethoxazole (Trovo *et al*. 2009). The ecotoxicity of transformation products is of major importance when assessing the suitability of water treatment options. Although UV by-products formed during the photolysis of several micropollutants have been identified, there is currently lack of information regarding their toxicity (Donner *et al*. 2013, Escher and Fenner 2011).

Several toxicity bioassays employing model organisms such as *Vibrio fischeri*, *Salmonella typhimorium* or *Daphnia magna* have been applied (Escher and Fenner 2011). Although only applicable to determine the toxicity related with endocrine disrupting compounds, a simpler and reliable bioassay - yeast estrogen screen (YES) assay - has been developed by Routledge and Sumpter (1996). This methodology has been successfully employed to evaluate the estrogenicity associated with many compounds such as estrogens, nonylphenol (Stanford and Weinberg 2010), bisphenol A, hydrocortisone, dieldrin, atrazine or methoxychlor (Bistan *et al*. 2012) when present in wastewater streams.

YES relies on the use of a human estrogen receptor (hER) transfected *Saccharomyces cerevisiae* that was developed to identify compounds that can interact with the human estrogen receptor (Routledge and Sumpter 1996). In this assay, the human estrogen receptor gene, which is integrated into the main genome, is expressed in a form capable of binding to estrogen response elements (ERE) within a hybrid promoter on an expression plasmid containing the reporter gene *Lac-Z*. The activation of hER, by binding of the estrogenic compound, leads to the expression of the reporter gene *Lac-Z that encodes* the enzyme β-galactosidase. When this enzyme is secreted into the medium, it is able to metabolise the chromogenic substrate chlorophenol red-β-D-galactopyranoside (CPRG), which is followed by a change of colour that is measurable by spectrophotometry (Routledge and Sumpter 1996).

1.5 PRESSURE-DRIVEN MEMBRANE PROCESSES

Membrane filtration has gained particular attention for the removal of a broad spectrum of contaminants from water and wastewater since the 1990's despite the demonstration of their potential since early 1960s. The growing interest in the use of membrane technology for water and wastewater treatment can be explained by the increasing demand for high quality water, the introduction of more stringent regulations, and the increasing interest in wastewater reuse (Van der Bruggen *et al.* 2008). The extended application of membrane technology was also motivated by the improvement of membrane materials and the development of membranes with enhanced chemical, thermal and mechanical properties or better permeability and selectivity, as well as the decrease of operation costs, namely membrane price due to enhanced use. Furthermore, membrane technologies present several advantages over conventional processes: do not involve the addition of chemical additives, usually present reduced plant footprint, and may be easily upscaled and retrofit to an existing facility or combined with other treatment processes (US EPA 2005, Fane *et al.* 2011).

Pressure-driven membrane processes are classified as reverse osmosis (RO), nanofiltration, ultrafiltration (UF), and microfiltration (MF), depending on the molecular weight cut-off (MWCO) of the respective membranes as well as transmembrane pressure. RO is commonly used for desalination of sea and brackish waters due to its ability to remove species with diameter as small as 0.1 nm like hydrated ions and molecules with low molecular weight. Nanofiltration is an intermeadiate process between RO and UF that is able to reject molecules with a size in the order of one nanometer. Ultrafiltration is characterised by the removal of molecules that have a molecular weight higher than approximately $2x10^3$ Da. Microfiltration membranes have the highest MWCO, allowing the removal of macromolecules with size above 0.1 μm (Bergman 2007, Eriksson 1988).

1.5.1 Nanofiltration

Nanofiltration is commonly applied for water softening operations due to its ability to remove multivalent ions such as magnesium and calcium. Van der Bruggen *et al*. (2001) reported extremely high rejections of hardness, up to 95%, using the NF membranes NF70, NF45, UTC-20, and UTC-60. In another study, rejections higher than 90% were attained for sulphate, calcium, and magnesium using the membrane UTC-20 (Schaep *et al*. 1998). NF membranes are also able to remove a wide range of microorganisms such as bacteria and viruses (e.g. Patterson *et al*. 2012). Very high removals from pure water were also obtained for the pesticides atrazine (97.5%), simazine (96.7%), malathion (99.64%), and chlorpyrifos (>99.95%), using a NTR-729HF nanofiltration membrane (Kiso *et al*. 2000). Likewise, several pharmaceuticals such as naproxen, ibuprofen, and carbamazepine were very efficiently removed at levels higher than 98% by a NF-90 membrane (Yangali-Quintanilla *et al*. 2009). Removals from surface water as high as 94%, using a NF-90 membrane, have been reported for NOM, a precursor of DBPs (Salvaterra *et al*. 2011). Removals of NOM between 72 and 94% have been also attained using synthetic waters with different ionic compositions and different thin film composite membranes (Schäfer *et al*. 2004). Nanofiltration is also suitable for the removal of low molecular weight organic compounds, as low as 200 Da, and is therefore expected to remove the pesticides and hormones presented in Tables 1.1 and 1.2.

Although the removal of these chemicals and microorganisms may also be achieved by reverse osmosis, the more compact structure with lower “free volume” of RO membranes requires the application of higher pressures to ensure high permeability. Furthermore, addition of essential salts of drinking water such as sodium and chloride is necessary after RO treatment to ensure ionic water balance since RO is able to demineralise water. Conversely, NF membranes may be efficiently operated at lower pressures, leading to energy cost savings (Bergman 2007) while ensuring ionic water balance without downstream salt addition due to its incomplete salt rejection. Therefore, nanofiltration is preferred whenever freshwater sources (groundwater or surface water) are available.

1.5.1.1 Membrane types and module configurations

A broad spectrum of NF membranes with different characteristics is available in the market and has been assessed for drinking water treatment applications. Polymeric NF membranes are generally manufactured from cellulose acetate or polyamide materials and their derivatives (US EPA 2005). Ceramic membranes are often composed of a variety of materials that include titania, alumina, silica, and zirconia. Ceramic membranes have relatively uniform pore structures, are less prone to fouling, due to their generally higher hidrophilicity, and have superior chemical, thermal, and mechanical stability (Kim and Van der Bruggen 2010, Van der Bruggen *et al*. 2003). Despite the advantages of ceramic over polymeric membranes, their commercialisation is yet very restricted because they are still under development. The membrane market is therefore dominated by polymeric membranes, which are significantly less expensive.

Even though several membrane configurations are available, the most common in water treatment applications are hollow-fiber and spiral-wound modules. Spiral-wound modules are often assembled using NF/RO semipermeable polymeric membranes, present moderate fouling tendency, and have low cost (Thorsen and Fløgstad 2006).

1.5.1.2 Selection of Desal 5DK membrane

The selection of a suitable membrane to carry out the studies described in the present thesis was based on the evaluation of the membranes NF-90, NF-270, and Desal 5DK in terms of their hydraulic permeability and ability to remove uncharged organic solutes. Among these three membranes, Desal 5DK was found to allow attaining an adequate balance between hydraulic permeability and rejection of uncharged solutes such as glycerol, glucose and saccharose and was therefore selected. A molecular weight cut-off of approximately 210 Da and a pore radius of 0.59 ± 0.01 nm were estimated for Desal 5DK during this PhD project by applying an hydrodynamic model described by Bowen and Welfoot (2002).

Desal 5DK is a negatively charged thin film composite membrane, characterised by a very dense and active layer of cross-linked aromatic polyamide, formed on a support layer manufactured from polysulphone. The wide applicability of thin film composite membranes relies on their high salt retention capacity and achievement of high fluxes at low operating pressures (Ozaki *et al*. 2002).

1.5.2 Membrane, solute and water-matrix interactions

Special attention has been devoted in the last decade on how interactions taking place between specific solutes/contaminants, membranes, and other water components impact the rejection of solutes with different geometry and physico-chemical properties. The comprehension of such interactions is essential for the improvement and selection of suitable membranes as well as for the development of tools that enable the prediction of NF efficiency towards a broad spectrum of micropollutants.

Size exclusion is often regarded as the most important mechanism of rejection. Although higher rejections are usually expected by membranes that present lower MWCO, organic solutes with molecular weight higher than membrane MWCO may also permeate. The prediction of steric hindrance effects upon rejection using information related with molecular size is often more adequate than using molecular weight (Bellona *et al*. 2004, Van der Bruggen *et al*. 1999). Furthermore, molecular weight is a poor predictor when molecules are charged or present high hydrophobicity (Kiso *et al*. 2001).

Most membranes are negatively charged due to the presence of functional groups like sulphonic and carboxylic acids that are deprotonated at neutral pH (Bellona *et al*. 2004). Experiments addressing the removal of the pesticide mecoprop from bank filtrate of a surface water showed that its dissociated form was the most rejected, with increases between 10 and 90% among the five NF membranes addressed as pH increased from 3 to 7 (Berg *et al*. 1997). The increase in rejection was related with repulsive electrostatic interactions between the dissociated molecule and the charged membrane.

Salts present in water may “shield” the charge of the functional groups of organic compounds and reduce the negative zeta potential of membranes, resulting in minimisation of repulsive electrostatic interactions. A reduction by up to 15% in rejection has been previously reported when several NF and RO membranes were evaluated to remove estrone from synthetic waters enriched with calcium, bicarbonate, and sodium (Nghiem *et al*. 2002). Conversely, an improvement upon the rejection of the pesticides atrazine, desethylatrazine, simazine, cyanazine, isoproturon, and diuron by approximately 5% (in the presence of calcium chloride) and 10% (in the presence of calcium sulphate) was reported for a NF-200 membrane while differences in rejection were not noteworthy using a Desal 5DK membrane (Boussahel *et al*. 2002). In addition, the decrease observed in the rejection of bisphenol A beyond 50 mM of sodium chloride using Desal 5DK was attributed to the reduction of the molecular hydrodynamic radius due to a “salting-out” effect (Zhang *et al*. 2006a). The effect of salts is, thus, dependent of salt concentration and membrane type (Zhang *et al*. 2006a).

The impact of NOM on micropollutants removal is not straightforward. Retention tends to rise with the presence of NOM due to the potential formation of complexes between micropollutants and NOM (Salvaterra *et al*. 2011, Devitt *et al.* 1998) that are, thus, rejected by size exclusion mechanisms. Retention, however, has been also reported to remain unchanged in the presence of NOM (Zhang *et al*. 2006a). The enhancement of interactions between humic substances and triazines in the presence of calcium improved triazines rejection, highlighting the different impact of NOM upon rejection (Plakas and Karabelas 2009). The different nature of commercial humic and fulvic acids as well as the respective molecular weight and concentrations usually applied to address the effect of NOM may explain the discrepancies reported. Furthermore, humic and fulvic acids addressed are often not representative of NOM found in real water matrices (Devitt and Wiesner 1998).

The diffusion of the molecules across the membrane is often facilitated through polar interactions between molecules and membranes. Polar interactions with the charged membranes NF45, NF-70, UTC-20, and NTR-7450 were related with the lower removals of diuron and isoproturon from groundwater relatively to less polar atrazine and simazine. These interactions led to minimisation of repulsive electrostatic interactions between dissociated molecules and charged membranes (Van der Bruggen *et al*. 1998).

Adsorption is an important rejection mechanism, particularly for hydrophobic compounds, often characterised by values of log K_{ow} higher than two (Yangali-Quintanilla *et al*. 2009, Kimura *et al*. 2003). Rejection due to adsorption mechanisms

---

is therefore expected for the aforementioned pesticides and hormones (Tables 1.1 and 1.2). PAHs such as naphthalene, anthracene, and benzo(a)pyrene were found to extensively absorb on Desal 5DK membrane during dead-end experiments with adsorption percentages higher than 92% (Sanches *et al*. 2011b). Adsorption interactions were also found to be driven by hydrogen bonding between the oxygen of hydroxyl and carbonyl groups of estrone and NF/RO membranes in a study carried out with synthetic water (Schäfer *et al*. 2003). Adsorptive interactions were found to play a relevant role in the overall rejection of estrone (Nghiem *et al*. 2004) and bisphenol A (Zhang *et al*. 2006a) in the early stage of filtration.

Although rejection mechanisms have been thoroughly investigated, discussion is mainly based on experiments conducted with pure or synthetic waters that are not representative of natural waters. Data obtained in a previous study during dead-end experiments carried out with pure water and four different raw natural waters using Desal 5DK membrane showed that, although significant variation in the removal of atrazine (32-37%) was not observed, noteworthy differences were attained in the rejection of alachlor (17-90%) and pentachlorophenol (11-68%) in different water sources (Sanches *et al*. 2011b). Further investigation is therefore still needed to elucidate the specific effect of organic and inorganic species present in natural waters or their combined effects upon rejection of these compounds.

1.5.3 Current use and challenges

High capacity drinking water plants are already employing nanofiltration for several years in Florida, The Netherlands, Spain, England, and France (Thorsen and Fløgstad 2006). The Méry-sur-Oise plant (France) is operational since the 1990s for the production of potable water from the Oise river using NF technology for a production capacity of 140 000 m^3 day^{-1}. It exhibits an outstanding performance towards the removal of organic matter and pesticides (Cyna *et al*. 2002).

A total treatment cost of €0.214 m^{-3} was estimated for a NF plant with a production capacity of 100 000 m^3 day^{-1} treating water from Tagus river (Costa and de Pinho 2006). These costs are comparable with those related with conventional processes. The cost estimated for the production of drinking water from surface water (encompassing pre-disinfection, coagulation, flocculation, sedimentation, filtration, and final disinfection) in a utility placed in McAllen, Texas, with a capacity of 31 230 m^3 day^{-1} was $US0.62 m^{-3} in 2006 (Rogers 2008). Even though treatment costs vary according with the plant capacity and updated data is not publicly available, nanofiltration has effectively become economically feasible and competitive to produce high quality water.

A major disadvantage of pressure-driven membrane processes is the occurrence of fouling that may result from the accumulation of organic and inorganic molecules, colloids and biological solids at the membrane surface and pores, ultimately leading to flux decline (Elimelech *et al*. 1997, Herzberg and Elimelech 2007, Nghiem *et al*. 2008, Wang and Tang 2011). As a consequence of fouling, the yield of permeate decreases and higher pressures are needed to maintain the flow rate, resulting in higher energy consumption and operating costs. Furthermore, frequent cleaning considerably reduces membrane life span (Van der Bruggen *et al*. 2008).

The generation of a retentate stream that is more concentrated than the feed stream in terms of suspended and dissolved constituents, is another intrinsic constraint of pressure driven membrane processes. Treatment of the retentate might consist in further concentration followed by disposal (landfilled or incinerated) or encompass the removal of specific components with subsequent discharge in surface water or groundwater (Van der Bruggen *et al*. 2008). In a previous study, costs related with the disposal of retentate from surface water were estimated as 17% of total operating costs (Costa and de Pinho 2006). The reduction of this cost would be very advantageous for the worldwide implementation of membrane processes by water utilities.

1.6 INTEGRATION OF UV PHOTOLYSIS AND NANOFILTRATION: OVERVIEW OF RECENT DEVELOPMENTS

Growing interest in the combination of UV and membrane processes has been observed in the last decade due to their expected potential to overcome some of the drawbacks associated with the individual application of these processes (described in sections 1.4.4 and 1.5.3).

A study from Molinari *et al.* (2002) reported the comparison of different configurations combining TiO_2 photocatalysis with ultrafiltration and nanofiltration: irradiation of the membrane (catalyst deposited, in suspension or entrapped) and irradiation of the recirculation tank using suspended catalyst. This latter configuration was considered the most interesting for industrial applications essentially due to the higher exposed catalytic surface area of the suspended TiO_2 comparatively with the immobilised form. Other studies have confirmed the advantage of applying the suspended catalyst. Additional trichloroethylene degradation of 20% were observed by Cho and co-workers (2005) using suspended catalyst relatively to the immobilised form. However, the photocatalytic efficiency of immobilised TiO_2 depends on the catalyst load (You *et al*. 2012) as well as the distribution of the catalyst that is related with the immobilisation methodology applied (Madaeni *et al*. 2011).

Most of the research studies combining UV photocatalysis with NF, UF or MF for drinking water treatment have focused on the application of suspended TiO_2, where the photocatalytic process takes place before filtration (e.g. Molinari *et al*. 2008, Benotti *et al*. 2009, Le-Clech *et al*. 2006, Patsios *et al*. 2013). Even though disinfection is the final stage of drinking water treatment, the positioning of UV photolysis upstream the membrane process is based on the required retention of TiO_2 nanoparticles.

The overall removal efficiency of humic acids during a sequential treatment comprising UV-A TiO_2 photocalysis and a submerged UF membrane relatively to photocatalysis alone increased from 52% to 83% as a result of the synergistic effects of photocatalytic oxidation and membrane filtration. A slight improvement was also observed comparatively to the application of UF alone (Patsios *et al*. 2013).

Gemfibrozil and tamoxifen were previously successfully photodegradeded during the operation of a sequential treatment but poor or none retention was observed for these compounds and respective by-products using a NTR 7410 nanofiltration membrane (Molinari *et al*. 2008). The identification of membranes that are able to simultaneously remove specific micropollutants and the respective UV by-products, which may have significantly low molecular weight, is therefore needed.

Pre-treatment of NOM soutions by LP/UV/TiO_2 photocatalysis using a titanium dioxide concentration of 0.5 g L^{-1} completely eliminated fouling of UF and MF membranes caused by NOM. The effectiveness in membrane fouling control was related with changes in the molecular characteristics of NOM (molecular weight and specific UV absorbance) due to the preferential removal and transformation of large and hydrophobic NOM molecules (Huang *et al*. 2008). The transformation of humic/hydrophobic NOM fractions and polysaccharides into less sorbable organic acids were also identified as the cause of the significant lower flux decline observed during the nanofiltration of groundwater carried out after a LP/UV/H_2O_2 oxidation pre-treatment (Song *et al*. 2004).

Formation of TiO_2 aggregates and the respective precipitation, that may take place due to catalyst insolubility, constitute a limitation of operations applying suspended catalyst (Li *et al*. 2010). pH plays a key role in the dispersion of the catalyst in aqueous suspensions since it determines the size of the particles and the respective number of catalytic active sites. Excessive disaggregation of the catalyst is avoided by working at a pH range of 7 ± 3 (Molinari *et al*. 2008). Benotti and co-workers (2009) addressed the photocatalysis of several endocrine disrupting compounds using a pilot system in which the membrane was back-pulsed every 60 seconds to prevent catalyst build-up. TiO_2 was recycled and reused, allowing for long-term operation.

Stable immobilisation of TiO_2 on membrane surface has been explored as an alternative to obtain membranes with photocatalytic and improved anti-fouling properties (e.g. Ma *et al*. 2010, Zhang *et al*. 2006b). In this case, membranes are irradiated to promote TiO_2 photocatalysis. While a variety of membrane materials may be applied using suspended catalyst, there is a limitation in terms of the type of the membranes that may be applied using immobilised TiO_2. Polymeric membranes are highly susceptible to UV radiation and radical species generated (Chin *et al*. 2006). Furthermore, the decrease of membrane permeability and increased rejection of membranes obtained using dipping techniques to immobilise TiO_2 (Tarabara 2009) as well as its detachment during cleaning procedures of membranes obtained by sol-gel precipitation (Su *et al*. 2012) and grafting (e.g. Madaeni *et al*. 2011) have been reported. Stable immobilisation of TiO_2 nanoparticles is currently a challenge.

1.7 OBJECTIVES AND THESIS OUTLINE

The main objective of the work developed and presented in this thesis is to evaluate a multi-barrier approach that integrates UV direct photolysis or TiO_2 photocatalysis with nanofiltration for drinking water treatment (Figure 1.1).

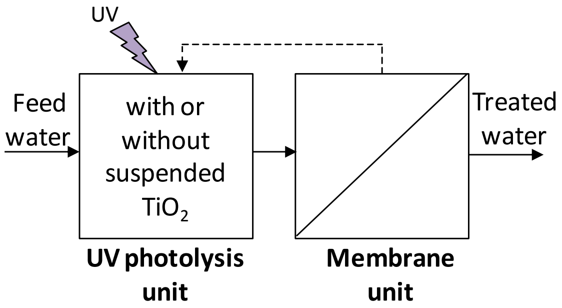


Figure 1.1 *Proposed configuration integrating UV direct photolysis or TiO_2 UV photocatalysis and nanofiltration.*

In this integrated treatment, the degradation of the selected organic micropollutants takes place by UV direct photolysis or TiO_2 photocatalysis, using suspended TiO_2 nanoparticles, at atmospheric pressure. A nanofiltration membrane unit is then subjected to applied pressure in the absence of UV radiation.

The evaluation of the integrated process is focused on its potential to remove the selected pesticides (atrazine, isoproturon, diuron, alachlor, pentachlorophenol, and chlorfenvinphos) and hormones (17β-estradiol, 17α-ethinylestradiol, estrone, estriol, and progesterone) as well as its ability to overcome the drawbacks associated with the individual application of UV and nanofiltration processes (Chapter 5). To achieve this goal, the potential application of the individual processes is firstly explored (Chapters 2, 3, and 4), focusing essentially on process optimisation as well as the

---

impact of specific natural water components and physico-chemical properties of the target compounds upon their removal efficiency.

The ultimate objective of this study is to provide a step forward towards the increasingly acceptance and implementation of UV and membrane processes while attempting to solve their main drawbacks, providing water producers with knowledge for their implementation.

This thesis is divided in 6 chapters. Chapter 1 consists of a revision of the state-of-the-art focusing on the occurrence of the target micropollutants in drinking water sources, the potential and benefits of applying UV photolysis and nanofiltration technologies over conventional drinking water treatment processes to remove micropollutants from water, as well as the challenges that these technologies currently face towards their implementation. Furthermore, the motivation of the conceptual and experimental approaches followed is provided throughout the text.

In Chapter 2, LP/UV direct photolysis, LP/UV/TiO_2 photocatalysis, and LP/UV/H_2O_2 oxidation of the selected pesticides is described. Laboratory grade water, surface water, and groundwater were selected to address the impact of water composition upon photodegradation efficiency and kinetics. Optimisation of the process was carried out by defining the main kinetic parameters that influence the photolysis of organic compounds - quantum yield and decadic molar absorption coefficient and the optimum concentration of TiO_2 for the photocatalytic process. A model was applied to provide other authors and drinking water producers with data that allows them to select the conditions that ensure an efficient degradation of the selected micropollutants.

Chapter 3 presents the potential of nanofiltration to remove the target micropollutants from ultrafiltered groundwater and surface water using a Desal 5DK membrane. The main mechanisms governing the rejection of the selected pesticides and hormones are discussed based on the impact of specific organic and inorganic components of natural waters as well as specific physico-chemical properties of target micropollutants. The role of adsorption upon the rejection of the selected micropollutants under extended adsorption conditions is also addressed by conducting membrane pre-adsorption experiments under static and dynamic conditions.

A comprehension of the factors affecting the rejection of the selected micropollutants from natural water matrices reported in Chapter 3 was not fully attained. Non-mechanistic models are useful tools to correlate large sets of data and unravel relationships between several variables. Chapter 4 describes the development of multivariate statistically-based models to assess which specific physico-chemical properties of the target micropollutants or operating related conditions are the most relevant to describe their rejection/adsorption during nanofiltration. The models developed allowed a better understanding of the mechanisms affecting the removal of the target compounds by nanofiltration.

The assembling and evaluation of the proposed combined treatment is described in Chapter 5. The efficiency of the individual processes and integrated treatment to remove the target micropollutants from surface water collected after the sedimentation process and the ability to produce high-quality drinking water is depicted. Emphasis is given to the potential of the integrated treatment to overcome the drawbacks related with the individual technologies through the monitoring of the concentration of the target compounds in the retentate, the identification of UV photolysis by-products, and flux decline. The toxicity of the treated water in terms of endocrine disrupting activity through the YES assay is also presented to further illustrate the quality of the water produced.

Chapter 6 summarises the main results obtained in the studies presented in this thesis and provides a discussion integrating the results obtained in the different chapters. Future developments and perspectives towards the implementation of the technologies evaluated for drinking water treatment are also described. Particular emphasis is given to the proposal of future work in view of the development of a new integrated configuration.

REFERENCES

Addamo M, Bellardita M, Di Paola A, Palmisano L (2006) Preparation and photoactivity of nanostructured anatase, rutile and brookite TiO_2 thin films. *Chem Commun* 47: 4943-4945.

Alhakimi G, Gebril S, Studnicki LH (2003) Comparative photocatalytic degradation using natural and artificial UV-light of 4-chlorophenol as a representative compound in refinery wastewater. *J Photoch Photobiol A* 157: 103-109.

Ardrey RE, Liquid chromatography - mass spectrometry: An introduction. John Wiley & Sons, England (2003).

ATSDR - US Agency for Toxic Substances and Disease Registry (2003) Toxicological profile for atrazine. Available online: http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=338&tid=59.

Autin O, Hart J, Jarvis P, MacAdam J, Parsons SA, Jefferson B (2012) Comparison of UV/H_2O_2 and UV/TiO_2 for the degradation of metaldehyde: Kinetics and the impact of background organics. *Water Res* 46: 5655-5662.

Aydin E, Talinli I (2013) Analysis, occurrence and fate of commonly used pharmaceuticals and hormones in the Buyukcekmece Watershed, Turkey. *Chemosphere* 90: 2004-2012.

Baeza A, Removal of pharmaceutical and endocrine disrupting chemicals by sequential photochemical and biological oxidation processes. ProQuest, Ann Arbor, USA (2008).

Balasubramanian G, Dionysiou DD, Suidan MT, Baudin I, Audin B, Laine JM (2004) Evaluating the activities of immobilised TiO_2 powder films for the photocatalytic degradation of organic contaminants in water. *Appl Catal B-Environ* 47: 73-84.

Battin TJ, Kammer FVD, Weilhartner A, Ottofuelling S, Hofmann T (2009) Nanostructures TiO_2: Transport behaviour and effects on aquatic microbial communities under environmental conditions. *Environ Sci Tecnol* 43: 8098-8104.

Bellona C, Drewes JE, Xu P, Amy G (2004) Factors affecting the rejection of organic solutes during NF/RO treatment - A literature review. *Water Res* 38: 2795-2809.

Benotti MJ, Stanford BD, Wert EC, Snyder SA (2009) Evaluation of a photocatalytic reactor membrane pilot system for the removal of pharmaceuticals and endocrine disrupting compounds from water. *Water Res* 43: 1513-1522.

Berg P, Hagmeyer G, Gimbel R (1997) Removal of pesticides and other micropollutants by nanofiltration. *Desalination* 113: 205-208.

Bergman R, Reverse osmosis and nanofiltration (2^{nd} ed.). American Water Works Association, Denver, CO (2007).

Birkett J, Sources of endocrine disrupters, in: Birkett J and Lester, JN (Eds.), Endocrine disrupters in wastewater and sludge treatment processes. CRC Press LLC, London, pp. 35-58 (2003).

Bistan M, Podgorelec M, Logar RM, Tisler T (2012) Yeast estrogen screen assay as a tool for detecting estrogenic activity in water bodies. *Food Technol Biotech* 50: 427-433.

Bolton J, Linden K (2003) Standardisation of methods for fluence (UV dose) determination in bench-scale UV experiments. *J Environ Eng-ASCE* 129: 209-215.

Boussahel R, Montiel A, Baudu M (2002) Effects of organic and inorganic matter on pesticide rejection by nanofiltration. *Desalination* 145: 109-114.

Bowen WR, Welfoot JS (2002) Modelling the performance of membrane nanofiltration - critical assessment and model development. *Chem Eng Sci* 57: 1121-1137.

Brunkard JM, Ailes E, Roberts VA, Hill V, Hilborn ED, Craun GF, Rajasingham A, Kahler A, Garrison L, Hicks L, Carpenter J, Wade TJ, Beach MJ, Yoder Msw JS, (2011) Surveillance for waterborne disease outbreaks associated with drinking water - United States, 2007-2008. Morbidity and mortality weekly report. *Surveillance summaries* 60: 38-68.

Buxton GV, Greenstock CL, Helman WP, Ross AB (1988) Critial review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals (OH/O^-) in aqueous-solution. *J Phys Chem Ref Data* 17: 513-886.

Cabeza Y, Candela L, Ronen D, Teijon G (2012) Monitoring the occurrence of emerging contaminants in treated wastewater and groundwater between 2008 and 2010. The Baix Llobregat (Barcelona, Spain). *J Hazard Mater* 239: 32-39.

Cessna AJ, Grover R (1978) Spectrophotometric determination of dissociation-constants of selected acidic herbicides. *J Agr Food Chem* 26: 289-292.

Chang H, Wu S, Hu J, Asami M, Kunikane S (2008) Trace analysis of androgens and progestogens in environmental waters by ultra-performance liquid chromatography-electrospray tandem mass spectrometry. *J* Chromatogr A 1195: 44-51.

ChemSpider: The free chemical database. Available online http://www.chemspider.com/. Last accessed: December 2012.

Chin SS, Chiang K, Fane AG (2006) The stability of polymeric membranes in a TiO_2 photocatalysis process. *J Membrane Sci* 275: 202-211.

Cho IH, Park JH, Kim YG (2005) Oxidative degradation and toxicity reduction of trichloroethylene (TCE) in water using TiO_2/solar light: Comparative study of TiO_2 slurry and immobilised systems. *J Environ Sci Heal A* 40: 1033-1044.

Comerton AM, Andrews RC, Bagley DM, Yang P (2007) Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds. *J Membrane Sci* 303: 267-277.

Costa AR, de Pinho MN (2006) Performance and cost estimation of nanofiltration for surface water treatment in drinking water production. *Desalination* 196: 55-65.

Costet N, Villanueva CM, Jaakkola JJK, Kogevinas M, Cantor KP, King WD, Lynch CF, Nieuwenhuijsen MJ, Cordier S (2011) Water disinfection by-products and bladder cancer: Is there a European specificity? A pooled and meta-analysis of European case-control studies. *Occup Environ Med* 68: 379-385.

Cyna B, Chagneau G, Bablon G, Tanghe N (2002) Two years of nanofiltration at the Mery-sur-Oise plant, France. *Desalination* 147: 69-75.

Decision 2004/248/EC of 10 March 2004 concerning the non-inclusion of atrazine in Annex I to Council Directive 91/414/EEC and the withdrawal of authorisations for plant protection products containing this active substance. Official Journal of European Union, L78/53 (2004).

Decision 2006/966/EC of 18 December 2006 concerning the non-inclusion of alachlor in Annex I to Council Directive 91/414/EEC and the withdrawal of authorisations for plant protection products containing this active substance. Official Journal of the European Union, L 397/28 (2006).

Decision 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. Official Journal of the European Communities, L 331/1 (2001).

De la Cruz N, Dantas RF, Giménez J, Esplugas S (2013) Photolysis and TiO_2 photocatalysis of the pharmaceutical propranolol: Solar and artificial light. *Appl Catal B-Environ* 130: 249-256.

Desbrow C, Routledge EJ, Brighty GC, Sumpter JP, Waldock M (1998) Identification of estrogenic chemicals in STW effluent. 1. Chemical fractionation and in vitro biological screening. Environ *Sci Technol* 32: 1549-1558.

Devitt EC, Ducellier F, Cote P, Wiesner MR (1998) Effects of natural organic matter and the raw water matrix on the rejection of atrazine by pressure-driven membranes. *Water Res* 32: 2563-2568.

Devitt EC, Wiesner MR (1998) Dialysis investigations of atrazine-organic matter interactions and the role of a divalent metal. *Environ Sci Technol* 32: 232-237.

Diamanti-Kandarakis E, Bourguignon J-P, Giudice LC, Hauser R, Prins GS, Soto AM, Zoeller RT, Gore AC (2009) Endocrine-disrupting chemicals: An endocrine society scientific statement. *Endocr Rev* 30: 293-342.

Directive 2013/39/EU of the European Parliament and of the council of 19 August 2013 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, L226/1 (2013).

Doll TE, Frimmel FH (2005) Removal of selected persistent organic pollutants by heterogeneous photocatalysis in water. *Catal Today* 101: 195-202.

Donner E, Kosjek T, Qualmann S, Kusk KO, Heath E, Revitt DM, Ledin A, Andersen HR (2013) Ecotoxicity of carbamazepine and its UV photolysis transformation products. *Sci Total Environ* 443: 870-876.

Elimelech M, Zhu XH, Childress AE, Hong SK (1997) Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes. *J Membrane Sci* 127: 101-109.

El Madani M, Guillard C, Perol N, Chovelon JM, El Azzouzi M, Zrineh A, Herrmann JM (2006) Photocatalytic degradation of diuron in aqueous solution in presence of two industrial titania catalysts, either as suspended powders or deposited on flexible industrial photoresistant papers. *Appl Catal B-Environ* 65: 70-76.

EPAL (2010) Qualidade da água para consumo humano - Relatório anual 2010. Available online: http://www.epal.pt/epal/DownloadsImgPdf.aspx?src=RelatQualidade&area=283&sub=5615&menu=5615.

Eriksson P (1988) Nanofiltration extends the range of membrane filtration. *Environ Prog* 7: 58-62.

Escher BI, Fenner K (2011) Recent advances in environmental risk assessment of transformation products. *Environ Sci Technol* 45: 3835-3847.

European Commission, Proposal for a Directive of the European Parliament and of the Council amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy, Brussels (2012).

Fane AG, Wang R, Jia Y, Membrane technology: Past, present, and future, in: Wang LK. Chen JP, Hung Y-T, Shammas NK (Eds.), Membrane and desalination technologies. Human Press, New York, USA (2011)

Fasnacht M, Blough N (2002) Aqueous photodegradation of polycyclic aromatic hydrocarbons. *Environ Sci Technol* 36: 4364-4369.

Fujishima A, Rao TN, Tryk DA (2000) Titanium dioxide photocatalysis. *J Photoch Photobio C* 1: 1-21.

Ge LK, Chen JW, Lin J, Cai XY (2009) Light-source-dependent effects of main water constituents on photodegradation of phenicol antibiotics: Mechanism and kinetics. *Environ Sci Technol* 43: 3101-3107.

Ge LK, Chen JW, Wei XX, Zhang SY, Qiao XL, Cai XY, Xie Q (2010) Aquatic photochemistry of fluoroquinolone antibiotics: Kinetics, pathways, and multivariate effects of main water constituents. *Environ Sci Technol* 44: 2400-2405.

Gerba C, Drinking water treatment and distribution, in: Maier RM, Pepper IL, Gerba CP (Eds.), Environmental Microbiology. Academic Press, San Diego, USA, pp. 535-541 (2000a).

Gerba C, Disinfection, in: Maier RM, Pepper IL, Gerba CP (Eds.), Environmental Microbiology. Academic Press, San Diego, USA, pp. 543-556 (2000b).

Grellier J, Bennett J, Patelarou E, Smith RB, Toledano MB, Rushton L, Briggs DJ, Nieuwenhuijsen MJ (2010) Exposure to disinfection by-products, fetal growth, and prematurity: A systematic review and meta-analysis. *Epidemiology* 21: 300-313.

Harries JE, Sheahan DA, Jobling S, Matthiessen P, Neall M, Sumpter JP, Taylor T, Zaman N (1997) Estrogenic activity in five United Kingdom rivers detected by measurement of vitellogenesis in caged male trout. *Environ Toxicol Chem* 16: 534-542.

Hayes TB, Anderson LL, Beasley VR, de Solla SR, Iguchi T, Ingraham H, Kestemont P, Kniewald J, Kniewald Z, Langlois VS, Luque EH, McCoy KA, Munoz-de-Toro M, Oka T, Oliveira CA, Orton F, Ruby S, Suzawa M, Tavera-Mendoza LE, Trudeau VL, Victor-Costa AB, Willingham E (2011) Demasculinisation and feminisation of male gonads by atrazine: Consistent effects across vertebrate classes. *J Steroid Biochem* 127: 64-73.

Health Canada (2012) Guidelines for Canadian drinking water quality - Summary table. Water, Air and Climate Change Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Ottawa, Ontario.
Available online: http://www.hc-sc.gc.ca/ewh-semt/alt_formats/pdf/pubs/water-eau/2012-sum_guide-res_recom/2012-sum_guide-res_recom-eng.pdf.

Hecker M, Hollert H (2011) Endocrine disrupter screening: Regulatory perspectives and needs. *Environ Sci Eur* 23: 1-15.

Herzberg M, Elimelech M (2007) Biofouling of reverse osmosis membranes: Role of biofilm-enhanced osmotic pressure. *J Membrane Sci* 295: 11-20.

Huang XH, Leal M, Li QL (2008) Degradation of natural organic matter by TiO_2 photocatalytic oxidation and its effect on fouling of low-pressure membranes. *Water Res* 42: 1142-1150.

Hurum DC, Agrios AG, Gray KA, Rajh T, Thurnauer MC (2003) Explaining the enhanced photocatalytic activity of Degussa P25 mixed-phase TiO_2 using EPR. *J Phys Chem B* 107: 4545-4549.

IJpelaar G, Harmsen DJH, Heringa M (2007) UV disinfection and UV/H_2O_2 oxidation: By-product formation and control - Report elaborated in the scope of the D2411 deliverable of Project TECHNEAU.

Jacobs LE, Weavers LK, Chin YP (2008) Direct and indirect photolysis of polycyclic aromatic hydrocarbons in nitrate-rich surface waters. *Environ Toxicol Chem* 27: 1643-1648.

Jardim WF, Montagner CC, Pescara IC, Umbuzeiro GA, Di Dea Bergamasco AM, Eldridge ML, Sodré FF (2012) An integrated approach to evaluate emerging contaminants in drinking water. *Sep Purif Technol* 84: 3-8.

Jeong CH, Wagner ED, Siebert VR, Anduri S, Richardson SD, Daiber EJ, McKague AB, Kogevinas M, Villanueva CM, Goslan EH, Luo W, Isabelle LM, Pankow JF, Grazuleviciene R, Cordier S, Edwards SC, Righi E, Nieuwenhuijsen MJ, Plewa MJ (2012) Occurrence and toxicity of disinfection by-products in European drinking waters in relation with the HIWATE epidemiology Study. *Environ Sci Technol* 46: 12120-12128.

Jin Y, Wang L, Fu Z (2013) Oral exposure to atrazine modulates hormone synthesis and the transcription of steroidogenic genes in male peripubertal mice. *Gen Comp Endocr* 184: 120-127.

Jmol: An open-source Java viewer for chemical structures in 3D. Available online: http://jmol.sourceforge.net/.

Jobling S, Nolan M, Tyler CR, Brighty G, Sumpter JP (1998) Widespread sexual disruption in wild fish. *Environ Sci Technol* 32: 2498-2506.

Kidd KA, Blanchfield PJ, Mills KH, Palace VP, Evans RE, Lazorchak JM, Flick RW (2007) Collapse of a fish population after exposure to a synthetic estrogen. *P Natl Acad Sci* USA 104: 8897-8901.

Kim J, Van der Bruggen B (2010) The use of nanoparticles in polymeric and ceramic membrane structures: Review of manufacturing procedures and performance improvement for water treatment. *Environ Pollut* 158: 2335-2349.

Kimura K, Amy G, Drewes J, Watanabe Y (2003) Adsorption of hydrophobic compounds onto NF/RO membranes: An artifact leading to overestimation of rejection. *J Membrane Sci* 221: 89-101.

Kiso Y, Nishimura Y, Kitao T, Nishimura K (2000) Rejection properties of non-phenylic pesticides with nanofiltration membranes. *J Membrane Sci* 171: 229-237.

Kiso Y, Sugiura Y, Kitao T, Nishimura K (2001) Effects of hydrophobicity and molecular size on rejection of aromatic pesticides with nanofiltration membranes. *J Membrane Sci* 192: 1-10.

Knauert S, Escher B, Singer H, Hollender J, Knauer K (2008) Mixture toxicity of three photosystem II inhibitors (atrazine, isoproturon, and diuron) toward photosynthesis of freshwater phytoplankton studied in outdoor mesocosms. *Environ Sci Technol* 42: 6424-6430.

Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, Buxton HT (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999-2000: A national reconnaissance. *Environ Sci Technol* 36: 1202-1211.

Konstantinou IK, Sakellarides TM, Sakkas VA, Albanis TA (2001) Photocatalytic degradation of selected s-triazine herbicides and organophosphorus insecticides over aqueous TiO_2 suspensions. *Environ Sci Technol* 35: 398-405.

Konstantinou IK, Sakkas VA, Albanis TA (2002) Photocatalytic degradation of propachlor in aqueous TiO_2 suspensions: Determination of the reaction pathway and identification of intermediate products by various analytical methods. *Water Res* 36: 2733-2742.

Kopecký J, Organic Photochemistry: A visual approach. VCH Publishers Inc, New York (1992).

Krieger R, Doull J, Ecobichon D, Gammon D, Hodgson E, Reiter L, Ross J, Handbook of pesticides toxicology: Principles. Elsevier Science, USA (2001).

Kuster M, José Lopéz de Alda M, Dolores Hernando M, Petrovic M, Martin-Alonso J, Barceló D (2008) Analysis and occurrence of pharmaceuticals, estrogens, progestogens and polar pesticides in sewage treatment plant effluents, river water and drinking water in the Llobregat river basin (Barcelona, Spain). *J Hydrol* 358: 112-123.

Larson RA, Zepp RG (1988) Reactivity of the carbonate radical with aniline derivatives. *Environ Toxicol Chem* 7: 265-274.

Le-Clech P, Lee EK, Chen V (2006) Hybrid photocatalysis/membrane treatment for surface waters containing low concentrations of natural organic matters. *Water Res* 40: 323-330.

Lee WJ, Hoppin JA, Blair A, Lubin JH, Dosemeci M, Sandler DP, Alavanja MCR (2004) Cancer incidence among pesticide applicators exposed to alachlor in the Agricultural Health Study American. *J Epidemiol* 159: 373-380.

Le Goff L, Khaldi S, Favennec L, Nauleau F, Meneceur P, Perot J, Ballet JJ, Gargala G (2010) Evaluation of water treatment plant UV reactor efficiency against *Cryptosporidium parvum* oocyst infectivity in immunocompetent suckling mice. *J Appl Microbiol* 108: 1060-1065.

Li G, Lv L, Fan H, Ma J, Li Y, Wan Y, Zhao XS (2010) Effect of the agglomeration of TiO_2 nanoparticles on their photocatalytic performance in the aqueous phase. *J Colloid Interf Sci* 348: 342-347.

Loos R, Gawlik BM, Locoro G, Rimaviciute E, Contini S, Bidoglio G (2009) EU-wide survey of polar organic persistent pollutants in European river waters. *Environ Pollut* 157: 561-568.

Loos R, Locoro G, Comero S, Contini S, Schwesig D, Werres F, Balsaa P, Gans O, Weiss S, Blaha L, Bolchi M, Gawlik BM (2010a) Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. *Water Res* 44: 4115-4126.

Loos R, Locoro G. Contini S (2010b) Occurrence of polar organic contaminants in the dissolved water phase of the Danube River and its major tributaries using SPE-LC-MS2 analysis. *Water Res* 44: 2325-2335.

Ma N, Zhang Y, Quan X, Fan X, Zhao H (2010) Performing a microfiltration integrated with photocatalysis using an Ag-TiO_2/HAP/Al_2O_3 composite membrane for water treatment: Evaluating effectiveness for humic acid removal and anti-fouling properties. *Water Res* 44: 6104-6114.

Madaeni SS, Zinadini S, Vatanpour V (2011) A new approach to improve antifouling property of PVDF membrane using in situ polymerisation of PAA functionalised TiO_2 nanoparticles. *J Membrane Sci* 380: 155-162.

Maldonado M, Passarinho P, Oller I, Gernjak W, Fernandez P, Blanco J, Malato S (2007) Photocatalytic degradation of EU priority substances: A comparison between TiO_2 and Fenton plus photo-Fenton in a solar pilot plant. *J Photoch Photobio A* 185: 354-363.

Marotta R, Spasiano D, Di Somma I, Andreozzi R (2013) Photodegradation of naproxen and its photoproducts in aqueous solution at 254 nm: A kinetic investigation. *Water Res* 47: 373-383.

McInnis P, Pesticides in Ontario's Treated Municipal Drinking Water 1986-2006. Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment (2010). Available online: http://www.ene.gov.on.ca/environment/en/resources/STD01_078819.html.

Mehrvar M, Venhuis SH (2005) Photocatalytic treatment of linear alkylbenzene sulfonate (LAS) in water. *J Environ Sci Heal A* 40: 1003-1012.

Meylan WM, Howard PH, Validation of water solubility estimation methods using log K_{ow} for application in PCGEMS & EPI. Syracuse Research Corporation, Environmental Science Center, New York (1994).

Molinari R, Palmisano L, Drioli E, Schiavello M (2002) Studies on various reactor configurations for coupling photocatalysis and membrane processes in water purification. *J Membrane Sci* 206: 399-415.

Molinari R, Caruso A, Argurio P, Poerio T (2008) Degradation of the drugs Gemfibrozil and Tamoxifen in pressurised and de-pressurised membrane photoreactors using suspended polycrystalline TiO_2 as catalyst. *J Membrane Sci* 319: 54-63.

Munger R, Isacson P, Hu S, Burns T, Hanson J, Lynch CF, Cherryholmes K, VanDorpe P, Hausler WJ (1997) Intrauterine growth retardation in Iowa communities with herbicide-contaminated drinking water supplies. *Environ Health Persp* 105: 308-314.

Nghiem LD, Schäfer AI, Waite TD (2002) Adsorption of estrone on nanofiltration and reverse osmosis membranes in water and wastewater treatment. *Water Sci Technol* 46: 265-272.

Nghiem L, Schäfer A, Elimelech M (2004) Removal of natural hormones by nanofiltration membranes: Measurement, modeling, and mechanisms. *Environ Sci Technol* 38: 1888-1896.

Nghiem LD, Espendiller C, Braun G (2008) Influence of organic and colloidal fouling on the removal of sulphamethoxazole by nanofiltration membranes. *Water Sci Technol* 58: 163-169.

NHMRC, NRMMC (2011) *Australian drinking water guidelines paper 6 - National water quality management strategy*. National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia, Canberra. Available online: http://www.nhmrc.gov.au/_files_nhmrc/publications/attachments/eh52_aust_drinking_water_guidelines.pdf.

Nickenig G, Strehlow K, Wassmann S, Baumer AT, Albory K, Sauer H, Bohm M (2000) Differential effects of estrogen and progesterone on AT(1) receptor gene expression in vascular smooth muscle cells. *Circulation* 102: 1828-1833.

Oki T, Kanae S (2006) Global hydrological cycles and world water resources. *Science* 313: 1068-1072.

Orton F, Lutz I, Kloas W, Routledge EJ (2009) Endocrine disrupting effects of herbicides and pentachlorophenol: In vitro and in vivo evidence. *Environ Sci Technol* 43: 2144-2150.

Ozaki H, Li HF (2002) Rejection of organic compounds by ultra-low pressure reverse osmosis membrane. *Water Res* 36: 123-130.

Patsios SI, Sarasidis VC, Karabelas AJ (2013) A hybrid photocatalysis–ultrafiltration continuous process for humic acids degradation. *Sep Purif Technol* 104: 333-341.

Patterson C, Anderson A, Sinha R, Muhammad N, Pearson D (2012) Nanofiltration membranes for removal of colour and pathogens in small public drinking water sources. *J Environ Eng-ASCE* 138: 48-57.

Pereira VJ, Linden KG, Weinberg HS (2007a) Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. *Water Res* 41: 4413-4423.

Pereira VJ, Weinberg HS, Linden KG, Singer PC (2007b) UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm. *Environ Sci Technol* 41: 1682-1688.

Pereira VJ, Galinha J, Barreto Crespo MT, Matos CT, Crespo JG (2012) Integration of nanofiltration, UV photolysis, and advanced oxidation processes for the removal of hormones from surface water sources. *Sep Purif Technol* 95: 89-96.

Pesticide Properties DataBase, Agriculture & Environment Research Unit (AERU). Available online: http://sitem.herts.ac.uk/aeru/footprint/en/index.htm; Last accessed: September 8, 2010.

Plakas KV, Karabelas AJ (2009) Triazine retention by nanofiltration in the presence of organic matter: The role of humic substance characteristics. *J Membrane Sci* 336: 86-100.

Postigo C, José Lopéz de Alda M, Barceló D, Ginebreda A, Garrido T, Fraile J. (2010) Analysis and occurrence of selected medium to highly polar pesticides in groundwater of Catalonia (NE Spain): An approach based on on-line solid phase extraction-liquid chromatography-electrospray-tandem mass spectrometry detection. *J Hydrol* 383: 83-92.

Purdom CE, Hardiman PA, Bye VVJ, Eno NC, Tyler CR, Sumpter JP (1994) Estrogenic effects of effluent from sewage treatmentworks. *Chem Ecol* 8: 275-285.

Rahman MB, Driscoll T, Cowie C, Armstrong BK (2010) Disinfection by-products in drinking water and colorectal cancer: A meta-analysis International. *J Epidemiol* 39: 733-745.

Rao KF, Lei BL, Li N, Ma M, Wang ZJ (2013) Determination of estrogens and estrogenic activities in water from three rivers in Tianjin, China. *J Environ Sci-China* 25: 1164-1171.

Regulation 2076/2002 of 20 November 2002 extending the time period referred to in Article 8(2) of Council Directive 91/414/EEC and concerning the non-inclusion of certain active substances in Annex I to that Directive and the withdrawal of authorisations for plant protection products containing these substances. Official Journal of the European Communities, L 319/3 (2002).

Rodriguez-Mozaz S, José López de Alda M, Barceló D (2004) Monitoring of estrogens, pesticides and bisphenol A in natural waters and drinking water treatment plants by solid-phase extraction–liquid chromatography–mass spectrometry. *J Chromatogr A* 1045: 85-92.

Rogers C, Economic costs of conventional surface-water treatment: A case study of the MCallen northwest facility (Master thesis). Texas A&M University, Texas, USA (2008).

Rosenfeldt E, Chen P, Kullman S, Linden K (2007) Destruction of estrogenic activity in water using UV advanced oxidation. *Sci Total Environ* 377: 105-113.

Routledge EJ, Sumpter JP (1996) Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast screen. *Environ Toxicol Chem* 15: 241-248.

Ruder AM, Yiin JH (2011) Mortality of US pentachlorophenol production workers through 2005. *Chemosphere* 83: 851-861.

Saito K, Niijima A, Kamite E, Watanabe M (2012) Bisphenol A and estrone-induced developmental effects in early chick embryos. *Environ Toxicol* 27: 58-62.

Salvaterra AF, Sarmento G, Minhalma M, de Pinho MN (2011) Nanofiltration of surface water for the removal of endocrine disruptors. *Desalin Water Treat* 35: 54-61.

Sanches S, Leitão C, Penetra A, Cardoso VV, Ferreira E, Benoliel MJ, Barreto Crespo MT, Pereira VJ (2011a) Direct photolysis of polycyclic aromatic hydrocarbons in drinking water sources. *J Hazard Mater* 192: 1458-1465.

Sanches S, Penetra A, Granado C, Cardoso VV, Ferreira E, Benoliel MJ, Barreto Crespo MT, Pereira VJ, Crespo JG (2011b) Removal of pesticides and polycyclic aromatic hydrocarbons from different drinking water sources by nanofiltration. *Desalin Water Treat* 27: 141-149.

Schaep J, Van der Bruggen B, Uytterhoeven S, Croux R, Vandecasteele C, Wilms D, Van Houtte E, Vanlergberghe F (1998) Removal of hardness from groundwater by nanofiltration. *Desalination* 119: 295-301.

Schäfer A, Nghiem L, Waite T (2003) Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis. *Environ Sci Technol* 37: 182-188.

Schäfer AI, Pihlajamaki A, Fane AG, Waite TD, Nyström M (2004) Natural organic matter removal by nanofiltration: Effects of solution chemistry on retention of low molar mass acids versus bulk organic matter. *J Membrane Sci* 242: 73-85.

Schwarzenbach RP, Gschwend PM, Imboden DM, In Environmental Organic Chemistry. John Wiley & Sons Inc, New York (1993).

Sharpless CM, Seibold DA, Linden KG (2003) Nitrate photosensitised degradation of atrazine during UV water treatment. *Aquat Sci* 65: 359-366.

Shemer H, Linden KG (2007a) Photolysis, oxidation and subsequent toxicity of a mixture of polycyclic aromatic hydrocarbons in natural waters. *J Photoch Photobio A-Chemistry* 187: 186-195.

Shemer H, Linden KG (2007b) Aqueous photodegradation and toxicity of the polycyclic aromatic hydrocarbons fluorene, dibenzofuran, and dibenzothiophene. *Water Res* 41: 853-861.

Shiklomanov IA, World fresh water resources, in: Gleick PH (Ed.), Water in crisis: A guide to the world's fresh water resources. Oxford University Press Inc, New York, pp. 13-24 (1993).

Shin GA, Linden KG, Faubert G (2009) Inactivation of *Giardia lamblia* cysts by polychromatic UV. *Lett Appl Microbiol* 48: 790-792.

Snyder SA, Adham S, Redding AM, Cannon FS, DeCarolis J, Oppenheimer J, Wert E, Yoon Y (2007) Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination* 202: 156-181.

Song W, Ravindran V, Koel BE, Pirbazari M (2004) Nanofiltration of natural organic matter with H_2O_2/UV pretreatment: Fouling mitigation and membrane surface characterisation. *J Membrane Sci* 241: 143-160.

Sosnowska B, Huras B, Nowacka-Krukowska H, Bukowska B (2013) Oxidative damage to human red blood cells treated with chlorfenvinphos, an organophosphate insecticide (in vitro). *Biologia* 68: 773-778.

Sousa MA, Gonçalves C, Pereira J, Vilar VJP, Boaventura RAR, Alpendurada MF (2013) Photolytic and TiO2-assisted photocatalytic oxidation of the anxiolytic drug lorazepam (Lorenin (R) pills) under artificial UV light and natural sunlight: A comparative and comprehensive study. *Sol Energy* 87: 219-228.

Stanford BD, Weinberg HS (2010) Evaluation of on-site wastewater treatment technology to remove estrogens, nonylphenols, and estrogenic activity from wastewater. *Environ Sci Technol* 44: 2994-3001.

Su Y-C, Huang C, Pan JR, Hsieh W-P, Chu M-C (2012) Fouling mitigation by TiO_2 composite membrane in membrane bioreactors. *J Environ Eng-ASCE* 138: 344-350.

Sun L, Yong W, Chu X, Lin J-M (2009) Simultaneous determination of 15 steroidal oral contraceptives in water using solid-phase disk extraction followed by high performance liquid chromatography-tandem mass spectrometry. *J Chromatogr A* 1216: 5416-5423.

Sunnotel O, Verdoold R, Dunlop PSM, Snelling WJ, Lowery CJ, Dooley JSG, Moore JE, Byrne JA (2010) Photocatalytic inactivation of *Cryptosporidium parvum* on nanostructured titanium dioxide films. *J Water Health* 8: 83-91.

Tarabara V, Multifunctional nanomaterial-enabled membranes for water treatment, in: Diallo M, Duncan J, Savage N, Sustich R, Street A (Eds.), Nanotechnology Applications for Clean Water. William Andrew Inc, New York, USA, pp. 59-75 (2009).

Teijon G, Candela L, Tamoh K, Molina-Diaz A, Fernandez-Alba AR (2010) Occurrence of emerging contaminants, priority substances (2008/105/CE) and heavy metals in treated wastewater and groundwater at Depurbaix facility (Barcelona, Spain). *Sci Total* Environ 408: 3584-3595.

Thorsen T, Fløgstad H (2006) Nanofiltration in drinking water treatment - Report elaborated in the scope of the deliverable D 534B of the TECHNEAU project.

Trovo AG, Nogueira RFP, Aguera A, Sirtori C, Fernandez-Alba AR (2009) Photodegradation of sulfamethoxazole in various aqueous media: Persistence, toxicity and photoproducts assessment. *Chemosphere* 77: 1292-1298.

Turan VK, Sanchez RI, Li JJ, Li SA, Reuhl KR, Thomas PE, Conney AH, Gallo MA, Kauffman FC, Mesia-Vela S (2004) The effects of steroidal estrogens in ACI rat mammary carcinogenesis: 17 beta-estradiol, 2-hydroxyestradiol, 4-hydroxyestradiol, 16 alpha-hydroxyestradiol, and 4-hydroxyestrone. *JEndocrinol* 183: 91-99.

US EPA (1996) Ultraviolet light disinfection technology in drinking water application – An overview (EPA 811-R-96-002). US Environmental Protection Agency, Office of Ground Water and Drinking Water, Washington DC.

US EPA (2003) Re-registration eligibility decision for diuron (document number 20460). US Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances, Washington DC.

US EPA (2005) Membrane filtration guidance manual (EPA 815-R-06-009). US Environmental Protection Agency, Office of Water, Washington DC.

US EPA (2006) Ultraviolet disinfection guidance manual for the final long term 2 enhanced surface water treatment rule (EPA 815-R-06-007). US Environmental Protection Agency, Office of Water, Washington, DC.

US EPA (2008) Reregistration eligibility decision for pentachlorophenol (EPA 739-R-08-008). US Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances, Washington DC.

US EPA (2009a) National primary drinking water regulations. Available online: http://water.epa.gov/drink/contaminants/basicinformation/alachlor.cfm.

US EPA (2009b) Drinking Water Contaminant Candidate List 3 –Final. Federal Register, Vol. 74, n. 194. Available online: http://water.epa.gov/scitech/drinkingwater/dws/ccl/ccl3.cfm.

US EPA (2012) Pesticides: Topical and chemical fact sheets. Available online: http://wwwepagov/pesticides/factsheets/atrazine_backgroundhtm. Last updated: May 5, 2012, last accessed: May 17, 2013.

Vajda AM, Barber LB, Gray JL, Lopez EM, Woodling JD, Norris DO (2008) Reproductive disruption in fish downstream from an Estrogenic wastewater effluent. *Environ Sci Technol* 42: 3407-3414.

Vajda AM, Barber LB, Gray JL, Lopez EM, Bolden AM, Schoenfuss HL, Norris DO (2011) Demasculinisation of male fish by wastewater treatment plant effluent. *Aquat Toxicol* 103: 213-221.

Van der Bruggen B, Schaep J, Maes W, Wilms D, Vandecasteele C (1998) Nanofiltration as a treatment method for the removal of pesticides from ground waters. *Desalination* 117: 139-147.

Van der Bruggen B, Schaep J, Wilms D, Vandecasteele C (1999) Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *J Membrane Sci* 156: 29-41.

Van der Bruggen B, Everaert K, Wilms D, Vandecasteele C (2001) Application of nanofiltration for removal of pesticides, nitrate and hardness from ground water: Rejection properties and economic evaluation. *J Membrane Sci* 193: 239-248.

Van der Bruggen B, Vandecasteele C, Van Gestel T, Doyen W, Leysen R (2003) A review of pressure-driven membrane processes in wastewater treatment and drinking water production. *Environ Prog* 22: 46-56.

Van der Bruggen B, Manttari M, Nyström M (2008) Drawbacks of applying nanofiltration and how to avoid them: A review. *Sep Purif Technol* 63: 251-263.

Van der Zande, A (2010) *Exploration of Management Options for Pentachlorophenol (PCP).* Paper for the 8th meeting of the UNECE CLRTAP Task Force on Persistent Organic Pollutants, Montreal, 18 -20 May 2010.

Velicu M, Suri R (2009) Presence of steroid hormones and antibiotics in surface water of agricultural, suburban and mixed-use areas. *Environ Monit Assess* 154: 349-359.

Verliefde A, Cornelissen E, Heijman S, Verberk J, Amy G, Van der Bruggen B, van Dijk J (2009) Construction and validation of a full-scale model for rejection of organic micropollutants by NF membranes. *J Membrane Sci* 339: 10-20.

Vidyasagar J, Karunakar N, Reddy MS, Rajnarayana K, Surender T, Krishna DR (2004) Oxidative stress and antioxidant status in acute organophosphorous insecticide poisoning. *Indian J Pharmacol* 36: 76-79.

Villanueva CM, Durand G, Coutte MB, Chevrier C, Cordier S (2005) Atrazine in municipal drinking water and risk of low birth weight, preterm delivery, and small-for-gestational-age status. *Occup Environ Med* 62: 400-405.

Vryzas Z, Papadakis EN, Vassiliou G, Papadopoulou-Mourkidou E (2012) Occurrence of pesticides in transboundary aquifers of North-eastern Greece. *Sci Total Environ* 441: 41-48.

Wang RC, Ren DJ, Xia SQ, Zhang YL, Zhao JF (2009) Photocatalytic degradation of Bisphenol A (BPA) using immobilised TiO_2 and UV illumination in a horizontal circulating bed photocatalytic reactor (HCBPR). *J Hazard Mater* 169: 926-932.

Wang YN, Tang CY (2011) Nanofiltration membrane fouling by oppositely charged macromolecules: Investigation on flux behavior, foulant mass deposition, and solute rejection. *Environ Sci Technol* 45: 8941-8947.

Wang Y, Chen Z, Ba T, Pu J, Chen T, Song Y, Gu Y, Qian Q, Xu Y, Xiang K, Wang H, Jia G (2013) Susceptibility of young and adult rats to the oral toxicity of titanium dioxide nanoparticles. *Small* 9: 1742-1752.

WHO (1996) Guidelines for drinking-water quality, Volume 2 - Health criteria and other supporting information (2nd ed.). *Wo*rld Health Organisation, Geneva.

Wilson AGE, Thake DC, Heydens WE, Brewster DW, Hotz KJ (1996) Mode of action of thyroid tumor formation in the male Long-Evans rat administered high doses of alachlor. *Fund Appl Toxicol* 33: 16-23.

Wlodyka-Bergier A, Bergier T (2011) The occurrence of haloacetic acids in Krakow water distribution system. *Arch Environ Prot* 37: 21-29.

Wong C, Chu W (2003) The direct photolysis and photocatalytic degradation of alachlor at different TiO_2 and UV sources. *Chemosphere* 50: 981-987.

Wu C, Linden KG (2008) Degradation and byproduct formation of parathion in aqueous solutions by UV and UV/H_2O_2 treatment. *Water Res* 42: 4780-4790.

Xia XH, Li GC, Yang ZF, Chen YM, Huang GH (2009) Effects of fulvic acid concentration and origin on photodegradation of polycyclic aromatic hydrocarbons in aqueous solution: Importance of active oxygen. *Environ Pollut* 157: 1352-1359.

Yangali-Quintanilla V, Sadmani A, McConville M, Kennedy M, Amy G (2009) Rejection of pharmaceutically active compounds and endocrine disrupting compounds by clean and fouled nanofiltration membranes. *Water Res* 43: 2349-2362.

You SJ, Semblante GU, Lu SC, Damodar RA, Wei TC (2012) Evaluation of the antifouling and photocatalytic properties of poly(vinylidene fluoride) plasma-grafted poly(acrylic acid) membrane with self-assembled TiO_2. *J Hazard Mater* 237: 10-19.

Yuan F, Hu C, Hu X, Qu J, Yang M (2009) Degradation of selected pharmaceuticals in aqueous solution with UV and UV/H_2O_2. *Water Res* 43: 1766-1774.

Zepp RG, Hoigné J, Bader H (1987) Nitrate-induced photooxidation of trace organic-chemicals in water. *Environ Sci Technol* 21: 443-450.

Zhang Y, Causserand C, Aimar P, Cravedi JP (2006a) Removal of bisphenol A by a nanofiltration membrane in view of drinking water production. *Water Res* 40: 3793-3799.

Zhang HM, Quan X, Chen S, Zhao HM, Zhao YZ (2006b) Fabrication of photocatalytic membrane and evaluation its efficiency in removal of organic pollutants from water. *Sep Purif Technol* 50: 147-155.

Zheng W, Yu H, Wang X, Qu W (2012) Systematic review of pentachlorophenol occurrence in the environment and in humans in China: Not a negligible health risk due to the re-emergence of schistosomiasis. *Environ Int* 42: 105-116.

Zhou X, Lian Z, Wang J, Tan L, Zhao Z (2011) Distribution of estrogens along Licun River in Qingdao, China. *Procedia Environ Sci* 10: 1876-1880.

CHAPTER 2

Drinking water treatment of pesticides using low pressure UV photolysis and advanced oxidation processes

Published in Water Research:

Sanches S, Barreto Crespo MT, Pereira VJ (2010) Drinking water treatment of priority pesticides using low pressure UV photolysis and advanced oxidation processes. *Water Res* 44(6): 1809-1818.

Sandra Sanches was involved in all the experimental work presented in this chapter. Modelling of experimental data was carried out by Vanessa Pereira, who also supervised all the work developed together with Teresa Crespo.

CONTENTS

ABSTRACT

This study reports the efficiency of low pressure UV photolysis for the degradation of pesticides identified as priority pollutants by the European Water Framework Directive 2000/60/EC. Direct low pressure UV photolysis and advanced oxidation processes (using hydrogen peroxide and titanium dioxide) experiments were conducted in laboratory grade water, surface water, and groundwater.

LP direct photolysis using a high UV fluence (1500 mJ cm^{-2}) was found to be extremely efficient to accomplish the degradation of all pesticides except isoproturon, whereas photolysis using hydrogen peroxide and titanium dioxide did not significantly enhance their removal. In all matrices tested the experimental photolysis of the pesticides followed the same trend: isoproturon degradation was negligible, alachlor, pentachlorophenol, and atrazine showed similar degradation rate constants, whereas diuron and chlorfenvinphos were highly removed. The degradation trend observed for the selected compounds followed the decadic molar absorption coefficients order with exception of isoproturon probably due to its extremely low quantum yield.

Similar direct photolysis rate constants were obtained for each pesticide in the different matrices tested, showing that the water components did not significantly impact degradation. Extremely similar photolysis rate constants were also obtained in surface water for individual compounds when compared to mixtures. The model fluence and time-based rate constants reported were very similar to the direct photolysis experimental results obtained, while overestimating the advanced oxidation results. This model was used to predict how degradation of isoproturon, the most resilient compound, could be improved.

2.1 INTRODUCTION

In recent years, a large group of organic compounds have been labelled as water emerging contaminants by the US Environmental Protection Agency and the European Union. The European Water Framework Directive (Decision 2455/2001/EC) identifies 33 priority substances that present high toxicity, high environmental persistence, and bioaccumulation potential. This directive includes pesticides such as atrazine, diuron, isoproturon, alachlor, pentachlorophenol, and chlorfenvinphos, which are of special interest due to their easy transport in the environment as well as potential for seriously threatening the aquatic environment and human health (Hincapié *et al.* 2005). The adverse health effects of these compounds include increased cancer risk as well as anaemia, eye, liver, kidney, spleen cardiovascular system, and reproductive problems (US EPA 2009). Among these pesticides, alachlor, atrazine and pentachlorophenol are also known to have endocrine disrupting capabilities.

These xenobiotics have been detected in drinking water sources such as surface water and groundwater at levels in the range of 2 to 13000 ng L^{-1} (Planas *et al.* 2006, Field *et al.* 2003).

Low pressure ultraviolet radiation, that emits primarily monochromatic light at 254 nm, is widely used for drinking water disinfection due to its effectiveness against a wide range of waterborne pathogens (Linden *et al.* 2002). The use of high UV fluences (1000-2000 mJ cm^{-2}) can also promote the degradation of photolabile organic compounds by direct photolysis due to their potential to absorb light (Sharpless and Linden 2003, Pereira *et al.* 2007a, Pereira *et al.* 2007b). However, some molecules do not strongly absorb the LP/UV radiation. For these stable micropollutants, advanced oxidation processes, using hydrogen peroxide and titanium dioxide , may be used to remove them from drinking water, due to the production of highly reactive, unselective and short-lived hydroxyl radicals (Pereira *et al.* 2007b). H_2O_2 has been widely described for water disinfection and degradation of pollutants (Sharpless and Linden 2003, Schwarzenbach *et al.* 1993, von Gunten 2003). TiO_2 recently emerged as a promising material to efficiently degrade pesticides in water. It presents several advantages related to its chemical and biological inertness, photostability, absence of toxicity, and low cost. To be catalytically active, TiO_2 requires irradiation with a wavelength lower than 380 nm, which induces the photoexcitation of an electron since it has an energy band gap of about 3.2 eV. Therefore, light sources such as low and medium pressure ultraviolet lamps as well as solar radiation are suitable to induce TiO_2 activity (Balasubramanian *et al.* 2004).

Several authors reported the degradation of the selected pesticides (atrazine, diuron, isoproturon, alachlor, pentachlorophenol, and chlorfenvinphos) by UV photolysis and AOPs (such as UV/H_2O_2 and UV/TiO_2), using solar (Hincapié *et al.* 2005, Malato *et al.* 2003, Haque and Muneer 2003) and UV-Visible radiation (Haque and Muneer 2003, Wong and Chu 2003a). Both direct photolysis and AOPs photolysis have proven to be very efficient although AOPs were usually more efficient (Haque and Muneer 2003, Wong and Chu 2003a).

LP lamps are the most commonly used lamps in drinking water facilities due to their extremely effective disinfection potential. To date, few studies have been conducted addressing the efficiency of LP lamps for the removal of the priority pesticides mentioned above and therefore further research is needed to address their degradation potential. LP/UV lamps have been reported to promote high degradation levels of some of the selected pesticides: atrazine by direct photolysis, UV/TiO_2, and UV/H_2O_2 (e.g. Bianchi *et al.* 2006); pentachlorophenol by direct photolysis (Vollmuth *et al.* 1994); diuron by direct and Photo-Fenton photolysis (Djebbar *et al.* 2008); and chlorfenvinphos by direct and UV/H_2O_2 (Acero *et al.* 2008).

Authors often describe the degradation of xenobiotics only as a function of time. These results provide insight on the efficiency of different systems to degrade the compounds, but cannot be compared directly with results obtained under different experimental setups. Reporting degradation in terms of UV fluence permits a standardisation of bench scale UV testing providing increased confidence in the data generated and the ability to compare results with other authors that report their results using the same method (Bolton and Linden 2003). The photolysis of xenobiotics is often studied for individual compounds and few studies compared these results to those obtained with mixtures where a competition effect could probably decrease the rate of degradation. In addition, studies addressing AOPs potential for the removal of the selected pesticides from water have been conducted mainly in laboratory grade water (LGW) and synthetic water matrices spiked with natural organic matter. Few studies concerning the removal of the selected micropollutants using real water matrices such as surface water and groundwater have been conducted to date (e.g. Acero *et al.* 2008, Rosenfeldt *et al.* 2006, Song *et al.* 2008). More studies using real source waters with different characteristics should therefore be conducted to address the potential of direct photolysis and AOPs to degrade organic compounds that may be present in those waters.

This study reports the effectiveness of LP/UV direct photolysis and AOPs (using H_2O_2 and TiO_2) for the degradation of the selected pesticides (isoproturon, alachlor, atrazine, pentachlorophenol, diuron, and chlorfenvinphos) identified as priority pollutants by the European Water Framework Directive. The degradation of these compounds was studied in laboratory grade water, surface water and groundwater. The pesticides were spiked individually in the different matrices and as mixtures in surface water to address if in real water systems, where a wide combination of compounds is expected to be present, different degradation trends could be expected. Several kinetic photolysis parameters were determined and used to model the photolysis results.

2.2 MATERIALS AND METHODS

2.2.1 Reagents

All pesticides and *para*-chlorobenzoic acid (pCBA) were purchased as solutions or solids of the highest grade commercially available (Sigma Aldrich, Germany). Aqueous suspension of bovine liver catalase with 40 000 - 60 000 units mg^{-1} protein was also obtained from Sigma Aldrich (one unit decomposed 1 μmol of H_2O_2). Hydrogen peroxide (30% w/w) was obtained from Panreac (Spain). Titanium dioxide Degussa® P25, a mixture of 70% anatase and 30% rutile, with an average particle size of 20 nm and a reactive surface area of 35-65 $m^2\ g^{-1}$ was used (Evonik Degussa, Germany). High performance liquid chromatography (HPLC) grade acetonitrile (ACN) and methanol (MeOH) from Lab Scan Analytical Sciences (Poland) were used for the chromatographic analysis and preparation of stock solutions. Laboratory grade water was produced by a Milli-Q (MQ) water system (Millipore, CA, USA) and the real water samples were collected in brown glass bottles, filtered through 0.45 μm mixed esters of cellulose filters (Millipore, CA, USA), and stored at 4 °C until used.

2.2.2 Experimental setup

2.2.2.1 UV photolysis experiments

UV photolysis experiments were conducted in a collimated beam bench-scale reactor (Trojan Technologies Inc., Canada) using a low pressure Hg lamp that emits mainly monochromatic light at 254 nm.

100 mL of laboratory grade water and two natural water matrices – surface water and groundwater - were spiked with the appropriate volume of the pesticides stock solutions to achieve concentrations of 1 mg L^{-1}. This concentration was set in order to follow the degradation of the compounds, spiked individually (in laboratory grade water, surface water, and groundwater) and as mixtures (in surface water), by direct injection using high performance liquid chromatography. 50 mL of sample were placed in a Petri dish and continuously stirred beneath the LP/UV source. The remaining 50 mL were used as control and kept in the dark under identical experimental conditions in order to determine possible pesticide losses due to evaporation or adsorption to the Petri dish walls. All experiments were conducted at room temperature (21 ± 2 °C).

The lamp irradiance was measured using a calibrated radiometer (IL1700, International Light, Newburyport, MA) which was placed at the same height of the water level in the Petri dish and the solution transmittance was measured by a UV photometer (P254C, Trojan Technologies Inc.). UV fluences of approximately 0, 40, 100, 500, 750, 1000, and 1500 mJ cm^{-2} were selected, taking into account the radiometer meter reading as well as petri, reflection, water and divergence factors (Bolton and Linden 2003), to establish the corresponding exposure times. At these exposure times, 200 μL of sample were taken to quantify the concentration of the compounds by HPLC analysis.

2.2.2.2 UV/H_2O_2 photolysis experiments

UV/H_2O_2 photolysis experiments were conducted similarly to direct photolysis experiments with the addition of 40 mg L^{-1} H_2O_2 and 500 μg L^{-1} pCBA to laboratory grade water and surface water spiked with the individual pesticides and mixtures. pCBA was added to the solution in order to determine indirectly, by competition kinetics, the second order rate constants between the selected micropollutants and the hydroxyl radicals, $k_{OH,M}$ (Elovitz and von Gunten 1999). At determined exposure times, 200 μL of sample were taken to vials containing catalase to quench the residual hydrogen peroxide. The residual H_2O_2 was determined at the beginning and end of each experiment using the I_3^- method described by Klassen *et al.* (1994).

2.2.2.3 UV/TiO_2 photolysis experiments

UV/TiO_2 photolysis experiments were conducted similarly to direct photolysis experiments with the addition of 2.5 mg L^{-1} TiO_2 and 500 μg L^{-1} pCBA to laboratory grade water spiked with the individual pesticides and surface water spiked with a mixture of the pesticides. During the degradation, samples (200 μL) were taken at each defined exposure time and filtered using 0.2 μm filters made of regenerated cellulose (Whatman, USA) to remove TiO_2 particles.

Even though different types of TiO_2 particles are available, Degussa® P25 TiO_2 (Evonik Degussa, Germany) was used because it has been referred by many authors as being the most efficient type of TiO_2 due to the presence of the more reactive anatase form (70%), surface area, and average particle size (Haque and Muneer 2003, Wong and Chu 2003b).

The UV/TiO_2 photocatalysis experiments in surface water were only conducted using a mixture of the pesticides isoproturon, alachlor, atrazine, diuron, and chlorfenvinphos. Pentachlorophenol was not added to the samples containing the mixture of pesticides due to analytical constrains and was not analysed individually because it was found to be significantly retained by the filters needed to remove the TiO_2 particles from the solutions.

2.2.2.4 Analytical methods

The selected pesticides and pCBA were analysed by reverse-phase high performance liquid chromatography using a Waters system equipped with an ultraviolet absorbance detector (Waters Chromatography, Milford, MA, USA).

The individual compounds, mixtures of each pesticide with pCBA, as well as mixtures containing all the selected pesticides were analysed using a Luna 5 μm C18(2) 100Å (150 x 3.0 mm) column (Phenomenex Inc., Torrance, CA, USA), different mobile phase compositions and monitored at compromise maximum absorbance wavelengths (detailed in Table A.1 in Appendix A.1). Pentachlorophenol was not added to the mixture samples because it could not be detected using the chromatography conditions used for the detection of the other pesticides. The Temperature Control Module was set at 34 ^{o}C for all analysis except the pesticide mixture samples that need to be analysed at room temperature to ensure appropriate separation of atrazine, diuron, and isoproturon.

2.3 RESULTS AND DISCUSSION

2.3.1 Direct photolysis

LP direct photolysis experiments were conducted to evaluate the degradation potential of pesticides with very different structures.

Figure 2.1 and Table 2.1 present the experimental and model direct photolysis results obtained using two real water matrices with very different compositions: surface water (Figure 2.1a) and groundwater (Figure 2.1b). The characterisation of the water matrices used is depicted in Appendix A.2 (Table A.6). In summary, the surface water matrix showed higher levels of total organic carbon and turbidity, whereas the groundwater samples presented higher alkalinity (Alk) and total hardness.

Different matrix compositions were taken into account in the fluence calculations. For the same UV fluence, different matrices were therefore subject to different exposure times calculated taking into account the absorbance of each matrix used. The direct photolysis fluence and time-based rate constants (k'_f and k'_t, respectively) obtained in LGW, surface water and groundwater (Table 2.1 and Table A.7 in Appendix A.2) show that for all the selected compounds except pentachlorophenol and chlorfenvinphos the rates slightly increased in surface water and groundwater. However, very similar time and fluence-based rate constants were obtained in all the tested matrices for all the compounds except chlorfenvinphos that presented lower rate constants in the real water matrices. Extremely similar rate constants were also obtained in surface water for the individual compounds and the mixtures.

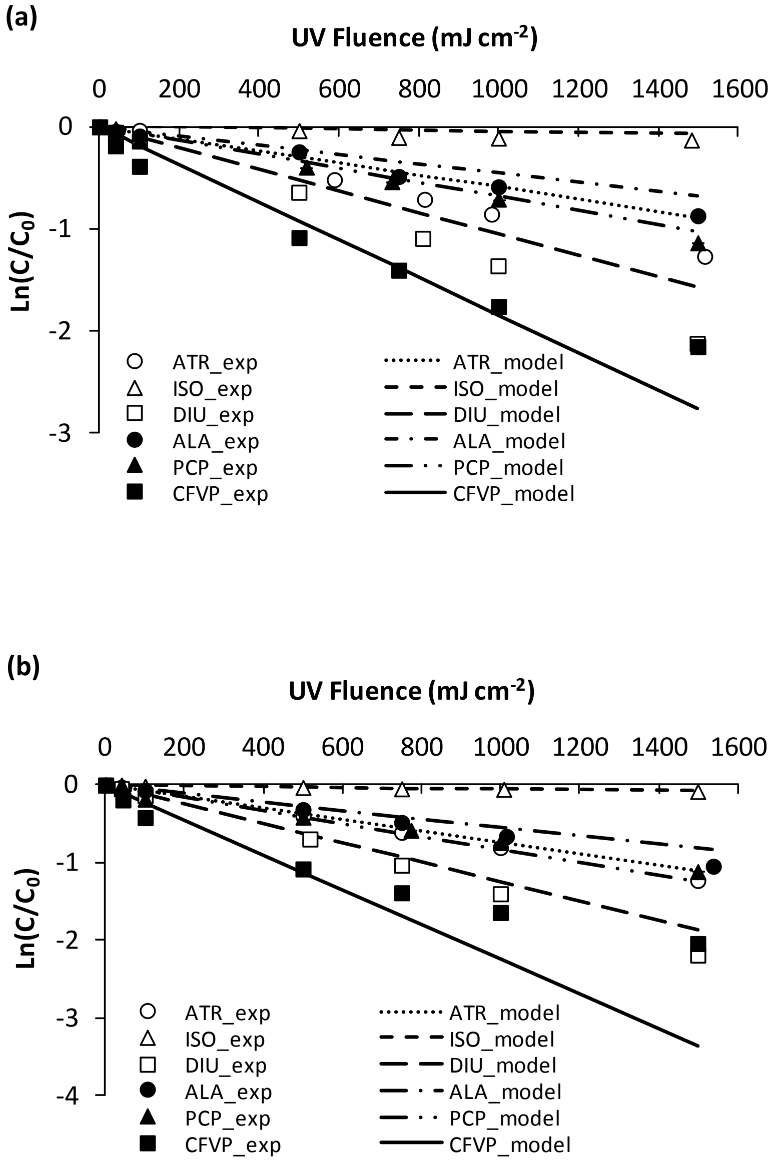


Figure 2.1 *Experimental (exp) and model low pressure direct photolysis of atrazine (ATR), isoproturon (ISO), diuron (DIU), alachlor (ALA), pentachlorophenol (PCP), and chlorfenvinphos (CFVP) in* ***(a)*** *surface water and* ***(b)*** *groundwater; experimental values are represented by symbols with error bars whereas the lines show the model results.*

Table 2.1 *Fluence-based direct photolysis (LP/UV) and AOPs (LP/UV/H_2O_2 and LP/UV/TiO_2) rate constants (k'_f) obtained for atrazine (ATR), isoproturon (ISO), diuron (DIU), alachlor (ALA), pentachlorophenol (PCP), and chlorfenvinphos (CFVP) in different water matrices: laboratory grade water (LGW), surface water (SW) and groundwater (GW) as individual compounds (ind) and mixtures (mix); standard errors are given in parenthesis and modelled results are given in square brackets.*

Pesticide	**k'_f x 10^4 (cm^2 mJ^{-1})**								
	LP/UV				**LP/UV/H_2O_2 – 40 mg L^{-1}**			**LP/UV/TiO_2 – 2.5 mg L^{-1}**	
	LGW_{ind}	**GW_{ind}**	**SW_{ind}**	**SW_{mix}**	**LGW_{ind}**	**SW_{ind}**	**SW_{mix}**	**LGW_{ind}**	**SW_{mix}**
ATR	7.56 (0.08) R^2=0.999 -	8.21 (0.03) R^2=0.999 [7.40]	8.51 (0.16) R^2=0.996 [5.94]	5.85 (0.04) R^2=0.999 -	7.43 (0.11) R^2=0.997 [59.4]	8.64 (0.06) R^2=0.999 [48.8]	6.16 (0.09) R^2=0.997 -	9.15 (0.06) R^2=0.999 [22.2]	10.17 (0.11) R^2=0.999 [17.3]
ISO	0.56 (0.07) R^2=0.850 -	0.53 (0.02) R^2=0.983 [0.55]	1.06 (0.17) R^2=0.769 [0.45]	0.12 (0.02) R^2=0.963 -	1.23 (0.04) R^2=0.987 [6.05]	0.16 (0.02) R^2=0.880 [4.95]	0.12 (0.03) R^2=0.843 -	0.47 (0.07) R^2=0.780 [1.73]	0.25 (0.05) R^2=0.920 [1.41]
DIU	13.05 (0.20) R^2=0.997 -	14.49 (0.15) R^2=0.999 [12.46]	14.04 (0.15) R^2=0.999 [10.47]	12.15 (0.09) R^2=0.999 -	13.52 (0.13) R^2=0.999 [91.6]	16.21 (0.10) R^2=0.999 [75.0]	12.96 (0.13) R^2=0.999 -	18.14 (0.29) R^2=0.997 [43.6]	14.59 (0.16) R^2=0.999 [33.0]
ALA	5.42 (0.16) R^2=0.991 -	6.80 (0.08) R^2=0.998 [5.47]	5.76 (0.18) R^2=0.988 [4.57]	6.71 (0.08) R^2=0.998 -	6.08 (0.11) R^2=0.996 [43.9]	6.20 (0.06) R^2=0.999 [36.9]	5.23 (0.07) R^2=0.998 -	7.03 (0.17) R^2=0.993 [8.63]	7.30 (0.18) R^2=0.993 [9.36]
PCP	8.38 (0.07) R^2=0.999 -	7.26 (0.22) R^2=0.989 [8.29]	7.34 (0.14) R^2=0.996 [6.86]	nd	9.57 (0.21) R^2=0.994 [69.9]	8.60 (0.33) R^2=0.983 [56.8]	nd	nd	nd
CFVP	22.52 (0.61) R^2=0.993 -	13.51 (0.85) R^2=0.955 [22.51]	14.44 (0.81) R^2=0.964 [18.50]	16.30 (0.47) R^2=0.990 -	20.16 (0.79) R^2=0.985 [152]	15.81 (0.67) R^2=0.979 [125]	16.96 (0.45) R^2=0.992 -	15.17 (0.56) R^2=0.984 [70.2]	18.54 (0.36) R^2=0.996 [56.7]

nd – not determined; R^2 – determination coefficient.

In all matrices tested the degradation of the pesticides followed the same trend (Table 2.1 and Figure 2.1). Isoproturon degradation was negligible, alachlor, pentachlorophenol and atrazine showed similar degradation rate constants, whereas diuron and chlorfenvinphos were highly removed. The same trend was observed when a mixture of the pesticides was degraded using direct photolysis.

There are two parameters – decadic molar absorption coefficient (ε) and quantum yield (ϕ) – that highly impact direct photolysis. Table 2.2 shows the decadic molar absorption coefficient and the quantum yield obtained for each pesticide. The decadic molar absorption coefficient presented represents the probability of the selected pesticides to absorb UV light at 254 nm, whereas the quantum yield can be defined as the ratio between the total number of molecules of isoproturon degraded to the total number of photons absorbed by the solution due to the compound's presence (Schwarzenbach *et al.* 1993). The degradation trend observed for the selected compounds followed the decadic molar absorption coefficients order with exception of isoproturon probably due to its extremely low quantum yield. All the decadic molar absorption coefficients and quantum yields obtained agree very well with previously reported values (Table 2.2).

***Table 2.2** Decadic molar absorption coefficient (ε), quantum yield (ϕ), and second-order rate constants for reaction of the micropollutants with OH radicals ($k_{OH,M}$) for the selected pesticides; literature values are given in square brackets (Acero et al. 2008, Song et al. 2008, Wong and Chu 2003b, Benitez et al. 2003, Benitez et al. 2006, De Laat et al. 1999, Beltran et al. 1993, Haag and Yao 1992).*

Compound	**ε ($M^{-1} cm^{-1}$)**	**ϕ (mol Einstein^{-1})**	**$k_{OH,M}$ x 10^{-9} ($M^{-1} s^{-1}$)**	
			LP/UV/H_2O_2	**LP/UV/TiO_2**
Atrazine	2647 [2847 – 3860]	0.060 [0.041- 0.05]	7.3 [18]	35.0
Isoproturon	5944 [6068]	0.002 [0.0037]	0.8 [5.2]	3.3
Diuron	16162 [15699]	0.019 [0.0115]	12.7 [4.6]	87.0
Alachlor	543 [428 – 467]	0.210 [0.095 - 0.140]	5.4 [7.0]	6.1
Pentachlorophenol	7400 [8500]	0.025 [0.0525]	9.0 [4.0]	nd
Chlorfenvinphos	8656 [7287]	0.056 [0.089]	18.5 [3.2]	132.5

nd – not determined

The experimental results depicted in Figure 2.1 were modelled using Equations A.1 to A.4 detailed in Appendix A.2 (Sharpless and Linden 2003, Schwarzenbach *et al.* 1993). The model used predicted extremely well the results obtained in groundwater for all the pesticides except chlorfenvinphos. In the surface water degradation experiments, the model slightly underestimated the experimental results for alachlor, atrazine and diuron. However, as can be seen in Table 2.1, the modelled direct photolysis fluence-based rate constants were similar to the experimental rate constants obtained.

2.3.2 Advanced oxidation processes

Experimental and model advanced oxidation of the selected pesticides was also tested using hydrogen peroxide and titanium dioxide (Table 2.1 and Figure 2.2).

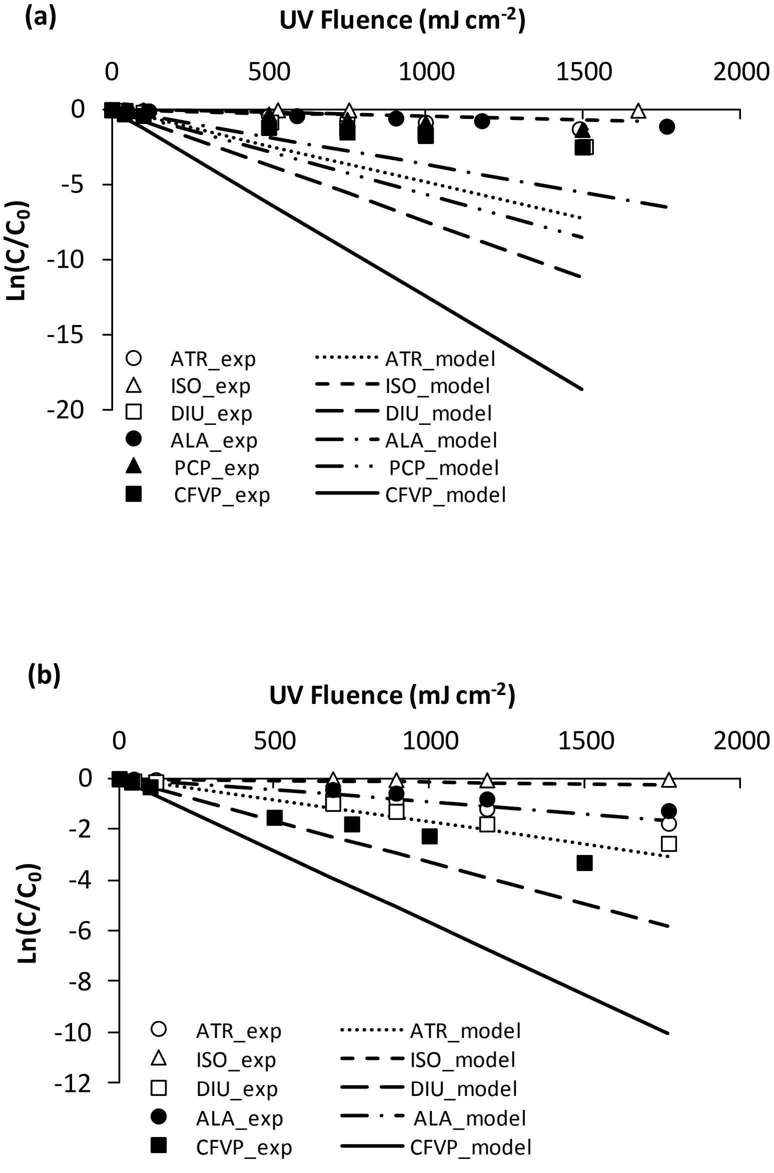


Figure 2.2 *Experimental (exp) and model low pressure photolysis of atrazine (ATR), isoproturon (ISO), diuron (DIU), alachlor (ALA), pentachlorophenol (PCP), and chlorfenvinphos (CFVP) in surface water using* ***(a)*** *40 mg L^{-1} hydrogen peroxide (H_2O_2) and* ***(b)*** *2.5 mg L^{-1} titanium dioxide (TiO_2); experimental values are represented by symbols with error bars whereas the lines show the model results.*

The experimental results represent, in these experiments, a combination of direct photolysis and AOP results and were modelled using Equations A.1 to A.11 presented in the Appendix A.2 (Sharpless and Linden 2003, Schwarzenbach *et al.* 1993, Klassen *et al.* 1994, Buxton *et al.* 1988, Huber *et al.* 2003, Neta and Dorfman 1968, Larson and Zepp 1988).

The LP/UV/H_2O_2 photolysis fluence-based rate constants obtained for atrazine, diuron, and alachlor slightly increased in surface water compared to laboratory grade water, similarly to what was observed in the LP/UV experiments (Table 2.1). Likewise, very similar time (Table A.7 in Appendix A.2) and fluence-based rate constants were obtained in both tested matrices for all the compounds except chlorfenvinphos that presented lower photolysis rate constants in the real water matrix. In the LP/UV/TiO_2 photolysis experiments similar time and fluence-based rate constants were obtained for all compounds in LGW and surface water. In addition, the exact same degradation trend was observed for the mixtures in the surface water matrix when comparing the LP/UV, the LP/UV/H_2O_2, and the LP/UV/TiO_2 results. The following order of degradation was observed: isoproturon, alachlor, atrazine, pentachlorophenol, diuron, and chlorfenvinphos. The results obtained when a mixture of the pesticides was subject to AOPs were again in agreement with the results obtained for the individual compounds.

Different concentrations of hydrogen peroxide (20, 60, 80, and 120 mg L^{-1}) and titanium dioxide (0.5, 5, and 10 mg L^{-1}) were tested but the results obtained showed no significant improvement in the photolysis rates obtained relatively to 40 mg L^{-1} H_2O_2 and 2.5 mg L^{-1} TiO_2.

The second-order rate constants for reaction of the micropollutants with OH radicals (Table 2.2) were determined by competition kinetics using pCBA as a reference compound (Elovitz and von Gunten 1999), according to Equations A.10 and A.11 detailed in Appendix A.2, and are similar to reported literature values.

The modelled results overestimated the AOP experimental values (Figure 2.2 and Table 2.1) especially when hydrogen peroxide was used to produce the OH radicals.

The model tested was also used to predict the degradation behaviour of the selected pesticides under different experimental conditions. The change in the direct photolysis time-based rate constants was therefore predicted at different distances from the UV source, z (Figure 2.3).

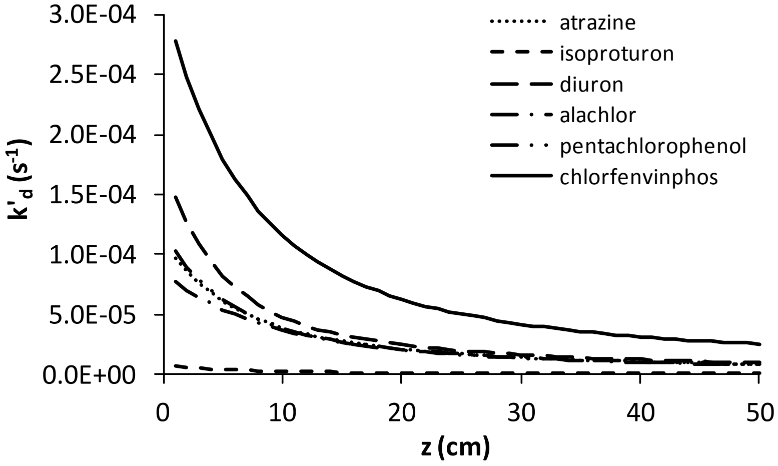


Figure 2.3 *Modelled time-based direct photolysis rate constants (k'$_d$).*

As expected, the distance to the UV source highly affects the degradation of the compounds at shorter pathlengths (up to approximately 20 cm), remaining almost constant at higher distances.

Figure 2.4 shows the AOPs time-based rate constants predicted for isoproturon, the most resilient compound, in surface water as a function of changes in the distance to the UV source and the hydrogen peroxide (Figure 2.4a) and titanium dioxide (Figure 2.4b) concentrations.

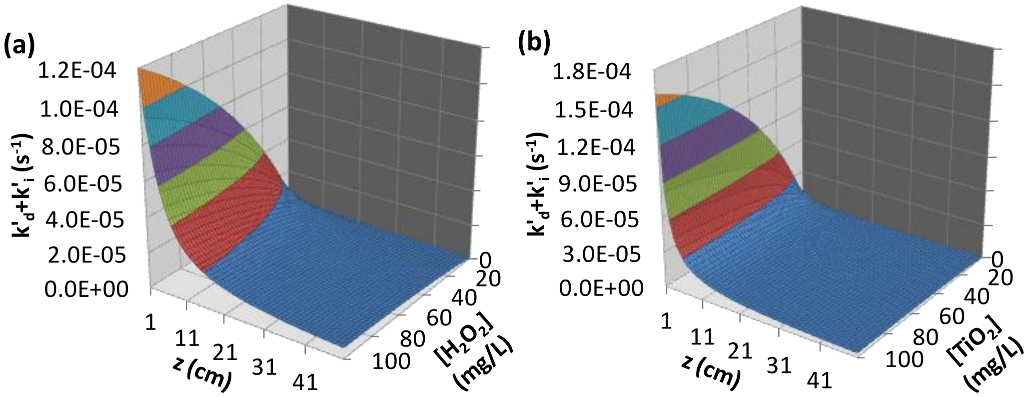


Figure 2.4 *Modelled time-based direct photolysis (k'_d) and AOPs (k'_i) rate constants obtained for isoproturon.*

At the distance to the source used in the collimated beam reactor (29 cm), the overall AOPs rate constants predicted were found to be fairly independent of the H_2O_2 and TiO_2 concentrations. However, under different experimental setups, the overall degradations rate constants obtained are likely to be more efficient using higher hydrogen peroxide and titanium dioxide concentrations at lower pathlengths.

Figure 2.5 presents a final comparison of the results obtained in the surface water matrix at a UV fluence of 1500 mJ cm^{-2} that was achieved after approximately 4 to 5 hours of degradation.

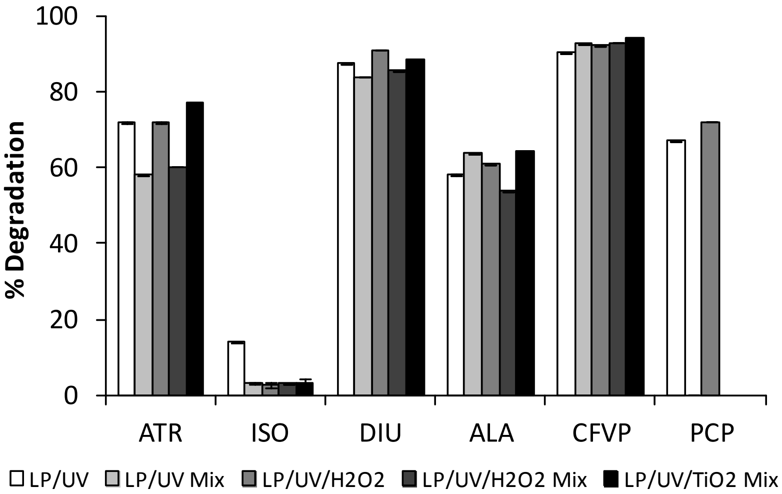


Figure 2.5 *LP/UV, LP/UV/H_2O_2, and LP/UV/TiO_2 percent degradation of atrazine (ATR), isoproturon (ISO), diuron (DIU), alachlor (ALA), chlorfenvinphos (CFVP), and pentachlorophenol (PCP) spiked in surface water as individual compounds and mixtures (Mix) using a UV fluence of 1500 mJ cm^{-2}.*

All the pesticides except isoproturon are expected to degrade significantly using LP/UV. Due to its extremely low quantum yield at 254 nm, isoproturon degradation using LP lamps will probably be very low even at higher UV fluences. Medium pressure lamps, that emit light at a broader range of wavelengths, have also proven to be inefficient for the degradation of isoproturon (Haque and Muneer 2003). To achieve isoproturon degradation, much higher H_2O_2 or TiO_2 concentrations would probably need to be used with a different reactor configuration that would allow shorter distances to the lamp (Figure 2.4).

The photolysis results obtained when mixtures of pesticides were degraded in surface water were extremely similar to the results obtained for the LP direct photolysis and AOPs using H_2O_2 of the individual compounds. The slight decrease in the degradation of the pesticides in most of the mixture samples may be due to competition between compounds and the OH radicals produced for the UV light. For all the selected pesticides, AOPs did not seem to enhance significantly their degradation using LP lamps. This tendency was already observed by other authors whenever direct photolysis efficiently degraded compounds such as alachlor (Wong and Chu 2003b), N-nitrosodimethylamine (Sharpless and Linden 2003), clofibric acid, and iohexol (Pereira *et al.* 2007b). Even though no significant enhancement of pesticides degradation was observed using AOPs, the two processes should be compared in terms of the levels of mineralisation achieved. Therefore, future studies should address if the LP photolysis of these priority pollutants enables accomplishment of mineralisation or if by-products may form as described by other authors for different light sources (Malato *et al.* 2003, Wong and Chu 2003a, Bianchi *et al.* 2006, Mills and Hoffmann 1993). Furthermore, the identified compounds may be different according to the UV systems used. The HPLC results obtained showed that as the UV fluence increased, the alachlor peak area decreased and a by-product peak was formed (Figure 2.6).

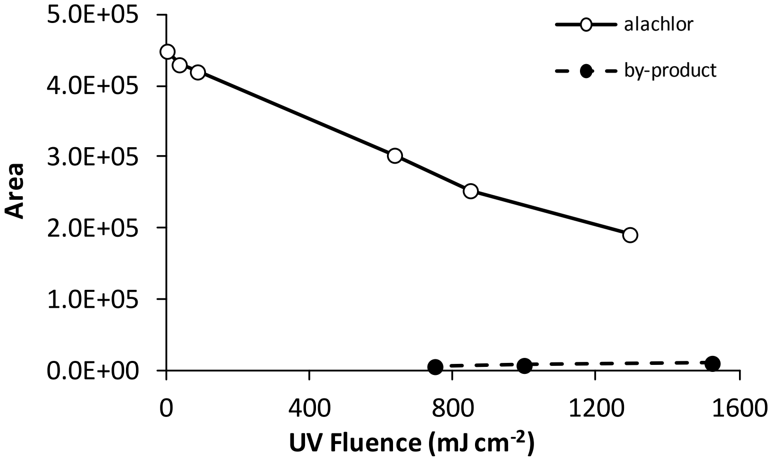


***Figure 2.6** Alachlor by-product detected by HPLC.*

This compound is probably similar in structure to alachlor since it was detected using the same HPLC chromatographic method. Even though this was the only by-product detected in our results, many other by-products may have been formed and could be identified using mass spectrometry analysis.

2.4 CONCLUSIONS

Besides being known as an extremely efficient process to inactivate microorganisms, the results of this work show that LP direct photolysis using high UV fluences may also prove to be very effective to ensure the degradation of several priority substances with different structures and it is therefore a promising technology for drinking water treatment.

ACKNOWLEDGEMENTS

We thank Cristina Leitão and Joana Ricardo for their technical assistance. This work was financed by Fundação para a Ciência e a Tecnologia (PTDC/AMB/66024/2006) and the European Economic Area Financial Mechanism, Empresa Portuguesa das Águas Livres, Município de Almada, and Instituto de Biologia Experimental e Tecnológica (through project PT0012). Vanessa J. Pereira acknowledges the financial support provided from Fundação para a Ciência e a Tecnologia through the grant SFRH/BPD/26990/2006. Empresa Portuguesa das Águas Livres is acknowledged for providing the real water matrices.

REFERENCES

Acero JL, Real FJ, Benitez EJ, Gonzalez A (2008) Oxidation of chlorfenvinphos in ultrapure and natural waters by ozonation and photochemical processes. *Water Res* 42: 3198-3206.

Balasubramanian G, Dionysiou DD, Suidan MT, Baudin I, Audin B, Laine JM (2004) Evaluating the activities of immobilised TiO_2 powder films for the photocatalytic degradation of organic contaminants in water. *Appl Catal B-Environ* 47: 73-84.

Beltran FJ, Ovejero G, Acedo B (1993) Oxidation of atrazine in water by ultraviolet radiation combined with hydrogen peroxide. *Water Res* 27: 1013-1021.

Benitez FJ, Acero JL, Real FJ, Garcia J (2003) Kinetics of photodegradation and ozonation of pentachlorophenol. *Chemosphere* 51: 651-662.

Benitez FJ, Real FJ, Acero JL, Garcia C (2006) Photochemical oxidation processes for the elimination of phenyl-urea herbicides in waters. *J Hazard Mater* 138: 278-287.

Bianchi CL, Pirola C, Ragaini V, Selli E (2006) Mechanism and efficiency of atrazine degradation under combined oxidation processes. *Appl Catal B-Environ* 64: 131-138.

Bolton J, Linden K (2003) Standardisation of methods for fluence (UV dose) determination in bench-scale UV experiments. *J Environ Eng-ASCE* 129: 209-215.

Buxton GV, Greenstock CL, Helman WP, Ross AB (1988) Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals (OH/O^-) in aqueous-solution. *J Phys Chem Ref Data* 17: 513-886.

Decision 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. Official Journal of the European Communities, L 331/1 (2001).

De Laat J, Gallard H, Ancelin S, Legube B (1999) Comparative study of the oxidation of atrazine and acetone by H_2O_2/UV, Fe(III)/UV, Fe(III)/H_2O_2/UV and Fe(II) or Fe(III)/H_2O_2. *Chemosphere* 39: 2693-2706.

Djebbar KE, Zertal A, Debbache N, Sehili T (2008) Comparison of Diuron degradation by direct UV photolysis and advanced oxidation processes. *J Environ Manage* 88: 1505-1512.

Elovitz MS, von Gunten U (1999) Hydroxyl radical/ozone ratios during ozonation processes. I. The Rct concept. *Ozone-Sci Eng* 21: 239-260.

Field JA, Reed RL, Sawyer TE, Griffith SM, Wigington PJ (2003) Diuron occurrence and distribution in soil and surface and groundwater associated with grass seed production. *J Environ Qual* 32: 171-179.

Haag W, Yao C (1992) Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ Sci Technol* 26: 1005-1013.

Haque MM, Muneer M (2003) Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspension of titanium dioxide. *J Environ Manage* 69: 169-176.

Hincapié M, Maldonado M, Oller I, Gernjak W, Sanchez-Perez J, Ballesteros M, Malato S (2005) Solar photocatalytic degradation and detoxification of EU priority substances. *Catal Today* 101: 203-210.

Huber MM, Canonica S, Park GY, Von Gunten U (2003) Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environ Sci Technol* 37: 1016-1024.

Klassen NV, Marchington D, McGowan HCE (1994) H_2O_2 Determination by the I_3^- method and by $KMNO_4$ titration. *Anal Chem* 66: 2921-2925.

Larson RA, Zepp RG (1988) Reactivity of the carbonate radical with aniline derivatives. *Environ Toxicol Chem* 7: 265-274

Linden K, Shin G, Faubert G, Cairns W, Sobsey M (2002) UV disinfection of *Giardia lamblia* cysts in water. *Environ Sci Technol* 36: 2519-2522.

Malato S, Caceres J, Fernandez-Alba A, Piedra L, Hernando M, Aguera A, Vial J (2003) Photocatalytic treatment of diuron by solar photocatalysis: Evaluation of main intermediates and toxicity. *Environ Sci Technol* 37: 2516-2524.

Mills G, Hoffmann M (1993) Photocatalytic degradation of pentachlorophenol on TiO_2 particles - identification of intermediates and mechanism of reaction. *Environ Sci Technol* 27: 1681-1689.

Neta P, Dorfman LM (1968) Pulse radiolysis studies XIII rate constants for reaction of hydroxyl radicals with aromatic compounds in aqueous solutions. *Adv Chem Ser* 81: 222-230.

Pereira VJ, Linden KG, Weinberg HS (2007a) Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. *Water Res* 41: 4413-4423.

Pereira VJ, Weinberg HS, Linden KG, Singer PC (2007b) UV degradation kinetics and modelling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm. *Environ Sci Technol* 41: 1682-1688.

Planas C, Puig A, Rivera J, Caixach J (2006) Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction - Estimation of the uncertainty of the analytical results. *J Chromatogr A* 1131: 242-252.

Rosenfeldt EJ, Linden KG, Canonica S, von Gunten U (2006) Comparison of the efficiency of $^{\bullet}OH$ radical formation during ozonation and the advanced oxidation processes O_3/H_2O_2 and UV/H_2O_2. *Water Res* 40: 3695-3704.

Schwarzenbach RP, Gschwend PM, Imboden DM, In Environmental organic chemistry. John Wiley & Sons Inc., New York (1993).

Sharpless C, Linden K (2003) Experimental and model comparisons of low- and medium-pressure Hg lamps for the direct and H_2O_2 assisted UV photodegradation of N-nitrosodimethylamine in simulated drinking water. *Environ Sci Technol* 37: 1933-1940.

Song W, Ravindran V, Pirbazari M (2008) Process optimisation using a kinetic model for the ultraviolet radiation-hydrogen peroxide decomposition of natural and synthetic organic compounds in groundwater. *Chem Eng Sci* 63: 3249-3270.

US EPA (2009) National primary drinking water regulations. Available online: http://water.epa.gov/drink/contaminants/basicinformation/alachlor.cfm.

Vollmuth S, Zajc A, Niessner R (1994) Formation of polychlorinated dibenzo-P-dioxins and polychlorinated dibenzofurans during the photolysis of pentachlorophenol-containing water. *Environ Sci Technol* 28: 1145-1149.

von Gunten U (2003) Ozonation of drinking water: Part I Oxidation kinetics and product formation. *Water Res* 37: 1443-1467.

Wong C, Chu W (2003a) The hydrogen peroxide-assisted photocatalytic degradation of alachlor in TiO_2 suspensions. *Environ Sci Technol* 37: 2310-2316.

Wong C, Chu W (2003b) The direct photolysis and photocatalytic degradation of alachlor at different TiO_2 and UV sources. *Chemosphere* 50: 981-987.

CHAPTER 3

Nanofiltration of hormones and pesticides in different real drinking water sources

Published in: Separation and Purification Technology

Sanches S, Penetra A, Rodrigues A, Ferreira E, Cardoso VV, Benoliel MJ, Barreto Crespo MT, Pereira VJ, Crespo JG (2012) Nanofiltration of hormones and pesticides in different real drinking water sources. *Sep Purif Technol* 94: 44-53.

Sandra Sanches was involved in all the experimental work presented in this chapter, except for: 1) the quantification of the target pesticides and hormones in the samples from nanofiltration experiments that was performed by Ana Penetra, Alexandre Rodrigues, and Vitor Cardoso at Empresa Portuguesa das Águas Livres, Portugal; 2) characterisation of the raw and ultrafiltered water samples that was carried out under the coordination and direction of Elisabete Ferreira and Maria João Benoliel, respectively, at Laboratório Central of EPAL, Portugal. Vanessa Pereira, João Crespo, and Teresa Crespo supervised all the experimental work carried out.

CONTENTS

ABSTRACT

This study addresses the efficiency of nanofiltration to remove different pesticides and hormones from different real water sources (surface water and groundwater) and the effect of the ionic composition of different water sources on the rejection of the target micropollutants. Ultrafiltration was performed prior to the nanofiltration process to remove particulate and large colloidal organic matter, that interfere in the rejection of micropollutants during nanofiltration, without affecting the concentration of ionic species and natural organic matter present in the water. The other aim of this study was to understand the role of adsorption on the rejection of the solutes selected, which was tested by conducting membrane pre-adsorption experiments using these micropollutants under static and dynamic conditions.

High percent rejections (67.4-99.9%) were obtained for the pesticides and hormones, often independently of the water composition. Size exclusion and hydrophobic interactions were found to highly influence the rejections obtained. The lower rejections (57.5-83.5%) obtained for pentachlorophenol could be explained by its increased solubility at the waters' pH. The overall nanofiltration efficiency to remove the selected compounds was not found to be considerably affected by the pre-adsorption of the compounds on the membrane under static and dynamic conditions, except for 17α-ethinylestradiol, estrone, and estriol in surface water.

3.1 INTRODUCTION

The occurrence of several xenobiotics like hormones, pesticides, polycyclic aromatic hydrocarbons, pharmaceuticals, and personal care products in drinking water sources has raised public concern in the last decades. Pesticides such as atrazine, alachlor, and pentachlorophenol are listed as priority pollutants by the European Union (Decision 2455/2001/EC) due to their high toxicity, persistence in the environment, and bioaccumulation potential. These organic compounds are used for agriculture purposes and wood-preservation and have been detected in groundwater and surface water at concentrations in the range of 2-13000 ng L^{-1} (Planas *et al.* 2006, Field *et al.* 2003). The hormones 17β-estradiol, 17α-ethinylestradiol, estrone, estriol, and progesterone have been also found in surface waters at ng L^{-1} levels (Snyder *et al.* 1999, Jardim *et al.* 2012). Natural hormones such as estrone and 17β-estradiol as well as the synthetic hormone 17α-ethinylestradiol present a very high endocrine disrupting potential (Johnson and Sumpter 2001, Ternes *et al.* 1999a, Ternes *et al.* 1999b). These three hormones have been reported to cause feminisation in male fish after exposure to levels as low as 1 ng L^{-1} during 21 days (Kolodziej *et al.* 2004, Routledge *et al.* 1998). Since the occurrence of pesticides and hormones in water sources have been linked to adverse effects in the aquatic environment and towards humans, further studies are needed to test the ability of different processes to cope with increasingly stringent regulations. In the last 20 years, nanofiltration (NF) has been described as very efficient for the removal of several xenobiotics (Van der Bruggen and Vandecasteele 2003, Bellona *et al.* 2004).

The rejection of organic compounds by nanofiltration membranes may be influenced by several mechanisms such as size exclusion, electrostatic interactions, and hydrophobic interactions, which may also lead to solute adsorption at the membrane surface. In particular, the different ion species present in the water may impact the removal of organic micropollutants by changing the interactions between the membrane and the organic compounds by “partially screening” the charge of the molecules functional groups (Nghiem *et al.* 2002a, Schäfer *et al.* 2003). Sodium, calcium, and bicarbonate were found to decrease the removal of organic molecules (Nghiem *et al.* 2002a, Devitt *et al.* 1998), although this behaviour may depend on the ion concentration and membrane type.

Several studies mentioned above, addressing the removal of the hormones using different nanofiltration membranes and experimental setups, reported that rejections are essentially related to adsorptive interactions of these molecules with the membrane and size exclusion mechanisms (Schäfer *et al.* 2003, Comerton *et al.* 2008, Nghiem *et al.* 2004, Bellona and Drewes 2007).

In a previous study, the potential of the nanofiltration membrane Desal 5DK for the removal of atrazine, alachlor, and pentachlorophenol from different natural water sources with very diverse compositions (groundwater, spring water, surface water, and surface water collected after sedimentation) was addressed using a dead-end filtration system (Sanches *et al.* 2011). Rejection values reported in that study are different from those reported by other authors using different nanofiltration systems (Boussahel *et al.* 2002, Yangali-Quintanilla *et al.* 2009). Very different rejection values can be expected depending on the fluid dynamic conditions. Therefore, it is very important to compare results generated by similar systems and under similar conditions because it is possible to obtain large variations in the rejection of one solute by varying the convective transport towards the membrane and the shear rate at the membrane surface during nanofiltration.

The adsorption of organic compounds on the membrane has been considered an extremely important removal mechanism. During the first stages of nanofiltration some compounds are strongly adsorbed on the membrane and therefore, adsorptive interactions are the main mechanism of rejection (Schäfer *et al.* 2003, Nghiem *et al.*

2004). However, as filtration proceeds, a decrease in rejection has been observed probably due to membrane site saturation since the adsorbed compounds may diffuse across the membrane once the equilibrium is accomplished. Therefore, several authors have suggested that the rejection of organic compounds should be determined in long term operations after the saturation of the membrane, to avoid an overestimation of nanofiltration efficiency (Schäfer *et al.* 2003, Nghiem *et al.* 2004, Bellona and Drewes 2007, Yangali-Quintanilla *et al.* 2009, Kimura *et al.* 2003). Further research is therefore necessary to address membrane efficiency under extended membrane saturation conditions using well characterised matrices.

Studies on the removal of micropollutants by nanofiltration have mainly been conducted in synthetic water matrices. Although these studies may give insights on the impact of specific water components in the removal of target micropollutants, further research addressing the performance of nanofiltration in well characterised real drinking water sources is necessary. Real water matrices are complex and therefore, the removal of micropollutants results from the combination of interactions between the micropollutants, the water components, and the membrane.

This study has two main objectives. The first one is the assessment of the effect of the composition of different well characterised real water matrices in terms of the concentration of different ion species. The water sources were subject to ultrafiltration prior to the nanofiltration treatment to remove particulate and large colloidal organic matter that interfere in the rejection of micropollutants during nanofiltration but will not affect considerably the water composition in terms of the concentration of ionic species and soluble matter. This approach therefore allows focusing on the evaluation of the effect of different ionic compounds and total organic carbon in the rejection of the selected micropollutants. The other focus of the present study is the comprehension of the adsorption role on the rejection of selected different micropollutants. The effects of static and dynamic pre-adsorption in the nanofiltration removal of pesticides and hormones from different natural water sources were tested.

This study was performed with a careful design of control experiments with the aim of assessing the stability of the compounds and the inertness of the system during long term operation procedures.

Nanofiltration efficiency is evaluated in terms of the potential to remove the target pesticides (atrazine, alachlor, and pentachlorophenol) and hormones (estrone, 17β-estradiol, 17α-ethinylestradiol, progesterone, and estriol) and relevant water components responsible for alkalinity, conductivity, total dissolved solids, and several ions from groundwater and surface water. Rejections obtained are also discussed in terms of the different structures and physico-chemical properties of the selected organic compounds as well as water matrices composition. The main rejection mechanisms are proposed.

3.2 MATERIALS AND METHODS

3.2.1 Chemical reagents and water matrices

The pesticides and hormones used were purchased as solutions or solids of the highest grade commercially available (higher than 98.9%, Sigma Aldrich, Germany).

High performance liquid chromatography grade acetonitrile and methanol (Fisher, UK) were used for the chromatographic analysis of the pesticides and the hormones and for the preparation of stock solutions. Milli-Q water used in the chromatographic analysis was produced by a Milli-Q water system (Millipore, CA, USA).

The natural water matrices used in the nanofiltration experiments, groundwater and surface water, were supplied by the drinking water utility Empresa Portuguesa das Águas Livres, S.A., that treats and supplies drinking water to approximately 2.8 million people in the region of Lisbon, Portugal. Surface water was collected in the abstraction zone of Tagus river in Valada do Ribatejo and groundwater was collected from a well located in the region of Alenquer. The real water samples were collected in 10 L bottles, characterised, and stored at 5 ± 3 °C until used.

3.2.2 Work plan and experimental procedure

Figure 3.1 presents a schematic representation of the experiments conducted in this study.

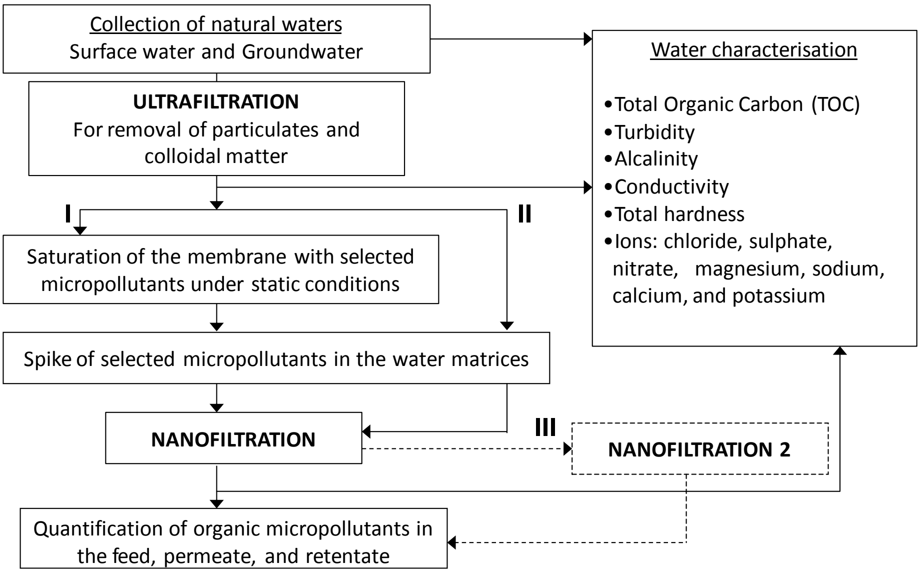


Figure 3.1 *Schematic representation of experimental procedure (---- experiments that were only conducted with the selected hormones).*

The water matrices studied (surface water and groundwater) were collected and immediately characterised in terms of the following parameters: pH, total organic carbon, total dissolved solids, turbidity, alkalinity, conductivity, total hardness, and several ionic components (chloride, sulphate, nitrate, magnesium, sodium, calcium, and potassium). These water matrices were ultrafiltered to remove particulates and colloidal matter - which may affect the rejection of the organic compounds during nanofiltration - while preserving the concentration of ions and soluble organic matter in the real waters. After ultrafiltration, the permeate was also characterised in terms of the parameters mentioned above to assess the changes in matrix composition. Nanofiltration experiments were conducted under different experimental conditions: with and without adsorption of the target organic micropollutants on the membrane prior to the nanofiltration process. In a set of experiments (Figure 3.1 - I), the membranes were previously placed in contact with solutions with the same composition as the solutions fed to the nanofiltration cell (ultrafiltered water permeates spiked with the selected organic compounds). The membranes were immersed in stirred solutions to promote the adsorption of the compounds on the membrane until a constant concentration in the bulk solution was achieved (Figure 3.1 - I). In these experiments, the adsorption of the compounds on the membrane was accomplished without permeation and these are therefore defined here as adsorption experiments conducted under static conditions.

In another set of experiments, the membranes used in the nanofiltration were not subject to a previous contact with the target organic contaminants (Figure 3.1 – II).

For the nanofiltration experiments, the target pesticides and hormones were spiked in the ultrafiltered water matrices and fed to the system. After nanofiltration, the spiked micropollutants were quantified in the feed, permeate, and retentate. The permeate was also characterised in terms of the physical-chemical parameters mentioned above.

The rejection of hormones was also tested after adsorption on the membrane under both static and dynamic conditions. Dynamic adsorption is defined here as adsorption that occurs during nanofiltration. A second nanofiltration (Nanofiltration 2 in Figure 3.1 - III) was therefore performed using the same membrane and a fresh feed solution.

3.2.2.1 Ultrafiltration experiments

The ultrafiltration of the natural water matrices was conducted using a Micro Carbosep® module associated to a positive displacement pump (Ismatec, Germany). A tubular membrane with an activated coating of zirconium oxide and titanium dioxide, with a molecular weight cut-off of 50 kDa, and an effective membrane area of 108 cm^2 (Orelis, France) was used. The ultrafiltration process was performed at 1 bar and the mean clean water permeability determined for this membrane was 69.4 ± 3.1 $L\ h^{-1}\ bar^{-1}\ m^{-2}$, at 21 ± 2 °C.

3.2.2.2 Static adsorption experiments

In the adsorption experiments conducted under static conditions, membranes were immersed in stirred solutions (200 mL of water matrices spiked with micropollutants at 500 $\mu g\ L^{-1}$) at room temperature (21 ± 2 °C). The adsorption of the compounds under these conditions was followed by taking samples (200 μL) over time until a constant concentration of the compounds in the bulk solution was achieved. After this procedure, membranes were placed in the cross-flow cell and the nanofiltration experiments were performed (as detailed in section 3.2.2.3).

During the static adsorption experiments, 100 mL of the spiked solutions were tested as controls since these experiments took several days and there was the risk of loss of the target compounds by degradation. The control samples were kept under the same experimental conditions as the solutions used for the static adsorption experiments - stirred at room temperature and in the dark – except for the absence of the membrane. Control samples (200 μL) were taken each time a sample was taken from the solution containing the membrane. The variation of the concentration of the target compounds in the control solution over time presented a variation below 9.5% for all the compounds except progesterone (45%). The concentration values obtained for the samples spiked with progesterone were therefore excluded from the discussion of the results obtained in the static adsorption experiments.

3.2.2.3 Nanofiltration experiments

The evaluation of nanofiltration efficiency to remove the selected organic compounds and several legislated physico–chemical parameters from different natural water sources was conducted in a laboratory scale unit shown schematically in Figure 3.2.

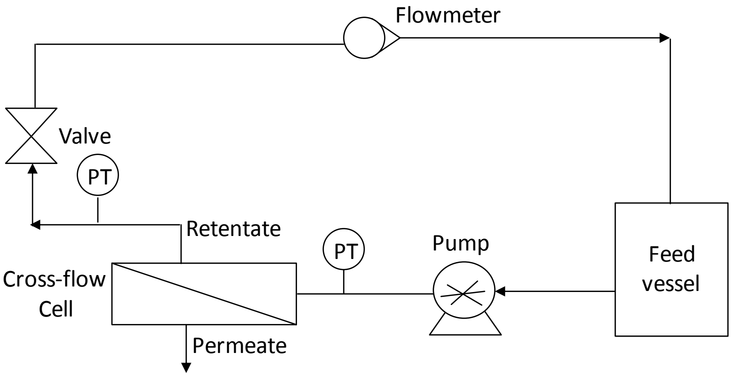


Figure 3.2 *Schematic representation of the experimental setup.*

This lab-scale unit consisted of two vessels for the feed and the permeate, a stainless steel cross-flow cell, a diaphragm pump (Hydra-cell G-13, Wanner Engineering, USA), as well a brass ball valve with an electric actuator (J2, J+JAutomation, UK) that allowed the pressure adjustment in the system. Two transmitters (8864, Trafag, Switzerland) were placed before and after the cross-flow cell to measure the inlet and outlet pressure and the temperature of the solution circulating in the system. The stainless steel cross-flow cell was designed and constructed expressly for these studies. This filtration cell was used with a 15 cm^2 flat-sheet Desal 5DK membrane (GE Osmonics, USA) that was placed between two rectangular cross-section channels (feed and permeate) measuring 150 mm x 10 mm x 1 mm (length x wide x height) each. Desal 5DK is a thin film composite membrane with a polysulphone support layer. This membrane presents a molecular weight cut-off of 150-300 Da (Boussahel *et al.* 2002) and is negatively charged at neutral pH (GE Osmonics, USA).

Before nanofiltration experiments, Desal 5DK membranes were compacted by filtration of laboratory grade water at 10 bar until a constant flux was obtained (approximately after 3 h of compaction). The deionised water permeability was then determined as 3.90 ± 0.21 L h^{-1} bar^{-1} m^{-2}, at 25 ± 2 °C.

Nanofiltration experiments using the spiked water matrices were conducted at 10 bar with a system recovery of 0.03% (v/v), defined as Q_p/Q_f (permeate flow rate/feed flow rate). The temperature in the cross-flow unit was controlled at 25 ± 2°C using a thermostatic bath. The retentate was continuously recirculated to the feed vessel during filtration while the permeate was collected in a different vessel for analysis.

Pesticides and hormones were grouped and spiked in the surface water and groundwater matrices according to their common analytical methods. The concentrations of the compounds in the feed solutions were as low as possible to mimic their levels in the environment, but set according to the detection limits of the respective analytical methods. Solutions containing pentachlorophenol (75 $\mu g\ L^{-1}$), solutions containing a mixture of atrazine and alachlor (150 $\mu g\ L^{-1}$ each), and solutions containing a mixture of all the selected hormones (150 $\mu g\ L^{-1}$ each) were prepared and individually assessed. The compounds were spiked in the water matrices using stock solutions prepared in methanol at very high concentrations to minimise the volume of methanol present in the water solutions. The percentage of methanol present in the water samples was always lower than 0.03% (v/v). Even though the concentrations used are slightly higher than the reported levels in the water sources, significant differences in their removal at these concentrations comparatively to the occurrence concentrations are not expected. Schäfer *et al.* (2003) studied the rejection of estrone at a range of concentrations between 1 and 1000 ng L^{-1} and concluded that the differences in the rejection of this molecule are not significant at different concentrations. Moreover, another study addressing the rejection of pesticides using higher concentrations ranging between 100 and 500 $\mu g\ L^{-1}$ (Van der Bruggen *et al.* 1998) also support these results.

Feed solutions were stored in amber bottles during all nanofiltration experiments to avoid possible degradation of the compounds due to light absorption. The nanofiltration experiments that assessed the removal of pentachlorophenol and hormones (3.0-3.5 L) were conducted during approximately 44-67 h, while the solutions containing atrazine and alachlor (approximately 4.5 L) were filtered during approximately 93h. The volume of feed solution filtered varied according to the permeate volume needed for analysis, since the analytical methods were different for the different compounds (as described in Appendix A.1).

Since nanofiltration experiments were long, controls were monitored in order to evaluate possible losses of the organic compounds due to degradation, evaporation, or adsorption to the vessels walls that could lead to an overestimation of nanofiltration efficiency. A volume of 100 mL of the feed solutions were used as control. In the beginning of each experiment, half of this volume (initial control) was taken to an amber flask and was immediately acidified to pH 2-3 with sulphuric acid to prevent the degradation of organic compounds that may occur due to the presence of microorganisms in the water sources. This solution was then stored at 5 ± 3 °C until analysis. The remaining 50 mL (final control) were transferred to another amber flask and kept during the nanofiltration procedure at the same experimental conditions as the nanofiltration solution in terms of temperature and light exposure: in the same thermostatic bath and in the dark. The final control was only acidified with sulphuric acid at the end of the filtration process and was then also stored at 5 ± 3 °C until analysis. Differences in the concentration of the micropollutants in the beginning and in the end of the experiments were not very significant; the percent changes obtained were always below 8% for all the compounds except progesterone (below 13%).

An additional control experiment was conducted to evaluate the potential loss of the compounds due to their adsorption to the system tubing and feed vessel. This experiment consisted in the circulation of a solution similar to the feed in the system, under identical experimental conditions as nanofiltration, but in the absence of a membrane. The percent change observed in the concentration of all the pesticides and hormones except progesterone and alachlor was below 9%. For alachlor and progesterone, a percent change of 14 and 34% was obtained, respectively, showing that these compounds (especially progesterone) may be retained in the system. The percent change obtained for progesterone in this control sample is high and similar to the percent change obtained for the control performed during the static adsorption experiments (section 3.2.2.2). The percent adsorption calculation for this compound was therefore excluded from the Results and Discussion section.

After nanofiltration, samples of feed, permeate, and retentate were acidified at pH 2-3 with sulphuric acid and stored in brown glass bottles at 5 ± 3 °C prior to analysis of the target pesticides and hormones, to avoid the degradation of the compounds. A

---

fraction of permeate was not acidified and was characterised in terms of the previously described organic and inorganic parameters. The pH of the samples was measured before and after acidification.

The apparent rejection (R_{app}) of the selected compounds was determined using Equation 3.1.

$$R_{app}(\%) = 100 \times \left(1 - \frac{C_p}{C_f} \right) \tag{3.1}$$

where C_p and C_f are the concentrations of a given compound in the permeate and feed, respectively.

The percentage of rejection due to adsorption on the membrane (A) was determined using Equation 3.2:

$$A(\%) = 100 \times \left(1 - \frac{C_p V_p + C_r V_r}{C_f V_f} \right) \tag{3.2}$$

where C_p, C_r, and C_f are the concentration of a given compound in the permeate, retentate, and feed, respectively, whereas V_p, V_r, and V_f are the volume of permeate, retentate, and feed, respectively.

3.2.3 Analytical Methods

3.2.3.1 Characterisation of natural water matrices

The natural water matrices were characterised in terms of pH, TOC, turbidity, alkalinity, conductivity, total hardness, and several ionic components (chloride, sulphate, nitrate, magnesium, sodium, calcium, and potassium). The pH was determined by an electrometric method (Standard Method 4500-H+B 1995), total organic carbon by persulfate-ultraviolet oxidation (EN1484 1997), turbidity by a nephelometric method (NPEN27027 1997), alkalinity by a titration method (Standard Method 2320B 1995), conductivity by conductimetry (Standard Method 2510-B 1995), and total hardness by a calculation method (Standard Method 2340-B 1995). The concentration of the ions was determined by ionic chromatography (chloride and sulphate), molecular absorption spectrometry (nitrate), as well as digestion and inductively coupled plasma spectroscopy (magnesium, sodium, calcium, and potassium).

3.2.3.2 Detection and quantification of target micropollutants

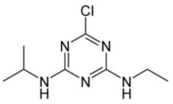
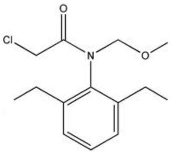
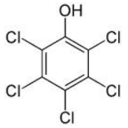
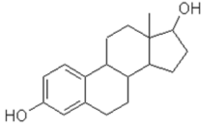
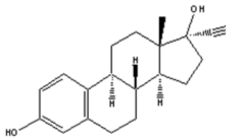
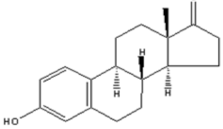
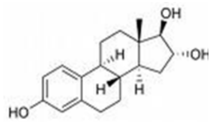
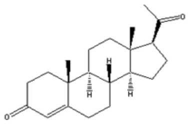
Analytical methods used to determine the concentrations of the studied organic micropollutants varied according to the concentrations of the analytes in the water samples. Therefore, the concentration of the hormones and pesticides during the experiments of adsorption under static conditions were followed by direct HPLC injection while the samples from nanofiltration experiments were subject to concentration prior to analysis due to the lower concentrations expected in the permeate samples. Briefly, samples from nanofiltration containing atrazine and alachlor were concentrated by solid phase extraction (SPE) and analysed by gas chromatography (GC) with mass spectrometry (MS) detection; samples containing the analyte pentachlorophenol were concentrated by microextraction and analysed by GC with electron capture detection; samples containing the hormones were concentrated by SPE and analysed by ultra-high-speed liquid chromatography (UPLC).

A detailed description of the analytical methods used is provided in Appendix A.1.

3.3 RESULTS AND DISCUSSION

The organic micropollutants selected for this study present very different structures and physico-chemical properties such as molecular weight, log K_{ow}, water solubility (W_s), dipole moment (μ), and pK_a that are detailed in Table 3.1.

Table 3.1 *Structure and physico-chemical properties of the selected pesticides and hormones.*

Compound	**Molecular formula**	**MW (Da)**	**log K_{ow}**	**W_s (mg L^{-1})**	**μ (D)**	**pK_a**
 Atrazine	$C_8H_{14}ClN_5$	215.7	2.56[1]	34.70[2]	3.40[3]	1.70[3]
 Alachlor	$C_{14}H_{20}ClNO_2$	269.8	3.52[4]	240[2]	3.60[4]	0.62[5]
 Pentachlorophenol	C_6HCl_5O	266.3	5.12[6]	14.00[2]	1.90[7]	4.70[8]
 17β-Estradiol	$C_{18}H_{24}O_2$	272.4	4.01[9]	3.60[2]	2.75[4]	10.40[9]
 17α-Ethinylestradiol	$C_{20}H_{24}O_2$	296.4	3.67[9]	11.30[2]	2.64[4]	10.40[9]
 Estrone	$C_{18}H_{22}O_2$	270.4	3.13[9]	30.00[2]	2.04[4]	10.40[9]
 Estriol	$C_{18}H_{24}O_3$	288.4	2.45[9]	441[2]	3.22[4]	10.40[9]
 Progesterone	$C_{21}H_{30}O_2$	314.5	3.87[9]	8.81[2]	2.70[10]	*

*no dissociation; **[1]** Schwarzenbach *et al.* 1993 **[2]** Meylan and Howard 1994 **[3]** Yangali-Quintanilla *et al.* 2009 **[4]** Comerton *et al.* 2007 **[5]** Pesticide Properties DataBase **[6]** Krieger *et al.* 2001 **[7]** Lu *et al.* 2005 **[8]** Cessna *et al.* 1978 **[9]** Snyder *et al.* 2007 **[10]** Gershfeld *et al.* 1971.

3.3.1 Ultrafiltration experiments

The natural water matrices used in this study were ultrafiltered prior to nanofiltration. The ultrafiltration process aimed to remove particulate and large colloidal organic matter, without affecting considerably the content in soluble matter and ions, in order to evaluate the contribution of each water matrix composition in the rejection of the selected compounds. Table 3.2 presents the characterisation of the two water matrices used after the ultrafiltration process. These analyses were performed by EPAL, Portugal, using accredited methods (ISO/IEC 17025: 2005).

Table 3.2 *Characterisation of groundwater and surface water after ultrafiltration.*

Parameter	**Groundwater**	**Surface Water**
pH	8.2	7.8
Turbidity (NTU)	< 0.40 ± 0.03	< 0.40 ± 0.03
Alkalinity (mg L^{-1} $CaCO_3$)	232 ± 19	57.9 ± 4.6
Conductivity (μS cm^{-1} 20 °C)	511 ± 26	357 ± 18
Total dissolved solids (mg L^{-1})	366	256
Nitrate (mg L^{-1})	3.12 ± 0.04	4.43 ± 0.53
Chloride (mg L^{-1})	34.6 ± 2.8	38.3 ± 3.1
Sulphate (mg L^{-1})	22.4 ± 1.8	nd
Total Hardness (mg L^{-1} $CaCO_3$)	259 ± 31	113 ± 14
Total Organic Carbon (mg L^{-1})	<1.00 ± 0.19	3.52 ± 0.35
Calcium (mg L^{-1})	87.0 ± 10.0	28.5 ± 3.4
Magnesium (mg L^{-1})	10.2 ± 1.5	10.1 ± 1.5
Sodium (mg L^{-1})	20.6 ± 2.1	29.3 ± 2.9
Potassium (mg L^{-1})	<1.00 ± 0.10	2.79 ± 0.28

nd - not determined

The two natural water matrices were very different in terms of organic and inorganic composition. Groundwater presented the higher levels of alkalinity, conductivity, total dissolved solids, and total hardness while surface water showed higher turbidity and TOC. After ultrafiltration, considerable differences were not detected in the groundwater matrix composition and only turbidity decreased in the surface water, which was the aim of the ultrafiltration process. The considerable decrease of turbidity in the surface water (from 2.6 NTU to levels below the detection limit of 0.4 NTU), without affecting the levels of TOC, demonstrates that the natural organic matter present in this matrix was maintained as expected. It is also important to mention that the concentration of the ionic species determined in the water sources studied was not affected by this ultrafiltration step. This approach allows the study to focus on the effect of the water composition and removes particles and colloids with high dimensions that may influence the efficiency of water treatment.

The conventional treatment of surface water in water treatment utilities often includes coagulation, flocculation, sedimentation, and sand filtration. After ultrafiltration, the surface water matrix presented an overall composition similar to the composition of the water obtained after conventional sedimentation and sand filtration processes (results not shown). Indeed, very low percent differences were obtained when the ultrafiltered surface water was compared with the water obtained after sedimentation (0.03-0.41%) and sand filtration (0.04-1.56%), in terms of several water quality indicator parameters (turbidity, conductivity, total hardness, total organic carbon, nitrate, calcium, magnesium, sodium, and potassium).

3.3.2 Static adsorption experiments

In the static adsorption experiments (adsorption on the membrane without permeation), the adsorption was followed over time until the concentration of the compounds in the bulk solution was constant. The results obtained for the adsorption of all compounds on the membrane as well as the time needed to achieve equilibrium, in the two matrices tested, are shown in Table 3.3.

Table 3.3 *Adsorption of the selected pesticides and hormones on the membrane during the experiments under static conditions and time (t) needed to achieve saturation of the membrane in the groundwater (GW) and surface water (SW) matrices.*

Source Water	**Compound**	**Adsorbed mass (μg)**	**Adsorbed molar mass (μmol)**	**Adsorbed mass/Area (μg cm^{-2})**	**Adsorbed molar mass/Area (10^{-3} μmol cm^{-2})**	**t (h)**
GW	Atrazine	37.9 ± 1.9	0.176 ± 0.010	0.9	4.0	95.4
	Alachlor	23.0 ± 1.1	0.085 ± 0.006	0.5	1.9	95.4
	Pentachlorophenol	13.0 ± 1.0	0.049 ± 0.003	0.3	1.1	27.5
	17β-Estradiol	20.2 ± 1.9	0.074 ± 0.005	0.5	1.7	101
	17α-Ethinylestradiol	29.9 ± 1.6	0.101 ± 0.007	0.7	2.3	98.4
	Estrone	23.9 ± 1.8	0.088 ± 0.006	0.5	2.0	101
	Estriol	16.8 ± 1.6	0.058 ± 0.004	0.4	1.3	123
SW	Atrazine	31.7 ± 4.6	0.147 ± 0.010	0.7	3.4	168
	Alachlor	25.2 ± 0.7	0.093 ± 0.006	0.6	2.1	149
	Pentachlorophenol	13.5 ± 0.7	0.051 ± 0.003	0.3	1.2	47.6
	17β-Estradiol	35.2 ± 1.6	0.129 ± 0.009	0.8	3.0	149
	17α-Ethinylestradiol	45.1 ± 3.0	0.152 ± 0.010	1.0	3.5	144
	Estrone	65.0 ± 4.6	0.241 ± 0.016	1.5	5.5	172
	Estriol	19.9 ± 1.9	0.069 ± 0.005	0.5	1.6	144

The adsorption behaviour of the organic compounds was different in terms of the adsorbed mass and the time needed to achieve equilibrium. However, in general, the adsorbed mass increased with the time needed to achieve equilibrium and the time needed to achieve equilibrium increased with the solubility of the target compounds. As expected, the most hydrophobic compounds (with higher log K_{ow} values and lower solubility) showed higher affinity to the membrane and achieved the equilibrium concentrations sooner. As a general trend, the mass adsorbed decreased with the decrease of log K_{ow}, for all the target compounds except pentachlorophenol and atrazine.

Differences were obtained in the adsorption of the compounds on the membrane under static conditions in groundwater and surface water. Generally, the time needed to achieve equilibrium as well as the level of adsorption of the compounds on the membrane was higher in the surface water matrix (Table 3.3). The fact that the adsorption equilibrium took longer in the surface water may be related to the competition between the selected compounds and the natural organic matter present in this matrix for the membrane adsorption sites or due to possible interactions between the natural organic matter and the target analytes. Comerton *et al.* (2007) also observed differences in the adsorption of several organic compounds (including alachlor, estriol, 17β-estradiol, 17α-ethinylestradiol, and estrone) in different water matrices: adsorption was generally higher in a surface water matrix comparatively to milli-Q water. In that study a correlation was also found in certain cases between adsorption to the membrane and the log K_{ow}. However, the adsorption of the organic compounds on different membranes (UE10, NF270, TS80, X20) was different depending on the membrane used, which supports the idea that other properties and interactions between the compounds and the membrane should also be considered. In fact, as previously reported in an earlier study of Schäfer *et al.*

(2003), water matrix components as well as electrostatic interactions, such as hydrogen bonding, are expected to play important roles in adsorption.

Although a direct linear correlation between adsorption and the hydrophobicity of all the compounds was not found, it was interesting to observe that estriol (log K_{ow}=2.45), which is the less hydrophobic compound, was one of the molecules that adsorbed to a lower extent to the membrane. Pentachlorophenol was the other compound that adsorbed the least to the membrane although it was the most hydrophobic compound selected (log K_{ow}=5.12). This behaviour could be explained by a combined effect of an increased solubility of the compound and higher charge repulsion between the molecule and the negatively charged membrane since, at the water pH, pentachlorophenol will be predominantly present in the deprotonated form (Comerton *et al.* 2007, Nghiem *et al.* 2005). Given the dissociation constant of pentachlorophenol and the pH values measured in the tested natural waters (higher than 7) the deprotonated form is expected to be present at levels higher than 99.45%. Kaiser and Valdmanis (1982) reported that octanol/water partition coefficient is expected to decrease significantly with the increase in pH. Likewise, Stapleton *et al.* (1994) reported that the total pentachlorophenol sorption is limited by the maximum sorption of the deprotonated form at high pH values. Between the pH values of 4 and 8.5, Stapleton *et al.* (1994) reported a decrease in sorption by three times and an increase in solubility by three orders of magnitude.

The establishment of direct correlations between adsorption and the properties of the target micropollutants or matrix components was not fully achieved since the interactions taking place are complex and therefore concurrent effects are expected to occur. Further analysis using a multivariable statistical approach may be useful.

3.3.3 Nanofiltration experiments

Nanofiltration experiments addressing the removal of the selected pesticides and hormones were conducted using different types of water (surface water and groundwater). The variation coefficient (standard deviation divided by the average expressed as a percentage) of the permeate flux observed during nanofiltration experiments was always lower than 10%. These results show that ultrafiltration of the water prior to nanofiltration effectively ensures a lower flux decline during nanofiltration. Therefore, the inclusion of an ultrafiltration process prior to nanofiltration will allow the removal of colloidal and particulate matter as well as fouling attenuation, which considerably enhances nanofiltration performance.

Nanofiltration experiments were conducted using different approaches: using a “fresh” membrane (without any previous adsorption of the compounds on the membrane); using a membrane that had been previously placed in contact with the compounds, to promote their adsorption on the membrane (adsorption under static conditions); and re-using a membrane that had been subject to adsorption under static conditions and used for nanofiltration (adsorption under dynamic conditions). This used membrane was therefore previously subject to adsorption under both static and dynamic conditions before being used in a second nanofiltration experiment to test the removal efficiency of hormones (Nanofiltration 2 shown in Figure 3.1). Figures 3.3 and 3.4 show the rejections obtained for the target organic compounds in these distinct experiments conducted in groundwater and surface water matrices. For the pesticides and hormones spiked in the surface water matrix, rejections between 67.4 and 99.9% were observed in the experiments conducted with a “fresh” membrane and rejections higher than 83.5% were obtained in the experiments conducted with pre-adsorption.

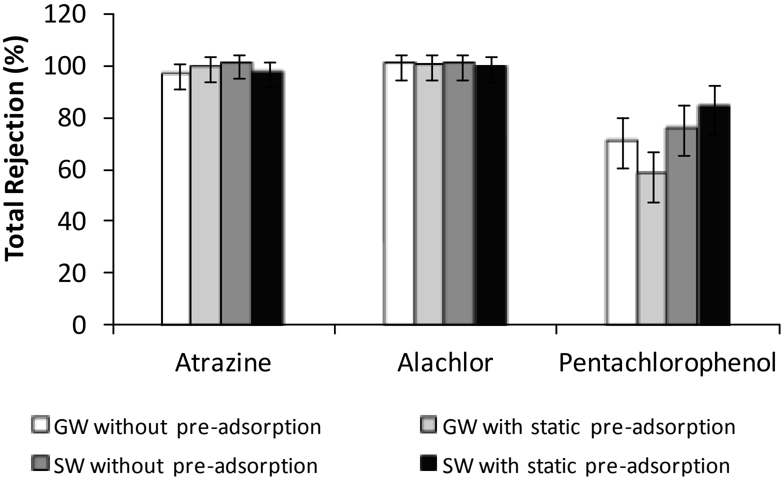


Figure 3.3 *Rejection of the selected pesticides (atrazine, alachlor, and pentachlorophenol) in the different nanofiltration experiments – without previous adsorption of the selected organic compounds on the membrane and with pre- adsorption under static conditions – in groundwater (GW) and surface water (SW) matrices (error bars correspond to the uncertainty related to analytical methods).*

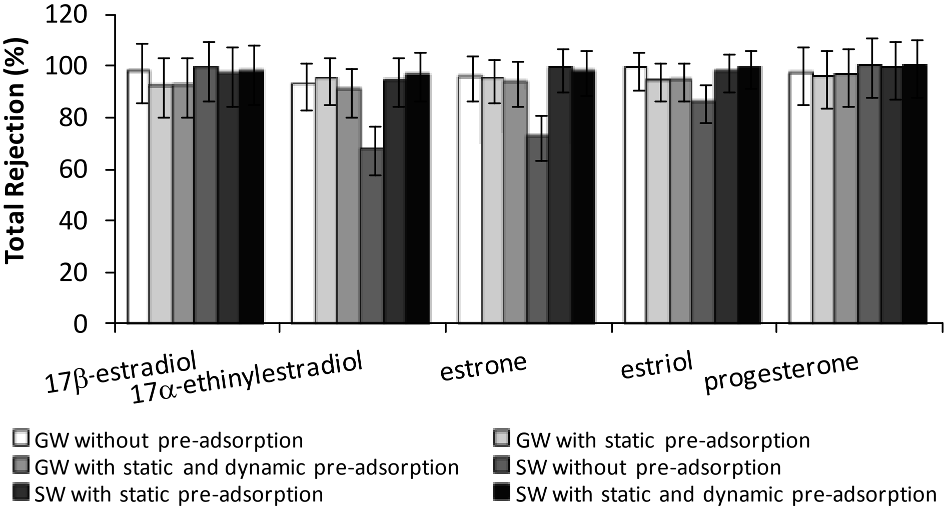


Figure 3.4 *Rejection of the selected hormones (17β-estradiol, 17α-ethinylestradiol, estrone, estriol, and progesterone) in the different nanofiltration experiments – without previous adsorption of the selected organic compounds on the membrane, with pre-adsorption under static conditions, and with pre-adsorption under both static and dynamic conditions – in groundwater (GW) and surface water (SW) matrices (error bars correspond to the uncertainty related to analytical methods).*

Extremely high rejections were obtained for all compounds in the groundwater (>90%), with the exception of pentachlorophenol. The rejections of pentachlorophenol obtained in both water matrices tested were generally lower when compared to the other organic compounds (Figure 3.3). The lower rejection of pentachlorophenol, as previously observed in another study using a dead-end filtration system (Sanches *et al.* 2011), may be explained by the fact that pentachlorophenol is an ionisable organic compound with a pK_a value of 4.7 (Cessna and Grover 1978) and therefore, its solubility is pH dependent and expected to increase at pH values higher than the pK_a. At pH values of 7 or 8 (the pH of the natural water matrices), the dominant species change towards the deprotonated form (Stapleton *et al.* 1994) and the solubility of this molecule increases, therefore decreasing its rejection.

The rejection of pentachlorophenol is also dependent on the water matrix composition, especially in the experiments conducted with pre-adsorption. The rejections obtained in the groundwater were 70.5 and 57.5% without and with static pre-adsorption, respectively while for the surface water, percent rejections of 75.4 and 83.5% without and with static pre-adsorption, respectively were observed. Although the adsorption of this compound on the membrane was important in its rejection in surface water (58-72% of the total rejection), the adsorption observed in the groundwater was not very significant (23 and 32% of the total rejection). Therefore, besides hydrophobic interactions, other rejection mechanisms play an important role in the rejection of this compound. The ionic composition of the two water matrices tested is very different: the groundwater matrix presents higher values of alkalinity, conductivity, total hardness, and calcium concentration (Table 3.2). The ions present in the water may have a “shielding” effect on the ionised molecule and the membrane surface charge, reducing the electrostatic interactions between the compound and the negatively charged membrane, leading to the observed decrease in the rejection of pentachlorophenol in the groundwater relatively to surface water. The decrease in the rejection of dissolved organic carbon with increasing ionic strength due to a “shielding” effect was also previously discussed (Schäfer *et al.* 2002). Furthermore, the ionic “shielding” of the molecules also reduces the length of the Debye layer of the molecules, which facilitates the breakthrough of the molecules across the membrane and decreases their rejection (Schäfer *et al.* 2003, Nyström *et al.* 1998). In particular, calcium has been reported as an ion that may influence the rejection of organic compounds due to the “shielding” effect (Boussahel *et al.* 2002). Since the concentration of calcium is much higher in the groundwater matrix (87.0 mg L^{-1} in the ultrafiltered groundwater and 28.5 mg L^{-1} in the ultrafiltered surface water), this ion may have a particular effect in the decrease of the rejection of pentachlorophenol in groundwater comparatively to the surface water matrix.

Extremely high rejections (higher than 96.2%) were obtained for atrazine and alachlor in both water matrices tested (Figure 3.3). The rejection of atrazine was found to be independent from the water matrix composition, which is in agreement with other studies using the same and other nanofiltration membranes as well as different types of natural and synthetic water matrices (Planas *et al.* 2006, Devitt *et al.* 1998, Sanches *et al.* 2011, Boussahel *et al.* 2002, Berg *et al.* 1997).

Table 3.4 shows the percent adsorption of the selected pesticides and hormones on the membrane during nanofiltration under different experimental conditions in terms of membrane pre-adsorption: without pre-adsorption, with static pre-adsorption, and with both static and dynamic pre-adsorption. Very high adsorption percentages were obtained for atrazine (73.3-96.9%) and alachlor (54.5-98.8%) in nanofiltration experiments, showing that hydrophobic interactions have an important impact on the rejection of these compounds.

Table 3.4 *Percent adsorption of the selected pesticides and hormones on the membrane during nanofiltration under different experimental conditions in terms of membrane saturation: without pre-adsorption of the compounds on the membrane, with static pre- adsorption on the membrane, as well as with both static and dynamic pre-adsorption on the membrane.*

Compound	**% Adsorption during nanofiltration**					
	Groundwater			**Surface water**		
	Without pre-adsorption	**With static pre-adsorption**	**With static and dynamic pre-adsorption**	**Without pre-adsorption**	**With static pre-adsorption**	**With static and dynamic pre-adsorption**
Atrazine	90.8	73.3	nd	96.9	nd	nd
Alachlor	98.8	97.2	nd	54.5	98.8	nd
Pentachlorophenol	16.4	18.1	nd	54.2	48.1	nd
17β-Estradiol	59.4	37.2	25.8	29.8	42.3	30.8
17α-Ethinylestradiol	37.3	47.8	9.1	12.3	20.4	23.1
Estrone	49.3	94.3	18.1	18.5	52.0	37.3
Estriol	39.2	nd	9.0	16.9	32.9	24.4

nd – not determined

Rejections obtained for atrazine and alachlor by other authors using cross-flow systems are in agreement with the results presented here: Yangali-Quintanilla *et al.* (2009) reported removals of atrazine from laboratory grade water with spiked dissolved organic carbon between 81.3 and 98.4% using NF-90 and NF-200 membranes, Van der Bruggen *et al.* (2001) obtained atrazine removals from groundwater higher than 90% using several nanofiltration membranes, and Comerton *et al.* (2008) observed rejections of alachlor above 90.9 in a filtered surface water using TS80 and NF-270 membranes.

For the hormones, extremely high rejections (higher than 90%) were obtained independently of the matrix tested in all the experiments conducted in groundwater and surface water, with the exception of lower percent rejections obtained for 17α-

---

ethinylestradiol, estrone, and estriol, (67.4, 72.4, and 85.4% respectively) in the experiments conducted in surface water without pre-adsorption (Figure 3.4). These results are in agreement with previously reported rejections for the selected hormones with other membranes (Comerton *et al.* 2008, Nghiem *et al.* 2004).

Most of the observed rejections of the hormones due to adsorption effects were lower than 52% (Table 3.4), showing that these effects are important mechanisms of rejection but are not the solely mechanisms. Percent adsorption values are not shown for progesterone in Table 3.4 since this molecule showed to be considerably retained (34%) in the system in the control samples (as mentioned in the Materials and Methods section). Since the water matrices pH (7-9) is lower than the pK_a of the hormones (10.4), these compounds are in the undissociated form and therefore, electrostatic interactions between the hormones and the membrane are not likely to occur. Adsorption effects and size exclusion are therefore expected to govern the rejection of these compounds since the selected hormones present similar and high molecular weights. Adsorption interactions take place since these are hydrophobic compounds (high log K_{ow}) and the structure of the hormones comprises hydroxyl and carbonyl groups that may form hydrogen bonding between the oxygen atoms of the molecule and the membrane polymer (Schäfer *et al.* 2003, Nghiem *et al.* 2002b, Van der Bruggen *et al.* 2008). Adsorption values lower than 50% obtained for estrone, estriol, 17β-estradiol, and 17α-ethinylestradiol by other authors (Dudziak and Bodzek 2009) concur with the results obtained in this study.

Even though the properties of the target compounds (log K_{ow}, solubility, molecular weight, and pK_a) and water characteristics (alkalinity, total hardness, and conductivity) have been related with the removal of the selected compounds, a full understanding of the individual effects on adsorption was not achieved. This fact is related with the complexity of the real waters and the consequent existence of combined removal effects, as previously discussed for the adsorption of the target micropollutants under static conditions. As mentioned above, the development of robust rejection models may require the use of a multivariable statistical approach.

Table 3.5 compares the natural water matrices composition in terms of several water quality indicator parameters, pesticides, and hormones before and after nanofiltration, shows their rejection values, and reports the regulated parametric values (Directive 98/83/EC). High percent rejection values were obtained for all the parameters except chloride, sodium, potassium, and nitrate. These are monovalent ions and were therefore expected to be less retained by nanofiltration (Table 3.5 and Figure 3.5).

***Table 3.5** Variation of the composition of the spiked groundwater (GW) and surface water (SW) subject to nanofiltration.*

Parameter	**Before nanofiltration**		**After nanofiltration**		**% Rejection**		**European legislation (98/83/EC)**
	GW	**SW**	**GW**	**SW**	**GW**	**SW**	
Alkalinity (mg L^{-1} CaCO$_3$)	232±19	57.9±4.6	41.7±3.8	18.5±6.1	82.0±1.7	68.1±10.6	
Conductivity (µS cm^{-1} 20 °C)	511±26	357±18	141±11	131±8	72.4±2.2	63.4±2.1	2500
Total dissolved solids (mg L^{-1})	366	256	134±11	124±7	63.4±3.0	51.7±2.8	
Nitrate (mg L^{-1} NO$_3$)	3.12±0.04	4.43±0.53	1.90±0.10	2.00±0.30	38.70±3.10	55.80±7.00	50
Chloride (mg L^{-1} Cl)	34.6±2.8	38.3±3.1	21.3±2.0	28.1±1.5	38.5±5.7	26.6±3.8	250
Sulphate (mg L^{-1} SO$_4$)	22.4±1.8	-	<10.0	<10.0	>55.4	>55.4	250
Total Hardness (mg L^{-1} CaCO$_3$)	259±31	113±14	32.2±8.4	< 20.0	89.6±5.8	> 82.3	
Calcium (mg L^{-1} Ca)	87.0±10.0	28.5±3.4	9.6±2.1	< 5.0	89.0±2.4	> 82.5	
Magnesium (mg L^{-1} Mg)	10.2±1.5	10.1±1.5	1.8±0.7	< 1.0	82.7±6.6	> 90.1	
Sodium (mg L^{-1} Na)	20.6±2.1	29.3±2.9	18.1±0.3	22.7±1.1	12.0±1.6	22.6±3.6	200
Potassium (mg L^{-1} K)	<1.0±0.10	2.8±0.3	<1.0±0.10	1.6±0.1	-	37.2±5.2	
Pesticides Individual (µg L^{-1})	77.0-166*	72.0-152*	0.1-49.0*	< 0.1-37.0*	70.5-99.9*	75.4-99.9*	0.1
Pesticides total (µg L^{-1})	328*	301*	52*	~37*			0.5
Hormones individual (µg L^{-1})	138-211*	132-186*	3.0-12.0*	1.0-59.0*	92.2-98.3*	67.4-99.6*	
Hormones total (µg L^{-1})	833*	803*	33.0*	127*			

*The results presented for the concentration and rejection of the spiked pesticides and hormones concern to the experiments conducted without pre-adsorption on the membrane.

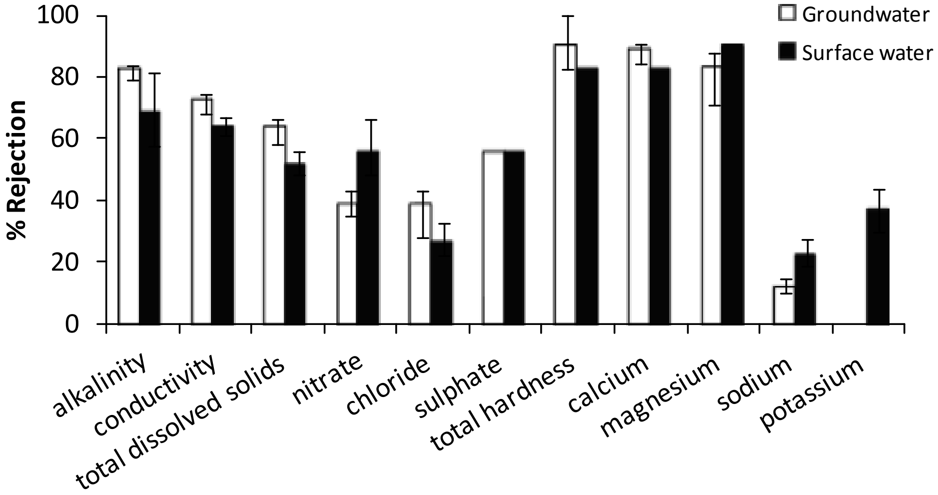


Figure 3.5 *Percent rejection of inorganic components of the natural water matrices during nanofiltration experiments (error bars correspond to minimum and maximum values obtained; error bars are not provided when the rejection of the components leaded to concentrations below detection limits).*

Even though slightly lower rejection values were often obtained in the surface water matrix, very similar rejection results were observed in both matrices. All physico - chemical parameters analysed were found to be present in the natural waters at concentrations below the legislated values (Tables 3.2 and 3.5). The selected compounds were spiked at levels slightly higher than the occurrence levels previously mentioned (Planas *et al.* 2006, Field *et al.* 2003). Therefore, it was possible to obtain these compounds at concentrations above the legislated values in the permeate even when high removals were obtained. Taking into account the removal percentages obtained, if the pesticides are present in the water at reported occurrence levels, we can expect to attain nanofiltered permeate concentrations in the range of 0.01-3.84 $\mu g\ L^{-1}$. Compliance with legislated values would therefore be ensured for atrazine and alachlor but not for pentachlorophenol, since lower rejection values were obtained for this pesticide (Table 3.5 and Figure 3.3) and the legislated value is 0.1 $\mu g\ L^{-1}$ (Directive 98/83/EC).

Since it was not possible to perform nanofiltration experiments during several months, to mimic real operation conditions in water treatment facilities, an attempt to mimic saturation conditions that are achieved during this operation was performed in this study by conducting nanofiltration experiments after pre-adsorption on the membrane under both static and dynamic conditions. Figures 3.3 and 3.4 show that significant differences were not obtained in the total rejection of the selected pesticides and hormones between the experiments carried out with and without pre-adsorption of the compounds on the membrane, with the exception of the hormones 17α-ethinylestradiol, estrone, and estriol. For these hormones, lower rejections were obtained in the experiments carried out without pre-adsorption on the membrane when compared to the experiments carried out with pre-adsorption in surface water. These three hormones are the less hydrophobic among the five hormones addressed in this study and therefore present higher solubility and are expected to adsorb to a lesser extent to the membrane and natural organic matter (Schäfer *et al.* 2010), which could explain the lower rejection observed in the surface water matrix.

Even though the experiments in this study were relatively long (44-93 h), the percent rejections obtained remained very high and similar, or even increased, in the nanofiltration assays conducted after static and dynamic adsorption (Figures 3.3 and 3.4). Therefore, results suggest that the rejection of the selected pesticides and hormones may not be considerably changed in a long term operation and that the membrane performance is not likely to be noticeably affected. Although a decrease in the rejection of organic compounds has been reported in previous studies, due to the decrease of their adsorption on the membrane surface and pores after achieving membrane saturation conditions within 10 to 96 h of operation (Nghiem *et al.* 2004, Yangali-Quintanilla *et al.* 2009, Kimura *et al.* 2003, Chang *et al.* 2002), studies conducted by Bellona and Drewes (2007) and Yangali-Quintanilla *et al.* (2009) concur with our findings.

The results obtained in Table 3.4 show that static pre-adsorption doesn’t seem to achieve saturation since, for many of the target hormones, there was still an additional membrane adsorption effect, observed in the nanofiltration experiments conducted after pre-adsorption. Even though static adsorption experiments were conducted until a constant concentration was obtained for all the target analytes in the solution (which took 27.5-168.4 h), the membranes obtained were still able to continue adsorbing the target compounds spiked in fresh solutions in the nanofiltration experiments. This observation may be explained by the fact that dynamic adsorption is likely to allow the organic compounds to access to additional membrane adsorption sites that were not easily accessed during pre-adsorption under static conditions.

In the dynamic assays conducted after nanofiltration preceded by static pre-adsorption (referred as Nanofiltration 2 in Figure 3.1), the additional adsorption on the membrane was found to be considerably lower comparatively to the additional adsorption obtained during the nanofiltration after static pre-adsorption (referred as Nanofiltration in Figure 3.1 - I). This fact may be explained by the possible partial membrane site saturation already achieved during static pre-adsorption. However, the total percent rejection remained extremely high and independent of the water matrix, showing that other rejection mechanisms besides adsorption may also play an important role. As previously mentioned, size exclusion is likely to be important for hormones rejection since these molecules have molecular weights very similar to the top value of the MWCO range of the membrane used (150-300 Da).

3.4 CONCLUSIONS

Ultrafiltration proved to be a suitable process to remove particles with high dimensions without affecting the concentration of ion species and soluble matter present in the water matrices allowing the study to focus on these components. This process will also decrease flux decline and fouling problems often associated with nanofiltration of waters with high turbidity.

Nanofiltration proved to be extremely efficient to remove all the priority pesticides and hormones selected, except pentachlorophenol, from different natural water sources with very different compositions (ultrafiltered surface water and groundwater) as well as several water quality parameters. For all the target analytes, size exclusion and hydrophobic interactions were found to have a very important role in rejection. The percent rejections obtained for all the water quality parameters, hormones, and pesticides tested except pentachlorophenol were found to be independent of the water matrix composition. Besides the deprotonation of this molecule at the water pH and its hydrophobic interactions with the membrane, the higher alkalinity, conductivity, and total hardness of the groundwater may decrease the removal of pentachlorophenol in this water matrix due to charge screening effects. Even though the adsorption of the organic compounds was attributed to some characteristics of the compounds and water matrices, a full comprehension was not attained since the real water matrices are very complex and concurrent effects still exist despite the methodology followed. Since this deterministic approach doesn’t allow a full understanding of the correlations between the variables analysed and the adsorption of the target micropollutants, a multivariable statistical analysis could be performed in future studies to assess the existence of simultaneous effects on the removal of the target compounds and explain the complex relationships affecting the mechanisms of rejection of the xenobiotics.

The efficiency of nanofiltration to remove the micropollutants of interest under membrane saturation conditions was also assessed. Even though it seems that saturation was not fully accomplished when pre-adsorption was performed under static conditions, results suggest that membrane efficiency with and without pre-adsorption on the membrane is not likely to be considerably different. The high efficiency of nanofiltration to remove the selected micropollutants under extended adsorption conditions suggests that nanofiltration is likely to be very efficient to produce high quality water under long term operations in water treatment utilities.

ACKNOWLEDGEMENTS

Financial support from Fundação para a Ciência e a Tecnologia, through the grants PTDC/AMB/66024/2006 and PEst-OE/EQB/LA0004/2011 as well as the fellowships BPD/26990/2006 and BD/72244/2010, is gratefully acknowledged.

The authors thank the EPAL team that collected the water samples. Sampling and organic compounds analyses had the financial support of EPAL.

REFERENCES

Bellona C, Drewes JE, Xu P and Amy G (2004) Factors affecting the rejection of organic solutes during NF/RO treatment - A literature review. *Water Res* 38: 2795-2809.

Bellona C, Drewes JE (2007) Viability of a low-pressure nanofilter in treating recycled water for water reuse applications: A pilot-scale study. *Water Res* 41: 3948-3958.

Berg P, Hagmeyer G, Gimbel R (1997) Removal of pesticides and other micropollutants by nanofiltration. *Desalination* 113: 205-208.

Boussahel R, Montiel A, Baudu M (2002) Effects of organic and inorganic matter on pesticide rejection by nanofiltration. *Desalination* 145: 109-114.

Cessna AJ, Grover R (1978) Spectrophotometric determination of dissociation-constants of selected acidic herbicides. *J Agr Food Chem* 26: 289-292.

Chang S, Waite TD, Schäfer AI, Fane AG (2002) Adsorption of trace steroid estrogens to hydrophobic hollow fibre membranes. *Desalination* 146: 381-386.

Comerton AM, Andrews RC, Bagley DM, Yang P (2007) Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds. *J Membrane Sci* 303: 267-277.

Comerton AM, Andrews RC, Bagley DM, Hao CY (2008) The rejection of endocrine disrupting and pharmaceutically active compounds by NF and RO membranes as a function of compound a water matrix properties. *J Membrane Sci* 313: 323-335.

Decision 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC, Official Journal of the European Communities, L 331/1 (2001).

Devitt EC, Ducellier F, Cote P, Wiesner MR (1998) Effects of natural organic matter and the raw water matrix on the rejection of atrazine by pressure-driven membranes. *Water Res* 32: 2563-2568.

Directive 98/83/EC of 3 November 1998 on the quality of the water intended for human consumption. Official Journal of the European Communities, L 330/32 (1998).

Dudziak M, Bodzek M (2009) Selected factors affecting the elimination of hormones from water using nanofiltration. *Desalination* 240: 236-243.

EN 1484: 1997. Water Analysis - Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC). The European Committee for Standardisation, Brussels, pp. 14 (1997).

Field, JA, Reed, RL, Sawyer, TE, Griffith, SM and Wigington, PJ (2003) Diuron occurrence and distribution in soil and surface and ground water associated with grass seed production. *J Environ Qual* 32: 171-179.

Gershfeld NL, Muramatsu M (1971) The interaction between steroid hormones nad lipid monolayers on water. *J Gen Physiol* 58: 650-666.

ISO/IEC 17025: 2005. General requirements for the competence of testing and calibration laboratories. International Organisation for Standardisation (2005).

Jardim WF, Montagner CC, Pescara IC, Umbuzeiro GA, Di Dea Bergamasco AM, Eldridge ML, Sodré FF (2012) An integrated approach to evaluate emerging contaminants in drinking water. *Sep Purif Technol* 84: 3-8.

Johnson AC, Sumpter JP (2001) Removal of endocrine-disrupting chemicals in activated sludge treatment works. *Environ Sci Technol* 35: 4697-4703.

Kaiser KLE, Valdmanis I (1982) Apparent octanol/water partition coefficients of pentachlorophenol as a function of pH. *Can J Chemistry* 60: 2104-2106.

Kimura K, Amy G, Drewes J, Watanabe Y (2003) Adsorption of hydrophobic compounds onto NF/RO membranes: An artifact leading to overestimation of rejection. *J Membrane Sci* 221: 89-101.

Kolodziej EP, Harter T, Sedlak DL (2004) Dairy wastewater, aquaculture, and spawning fish as sources of steroid hormones in the aquatic environment. *Environ Sci Technol* 38: 6377-6384.

Krieger R, Doull J, Ecobichon D, Gammon D, Hodgson E, Reiter L, Ross J, Handbook of Pesticides Toxicology: Principles. Elsevier Science, USA (2001).

Lu GH, Wang C, Yuan X, Lang PZ (2005) Quantitative structure-activity relationships for the toxicity of substituted benzenes to Cyprinus carpio. *Biomed Environ Sci* 18: 53-57.

Meylan WM, Howard PH, Validation of water solubility estimation methods using log K_{ow} for application in PCGEMS & EPI. Syracuse Research Corporation, Environmental Science Center, NY (1994).

Nghiem LD, Schäfer AI, Waite TD (2002a) Adsorption of estrone on nanofiltration and reverse osmosis membranes in water and wastewater treatment. *Water Sci Technol* 46: 265-272.

Nghiem LD, Schäfer AI, Waite TD (2002b) Adsorptive interactions between membranes and trace contaminants. *Desalination* 147: 269-274.

Nghiem L, Schäfer A, Elimelech M (2004) Removal of natural hormones by nanofiltration membranes: Measurement, modelling, and mechanisms. *Environ Sci Technol* 38: 1888-1896.

Nghiem L, Schäfer A, Elimelech M (2005) Pharmaceutical retention mechanisms by nanofiltration membranes. *Environ Sci Technol* 39: 7698-7705.

NP EN 27027: 1994. Water Quality: Determination of turbidity (1st ed.). The European Committee for Standardisation, Brussels, pp. 6 (1994).

Nyström M, Aimar P, Luque S, Kulovaara M, Metsamuuronen S (1998) Fractionation of model proteins using their physiochemical properties. *Colloid Surface A* 138: 185-205.

Pesticide Properties DataBase, Agriculture & Environment Research Unit (AERU). Available online: http://sitem.herts.ac.uk/aeru/ppdb/en/17.htm; Last accessed: September 8, 2010.

Planas C, Puig A, Rivera J, Caixach J (2006) Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction - Estimation of the uncertainty of the analytical results. *J Chromatogr A* 1131: 242-252.

Routledge EJ, Sheahan D, Desbrow C, Brighty GC, Waldock M, Sumpter JP (1998) Identification of estrogenic chemicals in STW effluent 2 In vivo responses in trout and roach. *Environ Sci Technol* 32: 1559-1565.

Sanches S, Penetra A, Granado C, Cardoso VV, Ferreira E, Benoliel MJ, Barreto Crespo MT, Pereira VJ, Crespo JG (2011) Removal of pesticides and polycyclic aromatic hydrocarbons from different drinking water sources by nanofiltration. *Desalin Water Treat* 27: 141-149.

Schäfer A, Mauch R, Waite T, Fane A (2002) Charge effects in the fractionation of natural organics using ultrafiltration. *Environ Sci Technol* 36: 2572-2580.

Schäfer A, Nghiem L, Waite T (2003) Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis. *Environ Sci Technol* 37: 182-188.

Schäfer AI, Nghiem LD, Meier A, Neale PA (2010) Impact of organic matrix compounds on the retention of steroid hormone estrone by a 'loose' nanofiltration membrane. *Sep Purif Technol* 73: 179-187.

Schwarzenbach RP, Gschwend PM, Imboden DM, In Environmental Organic Chemistry. John Wiley & Sons, Inc, New York (1993).

Snyder SA, Keith TL, Verbrugge DA, Snyder EM, Gross TS, Kannan K, Giesy JP (1999) Analytical methods for detection of selected estrogenic compounds in aqueous mixtures. *Environ Sci Technol* 33: 2814-2820.

Snyder SA, Adham S, Redding AM, Cannon FS, DeCarolis J, Oppenheimer J, Wert E, Yoon Y (2007) Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination 202*: 156-181.

Standard Method 2320B. Titration method, in: Standard methods for the examination of water and wastewater. American Water Works Association, Washington DC (1995).

Standard Method 2340-B. Hardness by calculation, in: Standard methods for the examination of water and wastewater. American Water Works Association, Washington DC (1995).

Standard Method 2510-B. Conductimetry method, in: Standard methods for the examination of water and wastewater. American Water Works Association, Washington DC (1995).

Standard Method 4500-H+B. Electrometric method, in: Standard methods for the examination of water and wastewater. American Water Works Association, Washington DC (1995).

Stapleton M, Sparks D, Dentel S (1994) Sorption of entachlorophenol to HDTMA-CLAY as a function of ionic-strength and pH. *Environ Sci Technol* 28: 2330-2335.

Ternes TA, Stumpf M, Mueller J, Haberer K, Wilken RD, Servos M (1999a) Behaviour and occurrence of estrogens in municipal sewage treatment plants - I Investigations in Germany, Canada and Brazil. *Sci Total Environ* 225: 81-90.

Ternes TA, Kreckel P, Mueller J (1999b) Behaviour and occurrence of estrogens in municipal sewage treatment plants - II Aerobic batch experiments with activated sludge. *Sci Total Environ* 225: 91-99.

Van der Bruggen B, Schaep J, Maes W, Wilms D, Vandecasteele C (1998) Nanofiltration as a treatment method for the removal of pesticides from ground waters. *Desalination* 117: 139-147.

Van der Bruggen B, Everaert K, Wilms D, Vandecasteele C (2001) Application of nanofiltration for removal of pesticides, nitrate and hardness from groundwater: Rejection properties and economic evaluation. *J Membrane Sci* 193: 239-248.

Van der Bruggen B, Vandecasteele C (2003) Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry. *Environ Pollut* 122: 435-445.

Van der Bruggen B, Manttari M, Nyström M (2008) Drawbacks of applying nanofiltration and how to avoid them: A review. *Sep Purif Technol* 63: 251-263.

Yangali-Quintanilla V, Sadmani A, McConville M, Kennedy M, Amy G (2009) Rejection of pharmaceutically active compounds and endocrine disrupting compounds by clean and fouled nanofiltration membranes. *Water Res* 43: 2349-2362.

CHAPTER 4

Assessment of phenomena underlying the removal of micropollutants during water treatment by nanofiltration using multivariate statistical analysis

Published in: Separation and Purification Technology

Sanches S, Galinha CF, Barreto Crespo MT, Pereira VJ, Crespo JG (2013) Assessment of phenomena underlying the removal of micropollutants during water treatment by nanofiltration using multivariate statistical analysis. *Sep Purif Technol* 118: 377-386.

Sandra Sanches was involved in all the modelling work presented in this chapter. The Matlab program used to develop multivariate statistical models was implemented by Cláudia Galinha, who was also closely involved in the development and discussion of all the models attained towards the establishment of the final models. João Crespo, Vanessa Pereira, and Teresa Crespo supervised all the work carried out.

CONTENTS

ABSTRACT

Multivariate statistically-based models were developed for the comprehension of the phenomena underlying the removal of several micropollutants during drinking water treatment. Projection to latent structures (PLS) modelling was used to describe the apparent rejection as well as adsorption using specific descriptors of the molecules (physico-chemical properties and molecular size parameters), descriptors of the membrane used and of the water matrices, and operating related conditions. Multilinear PLS models with good descriptive capability towards rejection were developed. Alkalinity, molecular size descriptors, molecular weight, molar volume, and log D were found to be the most relevant contributors for the rejection of the selected micropollutants, showing the impact of size exclusion and electrostatic interactions with minor contributions of hydrophobic interactions. The incorporation of molecular size descriptors demonstrated that the geometry of the molecule is important to determine rejection when molecules have very different geometry. Conversely, PLS modelling of adsorption required also the inclusion of quadratic and interaction terms to achieve good description. Adsorption of the selected compounds seems to be mainly determined by polar and electrostatic interactions rather than hydrophobic and may be described by polarisability as well as several specific interactions. Additionally, the incorporation of molecular size descriptors did not improve modelling of adsorption, showing that molecular geometry is not so important to describe this process as for rejection.

4.1 INTRODUCTION

The mechanisms that govern the removal of micropollutants from water during pressure-driven membrane processes have been thoroughly investigated. Depending on the physico-chemical properties of the micropollutants as well as membrane and water characteristics, removal may be attributed to one or several mechanisms. Adsorption is one of the main mechanisms contributing for the rejection of organic compounds by nanofiltration, in addition to columbic interactions, hydrogen bonding, and steric hindrance as revised by Karabelas and Plakas (2011).

Attempts for the comprehension of the phenomena underlying the removal of several micropollutants by nanofiltration were carried out by establishing correlations between their rejection or adsorption with specific properties of the molecules. Yangali-Quintanilla and co-workers (2009) attained good linear correlations of rejection with molecular weight and molecular size parameters (equivalent width and molecular width) in a study carried out in pure water spiked with several organic compounds and dissolved organic carbon. Interesting positive correlations of rejection with different molecular size parameters were also reported by other authors using different membranes (Van der Bruggen *et al.* 1999). In another study conducted with pure water, adsorption was found to positively correlate well with the logarithm of the octanol-water partition coefficient while rejection showed poor correlation (Kiso *et al.* 2001). Other parameters such as the charge of the molecule, polarity (dipole moment), and acid dissociation constant are also among the important factors that impact rejection (Karabelas and Plakas 2011, Van der Bruggen *et al.* 1999). Rejection of organic compounds may also vary considerably depending on the water composition in terms of pH, ionic composition, and presence of natural organic matter (e.g. Sanches *et al.* 2011, Salvaterra *et al.* 2011, Chang *et al.* 2012, Zhang *et al.* 2004). The charge and the molecular weight cut-off are the most relevant characteristics of the membranes that impact the process efficiency (Karabelas and Plakas 2011).

The experiments in this field were mostly carried out in pure or synthetic waters. This is the most suitable strategy to unravel the individual impact of specific water components and molecular properties on the removal of target compounds and has provided useful information. Nevertheless, this approach is not accurate enough to describe the removal of micropollutants during drinking water treatment since complex interactions are expected between the solutes, water components, and membranes as revised by Karabelas and Plakas (2011). As a result, the establishment of univariate correlations between the removal of micropollutants in natural waters and specific parameters is often not conclusive as reported in Chapter 3 (Sanches *et al.* 2012). This difficulty is probably related with the occurrence of synergies and concurrent effects that should be accounted to infer about the parameters that most impact the process. Another example is the study from Comerton and co-workers (2008) who reported that the correlation between rejection and log K_{ow} that was attained in milli-Q water was not observed in surface water. The identification of the key parameters that determine the removal of micropollutants from natural waters and the comprehension of the respective complex mechanisms is not straightforward and needs further assessment.

Multivariate statistical analysis has been successfully applied for monitoring several key performance parameters of membrane bioreactors for wastewater treatment as well as to correlate them with specific operating and analytical parameters (Galinha *et al.* 2012). The fact that non-mechanistic models may be useful to correlate large sets of data and unravel relationships between several variables might help to take a step forward towards the full comprehension of solute rejection in natural matrices.

In the present study, a mathematical approach based on projection to latent structures was applied to model data from cross-flow nanofiltration experiments carried out previously (Sanches *et al.* 2012) to address the removal of pesticides (atrazine, alachlor, and pentachlorophenol) and hormones (17β-estradiol, 17α-ethinylestradiol, estriol, estrone, and progesterone) from natural waters (surface water and groundwater). The optimisation of multilinear models was conducted to correlate apparent rejection and adsorption with specific physico-chemical properties, molecular size parameters, water media, and operating related parameters. The most important contributors were identified based on the analysis of the regression coefficients of the optimised models. These models were interpreted and discussed to infer about the mechanisms involved in rejection and adsorption of the target micropollutants.

4.2 MATERIALS AND METHODS

4.2.1 Cross-flow nanofiltration experiments

Nanofiltration experiments were carried out in a cross-flow filtration unit using a flat-sheet Desal 5DK membrane as described in Sanches *et al.* (2012) and presented in Chapter 3 of the present thesis.

4.2.2 Analytical methods

The analytical methods applied for the quantification of the target compounds were described in Sanches *et al.* (2012) and are presented in Appendix A.1.

4.2.3 Development of PLS models

Multivariate statistically-based models were developed to correlate apparent rejection and adsorption attained during cross-flow nanofiltration experiments with specific physico-chemical properties and molecular size descriptors of the target micropollutants as well as water media. Operating conditions were also incorporated in the model since some important differences are likely to have impacted the removal of the target micropollutants. PLS was applied to describe apparent rejection and adsorption (outputs) through multilinear correlations of several parameters (inputs).

PLS models were implemented in Matlab using the n-way tool box (Andersson and Bro 2000).

4.2.3.1 Description of the parameters used as inputs

The description of all parameters used as inputs in this study is presented in Table 4.1. Specific properties of the micropollutants – molecular weight (MW), logarithm of the octanol-water distribution ratio at pH 7.4 (log D), dipole moment (μ), inverse of the logarithm of the acid dissociation constant (pK_a), water solubility (W_s), molar volume (V_m), and polarisability (P) - as well as molecular size and geometry descriptors were used to develop the models. These descriptors were selected for being pointed out as key parameters to describe rejection and adsorption based on the literature available on the field (e.g. Yangali-Quintanilla *et al.* 2009, Van der Bruggen *et al.* 1999, Kiso *et al.* 2001, Van der Bruggen and Vandecasteele 2001, Comerton *et al.* 2007, Van der Bruggen *et al.* 2001).

Table 4.1 *Description of the selected inputs for model developing.*

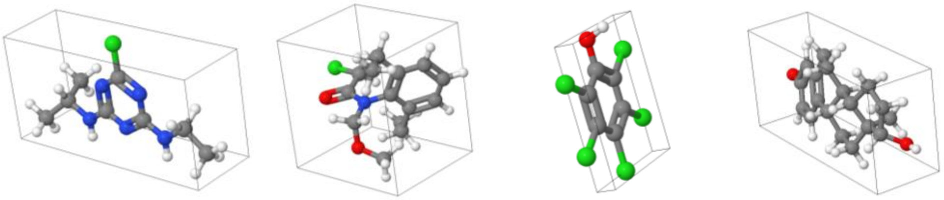
Descriptors of the molecules	**Descriptors of the water matrix**	**Descriptors of the membrane**	**Operating related conditions**
Physico-chemical properties - Molecular weight (MW) - Logarithm of the octanol-water distribution ratio at pH 7.4 (log D) - Dipole moment (μ) - Inverse of the logarithm of the acid dissociation constant (pK_a) - Water solubility (W_s) - Molar volume (V_m) - Polarisability (P) Molecular size parameters - Molecular length (M_l) - Molecular width (M_{wd}) - Molecular depth (M_d)	Alkalinity (Alk)	Permeability (L_p)	- Concentration of the micropollutants in the feed solution (C) - Filtered volume (V_{filt}) - Mass of micropollutants pre-adsorbed under static conditions (Stat ads) - Mass of micropollutants pre-adsorbed under dynamic conditions (Dyn ads)

Table 4.2 depicts the physico-chemical properties and size descriptors of the selected pesticides and hormones used as inputs for the development of the models. Molecular dimensions were determined based on their three-dimensional structure by taking the lengths of the edges of a box encompassing the molecules. The dimensions thus calculated reflect the molecular length (M_l), molecular width (M_{wd}), and molecular depth (M_d). The molecular visualisation software Jmol was used for this purpose. The three-dimensional structures obtained from Jmol are presented in Figure 4.1.

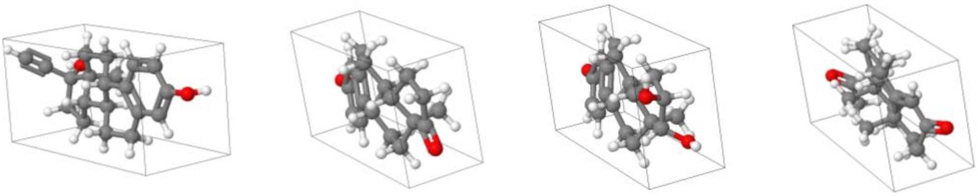
Table 4.2 *Physico-chemical properties and molecular size parameters of the selected pesticides and hormones.*

Molecule	**MW (Da)**	**log D at pH 7.4**	**μ (D)**	**pK_a**	**W_s ($mg\ L^{-1}$)**	**V_m ($cm^3\ mol^{-1}$)**	**$Px10^{23}$ (cm^3)**	**M_l (nm)**	**M_{wd} (nm)**	**M_d (nm)**
Atrazine	215.7	2.64[1]	3.40[2]	1.70[2]	34.7[3]	170[1]	2.32[1]	1.14[4]	0.55[4]	0.37[4]
Alachlor	269.8	3.05[1]	3.60[2]	0.62[5]	240[3]	241[1]	3.00[1]	0.71[4]	0.71[4]	0.58[4]
Pentachlorophenol	266.3	2.53[1]	1.90[2]	4.70[6]	14.0[3]	148[1]	2.09[1]	0.63[4]	0.54[4]	0.09[4]
17β-Estradiol	272.4	4.15[1]	2.75[2]	10.40[7]	3.6[3]	233[1]	3.15[1]	1.17[4]	0.57[4]	0.38[4]
17α -Ethinylestradiol	296.4	4.11[1]	2.64[2]	10.40[7]	11.3[3]	245[1]	3.42[1]	1.17[4]	0.55[4]	0.52[4]
Estrone	270.4	3.62[1]	2.04[2]	10.40[7]	30.0[3]	232[1]	3.09[1]	1.09[4]	0.56[4]	0.39[4]
Estriol	288.4	2.53[1]	3.22[2]	10.40[7]	441[3]	230[1]	3.21 [1]	1.17[4]	0.59[4]	0.39[4]
Progesterone	314.5	3.83[1]	2.70[2]	*	8.8[3]	289[1]	3.61 [1]	1.20[4]	0.58[4]	0.44[4]

*no dissociation; MW – molecular weight; log D – logarithm of the octanol-water distribution ratio; μ – dipole moment; pK_a –inverse of the logarithm of the acid dissociation constant; W_s – water solubility; V_m – molar volume; P – polarisability; M_l – molecular length; M_{wd} – molecular width; M_d – molecular depth; **[1]** Chemspider **[2]** Yangali-Quintanilla *et al.* 2009 **[3]** Meylan and Howard 1994 **[4]** Jmol software **[5]** Pesticide Properties DataBase **[6]** Cessna and Grover 1978 **[7]** Snyder *et al.* 2007.



Atrazine **Alachlor** **Pentachlorophenol** **17β-Estradiol**



17α-Ethinylestradiol **Estrone** **Estriol** **Progesterone**

Figure 4.1 *Molecular structures of the selected pesticides and hormones encompassed in a box used for the determination of measurements that reflect size parameters (grey – carbon; white – hydrogen; green – chloride; red – oxygen; blue – nitrogen) obtained from Jmol software.*

Since the present study assessed two different water matrices (ultrafiltered groundwater and surface water), only one input parameter is required to distinguish them in PLS modelling. Since the concentration of total organic carbon was under the detection limit for the groundwater, alkalinity (Alk) was selected over this parameter as representative of the water matrix (57.9 and 232 mg L^{-1} $CaCO_3$ in surface water and groundwater, respectively). Additionally, a previous study from the authors using pure water, groundwater, spring water, and surface water demonstrated that alkalinity is likely to play an important role in the rejection of alachlor (Sanches *et al.* 2011).

Operating related descriptors such as the concentration of the molecules in the feed solutions (C), filtered volume (V_{filt}) as well as the mass of micropollutants pre-adsorbed under static (Stat ads) and dynamic (Dyn ads) conditions were also used as inputs since there were differences in these parameters among the experiments carried out. Concentrations of the organic compounds spiked in the feed solutions were not the same as mentioned in Chapter 3. Furthermore, the concentrations used for model development were the concentrations determined by the analytical methods employed. Filtration volumes were also set in accordance with the volumes required for the analysis of each group of compounds.

Permeability was used as a membrane descriptor since it was different for the different water matrices assessed and it varied among the different experiments carried out. The performance of pre-adsorption of the target compounds on some of the membranes may also have contributed to some observed changes in their permeability.

All experimental data used in PLS models were previously normalised by subtracting to each value the average of the experimental data of the respective variable and dividing by the respective standard deviations. With this procedure all variables are fed to the model with comparable weights, regardless of the units used for each variable. The regression coefficients of each model obtained are, therefore, normalised and can be compared between them.

4.2.3.2 Optimisation and selection of the models

A group of 37 sampling events (observed data) were used for the development of the models (Appendix A.3). Sampling events were randomly divided into two sets: training and validation. The training set encompassed 75% of the sampling events and was used to calibrate the model while the remaining 25% were used to carry out validation. The same training and validation sets were used to develop the models for an output to allow direct comparison among the different models.

The selection of the number of latent variables of each PLS regression and model optimisation were made based on the lowest root mean square error of cross-validation (RMSECV). This parameter translates the error of the calibration set established through cross-validation, and was calculated using Equation 4.1:

$$\text{RMSECV}=\sqrt{\frac{\sum_{i=1}^{N}(\hat{y}_i-y_i)^2}{N}} \tag{4.1}$$

where y_i is the experimental value at the *i* event, $\hat{y}_i$ is the predicted value for the *i* event using the model obtained with *N-i* events, and N is the number of sampling events in the calibration set.

The first approach employed to predict the outputs was the development of simple multilinear PLS models:

$$y=a.x_1+b.x_2+c.x_3+\ldots \tag{4.2}$$

where *a*, *b*, and *c* are the regression coefficients and x_1, x_2, and x_3 are the useful predictors to describe the modelled output. Whenever this approach was not accurate enough to describe an output due to the existence of complex non-linear relationships, interaction and quadratic terms were also introduced as inputs. The models, thus, obtained reflect the crossed interferences between inputs as follows:

$$y=a.x_1+b.x_2+c.x_3+\ldots+d.x_1^2+e.x_1x_2+f.x_1x_3+\ldots \tag{4.3}$$

Three different mathematical approaches were used to select useful inputs: iterative stepwise elimination (ISE) (Boggia *et al.* 1997), stepwise elimination (Ryan 1997), and the Martens uncertainty test (Forina *et al.* 2004) using the jackknife standard deviations (Duchesne and MacGregor 2001). These methods enabled the elimination of non-useful inputs for each output, resulting in better prediction with fewer inputs. However, the different selection methods usually result in models with different number of inputs. The final models were then selected based not only on the RMSECV, but also on the root mean square error of prediction (RMSEP), training and validation determination coefficients, and the slopes of the fitting between observed and predicted data for the training and validation sets.

4.3 RESULTS AND DISCUSSION

4.3.1 Univariate analysis

The establishment of univariate correlations between the removal of micropollutants in natural waters and specific parameters is often not conclusive. Nevertheless, an attempt to establish simple univariated correlations between specific descriptors and apparent rejection or adsorption was carried out prior to multivariate analysis. The selection of the descriptors to establish these correlations was based on correlations obtained by other authors (Yangali-Quintanilla *et al.* 2009, Van der Bruggen *et al.* 1999, Kiso *et al.* 2001). As an example, Figure 4.2 depicts the variation of rejection with molecular weight (Figure 4.2a), dipole moment (Figure 4.2b), and molar volume (Figure 4.2c) as well as the variation of adsorption with log D (Figure 4.2d), in the experiments conducted without pre-adsorption in groundwater.

A correlation between apparent rejection or adsorption data and the selected descriptors cannot be established undoubtedly. Univariate analysis is, therefore, not sufficient to describe these variables probably due to the existence of complex interactions. To unravel these complex relationships, multivariate statistically-based models were developed as discussed below.

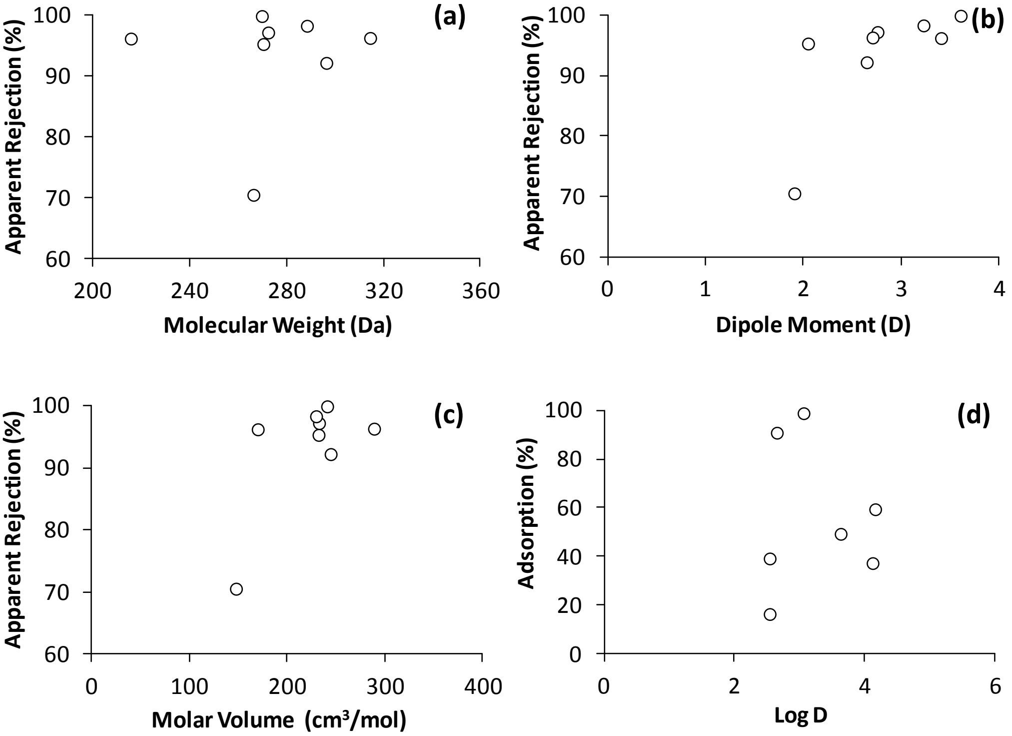


__Figure 4.2__ Univariated correlations between rejection and __(a)__ molecular weight, __(b)__ dipole moment, and __(c)__ molar volume as well as __(d)__ between adsorption and log D. Experimental data present in the plots were obtained for nanofiltration of groundwater spiked with the selected micropollutants carried out without pre-adsorption.

4.3.2 Multivariate statistical analysis

Besides its potential as a predictive tool, PLS modelling can be used to understand the relationships between the outputs and the respective input descriptors. In the present study, PLS models were developed aiming at the identification of the significant parameters that correlate with apparent rejection and adsorption.

Several PLS models were developed for each output. Optimisation was carried out aiming at selection of the relevant inputs and to simplify the interpretation of the correlations attained. The selected models as well as the regression coefficients of the

---

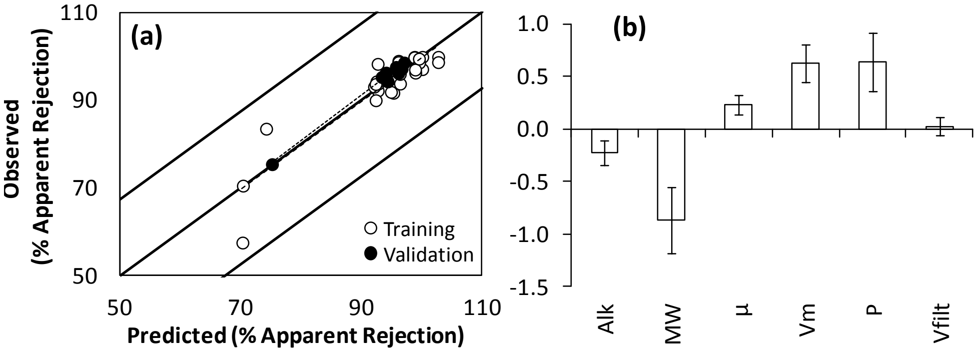
model inputs (contribution of the relevant inputs to the model) are depicted in the next sections. A detailed discussion about the relationships between the outputs and the corresponding descriptors established by the models is also provided.

4.3.2.1 Modelling of rejection

Figure 4.3 illustrates the optimised models obtained to describe apparent rejection where observed data is plotted versus modelled predictions (Figures 4.3a, c, and e). Regression coefficients relative to the inputs are also depicted for each model as bars (Figures 4.3b, d, and f) and correspond to regression coefficients of Equation 4.2. Comparison of regression coefficients values is possible since they were obtained from normalised data.

The first approach to model rejection (model 1) consisted in the development of a simple multilinear PLS model using as initial inputs the water matrix descriptor, all operating related conditions, permeability, and all physico-chemical properties depicted in Table 4.2 (Figures 4.3a and b). The optimised model requires six of these inputs to describe apparent rejection (water alkalinity, molecular weight, dipole moment, molar volume, polarisability, and filtered volume). Despite the model obtained resulted in an overall good description of apparent rejection, some of the lowest points modelled have high deviations (Fig. 3a). Therefore, an attempt to improve the prediction of these points was made through the incorporation of molecular geometric descriptors (length, width, and depth) as model inputs (model 2).

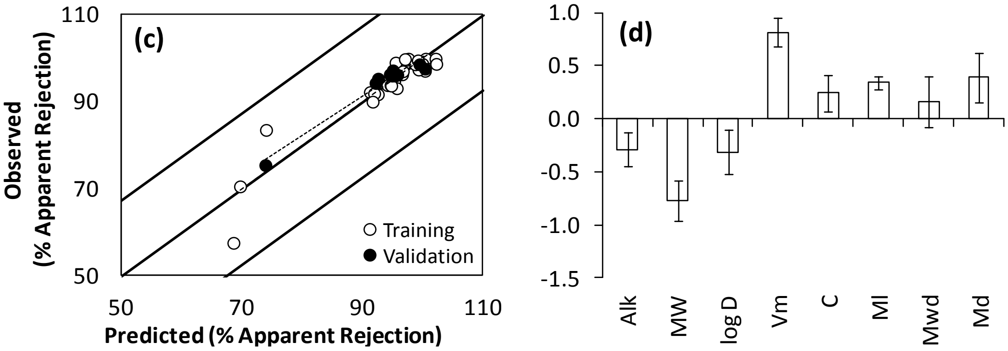
Model 1:



RMSEP= 1.6 % rejection
Training: R^2=0.84; slope=1.00

RMSECV=5.1 % rejection
Validation: R^2=0.98; slope=1.00

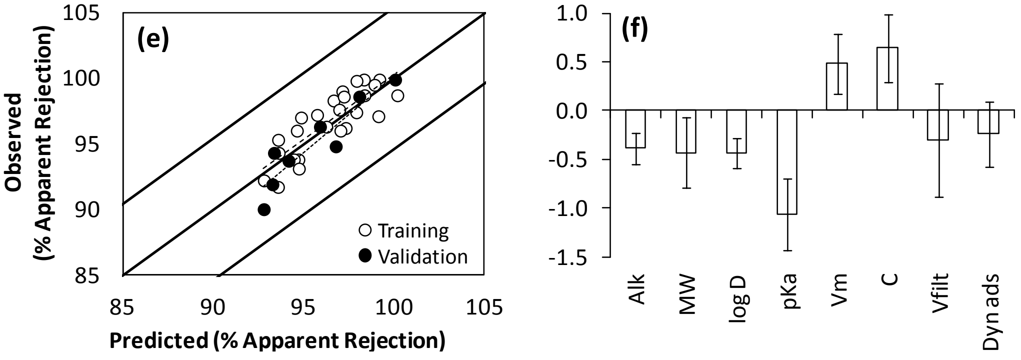
Model 2:



RMSEP=1.9 % rejection
Training: R^2=0.88; slope= 1.00

RMSECV=4.9 % rejection
Validation: R^2=0.95; slope=0.90

Model 3:



RMSEP= 1.4 % rejection
Training: R^2=0.70; slope=0.99

RMSECV=1.9 % rejection
Validation: R^2=0.86; slope=1.16

Figure 4.3 *Optimised multilinear models developed by PLS to predict apparent rejection and the respective normalised regression coefficients related to the relevant inputs: model 1 (a and b) was obtained using all observed data without including molecular size parameters; model 2 (c and d) was obtained using all observed data and molecular size parameters; model 3 (e and f) was obtained by excluding observations associated with pentachlorophenol without using molecular size parameters.* RMSEP, *RMSECV, R^2 values, and slopes of training and validation sets are provided for each model. Alk – alkalinity; MW – molecular weight; μ – dipole moment; V_m – molar volume; P – polarisability; V_{filt} – filtered volume; log D – logarithm of the octanol-water distribution ratio at pH 7.4; C – concentration; M_l – molecular length; M_{wd} – molecular width; M_d – molecular depth; pK_a – inverse of the logarithm of the acid dissociation constant; Dyn ads – mass of micropollutants pre-adsorbed under dynamic conditions.*

Even though the model obtained using molecular size parameters presents a slightly higher RMSEP (1.9%), comparatively to the first model (1.6%), the RMSECV was slightly improved from 5.1 to 4.9%, and the fitting of observed and predicted data in the two models is quite similar (Figures 4.3a and c), as demonstrated by R^2 coefficients of training (0.84 vs 0.88) and validation (0.98 vs 0.95). However, the introduction of geometry descriptors as initial inputs in PLS modelling led to the elimination of some relevant predictors selected in model 1 (dipole moment, polarisability, and filtered volume) and to the incorporation of the three molecular size parameters (Figures 4.3b and d), showing the relevance of size parameters as rejection descriptors over other parameters. Elimination of dipole moment and polarisability occurs because these descriptors enclose information that is already captured by molecular size parameters. Although dipole moment and polarisability may capture geometry related information, they do not capture all the variance that is captured by molecular size parameters.

Molecular length (M_l) and molecular depth (M_d) are the size parameters that most impacted rejection since significant differences are observed for these parameters among the selected molecules (Table 4.2 and Figure 4.1). In model 2, Log D and the concentration of the micropollutant in the feed solution, were also selected as relevant descriptors of apparent rejection. In the presence of the molecular size descriptors, log D and concentration appear to replace, respectively, the information relative to physico-chemical properties and operating related conditions previously provided by μ, P, and V_{filt} in model 1.

Since the experimental rejections obtained for pentachlorophenol (57.5-83.5%) were systematically lower comparatively to the other compounds (>90%), a model excluding the experimental observations attained for this molecule was developed (model 3) using the inputs described in Table 4.1, including and excluding molecular size parameters. This model was attained among several models generated through the establishment of different combinations of the inputs that were found relevant throughout the optimisation process. The best model was obtained without using molecular size descriptors as inputs (Figures 4.3e and f). The very different geometry of pentachlorophenol, relatively to the geometry of the other molecules addressed in this study, may explain the fact that molecular size descriptors were not found relevant inputs in this new model in opposition to model 2. As illustrated in Figure 4.1 and Table 4.2, this molecule is smaller and more plane than the others. To describe its removal, molecular depth is likely to assume particular significance since this size parameter is considerably lower for this molecule. Molecular size parameters such as the molecular length and molecular depth are considered important predictors in model 2 since they enclose information necessary to describe the removal of pentachlorophenol during nanofiltration. Furthermore, molecular size parameters are not essential to describe the rejection of the remaining molecules addressed, as suggested by the comparison of models 2 and 3, because of their more similar geometry. Pentachlorophenol is likely to break through the free volume of the membrane polymer more easily than the other molecules due to its smaller size and geometry, highlighting the importance of size exclusion mechanisms.

In model 1 both polarisability and dipole moment have a positive effect upon rejection when geometry is not accounted (Figure 4.3b). Polarisability is the ability for a molecule to be polarised and may be defined as a proportionality factor between induced dipole moment and the electrical field. The fact that polarisability was found to be a useful predictor of rejection, in addition to dipole moment, suggests the existence of a local electrostatic environment near the membrane surface that should be taken into consideration. For molecules with higher dipole moment, the solute dipole moment may orient towards the membrane surface, so that the side of the dipole with the opposite charge is closer to the membrane surface. As the dipole is directed towards the membrane, its penetration into the membrane structure is facilitated for polar molecules comparatively to non-polar with similar size, leading to a lower rejection of more polarised molecules (Van der Bruggen *et al.* 1999). Nevertheless, positive correlations were found between dipole moment/polarisability and rejection. Since dipole moment and polarisability were not selected in model 2 and 3, their presence in model 1 is probably an attempt to explain the lowest rejections of pentachlorophenol relatively to the other micropollutants since its polarisability (2.09×10^{-23} cm^3) and dipole moment (1.90 D) are the lowest among all the molecules addressed (>2.32×10^{-23} cm^3 and >2.04 D). The comparison of all models attained demonstrates that molecular size parameters are more relevant to describe the rejection of the micropollutants when the geometry of the compounds is significantly different between them. However, in the absence of major geometric differences other descriptors (polarisability and dipole moment) are preferred to describe the rejection.

As illustrated in Figure 4.3d, besides geometric descriptors, alkalinity, molecular weight, log D, molar volume, and concentration are also relevant for the description of rejection according with model 2. The negative correlation found between alkalinity and rejection in the present study corroborates data from a previous study from the authors (Sanches *et al.* 2011) in which it was proposed that ionic species present in the water may “shield” the solutes and the membrane surface charge. Electrostatic interactions between the organic compounds and the negatively charged membrane may be therefore reduced, ultimately leading to a decreased rejection. The presence of ionic compounds in solution may also contribute to facilitate the breakthrough of the target solute molecules across the membrane by reducing the length of their Debye double layer.

The negative correlation of rejection with molecular weight (found in the three models – 1, 2 and 3) is apparently unexpected, since a positive correlation is usually reported in literature (Karabelas and Plakas 2011). Although molecular weight is a useful indicator of rejection, the combination of molecular size parameters is pointed out as better predictor of steric hindrance effects upon the rejection of molecules by nanofiltration membranes. Molecules with similar molecular weights do not necessarily have larger molecular dimensions, as demonstrated by comparing the molecular weight and molecular size parameters of pentachlorophenol and the other micropollutants (Table 4.2). In the present study, molecular weight was selected as one of the most relevant parameters to describe apparent rejection, however, the molar volume was also found to be a relevant descriptor. In fact, molar volume is a more reliable measure of molecular size than molecular weight, has a similar weight as input parameter in all models (models 1, 2 and 3), and it correlates positively with rejection, as expected. These two parameters may therefore account together the size of the molecule in the optimised models.

Models 2 and 3 also negatively correlate apparent rejection with log D (Figures 4.3d and f). Even though log D is a useful indicator of adsorption interactions between the molecules and membranes, it may also impact rejection. The explanation following this correlation is that molecules with higher log D values are usually more concentrated at the membrane surface and when adsorption equilibrium is achieved, molecules are more prone to diffuse across the membrane, leading to a decrease in rejection (Kimura *et al.* 2003).

pK_a was only found to be a relevant descriptor of rejection in model 3 (Figure 4.3f). The negative correlation found between pK_a and rejection is supported by the dissociation state of the molecules with lower pK_a at the pH of the natural waters (7.8 and 8.2 for surface water and groundwater, respectively). Thus, repulsive electrostatic interactions between dissociated molecules and the negatively charged membranes are expected to occur, leading to enhanced rejections.

The micropollutant concentration was also found to correlate positively with the apparent rejection in models 2 and 3 with a minor contribution in model 2 (Figures 4.3d and f). Although the compounds were not spiked at the exactly same concentration in water matrices, a similar concentration was always applied in all experiments for a given compound (as explained in Chapter 3). In model 2, this input may, therefore, not only reflect the variability of concentration of the compounds present but also the significantly different concentration of pentachlorophenol. Its interpretation is, therefore, not straightforward.

Besides micropollutants concentration, the filtered volume and dynamic pre-adsorption are the only operating related conditions also relevant to describe rejection (filtered volume in models 1 and 3, and dynamic pre-adsorption in model 3). Error bars associated with the regression coefficients related to filtered volume in models 1 and 3 are significantly high (Figures 4.3b and f). Likewise, a significant error bar was also obtained for the descriptor dynamic pre-adsorption in model 3 (Figure 4.3f). Thus, despite required, the impact of these descriptors is minor and difficult to define.

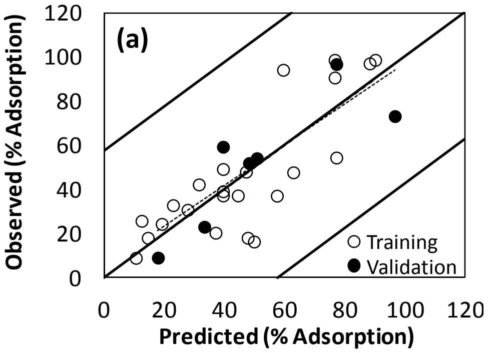
Based on the type and contribution degree of the relevant inputs associated with the three models developed to predict the apparent rejection of the selected micropollutants, size exclusion and electrostatic interactions are the most important mechanisms of rejection, with minor contributions of hydrophobic interactions. Besides these findings, the models obtained highlight the potential of this modelling approach. Such models, when properly calibrated, can thus be used as predictive tools to assess the ability to remove a determined micropollutant from water using a pressure-driven membrane process.

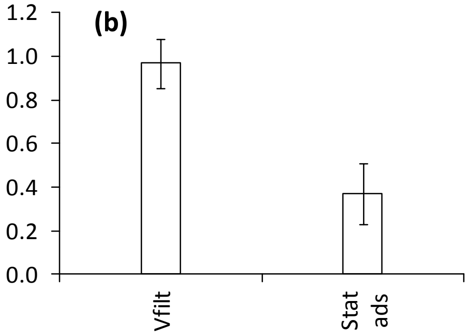
4.3.2.2 Modelling of adsorption

An effort to better understand the factors that impact adsorption was carried out in this study, since an important role in the overall apparent rejection is often attributed to adsorption. Molecules adsorb at the membrane surface due to physico-chemical interactions such as hydrophobic interactions, polar interactions (dipole-dipole and dipole-induced-dipole forces), and hydrogen bonding (Van der Bruggen and Vandecasteele 2001).

Modelling of adsorption was firstly attempted by developing a simple multilinear PLS model (model 4) using all the descriptors depicted in Table 4.1 with the exception of molecular size parameters (Figures 4.4a and b).

Model 4:

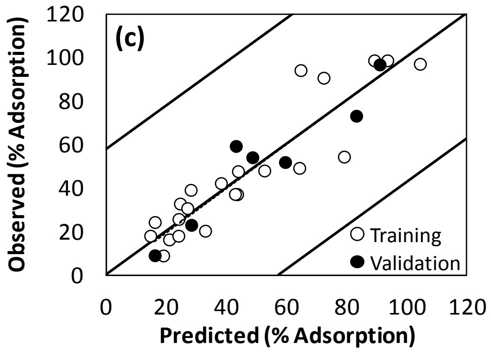


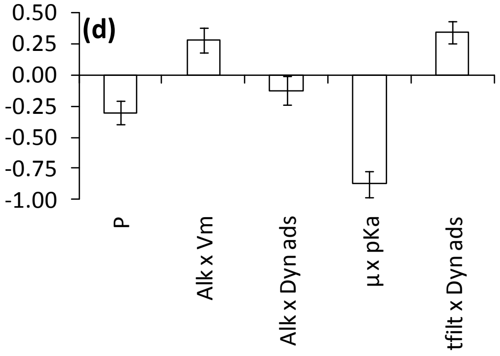


RMSEP= 14.8 % adsorption
Training: R^2=0.67; slope=0.99

RMSECV=17.4 % adsorption
Validation: R^2=0.71; slope=0.93

Model 5:

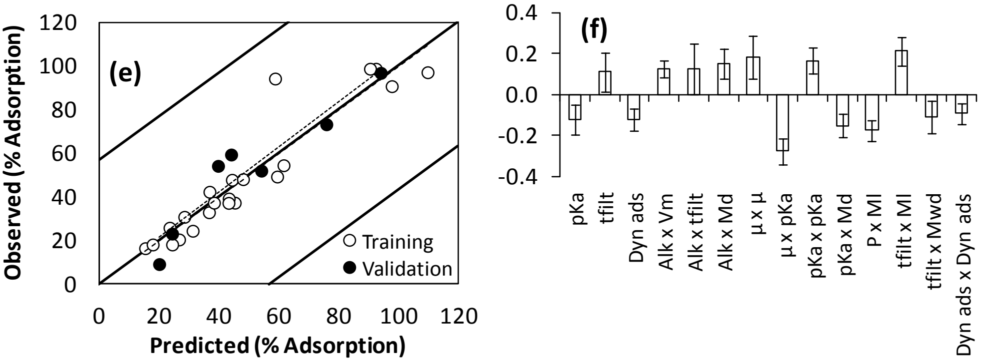




RMSEP= 8.9 % adsorption
Training: R^2=0.84; slope=1.00

RMSECV=13.6 % adsorption
Validation: R^2=0.89; slope=1.02

Model 6:



RMSEP= 9.1 % adsorption *RMSECV=13.3 % adsorption*

Training: R^2=0.88; slope=0.99 *Validation: R^2=0.90; slope=1.04*

Figure 4.4 *Optimised models developed by PLS to predict adsorption and the respective normalised regression coefficients related to the relevant inputs: model 4 (a and b) was obtained without using molecular size parameters; model 5 (c and d) was obtained by incorporating quadratic and interaction terms of the input parameters without using molecular size parameters; model 6 (e and f) was obtained by incorporating quadratic and interaction terms of the input parameters and using molecular size parameters. RMSEP, RMSECV, R^2 values, and slopes of training and validation sets are provided for each model. V_{filt} – filtered volume; Stat ads – mass of micropollutants pre-adsorbed under static conditions; P – polarisability; Alk – alkalinity; V_m – molar volume; Dyn ads – mass of micropollutants pre-adsorbed under dynamic conditions; μ – dipole moment; pK_a – inverse of the logarithm of the acid dissociation constant; filtration time (t_{filt}).*

The model obtained has relatively low descriptive capability since it presents a significant RMSEP value of 14.8%. Moreover, the model fitting is poor as R^2 coefficients below 0.8 were obtained for the training and validation sets (0.67 and 0.71, respectively). The inclusion of molecular size parameters as inputs did not result in model improvement (data not shown), demonstrating that the geometry of the molecule is not useful to describe adsorption through a multilinear correlation. Simple multilinear models seem not to be sufficient to describe adsorption.

Since the multilinear approach was not succeeded in developing a good model to predict the output, interaction and quadratic terms were included in the model. This approach is more complex since it can reflect the crossed interferences between inputs. Furthermore, the introduction of an additional descriptor – filtration time (t_{filt}) – was required. Even though filtration time is function of the filtered volume and membrane permeability, its introduction significantly improved the descriptive capability of the PLS models. In fact, adsorption of organic micropollutants is dependent of the filtration time and it increases until equilibrium at the membrane surface is achieved (Kimura *et al.* 2003, Verliefde *et al.* 2007).

The optimised model (model 5) was established based on the results obtained throughout the optimisation process. Substantial better fitting was observed with the incorporation of quadratic and interaction terms comparatively to the simple multilinear model, with training and validation R^2 of 0.84 and 0.89, respectively (Figure 4.4c). The predictive capability of the model was also improved as illustrated by the decrease of the RMSEP value to 8.9%. Like for rejection, the impact of the molecular geometry was further addressed by including molecular size parameters as inputs of a PLS model with quadratic and interaction terms (model 6; Figures 4.4e and f). Slightly better R^2 was obtained for the training set when size parameters were included (0.88 vs 0.84). On the other hand, the descriptive ability of the model slightly decreased since RMSEP value increased from 8.9% to 9.1%. Even though the fitting of the two models (Figures 4.4c and e) is very equivalent, the incorporation of geometry descriptors not only did not significantly improve the description of adsorption as it also increased the complexity of the model by greatly enlarging the number of relevant inputs from 5 to 14 (Figure 4.4d and f). Molecular geometry is therefore, not likely to be determinant to describe adsorption. Furthermore, while molecular length and molecular depth are important contributors for rejection (Figure 4.3d), size parameters are only important to predict adsorption if in interaction with several other parameters (Figure 4.4f).

Model 5 is therefore a good model to describe adsorption using only 5 relevant inputs: polarisability, alkalinity x molar volume, alkalinity x dynamic pre-adsorption, dipole moment x pK_a, and filtration time x dynamic pre- adsorption. It is noteworthy that two parameters (alkalinity and dynamic adsorption) contribute to adsorption by interacting with more than one parameter, highlighting the complexity of the relationships between the inputs.

Among the relevant descriptors of model 5, only polarisability correlates linearly with adsorption. Following the previous discussion about the correlation between this descriptor and rejection, adsorption of organic compounds on charged membranes is often favoured by a high polarisability or polarity due to minimisation of repulsive interactions between the solutes and the charged membrane (e.g. Van der Bruggen and Vandecasteele 2001). Nevertheless, a negative correlation was found between adsorption and polarisability. Table 4.2 shows that hormones, which adsorbed less on the membrane, are more polarised than pesticides. The model might, therefore, be taking this relation into consideration. Inferring about this correlation must be carefully done.

The effect of polarity is also accounted in the most relevant correlation of the model that was established between adsorption and the combined effects of dipole moment and pK_a (Figure 4.4d). pK_a was expected to impact adsorption since it determines the level of dissociation of the molecules, that in turn influences the electrostatic interactions taking place between them and the negatively charged membrane.

Following the previous discussion related with the effect of alkalinity upon rejection, repulsive interactions between the molecules and the negatively charged membrane may also influence adsorption. Additionally, other characteristics of water matrices, such as the natural organic content may also be determinant in the adsorption of micropollutants to the membrane.

Dynamic pre-adsorption was expected to influence the adsorption of the compounds since adsorption has already occurred at some extent on the membrane surface and pores. The establishment of two correlations including dynamic pre-adsorption and none including static pre-adsorption probably relies on the much higher adsorption observed under dynamic conditions. Dynamic conditions are likely to allow the molecules to access additional membrane adsorption sites that were not easily accessed under static conditions.

Although adsorption is often associated with hydrophobic-hydrophobic interactions, the most representative parameter of this kind of interactions - log D - was systematically considered not essential to predict adsorption throughout model optimisation. For the selected organic compounds, polar and electrostatic interactions are the predominant physico-chemical interactions leading to adsorption.

4.4 CONCLUSIONS

The models obtained have good descriptive capability and contributed for an overall comprehension of rejection and adsorption mechanisms of the micropollutants selected in the present study. Size exclusion and electrostatic interactions with minor contributions of hydrophobic interactions are important rejection mechanisms. Molecular geometry is very important to describe rejection when molecules have very different geometry. Alkalinity, molecular weight, log D, and molar volume are also among the most relevant contributors for rejection. Conversely, molecular geometry is not essential to describe adsorption. Hence, adsorption occurs mainly through polar and electrostatic interactions rather than hydrophobic and it is determined by polarisability as well as several specific interactions.

The correlations established between the outputs and the useful predictors of the models developed corroborate the hypotheses initially formulated that synergies and concurrent effects might effectively impact the removal of the selected micropollutants during nanofiltration.

Since the models developed were calibrated with a limited number of compounds, experimental conditions, and low variation of rejection/adsorption values, generalised conclusions from the present work should be taken with care. The mathematical approach used proved to be suitable to disclose relationships between the predictors and the outputs studied. This multivariate data analysis showed, then, to have the potential to be further applied in the prediction of nanofiltration performance for the removal of micropollutants from water. This mathematical approach may be either applied to study other specific processes, within limited experimental conditions, or be applied to a larger set of data, to highlight the general mechanisms and process conditions involved in the removal of target compounds (aiming process optimisation).

The extension of the application range of the models obtained can be further conducted using data from the nanofiltration of other molecules with different physico-chemical properties and geometry. More comprehensive models may also be accomplished by the inclusion of data obtained using other membrane types as well as by assessing other natural waters. The assessment of other water matrices would allow the establishment of correlations between more than one relevant water component and rejection/adsorption, namely natural organic matter and total hardness.

ACKNOWLEDGEMENTS

Financial support from Fundação para a Ciência e a Tecnologia - through the project PTDC/AMB/66024/2006, the grant PEst-OE/EQB/LA0004/2011, and the fellowships BPD/26990/2006 and BD/72244/2010 is gratefully acknowledged.

REFERENCES

Andersson CA, Bro R (2000) The N-way toolbox for MATLAB, *Chemometr Intell Lab* 52: 1-4.

Boggia R, Forina M, Fossa P, Mosti L (1997) Chemometric study and validation strategies in the structure-activity relationships of new cardiotonic agents. *Quant Struct-Act Rel* 16: 201-213.

Cessna AJ, Grover R (1978) Spectrophotometric determination of dissociation-constants of selected acidic herbicides. *J Agr Food Chem* 26: 289-292.

Chang EE, Chang Y-C, Liang C-H, Huang C-P, Chiang P-C (2012) Identifying the rejection mechanism for nanofiltration membranes fouled by humic acid and calcium ions exemplified by acetaminophen, sulfamethoxazole, and triclosan. *J Hazard Mater* 221–222: 19-27.

ChemSpider: The free chemical database. Available online http://www.chemspider.com/. Last accessed: December 2012.

Comerton AM, Andrews RC, Bagley DM, Yang P (2007) Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds. *J Membrane Sci* 303: 267-277.

Comerton AM, Andrews RC, Bagley DM, Hao CY (2008) The rejection of endocrine disrupting and pharmaceutically active compounds by NF and RO membranes as a function of compound a water matrix properties. *J Membrane Sci* 313: 323-335.

Duchesne C, MacGregor JF (2001) Jackknife and bootstrap methods in the identification of dynamic models. *J Process Contr* 11: 553-564.

Forina M, Lanteri S, Oliveros MCC, Millan CP (2004) Selection of useful predictors in multivariate calibration. *Anal Bioanal Chem* 380: 397-418.

Galinha CF, Carvalho G, Portugal CAM, Guglielmi G, Reis MAM, Crespo JG (2012) Multivariate statistically-based modelling of a membrane bioreactor for wastewater treatment using 2D fluorescence monitoring data. *Water Res* 46: 3623-3636.

Jmol: an open-source Java viewer for chemical structures in 3D. Available online: http://jmol.sourceforge.net/.

Karabelas A, Plakas K, Membrane treatment of potable water for pesticides removal, In: Soloneski S and Larramendy ML (Eds.), Herbicides, theory and applications. InTech, pp. 370-408 (2011). Available online: http://www.intechopen.com/books/herbicides-theory-and-applications/membrane-treatment-of-potable-water-for-pesticides-removal.

Kimura K, Amy G, Drewes J, Watanabe Y (2003) Adsorption of hydrophobic compounds onto NF/RO membranes: an artifact leading to overestimation of rejection. *J Membrane Sci* 221: 89-101.

Kiso Y, Sugiura Y, Kitao T, Nishimura K (2001) Effects of hydrophobicity and molecular size on rejection of aromatic pesticides with nanofiltration membranes. *J Membrane Sci* 192: 1-10.

Meylan WM, Howard PH, Validation of water solubility estimation methods using log K_{ow} for application in PCGEMS & EPI. Syracuse Research Corporation, Environmental Science Center, NY (1994).

Pesticide Properties DataBase, Agriculture & Environment Reasearch Unit (AERU). Available online: http://sitem.herts.ac.uk/aeru/footprint/. Last accessed: September 8, 2010.

Ryan TP, Modern regression methods. John Wiley & Sons, Inc, New York (1997).

Salvaterra AF, Sarmento G, Minhalma M, de Pinho MN (2011) Nanofiltration of surface water for the removal of endocrine disruptors. *Desalin Water Treat* 35: 54-61.

Sanches S, Penetra A, Granado C, Cardoso VV, Ferreira E, Benoliel MJ, Barreto Crespo MT, Pereira VJ, Crespo JG (2011) Removal of pesticides and polycyclic aromatic hydrocarbons from different drinking water sources by nanofiltration. *Desalin Water Treat* 27: 141-149.

Sanches S, Penetra A, Rodrigues A, Ferreira E, Cardoso VV, Benoliel MJ, Barreto Crespo MT, Pereira VJ, Cresp, JG (2012) Nanofiltration of hormones and pesticides in different real drinking water sources. *Sep Purif Technol* 94: 44-53.

Snyder SA, Adham S, Redding AM, Cannon FS, DeCarolis J, Oppenheimer J, Wert EC, Yoon Y (2007) Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination* 202: 156-181.

Van der Bruggen B, Schaep J, Wilms D, Vandecasteele C (1999) Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *J Membrane Sci* 156: 29-41.

Van der Bruggen B, Everaert K, Wilms D, Vandecasteele C (2001) Application of nanofiltration for removal of pesticides, nitrate and hardness from ground water: Rejection properties and economic evaluation. *J Membrane Sci* 193: 239-248.

Van der Bruggen B, Vandecasteele C (2001) Flux decline during nanofiltration of organic components in aqueous solution. *Environ Sci Technol* 35: 3535-3540.

Verliefde ARD, Heijman SGJ, Cornelissen ER, Amy G, Van der Bruggen B, van Dijk JC (2007) Influence of electrostatic interactions on the rejection with NF and assessment of the removal efficiency during NF/GAC treatment of pharmaceutically active compounds in surface water. *Water Res* 41: 3227-3240.

Yangali-Quintanilla V, Sadmani A, McConville M, Kennedy M, Amy G (2009) Rejection of pharmaceutically active compounds and endocrine disrupting compounds by clean and fouled nanofiltration membranes. *Water Res* 43: 2349-2362.

Zhang Y, Van der Bruggen B, Chen GX, Braeken L, Vandecasteele C (2004) Removal of pesticides by nanofiltration: Effect of the water matrix. *Sep Purif Technol* 38: 163-172.

CHAPTER 5

Removal of pesticides and hormones from water combining low pressure UV photolysis with nanofiltration

---

Adapted from:

Sanches S, Penetra A, Rodrigues A, Cardoso VV, Ferreira E, Benoliel MJ, Barreto Crespo MT, Crespo JG, Pereira VJ (2013) Removal of pesticides from water combining low pressure UV photolysis with nanofiltration. *Sep Purif Technol* 115: 73-82.

and

Sanches S, Rodrigues A, Cardoso VV, Ferreira E, Benoliel MJ, Barreto Crespo MT, Crespo JG, Pereira VJ (2013). Combination of UV photolysis and nanofiltration to overcome their drawbacks and remove endocrine disrupting compounds from a drinking water source. Re-submitted after revision to Desalination.

Sandra Sanches was involved in all the experimental work presented in this chapter, except for: 1) the quantification of the target pesticides and hormones in the samples from permeate of nanofiltration and combined treatment experiments that was performed by Ana Penetra and Alexandre Rodrigues at Laboratório Central of EPAL, Portugal, under the direction of Vitor Cardoso, Elisabete Ferreira, and Maria João Benoliel; 2) identification of UV by-products generated that was carried out by Vanessa Pereira and Vitor Cardoso. Vanessa Pereira, João Crespo, and Teresa Crespo supervised all the experimental work carried out.

CONTENTS

ABSTRACT

A sequential water treatment combining UV photolysis with nanofiltration was evaluated to remove several pesticides (atrazine, isoproturon, diuron, alachlor, and chlorfenvinphos) and hormones (17β-estradiol, 17α-ethinylestradiol, estrone, estriol, and progesterone) as well as the respective estrogenic activity. Generally, the individual processes were found to efficiently remove the target compounds. The combined treatment was able to remove the target compounds (removals higher than 85.1%) as well as the respective endocrine disrupting activity from the water containing a mixture of pesticides (64.4-93.8%) and hormones (95.4-99.6%) after 6 h of treatment. The ability of this treatment to overcome the drawbacks associated with the individual processes (production of a concentrated retentate and formation of toxic by-products) was also assessed. The retentate produced by the nanofiltration unit when operated in the integrated process was much less concentrated, suggesting that the combined treatment might effectively reduce the need to further treat/dispose the retentate. The concentration of the by-products formed and the estrogenic activity of the nanofiltration permeate was found to be always very low during the treatment, showing that the by-products formed during photolysis were generally efficiently retained by the nanofiltration process. The combination of direct LP/UV photolysis with nanofiltration is promising for a drinking water utility that needs to cope with sudden punctual discharges or deterioration of the water quality and wants to decrease the levels of chemicals in the nanofiltration retentate.

5.1 INTRODUCTION

The presence of pesticides and hormones in drinking water sources has recently attracted much attention. Several pesticides like atrazine, isoproturon, diuron, alachlor, and chlorfenvinphos, which occur in surface water and groundwater at 0.27-9950 ng L^{-1} (Cabeza *et al.* 2012, Postigo *et al.* 2010), are characterised by their negative impact in the environment given their toxicity, persistence, and potential of bioaccumulation. The hormones 17β-estradiol, 17α-ethinylestradiol, estrone, estriol, and progesterone, also highly impact the aquatic ecosystem due to their exceptional endocrine disrupting capabilities (Johnson and Sumpter 2001, Kolodziej *et al*. 2004, Ternes *et al*. 1999), even at concentrations below their occurrence levels in drinking water sources (0.07-180 ng L^{-1}) (Chang *et al.* 2008, Zhou *et al.* 2011). Endocrine disrupting activity has been also reported for pesticides such as atrazine and alachlor (Danzo 1997, Wilson *et al.* 1996). The increasing evidence of their impact and their detection in treated waters (McInnis 2010, Rodriguez-Mozaz *et al*. 2004, Kuster *et al.* 2008) demands the development of new technologies that allow utilities to provide high quality water.

UV photolysis and titanium dioxide photocatalysis as well as nanofiltration have been pointed out as alternative effective processes for the removal of a wide range of organic micropollutants including several pesticides and hormones (Braeken and Van der Bruggen 2009, Dudziak and Bodzek 2009, Leech *et al.* 2009, Pereira *et al.* 2012, Sanches *et al.* 2010, Sanches *et al.* 2012, Zhang *et al*. 2007). Although promising for water treatment applications, these processes present specific well known drawbacks. The partial oxidation of the micropollutants during UV processes may lead to the formation of oxidation products with higher toxicity than the parent compounds, as previously reported during the direct photolysis of carbamazepine using a medium pressure lamp (Donner *et al*. 2013). By-products of carbamazepine, acridine and acridone, were found to be more toxic than carbamazepine, using

---

several toxicological approaches. In addition, the scaling up of technologies using TiO_2 is limited due to the need to remove the photocatalyst from the treated water. The limitations associated with the application of pressure-driven membrane processes include the occurrence of fouling as well as the production of a retentate highly concentrated in suspended and dissolved constituents that requires additional treatment and/or disposal. Thus, operation costs associated with the treatment/disposal of retentate as well as frequent membrane cleanings and replacement are noteworthy (Braeken *et al*. 2006).

The integration of UV photolysis/TiO_2 photocatalysis and nanofiltration might attenuate these drawbacks. Nanofiltration is expected to retain the selected micropollutants, UV photolysis by-products, and TiO_2 nanoparticles while UV photolysis is likely to allow the production of a less concentrated retentate.

Nanofiltration followed by direct and indirect photolysis (using hydrogen peroxide) were previously tested using batch laboratory scale reactors and proved to be extremely efficient to remove hormones from a surface water matrix (Pereira *et al*. 2012). Some configurations combining a TiO_2 oxidation pre-treatment with membrane filtration have been proposed (Benotti *et al*. 2009, Bosc *et al*. 2005, Djafer *et al*. 2010, Le-Clech *et al*. 2006, Ma *et al*. 2010, Molinari *et al*. 2008, Molinari *et al*. 2002, Molinari *et al*. 2006). Even though many studies reported that the integration of these processes is promising, the removal of the micropollutants was mainly achieved by the oxidation step since the membranes tested were not suitable for their retention in many cases (Molinari *et al*. 2008, Molinari *et al*. 2006). Other membranes, in particular nanofiltration membranes, should therefore be evaluated.

The incomplete mineralisation of organic micropollutants during UV photolysis (Malato *et al*. 2003, Molinari *et al*. 2007) suggests that it is important to address the formation of intermediate compounds and understand if these compounds may also be retained in the filtration step. Although an efficient removal of the parent compounds may be achieved, permeate toxicity may increase as a result of the possible breakthrough of potentially toxic by-products (Escher and Fenner 2011, Rizzo 2011). Therefore, the ability of integrated processes to reduce the water toxicity requires further evaluation in particular, in natural water matrices.

This study aims to address the efficiency of a two-stage integrated system that combines UV direct photolysis and TiO_2 photocatalysis with nanofiltration to remove several pesticides (atrazine, isoproturon, diuron, alachlor, and chlorfenvinphos) and hormones (17β-estradiol, 17α-ethinylestradiol, estrone, estriol, and progesterone) from surface water collected after the sedimentation process in a water treatment utility. The processes take place sequentially: UV photolysis of the target micropollutants is followed by nanofiltration occurring in the absence of irradiation. The potential of this integrated process to decrease the estrogenic activity of the water is also evaluated through the identification of the UV photolysis by-products formed and the determination of their overall estrogenic activity using the YES assay.

5.2 MATERIALS AND METHODS

5.2.1 Chemical reagents

The pesticides and hormones as well as the aminoacids and salts used in the YES assay were purchased as solids of the highest grade commercially available (Sigma Aldrich, Germany).

Sabouraud dextrose agar (Oxoid, UK) supplemented with chloramphenicol (Oxoid, UK) was used to prepare the yeast culture media.

Titanium dioxide Degussa® P25, a mixture of 70% anatase and 30% rutile, with an average particle size of 20 nm and a reactive surface area of 35-65 m^2 g^{-1} (Evonik Degussa, Germany) was used in the photocatalytic experiments.

High performance liquid chromatography grade methanol and acetonitrile (Fisher, UK) was used for the chromatographic analysis of the pesticides and hormones as well as for the preparation of stock solutions. Milli-Q water used in the chromatographic analysis was produced by a Milli-Q water system (Millipore, CA, USA).

5.2.2 Natural water matrix

The water matrix was supplied by the water utility Empresa Portuguesa das Águas Livres, S.A. that treats and supplies drinking water to approximately 2.8 million people in the region of Lisbon, Portugal. Surface water from the abstraction zone of Tagus River in Valada do Ribatejo was collected after the sedimentation process in 10 L jerricans and stored at 4 ± 3 °C until used. The micropollutants targeted in this study were not detected in the water collected for this study.

All the experiments performed were carried out at a pH value of 7.8, without any pH adjustment. Molinari *et al*. (2008) reported that the optimum pH for the degradation of organic compounds by TiO_2 photocatalysis is 7.0 ± 3.0.

5.2.3 Experimental setup

The experiments were performed in a laboratory scale unit shown schematically in Figure 5.1.

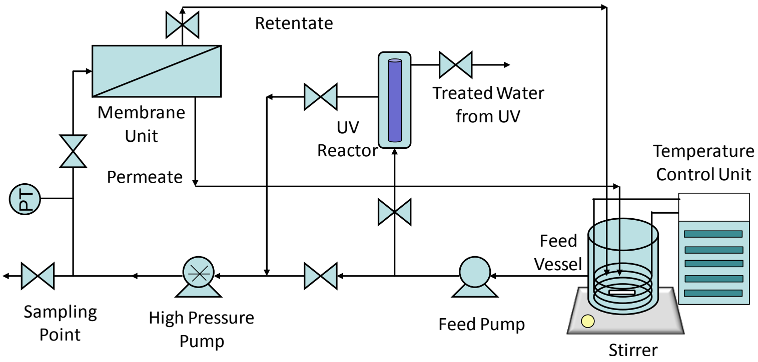


Figure 5.1 *Schematic representation of the experimental setup.*

This unit is equipped with a feed vessel, a recirculation magnetic drive pump (model MD-15RV, IWAKI, Massachusetts, USA), a Puro-Tap UV reactor with a low pressure mercury lamp that emits primarily monochromatic light at 254 nm (PURO, Italy), an high pressure diaphragm pump (Hydra-Cell model D/G-03-X, Wanner Engineering, USA), and a membrane unit equipped with a spiral-wound Desal 5DK membrane (model DK2540F1073, GE Water & Process Technologies, USA). The nanofiltration filter element presented 1.27 mm spacers, an active area of 1.6 m^2, a water permeability of 5.0 ± 0.2 $L\ h^{-1}\ bar^{-1}\ m^{-2}$, and an $MgSO_4$ average rejection of 98%. The maximum operating pressure of the membrane module is 41 bar. A transmitter (8864, Trafag, Switzerland) was placed upstream the membrane unit to measure the pressure and temperature of the water circulating in the system. The pressure was adjusted on the retentate side with a brass ball valve. The temperature of the feed water was controlled at 25 ± 2 °C using a temperature control unit equipped with a stainless steel heat exchanger coil that was submerged into the feed reservoir. Stirring was provided to the feed solution during the experiments to ensure the homogeneity of the solution and to avoid TiO_2 deposition. The tubing of the system was made of polyvinylidene difluoride to minimise the adsorption of the organic compounds.

This unit was designed to allow to carry out different studies: degradation of the selected compounds by UV photolysis/TiO_2 photocatalysis (using only the UV lamp), removal by nanofiltration (using only the membrane module), and integration of both processes (using the UV reactor followed by nanofiltration).

5.2.4 UV photolysis

LP/UV direct photolysis and TiO_2 photocatalysis experiments were performed to assess the degradation of the selected organic compounds over time. Surface water collected after sedimentation (2 L) was spiked with a mixture of the selected pesticides or hormones to achieve a concentration of approximately 500 μg L^{-1}. Even though the target compounds occur in the aquatic environment at ng L^{-1} to low μg L^{-1} range (see Tables 1.1 and 1.2 in Chapter 1), higher levels were spiked in the feed water used in these and the other experiments described in this chapter. These higher levels enabled to follow the degradation of the compounds by HPLC direct injection and to identify some UV by-products formed, since the detection limits of the methods (see section 5.2.7) could prevent the follow-up of the pesticides and hormones degradation if the compounds were spiked at their occurrence levels.

The UV lamp was turned on approximately 30 min before the assays to stabilise the radiation intensity while laboratory grade water was recirculated through the UV system. The water solutions containing the mixture of pesticides or the mixture of hormones were then totally recirculated through the UV reactor during approximately 3-7 h in the absence (direct photolysis) and presence of 50 mg L^{-1} TiO_2 (optimum TiO_2 concentration; data not shown). Samples (2 mL) were taken at regular time intervals during the assays, filtered with 0.2 μm filters made of regenerated cellulose (Whatman, USA) to remove TiO_2 particles, and analysed by HPLC to determine the percent degradation of the compounds. These filters were selected among several filters evaluated since they are able to minimise the adsorption of the selected compounds onto the filter material, with percent adsorptions lower than 12.1% (0.3% for atrazine, 5.0% for isoproturon, 3.0% for diuron, 8.0% for alachlor, 11.0% for chlorfenvinphos, 6.5% for 17β-estradiol, 12.1% for 17α-ethinylestradiol, 6.3% for estrone, 4.9% for estriol, and 8.1% for progesterone).

The UV fluence provided by the UV lamp was determined by using the data obtained for atrazine since this compound is often used for actinometry purposes. Besides the concentration of atrazine before and after LP/UV photolysis in this study, the fluence-based direct photolysis rate constant provided in Chapter 1, obtained using a well defined collimated beam batch reactor (Sanches *et al*. 2010), was also used for the UV fluence determination. The UV fluence determined for the LP/UV lamp was approximately 465mJ cm^{-2}.

Control experiments were performed to assess the loss of the organic compounds due to degradation or adsorption on the system. These experiments were conducted under the exact same conditions as the direct photolysis and photocatalysis assays with the exception of the fact that the UV lamp was turned off. Samples were also taken over time and analysed by HPLC. A concentration decline lower than 12% was determined for atrazine, isoproturon, diuron, 17β-estradiol, and estriol while decreases of 34, 39, 22, 21, and 59% were obtained for alachlor, chlorfenvinphos, 17α-ethinylestradiol, estrone, and progesterone, respectively. These values were used to correct the degradations attained during photolysis assays.

5.2.5 Nanofiltration

Nanofiltration experiments were conducted with total recirculation of permeate and retentate to simulate an extended exposure of the membrane to a water stream containing the target micropollutants. Much larger volumes of feed solutions would be needed to follow the removal of the compounds over time in the absence of total recirculation since the dead volume of the system is approximately 800 mL. Furthermore, a considerable quantity of the selected organic compounds would therefore be needed, which is unaffordable.

Surface water collected after the sedimentation process (5 L) was spiked with the appropriate volume of a mixture of pesticides or a mixture of hormones to achieve a concentration of approximately 500 μg L^{-1}. These solutions were recirculated in the nanofiltration system with a by-pass to the UV system at 0.2 m^3 h^{-1} and 10 bar during 6 hours. The volume of feed was maintained constant after each sampling through the addition of fresh solution to the feed vessel.

Samples of feed, permeate, and retentate were taken throughout the experiments and acidified to prevent degradation of the organic compounds until analysis to determine the concentration of the target pesticides and hormones.

5.2.6 Integration of UV photolysis/TiO_2 photocatalysis and nanofiltration

This configuration was evaluated under different experimental conditions that were set to mimic the real conditions in water treatment utilities. Two different strategies were followed to evaluate the potential of the integrated sequential process to cope with different loadings of micropollutants throughout the treatment: 1 - total recirculation without the addition of fresh feed solution during the experimental study and; 2 - total recirculation at constant volume with the repeated addition of fresh feed solution for replenishment of the volumes of samples extracted at different experimental times. The experiments were conducted with total recirculation of permeate and retentate, for the same reasons detailed in section 5.2.5 for nanofiltration experiments.

The experiments combining UV photolysis and nanofiltration were conducted in the absence and presence of 50 mg L^{-1} suspended TiO_2. In both assays, surface water collected after the sedimentation process (5 L) was spiked with a mixture of the selected pesticides or a mixture of the selected hormones to achieve a final concentration of 500 μg L^{-1}. In the UV reactor, the degradation of the target compounds took place due to LP/UV irradiation at atmospheric pressure. In the membrane unit, nanofiltration was performed at 10 bar in the absence of irradiation. Operation was carried out in sequential steps (reaction, filtration, recirculation) during 6 h. Samples of feed, permeate, and retentate were taken at regular intervals to follow the removal of the selected compounds and identify UV photolysis by-products formed as well as to evaluate the variation of the relative estrogenic activity of the water using the YES assay (described in section 5.2.8).

5.2.7 Analytical methods

Different analytical methods were used according with the different micropollutants and their concentrations in the samples. The concentration of the mixture of pesticides and the mixture of hormones in the samples of feed and retentate was followed by direct HPLC injection. The detection limits achieved by direct injection of the target compounds are the following: 5 μg L^{-1} (estriol and atrazine), 12.5 μg L^{-1} (diuron and chlorfenvinphos), 20 μg L^{-1} (isoproturon), 25 μg L^{-1} (estrone and progesterone), 50 μg L^{-1} (alachlor and 17β-estradiol), and 100 μg L^{-1} (17α-ethinylestradiol).

Analytical methodologies that include a previous concentration step were employed to monitor the concentration of the target analytes in the permeate due to the low concentrations expected (below the detection limits mentioned above) and to evaluate the formation of UV by-products. Briefly, atrazine, alachlor, and chlorfenvinphos were concentrated by solid phase extraction and analysed by gas chromatography with mass spectrometry detection while the analytes diuron and isoproturon were concentrated by SPE and analysed by HPLC-MS/MS. Solid-phase extraction was also carried out prior to quantification of hormones by UPLC-MS/MS. The uncertainties related with the methodologies comprising a concentration step are the following: 9.5% (atrazine), 18.3% (isoproturon), 17.9% (diuron), 9.8% (alachlor), 13.4% (chlorfenvinphos), 23.1% (17β-estradiol), 18.7% (17α-ethinylestradiol), 17.2% (estrone), 14.7% (estriol), and 22.5% (progesterone).

A detailed description of the analytical methods employed to quantify the target compounds (by direct injection and after concentration) and identify the by-products formed is provided in Appendix A.1.

5.2.8 Yeast estrogen screen assay

A YES assay using a human estrogen receptor transfected *Saccharomyces cerevisiae* strain was performed to evaluate the variation of the relative estrogenic activity of the permeate and retentate samples from the integrated process throughout the experiments. The human estrogen receptor transfected *Saccharomyces cerevisiae* employed in the YES assay was used under agreement with Professor J. P. Sumpter at Brunel University, UK. This assay was conducted according to the procedure described by Routledge and Sumpter (1996) and specific modifications introduced by Stanford and Weinberg (2010). A detailed description is provided in Appendix A.4.

In this assay, 17β-estradiol is used as a reference in terms of estrogenic activity response. The concentrations of 17β-estradiol and samples tested that induce 50% of the maximum response (EC_{50}) were determined and used to obtain and compare the estradiol equivalents (EEQ) of the samples over time. Estradiol equivalents are a measure of the relative estrogenic activity of the samples and were determined using Equation 5.1.

$$Estradiol Equivalents=\frac{EC_{50,17\beta-Estradiol}}{EC_{50,Sample}} \tag{5.1}$$

5.3 RESULTS AND DISCUSSION

5.3.1 UV photolysis

LP/UV direct photolysis and TiO_2 photocatalysis were evaluated for the degradation of the selected pesticides and hormones. These compounds were addressed as a mixture of pesticides or as a mixture of hormones since these micropollutants are present in the water as a cocktail of compounds and concurrent effects may influence their degradation rates.

Two water matrices with very different compositions were initially tested and compared in terms of the degradation of the target compounds by direct photolysis – laboratory grade water and surface water collected after the sedimentation process in a water treatment utility. Surface water collected after sedimentation was selected instead of untreated surface water because, at this stage of the treatment, the suspended, colloidal, and particulate matter that contribute to scavenging of UV light, membrane fouling, and flux decline were already highly removed (Sanches *et al.* 2012). The degradation of the pesticides was not generally very influenced by the water matrix while a considerable improvement was observed in laboratory grade water comparatively with the surface water collected after sedimentation for the hormones (percent change of 9% for atrazine, 13% for isoproturon, 10% for diuron, 30% for alachlor, 5% for chlorfenvinphos, 52% for 17β-estradiol, 77% for 17α-ethinylestradiol, 22% for estrone, 24% estriol, and 33% for progesterone). This behaviour is probably related with the competition between the target compounds and resilient natural organic matter constituents for the absorption of the UV radiation. All the subsequent experiments were conducted in the real water matrix: surface water collected after sedimentation.

The linearity between TiO_2 concentration and its absorbance in the concentration range of 10 to 1000 mg L^{-1} was evaluated by UV-vis spectrophotometry (340 nm). Results (data not shown) showed that there is no linearity between the concentration of TiO_2 and absorbance above 100 mg L^{-1}. Then, the ability to maintain the concentration of TiO_2 constant over time at these levels in the feed vessel and therefore, in the UV lamp circuit, was addressed by totally recirculating solutions with TiO_2 concentrations of 50 and 100 mg L^{-1} through the tubes of the system during the same time of the photolysis experiments (approximately 6 h). Even though the feed solution was powerfully stirred during all the experiments to avoid deposition of the catalyst, there was a loss of TiO_2 due to adsorption on the system and vessel walls using both concentrations. Approximately 39% and 60% loss of catalyst was detected at 50 and 100 mg L^{-1}, respectively. Even though a constant TiO_2 concentration is intended during the experiment to ensure the same catalytic conditions, our results show that a significant loss of catalyst can be expected. All experiments involving the use of TiO_2 were conducted at 50 mg L^{-1} to ensure a lower catalyst loss.

The degradation of the compounds was followed over time and time-based pseudo-first-order rate constants (k'_t) were determined from the slope of the linear regression described by Equation 5.2:

$$-\frac{d[C]}{dt} = k'_t [C] \Rightarrow ln\frac{[C]}{[C_0]} = -k'_t \times t \tag{5.2}$$

The rate constants obtained are provided in Table 5.1.

Table 5.1 *Time-based pseudo-first order direct and AOP rate constants (k'_t) obtained for the selected pesticides and hormones in surface water collected after the sedimentation process and the respective determination coefficients (R^2).*

Compound	**Direct photolysis**		**AOP/TiO_2 (50 mg L^{-1})**	
	k'_t x10^3 (min^{-1})	**R^2**	**k'_t x10^3 (min^{-1})**	**R^2**
Atrazine	26.8 ± 0.3	0.99	19.3 ± 0.4	0.99
Isoproturon	3.7 ± 0.1	0.99	4.1 ± 0.1	0.99
Diuron	42.0 ± 0.3	0.99	33.3 ± 0.7	0.99
Alachlor	8.0 ± 1.0	0.88	8.9 ± 0.7	0.95
Chlorfenvinphos	41.7 ± 5.5	0.94	11.6 ± 2.4	0.80
17β-Estradiol	2.0 ± 0.1	0.94	17.1 ± 0.2	0.99
17α-Ethinylestradiol	1.3 ± 0.1	0.95	16.6 ±0.3	0.99
Estrone	24.5 ± 2.8	0.91	33.2 ±0.8	0.99
Estriol	1.9 ± 0.1	0.98	20.1 ± 1.0	0.97
Progesterone	34.7 ± 4.7	0.90	22.7 ± 2.5	0.93

When comparing the time-based pseudo-first order direct and indirect photolysis rate constants reported in Table 5.1, an increase not very high was observed in the degradation of isoproturon, alachlor, and estrone using the AOP (percent changes between 5 and 15%) while for the other pesticides and progesterone, the AOP even hinder their degradation. Therefore, it may be concluded that there is no significant advantage in using TiO_2 to degrade the selected pesticides, as reported in Chapter 2, for experiments carried out using a batch collimated beam reactor (Sanches *et al*. 2010). However, the levels of mineralisation achieved in both processes may have been different. The negligible effect of TiO_2 is mainly the result of the very effective LP/UV direct photolysis decay. Furthermore, TiO_2 nanoparticles may compete with the pesticides by the absorption of the UV radiation and present a hindrance effect. Conversely, a significant improvement in the degradation of 17β-estradiol, 17α-ethinylestradiol, and estriol was observed in the present study by TiO_2 photocatalysis. This improvement (percent change between 79 and 86%) shows that the hydroxyl radical mediated advanced oxidation becomes the dominant degradation mechanism. These results are in line with a previous study that compared the photodegradation of several hormones in a raw surface water by direct photolysis and an H_2O_2 based AOP using a batch collimated beam reactor (Pereira *et al*. 2012). Despite the difference in the experimental conditions of the two studies, the degradation of 17β-estradiol, 17α-ethinylestradiol, and estriol was also highly enhanced by the presence of H_2O_2 in that study while only a slight increase was obtained for estrone and progesterone. A considerable improvement in the degradation of these three hormones was also reported by Rosenfeldt and Linden (2004) in the presence of H_2O_2 using medium pressure lamps and by Puma *et al*. (2010) when UV-A and UV-C lamps were tested.

Figure 5.2 shows the percent degradation attained for the selected pesticides (Figure 5.2a) and hormones (Figure 5.2b) during direct photolysis.

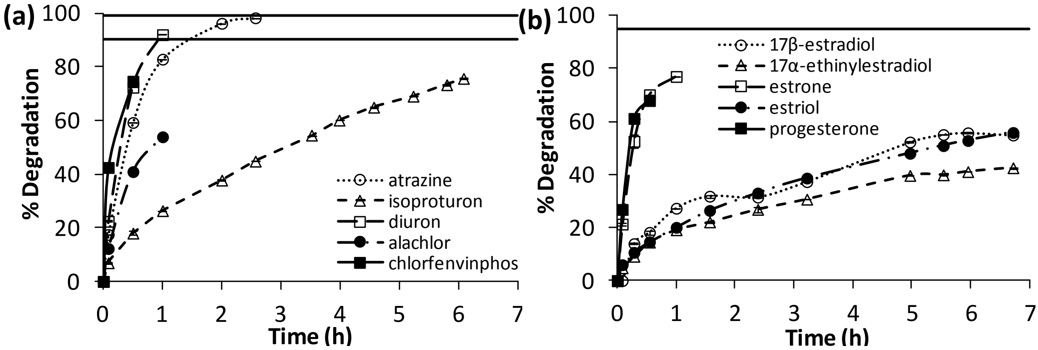


Figure 5.2 Degradation of the selected ***(a)*** *pesticides and* ***(b)*** *hormones by LP/UV direct photolysis over a 6-7 h experimental period (duplicate injections are provided as error bars; degradations higher than limits of detection are not represented). Horizontal lines in (a) represent % degradations that correspond to the lowest and highest limits of detection of the target pesticides (5-50 μg L^{-1}); the horizontal line in (b) correspond to the detection limit for the hormones estrone and progesterone (25 μg L^{-1}).*

All pesticides and hormones were analysed over the 6-7 h experimental periods. Whenever the concentrations of the compounds were below the detection limits of the analytical methods, the respective degradations (>90% and >95% for the pesticides and hormones, respectively) were not provided in the plot. Results obtained illustrate the high efficiency of direct photolysis towards the selected pesticides since removals higher than 90% were obtained after 2.6 h for all pesticides, except isoproturon (76% after 6.1 h). Extremely high degradations (>95%) were also attained for the hormones estrone and progesterone after the first hour of treatment. Conversely, 17β-estradiol, 17α-ethinylestradiol, and estriol were poorly degraded by direct photolysis. These differences might be explained by the decadic molar absorption coefficient (probability of the selected compounds to absorb UV light at 254 nm) and quantum yield (ratio between the total number of molecules of compound degraded to the total number of photons absorbed by the solution due to the compound's presence) of the selected hormones. Although estrone presents a low decadic molar absorption coefficient (2215 M^{-1} cm^{-1}), the highest quantum yields were determined for this molecule (5.45 mol $Einstein^{-1}$) and progesterone (2.82 mol

---

Einstein^{-1}) relatively to the other hormones (0.06, 0.09, and 0.40 mol Einstein^{-1} for 17β-estradiol, 17α-ethinylestradiol, and estriol, respectively) in a previous study (Pereira *et al*. 2012).

Isoproturon, that was previously found to be extremely resilient to degradation (<14%) during batch collimated beam UV photolysis (Sanches *et al*. 2010), was degraded more efficiently in the present study. The improvement of the degradation of isoproturon had been previously predicted, as described in Chapter 1, by modelling the results obtained in a batch experimental set up if a reactor that allows lower distances between the UV lamp and the water could be used (Sanches *et al*. 2010). Indeed, much lower distances from the UV source are provided by this system (approximately 0.5 cm vs 29 cm), which results in higher UV fluences. In the present study, 1 h of circulation in the system corresponds to approximately 2200 mJ cm^{-2}.

Figure 5.3 depicts the degradation of the selected pesticides (Figure 5.3a) and hormones (Figure 5.3b) during TiO_2 photocatalysis.

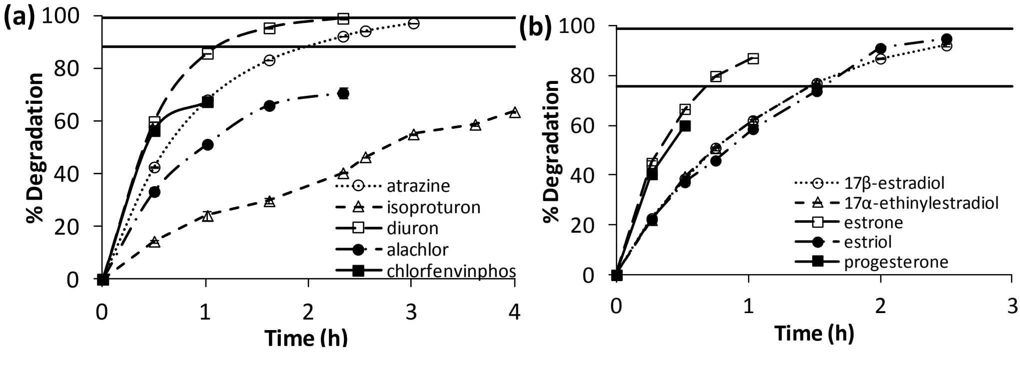


Figure 5.3 *Degradation of the selected* ***(a)*** *pesticides and* ***(b)*** *hormones by* TiO_2 *photocatalysis over a 3-4 h experimental period (50 mg/L* TiO_2*; duplicate injections are provided as error bars; degradations higher than limits of detection are not represented). Horizontal lines in (a) represent % degradations that correspond to the lowest and highest limits of detection of the target pesticides (5-50 μg* L^{-1}*); horizontal lines in (b) correspond to the lowest and highest limits of detection of the target hormones (5-100 μg* L^{-1}*).*

Even though all the compounds were analysed over the 3-4 h experimental period, only isoproturon was detected throughout all assay. Whenever pesticides and hormones were not detected because of their concentrations below the detection limits of the analytical methods employed, the respective degradations (>88% for the pesticides and >76% for the hormones) were not provided in the plot. Among the hormones, only estriol and 17β-estradiol were still present after 2.5 h of photocatalysis at concentrations that enabled detection and that correspond to removals of 95 and 92%, respectively, showing that LP/UV/TiO_2 is extremely efficient to accomplish the degradation of the hormones poorly degraded by direct photolysis.

5.3.2 Nanofiltration

A Desal 5DK membrane was selected for this study since it proved to be extremely effective for the removal of the pesticides atrazine and alachlor as well as the hormones addressed in a flat-sheet configuration using a cross-flow membrane unit (Sanches *et al*. 2012).

The apparent rejection of the selected compounds was determined taking all mechanisms that affect the retention of solutes into consideration using Equation 5.3.

$$R_{app}(\%) = 100 \times \left(1 - \frac{C_{p_t}}{C_{f_0}} \right) \tag{5.3}$$

where C_{p_t} and C_{f_0} are the concentrations of a given compound in the permeate over time (t) and in the feed solution at t=0, respectively.

Figure 5.4 shows the apparent rejection obtained for all pesticides (Figure 5.4a) and hormones (Figure 5.4b) over 6 hours of nanofiltration.

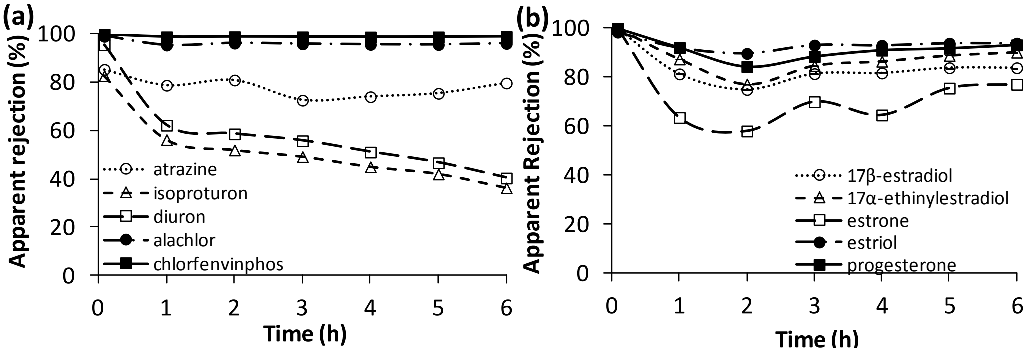


Figure 5.4 *Apparent rejections of the selected **(a)** pesticides and **(b)** hormones throughout the nanofiltration assay.*

The apparent rejections observed were very high for all the pesticides in the beginning of the experiment (>83%). Even though the rejections attained for alachlor, chlorfenvinphos, and atrazine were very high throughout the assay, the rejections obtained for isoproturon and diuron decreased significantly within the first hour of treatment and were determined as approximately 40% at the 6th hour of operation.

All pesticides adsorbed on the membrane during the early stage of nanofiltration and then a decrease in the adsorption was generally observed (data not shown). The decrease observed in the rejection of isoproturon and diuron may be related with the decrease observed in their adsorption. The decrease in the overall rejection and adsorption over time has been previously reported by other authors (Kimura *et al.* 2003, Nghiem *et al.* 2004). In the first stages of nanofiltration, some compounds are strongly adsorbed on the membrane and therefore, adsorptive interactions are the main rejection mechanism. However, as filtration proceeds, membrane site saturation may be achieved and, therefore, other mechanisms may play role. In the present study, the impact of the adsorption decrease on the rejection of isoproturon and diuron may have been higher than for chlorfenvinphos and alachlor, probably because of their lower molecular weight. Moreover, the rejections attained for atrazine, isoproturon, and diuron were lower comparatively to alachlor and chlorfenvinphos, particularly after one hour of operation in the case of diuron and isoproturon. This behaviour is consistent with the molecular weight of the molecules since alachlor and chlorfenvinphos present higher molecular weights (269 and 359 Da, respectively) than isoproturon, atrazine, and diuron (206, 215, and 233 Da, respectively) and were consequently more rejected by the membrane. Size exclusion is therefore also an important mechanism for the rejection of the selected pesticides.

The rejections obtained in this study for atrazine and alachlor, particularly alachlor, are quite similar to those obtained in a previous study using a flat-sheet Desal 5DK membrane and a cross-flow cell (Sanches *et al*. 2012).

The rejections obtained for the hormones throughout nanofiltration were often higher than 77.2%, with the exception of estrone (58.0-99.9%), showing that the process is also effective to remove these molecules even when they are spiked in surface water at levels higher than their reported occurrence levels (Figure 5.4b). In Chapter 3, very high removals of these hormones were also reported (higher than 90.0% and 67.4% in groundwater and surface water, respectively) using the same membrane in a flat-sheet configuration (Sanches *et al*. 2012). Generally, removals attained by Pereira *et al*. (2012) for the majority of these hormones using a NF-270 membrane also concur with these findings.

As for the pesticides, apparent rejection of hormones after 1 h of operation was generally higher for the molecules having the highest molecular weights. Nevertheless, size exclusion mechanisms do not seem to play an important role in the early stage of the process since very similar and extremely high removals were obtained for all hormones. Conversely, hydrophobic interactions may play a significant role in the beginning of the assay, contributing to higher rejections. After 1 hour of treatment, some variation is observed in the rejection of some hormones, particularly estrone, which is probably related with the uncertainties associated with the analytical methodologies employed for the determination of micropollutants concentrations.

5.3.3 Integration of UV photolysis/TiO_2 photocatalysis and nanofiltration

The integrated process was evaluated in the absence and presence of 50 mg L^{-1} suspended TiO_2. However, the complete deposition of TiO_2 on the membrane was observed within the first five minutes of operation. As a result, the removal of the target compounds was similar to the one obtained in the absence of the catalyst since nanoparticles were removed from the reaction environment. Therefore, only the results obtained in the absence of TiO_2 are provided in this chapter.

Since the degradation of 17β-estradiol, 17α-ethinylestradiol, and estriol is considerably improved in the presence of TiO_2, another configuration combining TiO_2 photocatalysis with nanofiltration could be pursued to take advantage of the benefits of integrating both technologies. An interesting approach could be the irradiation of TiO_2 immobilised on the membrane surface, which would prevent agglomeration of suspended nanoparticles and their deposition.

5.3.3.1 Experiments carried out with total recirculation without feed solution addition

Table 5.2 shows the global removal of the target pesticides and hormones throughout the integrated process without addition of fresh feed solution, reflecting the quality of the drinking water produced (permeate).

Table 5.2 Removal of the selected pesticides and hormones during the integrated treatment without fresh feed solution addition.

Compound	**Removal (%)**		
	0.1 h	**3 h**	**6 h**
Atrazine	99.9	99.9	>99.9
Isoproturon	99.7	95.3	95.0
Diuron	99.9	95.8	97.4
Alachlor	99.9	99.9	>99.9
Chlorfenvinphos	99.9	99.9	99.9
17β-Estradiol	99.9	85.6	85.1
17α-Ethinylestradiol	99.9	94.7	93.8
Estrone	99.9	93.3	95.2
Estriol	99.9	88.6	91.0
Progesterone	99.9	98.8	97.6

The integrated treatment was very effective since the removals attained using Equation 5.3 were higher than 99.7% within the first stages of operation. Slightly lower removals were observed for the majority of the compounds at the 3rd and 6th hours probably due to their diffusion through the membrane when the equilibrium was achieved.

The removals attained are in agreement with the removals obtained by nanofiltration alone (Figure 5.4) for the majority of the compounds with percent changes lower than 2% at the 6th hour of treatment. An improvement was, however, observed for atrazine, isoproturon, diuron, and estrone when the combined treatment was applied with percent changes of 11, 45, 41, and 11%, respectively. Thus, there is advantage in the use of the integrated treatment in terms of the quality of the water produced.

The potential of this treatment to produce a less concentrated retentate was assessed by determining the removal of the selected micropollutants from the retentate ($Removal_{retentate}$) over time using Equation 5.4.

$$Removal_{retentate}\,(\%) = 100 \times \left(1 - \frac{C_{r_t}}{C_{r_{t0}}} \right) \tag{5.4}$$

where C_{r_t} and $C_{r_{t0}}$ are the concentrations of a given compound in the retentate over time (t) and in the beginning of the experiment (t_0), respectively.

Figures 5.5a and c depict the removal of the selected pesticides and hormones from the retentate while Figures 5.5b and d show the removal of the estrogenic activity throughout the assay carried out without the repeated addition of fresh feed solution.

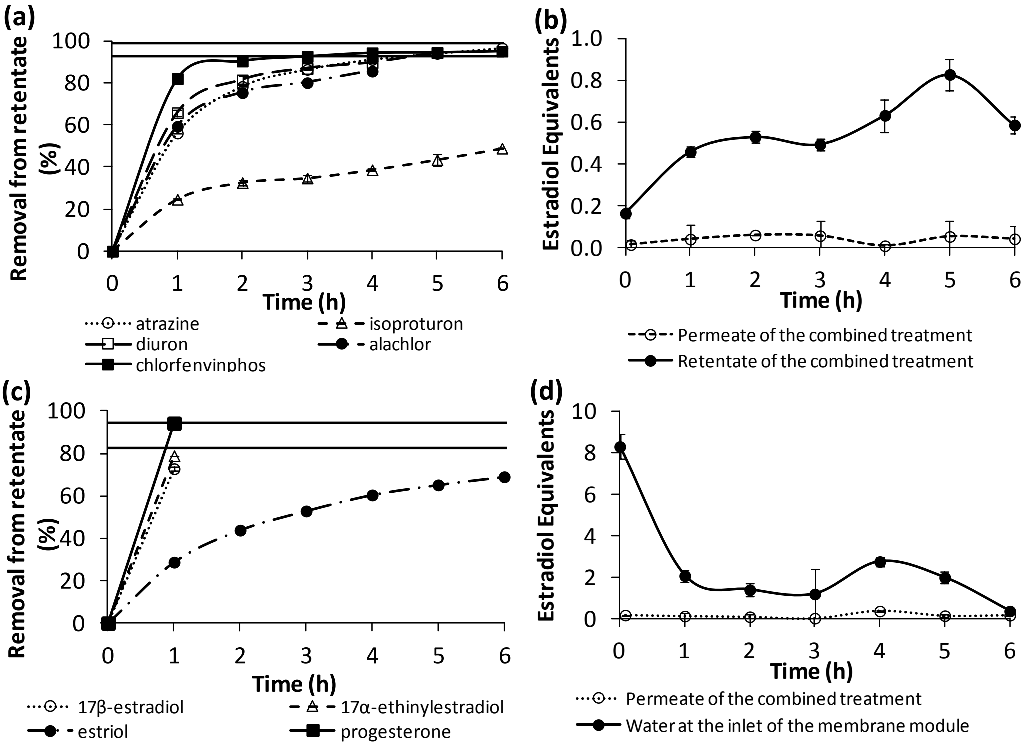


Figure 5.5 *Removal of the selected pesticides from the retentate* ***(a)*** *and variation of the respective Estradiol Equivalents in the permeate and retentate* ***(b)****; removal of the selected hormones from the retentate* ***(c)*** *and variation of the respective Estradiol Equivalents in the permeate and at the inlet of the membrane module* ***(d)*** *throughout the integrated treatment conducted without fresh feed solution addition in the absence of TiO_2 over a 6h experimental period (duplicate experiments are provided as error bars; degradations higher than limits of detection are not represented). Horizontal lines in (a) represent % degradations that correspond to the lowest and highest limits of detection of the target pesticides (5-50 $\mu g\ L^{-1}$); horizontal lines in (c) represent the % degradations that correspond to the lowest and highest detection limits of the hormones not detected after 1 h of operation (25-100 $\mu g\ L^{-1}$).*

Even though all pesticides and hormones were analysed over the 6 h experimental period, the concentrations of the pesticides diuron and alachlor as well as all hormones except estriol were below the detection limits of the analytical methods employed in the later stage of the treatment. The respective degradations are therefore not provided.

After 6 h of operation, removals from retentate higher than 92% were obtained for all the pesticides, except isoproturon (49%), which can be attributed to UV degradation as well as to adsorption on the membrane (Figure 5.5a). Removals from the retentate higher than 79% were obtained for all the hormones except estriol at the first hour of treatment (Figure 5.5c). Estriol was still detected in the retentate at the 6th hour with a removal of 69% while estrone was not detected above the detection limits even at the sample taken at the 1st hour (removal higher than 92%).

The significant decrease observed in the concentration of the selected pesticides and hormones in the retentate is very important since it is likely to reduce the need for additional treatment and disposal procedures of retentate, which costs represent a major drawback of common filtration processes.

Even though the integrated process was very efficient towards the target compounds in terms of the quality of the water produced as well as the retentate, the formation of UV photolysis by-products that may increase the toxicity of the water needs to be accounted. Although the concentration of the pesticides in the retentate decreased over the treatment (Figure 5.5a), the relative estrogenic activity of the retentate, reported as the equivalent concentration of 17β-estradiol, increased until the 5th hour of treatment (Figure 5.5b). This increase is likely to be related with the presence of estrogenically active transformation compounds generated during UV photolysis that present higher levels of estrogenicity than the parent compounds. Despite this increase, a decreasing tendency was observed for the retentate between the 5th and 6th hours. Data obtained suggest that the decrease of the estrogenic activity is probably only accomplished after several hours due to the production of photolysis by-products. Even though the relative estrogenic activity determined for the retentate containing pesticides increased during UV photolysis, the by-products produced were retained by the membrane since the estrogenic activity of the permeate was always very low and did not increase throughout the assay.

For the hormones, a noteworthy estrogenic removal of 75% was attained at the inlet of the membrane within the first hour of treatment (Figure 5.5d). However, a slight increase was observed between the 3rd and the 4th hours in both permeate and water at the inlet of the membrane. This increase in the estrogenic activity may be explained by the formation of estrogenically active transformation compounds. The simultaneous increase of estrogenic activity in the permeate and in the water at the inlet of the membrane suggests the breakthrough of by-products at this period, which should be further addressed. The efficient removal of the endocrine disrupting activity associated to 17β-estradiol and 17α-ethinylestradiol during photolysis using low pressure and media pressure lamps was also previously reported (Rosenfeldt *et al*. 2007).

Estradiol equivalents obtained in the permeate from the experiment carried out with pesticides (0.01-0.06) and hormones (0.04-0.38) were always largely below the estradiol equivalents determined in the initial feed solutions of pesticides (0.16) and hormones (8.32) (Figures 5.5 b and d). These results reflect removals of estrogenic activity of 64.4-93.8% and 95.4-99.6% for the pesticides and hormones, respectively. The results show that the combined treatment is not only extremely efficient to accomplish the removal of the target compounds but also the removal of formed by-products with estrogenic activity.

5.3.3.2 Experiments carried out with total recirculation at constant volume with repeated addition of feed solution

Similar quality of the permeate was attained in the assays conducted with and without the repeated addition of feed solution containing the mixture of the pesticides or the mixture of hormones (data not shown).

When repeated addition of feed solution was conducted throughout the assay, the removal of the selected pesticides and hormones from the retentate was less efficient (Figures 5.6a and c) comparatively to the previous assay (Figures 5.5a and c).

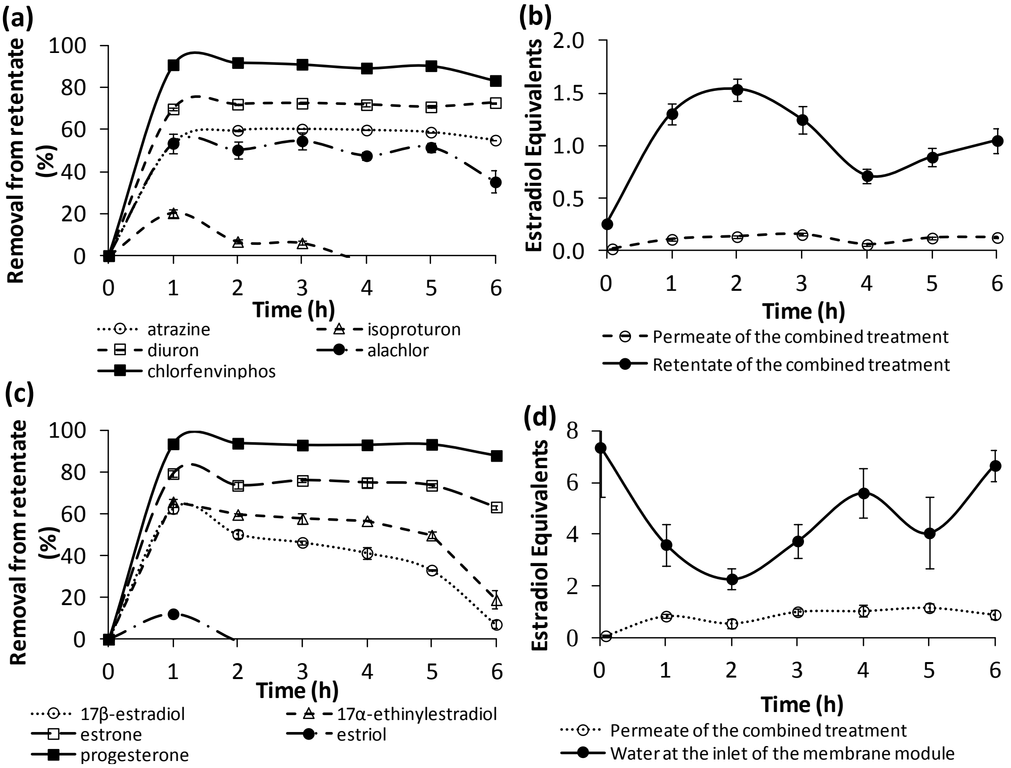


Figure 5.6 *Removal of the selected pesticides from the retentate* ***(a)*** *and variation of the respective Estradiol Equivalents in the permeate and retentate* ***(b)****; removal of the selected hormones from the retentate* ***(c)*** *and variation of the respective Estradiol Equivalents in the permeate and at the inlet of the membrane module* ***(d)*** *throughout the integrated treatment conducted with the addition of fresh feed solution in the absence of* TiO_2 *over a 6 h experimental period (duplicate experiments are provided as error bars).*

This observation was expected due to the accumulation of the non-degraded compounds. The average hydraulic residence time of the water solution was determined as 2.5 h since this experiment was conducted at a constant volume of 5 L with the addition of 2 L of fresh feed solution every hour, similarly to a fed-batch experiment. This hydraulic residence time was found to be short to achieve an effective degradation and should therefore be increased.

The higher concentration of the target compounds determined in the retentate during this assay is also reflected in the relative estrogenic activity which is approximately the double for the pesticides (Figures 5.5b and 5.6b) and eighteen times higher for the hormones (Figures 5.5d and 5.6d) in the end of the treatment.

The increase of the relative estrogenic levels associated with the pesticides in the retentate was observed until the 2nd hour of treatment, which is likely to be related with the formation of UV photolysis by-products since the concentration of all pesticides except isoproturon decreased in the beginning of the experiment and then remained fairly constant.

Isoproturon was accumulated in the system since the beginning of the experiment due to its lower degradation rate constant as previously discussed. Likewise, estriol was particularly poorly removed among the hormones. A significant decrease of estradiol equivalents was observed in the water containing the target hormones at the inlet of the membrane during the initial two hours of treatment (69%). However, successive increases and decreases of estrogenic activity were observed after this period (Figure 5.6d) probably because of the combined accumulation of the target compounds (Figure 5.6c) and the respective photolysis by-products. Even though higher estradiol equivalents were determined in the permeate throughout the treatment when feed solution containing the hormones mixture was repeatedly added (0.04-0.38 versus 0.08-1.16), the removal observed under repeated addition of feed was still considerably high throughout the assay, above 84% (Figure 5.6d). These data suggest the retention of the estrogenically active transformation compounds generated by the membrane.

Permeate, retentate, and feed samples collected after 0, 1, 3, and 6 hours of operation were also analysed using the GC/MS, HPLC/MS, and UPLC-MS/MS methods detailed in Appendix A.1 to determine the presence of by-products in the experiments conducted with the repeated addition of feed solution. By-products generated during the degradation of the hormones were not detected probably due to their presence at extremely low concentrations that did not enable detection. Conversely, six major by-products were detected in the retentate collected at times 1, 3, and 6 hours in the experiments conducted with the pesticides. The mass spectra of these compounds are presented in Appendix A.5 while a summary of the mass spectra data analysis showing the parent compound, the major daughter ions, their relative abundance, and proposed structures is shown in Table 5.3.

***Table 5.3** Summary results obtained by mass spectra analysis of the major by-products detected - parent compound, major daughter ions, their relative abundance, and proposed fragments.*

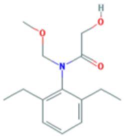
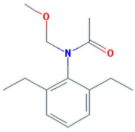
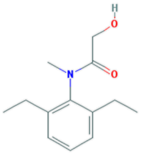
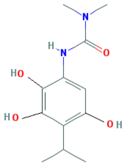
Presumed by-product	Detection method (correspondent mass spectra in Figure A.1)	Retention time (min)	Parent compound ($[M+H]^+$ or $[M+Na]^+$) and major daughter ions (relative percent abundances)	Proposed structure and molecular formula
Alachlor by-product 1	GC/MS Figure A.1a	23.6	251 (2); 219 (32); 188 (100); 160(90); 146(74); 132(50);117(36)	 $C_{14}H_{21}NO_3$
Alachlor by-product 2	GC/MS Figure A.1b	20.9	233 (9); 201(72); 186(100); 146(54)	 $C_{14}H_{21}NO_3 - H_2O$
Alachlor by-product 3	GC/MS Figure A.1c	15.6	221 (2);189(56); 146(100); 132(50); 118(22)	 $C_{14}H_{21}NO_3 - CH_3O$
Alachlor by-product 4	GC/MS Figure A.1d	25.3	251 (8); 219 (10); 190 (100); 162(70); 155(48); 132(38);119(22)	Isomer of alachlor by-product 1 $C_{14}H_{21}NO_3$
Isoproturon by-product 1	HPLC/MS Figure A.1e	11.9	296(18); 260(26); 230(30); 191(100); 163(14); 148(12)	 $C_{12}H_{18}N_2O_4$
Isoproturon by-product 2	HPLC/MS Figure A.1f	14.7	296(8); 274(100); 252(12); 220(6); 190(32); 162(54)	Isomer of isoproturon by-product 1 $C_{12}H_{18}N_2O_4$

Figure A.2 in Appendix A.5 shows the relative areas of the different by-products detected in the retentate after 1, 3, and 6 hours of operation. The results obtained show that the relative area/intensity of all major by-products detected except one (by-product 1 of isoproturon) increased with operation time. For the isoproturon by-product with a mass to charge ratio of 296 (isoproturon by-product 1), which was proposed that could correspond to a tri-hydroxylated isoproturon, the peak area decreased after 6 h of operation, showing that a considerable decrease of this by-product can be expected using the applied treatment.

In the permeate samples, isoproturon by-products were not detected and alachlor by-products were detected at extremely low levels (peak intensity percentage values of 1 to 2%) compared to the retentate samples, showing that the membrane was able to effectively retain the by-products formed.

Previously, other sequential treatments have been studied combining UV photolysis with nanofiltration or ultrafiltration membranes (Molinari *et al*. 2008, Molinari *et al*. 2006). In many cases, the removal of the compounds was mainly achieved by the oxidation step since the membranes tested were not suitable for the retention of several pharmaceuticals as well as the respective by-products. In the present study, a membrane with lower molecular weight cut-off was applied and both LP/UV photolysis and nanofiltration were efficient to attain high removals of the selected compounds. Furthermore, the very low estrogenic activity observed in the permeate shows that the combined treatment is not only extremely efficient at removing the parent compounds but also the estrogenically active by-products formed.

The permeate flux measurements throughout experiments indicated that the flux was fairly constant over time. Starting with a flux of 54 and 48 L h^{-1} m^{-2} for the pesticides and hormones solutions, respectively, variation coefficients of approximately 5% (solution containing the pesticides) and 8% (solution containing the hormones) were determined. The degradation of natural organic matter present in the water by LP/UV radiation is likely to have contributed to minimise fouling and promote a relatively constant flux. Furthermore, the natural water matrix used presents low concentrations of particulates and colloidal organic matter that usually contribute to membrane fouling and consequently to flux decline.

5.3.4 Comparison of the different treatment technologies

LP/UV direct photolysis was extremely efficient to degrade several pesticides and hormones. Lower effectiveness towards the degradation of isoproturon, 17β-estradiol, 17α-ethinylestradiol, and estriol were attained. Nevertheless, TiO_2 photocatalysis was able to improve the degradation of the more resilient hormones, for which removals higher than 76% were achieved by photocatalysis.

UV photolysis was considerably more effective than nanofiltration to remove diuron. Furthermore, the removal of atrazine, isoproturon, diuron, and estrone (particularly, isoproturon and diuron) was enhanced during the combined treatment relatively to nanofiltration alone. Although the combined treatment did not improve the removal of the other compounds, mainly because of their already high removals, the quality of the retentate was significantly improved in the combined treatment conducted at lower loadings of micropollutants throughout the 6 h period (without feed solution addition). The combined treatment is therefore the most effective treatment addressed. Similar global removals were attained by the combined treatment, when assessed at different loadings of micropollutants (with and without the addition of fresh feed solution), and improved retentate treatment is likely to be achieved through the increase of the residence time, in the case of higher loadings (with fresh feed solution addition).

5.4 CONCLUSIONS

Even though LP/UV/TiO_2 was found to be extremely efficient to achieve degradation of 17β-estradiol, 17α-ethinylestradiol, and estriol, when the photocatalysis process was coupled with nanofiltration, complete deposition of TiO_2 on the membrane was observed within the first five minutes of operation. Future work should focus on other configurations combining TiO_2 photocatalysis with nanofiltration that could take advantage of the benefits of integrating both technologies.

The combination of UV photolysis and nanofiltration improved the water quality attained by their individual application in terms of the concentration of atrazine, isoproturon, diuron, and estrone. Even though the quality of the treated water obtained by the individual technologies and the integrated treatment is similar for some of the compounds addressed, the quality of the retentate will be increased in the integrated treatment when the compounds are present at lower concentrations (without feed solution addition). Under these conditions, it might be effectively possible to reduce the need to further treat/dispose the retentate. Nevertheless, the increment of the hydraulic residence time is recommended to attain the same removal efficiency at higher loadings of micropollutants.

Generally, the membrane applied was also able to retain the by-products formed during UV photolysis, highlighting the advantage of combining these two processes to overcome this photolysis drawback.

Globally, the proposed treatment allows the production of high quality water in terms of the target micropollutants, formed by-products, and the respective estrogenic activity, assuring the protection of consumers against their potential deleterious health effects. The integration of the proposed technologies is also expected to be advantageous for the removal of other organic compounds. Moreover, its application could also reduce the doses of disinfectants applied during water treatment, leading to the decrease of the potential formation of hazardous disinfection by-products in the treated water.

ACKNOWLEDGEMENTS

We thank Dr. José María Navas and Dr. Beate Escher for the yeast strains used in the Yeast Estrogen Screen Assay and Dr. Benjamin Stanford for his help implementing the YES method.

Financial support from Fundação para a Ciência e a Tecnologia - through the project PTDC/AMB/66024/2006, the grant PEst-OE/EQB/LA0004/2011, and the fellowships BPD/26990/2006 and BD/72244/2010 is gratefully acknowledged.

Vanessa J. Pereira thanks the Department of Geography and Environmental Engineering at Johns Hopkins University for hosting her as a Visiting Scholar during the academic year 2012/2013.

REFERENCES

Benotti MJ, Stanford BD, Wert EC, Snyder SA (2009) Evaluation of a photocatalytic reactor membrane pilot system for the removal of pharmaceuticals and endocrine disrupting compounds from water. *Water Res* 43: 1513-1522.

Bosc F, Ayral A, Guizard C (2005) Mesoporous anatase coatings for coupling membrane separation and photocatalysed reactions. *J Membrane Sci* 265: 13-19.

Braeken L, Van der Bruggen B, Vandecasteele C (2006) Flux decline in nanoriltration due to adsorption of dissolved organic compounds: Model prediction of time dependency. *J Phys Chem B* 110: 2957-2962.

Braeken L, Van der Bruggen B (2009) Feasibility of nanofiltration for the removal of endocrine disrupting compounds. *Desalination* 240: 127-131.

Cabeza Y, Candela L, Ronen D, Teijon G (2012) Monitoring the occurrence of emerging contaminants in treated wastewater and groundwater between 2008 and 2010. The Baix Llobregat (Barcelona, Spain). *J Hazard Mater* 239: 32-39.

Chang H, Wu S, Hu J, Asami M, Kunikane S (2008) Trace analysis of androgens and progestogens in environmental waters by ultra-performance liquid chromatography-electrospray tandem mass spectrometry. *J* Chromatogr A 1195: 44-51.

Danzo BJ (1997) Environmental xenobiotics may disrupt normal endocrine function by interfering with the binding of physiological ligands to steroid receptors and binding proteins. *Environ Health Persp* 105: 294-301.

Djafer L, Ayral A, Ouagued A (2010) Robust synthesis and performance of a titania-based ultrafiltration membrane with photocatalytic properties. *Sep Purif Technol* 75: 198-203.

Donner E, Kosjek T, Qualmann S, Kusk KO, Heath E, Revitt DM, Ledin A, Andersen HR (2013) Ecotoxicity of carbamazepine and its UV photolysis transformation products. *Sci Total Environ* 443: 870-876.

Dudziak M, Bodzek M (2009) Selected factors affecting the elimination of hormones from water using nanofiltration. *Desalination* 240: 236-243.

Escher BI, Fenner K (2011) Recent advances in environmental risk assessment of transformation products. *Environ Sci Technol* 45: 3835-3847.

Johnson AC, Sumpter JP (2001) Removal of endocrine-disrupting chemicals in activated sludge treatment works. *Environ Sci Technol* 35: 4697-4703.

Kimura K, Amy G, Drewes J, Watanabe Y (2003) Adsorption of hydrophobic compounds onto NF/RO membranes: An artifact leading to overestimation of rejection. *J Membrane Sci* 221: 89-101.

Kolodziej EP, Harter T, Sedlak DL (2004) Dairy wastewater, aquaculture, and spawning fish as sources of steroid hormones in the aquatic environment. *Environ Sci Technol* 38: 6377-6384.

Kuster M, José Lopéz de Alda M, Dolores Hernando M, Petrovic M, Martin-Alonso J, Barceló D (2008) Analysis and occurrence of pharmaceuticals, estrogens, progestogens and polar pesticides in sewage treatment plant effluents, river water and drinking water in the Llobregat river basin (Barcelona, Spain). *J Hydrol* 358: 112-123.

Le-Clech P, Lee EK, Chen V (2006) Hybrid photocatalysis/membrane treatment for surface waters containing low concentrations of natural organic matters. *Water Res* 40: 323-330.

Leech DM, Snyder MT, Wetzel RG (2009) Natural organic matter and sunlight accelerate the degradation of 17 beta-estradiol in water. *Sci Total Environ* 407: 2087-2092.

Ma N, Zhang Y, Quan X, Fan X, Zhao H (2010) Performing a microfiltration integrated with photocatalysis using an Ag-TiO_2/HAP/Al_2O_3 composite membrane for water treatment: Evaluating effectiveness for humic acid removal and anti-fouling properties. *Water Res* 44: 6104-6114.

Malato S, Caceres J, Fernandez-Alba A, Piedra L, Hernando M, Aguera A, Vial J (2003) Photocatalytic treatment of diuron by solar photocatalysis: Evaluation of main intermediates and toxicity. *Environ Sci Technol* 37: 2516-2524.

McInnis P, Pesticides in Ontario's Treated Municipal Drinking Water 1986-2006. Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment (2010). Available online: http://www.ene.gov.on.ca/environment/en/resources/STD01_078819.html.

Molinari R, Palmisano L, Drioli E, Schiavello M (2002) Studies on various reactor configurations for coupling photocatalysis and membrane processes in water purification. *J Membrane Sci* 206: 399-415.

Molinari R, Pirillo F, Loddo V, Palmisano L (2006) Heterogeneous photocatalytic degradation of pharmaceuticals in water by using polycrystalline TiO_2 and a nanofiltration membrane reactor *Catal Today* 118: 205-213.

Molinari R, Argurio P, Poerio T, Bonaddio F (2007) Photo assisted fenton in a batch and a membrane reactor for degradation of drugs in water. *Sep Sci Technol* 42: 1597-1611.

Molinari R, Caruso A, Argurio P, Poerio T (2008) Degradation of the drugs Gemfibrozil and Tamoxifen in pressurised and de-pressurised membrane photoreactors using suspended polycrystalline TiO_2 as catalyst. *J Membrane Sci* 319: 54-63.

Nghiem L, Schäfer A, Elimelech M (2004) Removal of natural hormones by nanofiltration membranes: Measurement, modelling, and mechanisms. *Environ Sci Technol* 38: 1888-1896.

Pereira VJ, Galinha J, Barreto Crespo MT, Matos CT, Crespo JG (2012) Integration of nanofiltration, UV photolysis, and advanced oxidation processes for the removal of hormones from surface water sources. *Sep Purif Technol* 95: 89-96.

Postigo C, José Lopéz de Alda M, Barceló D, Ginebreda A, Garrido T, Fraile J. (2010) Analysis and occurrence of selected medium to highly polar pesticides in groundwater of Catalonia (NE Spain): An approach based on on-line solid phase extraction-liquid chromatography-electrospray-tandem mass spectrometry detection. *J Hydrol* 383: 83-92.

Puma GL, Puddu V, Tsang HK, Gora A, Toepfer B (2010) Photocatalytic oxidation of multicomponent mixtures of estrogens (estrone (El), 17 beta-estradiol (E2), 17 alpha-ethynylestradiol (EE2) and estriol (E3)) under UVA and UVC radiation: Photon absorption, quantum yields and rate constants independent of photon absorption. *Appl Catal B-Environ* 99: 388-397.

Rizzo L (2011) Bioassays as a tool for evaluating advanced oxidation processes in water and wastewater treatment. *Water Res* 45: 4311-4340.

Rodriguez-Mozaz S, José López de Alda M, Barceló D (2004) Monitoring of estrogens, pesticides and bisphenol A in natural waters and drinking water treatment plants by solid-phase extraction–liquid chromatography–mass spectrometry. *J Chromatogr A* 1045: 85-92.

Rosenfeldt EJ, Linden KG (2004) Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes. *Environ Sci Technol* 38: 5476-5483.

Rosenfeldt E, Chen P, Kullman S, Linden K (2007) Destruction of estrogenic activity in water using UV advanced oxidation. *Sci Total Environ* 377: 105-113.

Routledge EJ, Sumpter JP (1996) Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast screen. *Environ Toxicol Chem* 15: 241-248.

Sanches S, Barreto Crespo MT, Pereira VJ (2010) Drinking water treatment of priority pesticides using low pressure UV photolysis and advanced oxidation processes. *Water Res* 44, 1809-1818.

Sanches S, Penetra A, Rodrigues A, Ferreira E, Cardoso VV, Benoliel MJ, Barreto Crespo MT, Pereira VJ, Crespo JG (2012) Nanofiltration of hormones and pesticides in different real drinking water sources. *Sep Purif Technol* 94: 44-53.

Stanford BD, Weinberg HS (2010) Evaluation of on-site wastewater treatment technology to remove estrogens, nonylphenols, and estrogenic activity from wastewater. *Environ Sci Technol* 44: 2994-3001.

Ternes TA, Stumpf M, Mueller J, Haberer K, Wilken RD, Servos M (1999) Behaviour and occurrence of estrogens in municipal sewage treatment plants - I. Investigations in Germany, Canada and Brazil. *Sci Total Environ* 225: 81-90.

Wilson AGE, Thake DC, Heydens WE, Brewster DW, Hotz KJ (1996) Mode of action of thyroid tumor formation in the male Long-Evans rat administered high doses of alachlor. *Fundam Appl Toxicol* 33: 16-23.

Zhang Y, Zhou JL, Ning B (2007) Photodegradation of estrone and 17 beta-estradiol in water. *Water Res* 41: 19-26.

Zhou X, Lian Z, Wang J, Tan L, Zhao Z (2011) Distribution of estrogens along Licun River in Qingdao, China. *Procedia Environ Sci* 10: 1876-1880.

CHAPTER 6

Discussion and Future work

CONTENTS

The main objective of the work presented in this thesis was to address the potential of combining low pressure UV photolysis/TiO_2 photocatalysis with nanofiltration to treat water containing environmental relevant micropollutants while overcoming specific drawbacks related with the individual application of these technologies. The main achievements are highlighted in this section with a particular emphasis on future developments and perspectives towards the implementation of the proposed technologies for drinking water treatment, namely the proposal of a new configuration.

6.1 Potential of the individual technologies for drinking water treatment

6.1.1 UV photolysis

The very efficient LP/UV direct photolysis/TiO_2 photocatalysis of several pesticides and hormones, associated with their proven high potential towards the inactivation of a wide range of microorganisms (Le Goff *et al*. 2010, Shin *et al*. 2009), demonstrates the suitability of this technology for drinking water treatment. Even though direct photolysis alone is sufficient to degrade the majority of the compounds addressed, TiO_2 photocatalysis significantly improved the degradation of the hormones 17β-estradiol, 17α-ethinylestradiol, and estriol. Moreover, LP/UV radiation is expected to be also effective to remove the target compounds in the presence of other micropollutants during water treatment.

The model applied towards the predictions of direct photolysis of the target pesticides in different water matrices under different experimental conditions showed good agreement with experimental data attained. Modelling of experimental data gave insights for the optimisation of operating conditions during the sequential treatment in terms of TiO_2 concentration and distance to the UV source, particularly for the degradation improvement of the most resilient pesticide, isoproturon. The determination of UV photolysis kinetic parameters (decadic molar absorption coefficient, the pseudo-first order rate constants, and the second-order rate constants for reaction of the pesticides with OH radicals) provides drinking water utilities with useful information for process implementation.

Although many studies report the degradation of organic compounds as function of time, the ability to compare data obtained using different systems is not possible. In the present thesis, a significant amount of data is reported as a function of UV fluence, allowing a standardisation of UV testing as well as providing increased confidence in the data generated and the ability to compare data obtained using other lamps/systems in view of process implementation. An important contribution is, thus, made in terms of the UV fluences that are needed to cope with the target compounds.

6.1.2 Nanofiltration

Nanofiltration using the membrane Desal 5DK was able to remove the majority of the target micropollutants very efficiently. It is, however, noteworthy that diuron is better removed by UV photolysis than by nanofiltration (Chapter 5). Furthermore, the rejection of the selected pesticides and hormones is not expected to be considerably changed in a long term operation and membrane performance is not likely to be noticeably affected. The removals attained for the pesticides atrazine and alachlor as well for the hormones using the flat-sheet Desal 5DK membrane were generally in line with those obtained using the same membrane in a spiral-wound configuration. The differences observed are within the uncertainties of the analytical methods employed to determine the concentration of the compounds. Furthermore, removal and fouling development were similar despite the different pre-treatment of the surface water applied in both studies (ultrafiltered surface water and surface water collected after conventional sedimentation).

The application of ultrafiltration prior to nanofiltration was an appropriate strategy to remove particulate and large colloidal organic matter, without affecting the concentration of ionic species and NOM. Even though an attempt to correlate the nanofiltration rejection of the micropollutants with relevant parameters (water composition, physico-chemical properties of the target micropollutants, and operating conditions) was carried out, the interpretation of experimental data was not totally satisfactory.

The application of multivariate statistical analysis demonstrated the complexity of the relationships (synergies and concurrent effects) that impact process efficiency, highlighting the difficulty of taking conclusions from univariate analysis as first attempted.

The rejection of the selected pesticides and hormones were found to be determined by the combination of size exclusion, electrostatic interactions, and hydrophobic interactions (Chapters 3, 4, and 5). The properties of the molecules that most contribute for this phenomenon are molecular weight, molar volume, molecular size, and log D. The geometry of the molecule, given by molecular length, molecular width, and molecular depth, was found extremely relevant to explain the lower rejections obtained for pentachlorophenol compared with the other molecules addressed (57.5-83.5% vs 67.4-99.9%) since the geometry of this molecule is very different. The lower rejections are more likely to be determined by the molecular geometry of pentachlorophenol rather than its increased solubility at the pH of the waters as initially proposed. Multivariate statistics suggested that the characteristics of the water matrix are also likely to impact rejection, as observed in a previous work addressing the removal of alachlor and pentachlorophenol during a dead-end filtration (Sanches *et al*. 2011). Nevertheless, additional clarification regarding the impact of several specific water components upon micropollutants rejection was not accomplished. Further assessment should be conducted through the performance of experiments using other natural waters with different characteristics to increase the variability of the data set. Adsorption was found important for the removal of several compounds, particularly atrazine and alachlor. Hydrophobic interactions were pointed out as the adsorption mechanism in Chapter 3. Even though PLS models developed (Chapter 4) suggested that polar and electrostatic interactions may have an important impact on adsorption, hydrophobic interactions may also play a role.

Generalised conclusions from the models developed should, however, be taken with care since the variability of the experimental data used was not high and the models were calibrated with a limited number of compounds and experimental conditions. The application range of the models developed could be further extended through the inclusion of data obtained for micropollutants with different physico-chemical properties, other membranes, and other natural waters. An increased variability in the experimental data set would be therefore expected, enlarging the range of rejections. The potential of nanofiltration to remove other environmental relevant micropollutants from water could be then predicted avoiding empirical rejections.

6.2 Integrated treatment

The combination of nanofiltration with direct LP/UV photolysis was able to enhance the removals obtained by nanofiltration (using the same membrane) for atrazine, diuron, isoproturon, and estrone while maintaining the removal of the other micropollutants fairly constant. An improvement of the water quality in terms of the removal of isoproturon was also observed using the combined treatment relatively to UV processes since this compound was found to be very resilient to UV degradation.

Besides the potential to produce high quality water in terms of the target micropollutants and endocrine disrupting activity, data herein presented demonstrates that the combined treatment is able to attenuate the drawbacks related with the individual processes.

The effective removal of the target micropollutants from the retentate as well as the extremely high reduction of the respective endocrine disrupting activity (particularly in the case of the hormones) demonstrates that the need to treat/dispose the nanofiltration retentate and the respective costs are potentially highly reduced. Higher residence times are, however, needed for a continuous loading of high concentrations of the target pesticides and hormones, which is a less probable scenario. Furthermore, the concentrations applied in this study were higher than the occurrence concentrations and, therefore, UV direct photolysis/TiO_2 photocatalysis might be expected to be even more effective under real conditions.

Further significant economical benefits in terms of operating costs related with energy consumption and membrane cleaning/replacement are also expected since very low fouling was observed during the combined treatment (5-8% of flux decline). The fouling development control is likely to be related with the UV degradation of organic matter. This feature is particularly important for the treatment of waters containing high concentrations of NOM like surface waters.

UV by-products from the degradation of alachlor and isoproturon were identified in the samples taken from the retentate of the integrated treatment. These molecules were successfully retained by the membrane or were present at very low concentrations since their detection in the treated water was not achieved. The low concentration of the by-products formed and estrogenic activity of the treated water throughout the treatment showed that the photolysis by-products formed were

---

generally efficiently retained by the nanofiltration process. These results highlight the advantage of the multi-barrier approach comparatively with UV photolysis alone.

6.3 Future work

6.3.1 Further assessment of the proposed integrated treatment

Besides the UV by-products identified during the combined process, many others may have been generated at extremely low levels that did not enable detection. Further research should be carried out at higher concentrations to achieve detection of such compounds. Although the endocrine disrupting activity of the treated water was found to be very low, other toxicological methodologies could be further applied to determine different toxicological effects. As an example, the Ames test provides information related with mutagenicity potential.

The combined treatment was assessed at concentrations that are higher than the occurrence concentrations of the selected micropollutants in the aqueous environment. The reasons supporting this strategy, which was also applied for the assessment of the individual processes, were largely discussed in Chapters 3 and 5. It would be interesting to evaluate the combined treatment at the pilot-scale and at occurrence levels for further process validation. Much larger volumes of water could then be processed in a continuous mode.

6.3.2 Proposal of a new configuration

Even though the removal of the pesticides and the hormones estrone and progesterone was not considerably improved by TiO_2 photocatalysis, a significant improvement in the removal of 17β-estradiol, 17α-ethinylestradiol, and estriol was demonstrated. To take advantage of TiO_2 photocatalytic properties and avoid the deposition of the suspended catalyst, another configuration in which TiO_2 is immobilised on the top surface of a nanofiltration membrane, forming a reactive thin film, could be developed and evaluated. In this case, photocatalysis would take place through membrane irradiation.

Magnetron sputtering is a well established physical vapour deposition technique. It became the number one choice for the deposition of a wide range of industrially relevant coatings, namely TiO_2 coatings, in a variety of surfaces due to its ability to produce high-purity and high-quality well-adhered functional films at large surface areas (Kelly and Bradley 2009, Ehiasarian 2010). The application of this technique for the introduction of a built-in oxidative functionality on filtration membranes could be a suitable alternative to traditional techniques that often lead to low film stability (Su *et al*. 2012, Madaeni *et al*. 2011) and low homogeneity distribution (Madaeni *et al*. 2011). Indeed, homogeneous TiO_2 thin films were recently developed on the surface of a commercial ceramic membrane from Fraunhofer, composed of aluminium oxide and non reactive titanium dioxide, by pulsed direct current (DC) reactive magnetron sputtering. Different conditions in terms of distance to the target, current intensity, and immobilisation time were applied (Figure 6.1). The scanning electron microscopy images presented in Figure 6.1 were obtained by Clarisse Nunes from Laboratório Nacional de Energia e Geologia in the context of a collaboration established in the scope of this thesis and its future development.

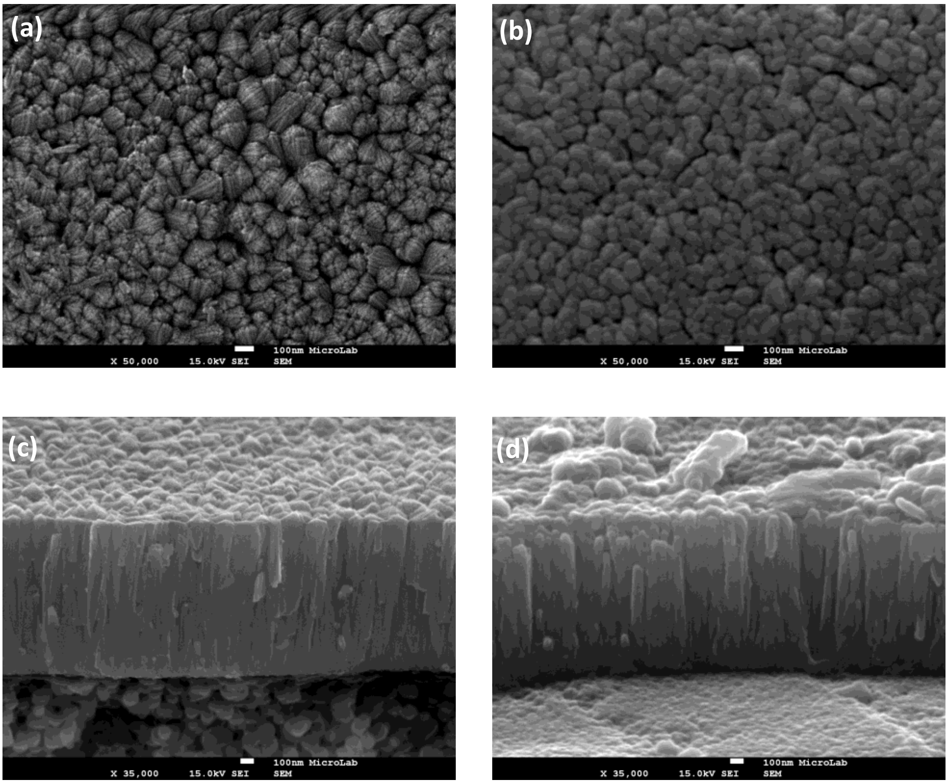


Figure 6.1 *Scanning electron microscopy images of the top view (Figures* ***(a)*** *and* ***(b)****) and cross section (Figures* ***(c)*** *and* ***(d)****) of the* TiO_2 *thin films obtained on the surface of a commercial ceramic membrane by pulsed DC reactive magnetron sputtering. The following sputtering conditions were applied to obtain the film depicted in Figures* ***(a)*** *and* ***(c)****: distance to the target – 9 cm, immobilisation time – 8 h, current intensity – 0.7 A, pressure –* $1.2x10^{-2}$ *mbar and argon:oxygen ratio – 2:1. To obtain the film depicted in Figures* ***(b)*** *and* ***(d)****, the following conditions were applied: distance to the target – 15 cm, immobilisation time – 11.5 h, current intensity – 1 A, pressure –* $1.2x10^{-2}$ *mbar and argon:oxygen ratio – 2:1.*

Although well defined vertically aligned TiO_2 nanostructured columns and a similar thin film thickness (approximately 1 μm) were obtained with both condition sets, different thin films morphologies were observed, depending on the sputtering conditions applied. Lower width nanocolumns were generally observed in the TiO_2 film obtained applying higher distance to the target, deposition time, and current intensity (38-119 nm vs 118-222 nm). The permselectivity properties of the coated membranes relatively to the uncoated membrane were modified. The significant improvement in the rejection of 17β-estradiol and estriol using the film presenting the lowest width columns (from 79 to 94% and from 65 to 87%, respectively) relatively to the uncoated membrane was accompanied by an expected decrease of membrane hydraulic permeability. Further studies should address the viability of magnetron sputtering to obtain a membrane that simultaneously present high permeability and rejection as well as adequate photocatalytic activity and enhanced membrane anti-fouling properties. The formation of TiO_2 films that comprises all these features is not straightforward and requires further optimisation in terms of the aforementioned parameters.

Given the versatility of magnetron sputtering to immobilise a large spectrum of nanoparticles, other nanoparticles or combinations of TiO_2 with other nanoparticles could be also evaluated for drinking water treatment. Fe_2O_3 is a potential candidate since hydroxyl radicals produced at the surface of ceramic membranes containing Fe_2O_3 has been related with the improvement of NOM degradation (Karnik *et al*. 2005). The combination of silica with TiO_2 has also been reported to improve photocatalytic activity through the increase of surface area and cristalinity (Iwamoto *et al*. 2000, 2005). For the treatment of waters containing high levels of microorganisms, the inclusion of silver nanoparticles may be advantageous since silver has been shown to avoid fouling, mainly through biofouling mitigation (Kim and Van der Bruggen 2010).

Since magnetron sputtering is widely known for its ability to generate well adhered TiO_2 thin films, the release of nanoparticles to the water is not expected. Nevertheless, the potential release of TiO_2 nanoparticles from specific membrane materials, namely ceramic materials, should be carefully addressed in order to avoid environmental issues. Furthermore, potential membrane damage caused by the UV radiation should also be investigated.

Despite the proven benefits of TiO_2 for the degradation of some micropollutants and improved membrane performance, the impact of TiO_2 nanoparticles should also be determined from the eco(toxicological) point of view. Although the absence of toxicity of TiO_2 has been widely pointed out as one of the most relevant characteristics supporting its application for water treatment (Doll and Frimmel 2005), evidence of toxic effects of these engineered nanoparticles on model organisms has recently emerged (e.g. Wang *et al*. 2013, Battin *et al*. 2009). Implications of TiO_2 for the functioning and health of ecosystems needs, therefore, further assessment prior to its application for drinking water treatment.

If proven stable and non toxic, these films could be produced on large membrane surfaces to be implemented in water treatment utilities. Furthermore, plant footprint could be significantly reduced comparatively to the sequential treatment.

6.3.3 Economical evaluation

The implementation of UV treatment for both inactivation and micropollutants degradation is likely to increase the costs associated with UV inactivation since much higher UV fluences must be provided to achieve effective degradation (>1500 mJ cm^{-2} vs 200 mJ cm^{-2}). Conversely, operating costs related with fouling development and treatment/disposal of retentate are expected to considerably decrease through the application of the integrated treatment. Furthermore, it is noteworthy that a considerable improvement of water quality is expected due to micropollutants removal and the reduction of chlorination by-products produced through the decrease of chlorine doses needed to achieve effective disinfection. An economical evaluation should be carried out to address the implementation viability of the integrated treatment addressed in this thesis. Moreover, the comparison of the costs and scientific advantages associated with this integrated process and the integrated process proposed in section 6.3.2 would be interesting to determine the best multi-barrier treatment.

Even though economic aspects are often barriers for the implementation of technologies by water producers, attention must be given to the trade-off between costs and benefits in terms of the quality of the water produced.

ACKNOWLEDGEMENTS

The support of Dr. Clarisse Nunes from Laboratório Nacional de Energia e Geologia with the development of the coated membranes by DC reactive magnetron sputtering as well as the fruitful discussions is gratefully acknowledged.

REFERENCES

Battin TJ, Kammer FVD, Weilhartner A, Ottofuelling S, Hofmann T (2009) Nanostructures TiO_2: Transport behaviour and effects on aquatic microbial communities under environmental conditions. *Environ Sci Tecnol* 43: 8098-8104.

Doll TE, Frimmel FH (2005) Removal of selected persistent organic pollutants by heterogeneous photocatalysis in water. *Catal Today* 101: 195-202.

Ehiasarian AP (2010) High-power impulse magnetron sputtering and its applications. *Pure Appl Chem* 82: 1247-1258.

Iwamoto S, Tanakulrungsank W, Inoue M, Kagawa K, Praserthdam P (2000) Synthesis of large-surface area silica-modified titania ultrafine particles by the glycothermal method. *J Mater Sci Lett* 19: 1439-1443.

Iwamoto S, Inoue M, Yoshida H, Tanaka T, Kagawa K (2005) XANES and XPS study of silica-modified titanias prepared by the glycothermal method. *Chem Mater* 17: 650-655.

Karnik BS, Davies SH, Baumann MJ, Masten SJ (2005) Fabrication of catalytic membranes for the treatment of drinking water using combined ozonation and ultrafiltration. *Environ Sci Technol* 39: 7656-7661.

Kelly PJ, Bradley JW (2009) Pulsed magnetron sputtering - Process overview and applications. *J Optoelectron Adv M* 11: 1101-1107.

Kim J, Van der Bruggen B (2010) The use of nanoparticles in polymeric and ceramic membrane structures: Review of manufacturing procedures and performance improvement for water treatment. *Environ Pollut* 158: 2335-2349.

Le Goff L, Khaldi S, Favennec L, Nauleau F, Meneceur P, Perot J, Ballet JJ, Gargala G (2010) Evaluation of water treatment plant UV reactor efficiency against *Cryptosporidium parvum* oocyst infectivity in immunocompetent suckling mice. *J Appl Microbiol* 108: 1060-1065.

Madaeni SS, Zinadini S, Vatanpour V (2011) A new approach to improve antifouling property of PVDF membrane using in situ polymerization of PAA functionalized TiO_2 nanoparticles. *J Membrane Sci* 380: 155-162.

Sanches S, Penetra A, Granado C, Cardoso VV, Ferreira E, Benoliel MJ, Barreto Crespo MT, Pereira VJ, Crespo JG (2011) Removal of pesticides and polycyclic aromatic hydrocarbons from different drinking water sources by nanofiltration. *Desalin Water Treat* 27: 141-149.

Shin GA, Linden KG, Faubert G (2009) Inactivation of *Giardia lamblia* cysts by polychromatic UV. *Lett Appl Microbiol* 48: 790-792.

Su Y-C, Huang C, Pan JR, Hsieh W-P, Chu M-C (2012) Fouling mitigation by TiO_2 composite membrane in membrane bioreactors. *J Environ Eng-ASCE* 138: 344-350.

Wang Y, Chen Z, Ba T, Pu J, Chen T, Song Y, Gu Y, Qian Q, Xu Y, Xiang K, Wang H, Jia G (2013) Susceptibility of young and adult rats to the oral toxicity of titanium dioxide nanoparticles. *Small* 9: 1742-1752.

APPENDICES

CONTENTS

A.1 Analytical methods

A.1.1 Direct HPLC injection of pesticides and hormones

Samples from the batch LP/UV photolysis experiments (described in Chapter 2) were analysed by HPLC using a Waters system equipped with ultraviolet and fluorescence detectors (Waters Chromatography, Milford, MA, USA) and a Luna 5 μm C18(2) 100 A (150 x 3.0 mm) column (Phenomenex Inc., Torrance, CA, USA). The analytical methods employed are described in Table A.1.

Table A.1 *HPLC methods used for the detection of the pesticides atrazine (ATR), isoproturon (ISO), diuron (DIU), alachlor (ALA), pentachlorophenol (PCP), and chlorfenvinphos (CFVP) as well as para-chlorobenzoic acid (pCBA) in the direct photolysis and AOPs experiments.*

Type of photolysis experiment	Compound	Mobile phase composition (%)	Injection volume (μL)	Flow rate (mL min^{-1})	λ_{UV} (nm)
Direct photolysis	DIU	50 ACN/50 H_2O	20	1.0	240
	ISO	50 ACN/50 H_2O	20	1.0	240
	ATR	50 ACN/50 H_2O *	50	1.0	240
	ALA	70 ACN/30 H_2O *	50	1.0	220
	CFVP	70 ACN/30 H_2O	20	1.0	258
	PCP	85 ACN/15 H_2O **	50	0.4	230
	pCBA	65 ACN/35 H_2O **	20	0.5	240
AOPs	DIU + pCBA	55 MeOH/45 H_2O **	10	0.7	238
	ISO + pCBA	47 MeOH/53 H_2O **	10	1.0	238
	CFVP + pCBA	65 MeOH/35 H_2O **	50	1.0	238
	PCP + pCBA	0-3min: 68 MeOH/32 H_2O ** 3.5-13min: 90 MeOH/10 H_2O ** 13.5-15min: 68 MeOH/32 H_2O **	30	1.0	238
	Mixture	0-5min: 38 ACN/62 H_2O 19min: 47 ACN/53 H_2O 20-24min: 75 ACN/25 H_2O 26-36min: 38 ACN/62 H_2O	50	0.5	220

*used for the analysis of the compounds in direct photolysis and AOPs experiments; **acidic milli-Q water (containing 10 mM phosphoric acid); λ_{UV} – ultraviolet wavelength; H_2O – milli-Q water.

Samples containing the selected pesticides or hormones from pre-adsorption experiments preceding nanofiltration assays (described in Chapter 3) were analysed using the chromatographic system aforementioned under the conditions described in Table A.2.

Table A.2 *HPLC methods used for the detection of pesticides and hormones in the direct HPLC analysis of samples from pre-adsorption experiments preceding nanofiltration assays.*

Compound	**Mobile phase composition (%)**	**T (°C)**	**Flow rate (mL min^{-1})**	**HPLC/UV**	**HPLC/FL**		**Detection limit* (μg L^{-1})**
				λ_{UV} (nm)	**λ_{em} (nm)**	**λ_{exc} (nm)**	
Atrazine Alachlor	70 ACN/30 H_2O	34	0.8	220	-	-	50 100
Pentachlorophenol	85 MeOH/15 H_2O containing 10 mM phosphoric acid	34	0.8	220	-	-	25
17β-Estradiol 17α-Ethinylestradiol Estriol Estrone Progesterone	0-6min: 40 ACN/60 H_2O 9-20min: 62 ACN/38 H_2O 23-30min: 40 ACN/60 H_2O	35	1.0	220	300	217	50 100 100 25 25

*direct injection; T – temperature; ACN – acetonitrile; MeOH – methanol; H_2O – milli-Q water; UV – ultraviolet; FL – fluorescence; λ_{em} – emission wavelength; λ_{exc} – excitation wavelength; λ_{UV} – ultraviolet wavelength; Volume of injection: 50μL.

Samples from LP/UV photolysis experiments as well as feed, retentate, and control samples from nanofiltration and the combined treatment experiments (described in Chapter 5) were analysed by HPLC using a Waters system (Alliance e2695 Separations Module), equipped with a photodiode array detector (2998, Waters Chromatography, Milford, MA, USA), a Multi λ Fluorescence detector (2475, Waters Chromatography, Milford, MA, USA), and a Luna 5 μm C18(2) 100 A (150 x 3.0 mm) column (Phenomenex Inc., Torrance, CA, USA). The analytical methods employed are described in Table A.3.

Table A.3 *HPLC methods used for the detection of the selected pesticides and hormones in the direct HPLC analysis of samples from the LP/UV photolysis experiments as well as feed, retentate, and control samples from nanofiltration and combined treatment experiments.*

Compound	**Mobile phase composition (%)**	**T (°C)**	**Flow rate (mL min^{-1})**	**HPLC/UV**	**HPLC/FL**		**Detection limit* (μg L^{-1})**
				λ_{UV} (nm)	**λ_{em} (nm)**	**λ_{exc} (nm)**	
Atrazine							5
Isoproturon	0-11min: 55 MeOH/45 H_2O			220			20
Diuron	12.5-9min: 77 MeOH/23 H_2O	25	0.5	240	-	-	12.5
Alachlor	21-28min: 55 MeOH /45 H_2O			250			50
Chlorfenvinphos							12.5
17β-Estradiol							50
17α-Ethinylestradiol	0-6min: 40ACN/60H_2O						100
Estriol	6.5-9.5: 65ACN/35H_2O	35	1.0	220	300	217	5
Estrone	10.5-15min: 40ACN/60H_2O						25
Progesterone							25

*direct injection; T – temperature; ACN – acetonitrile; MeOH – methanol; H_2O – milli-Q water; UV – ultraviolet; FL – fluorescence; λ_{em} – emission wavelength; λ_{exc} – excitation wavelength; λ_{UV} – ultraviolet wavelength; volume of injection: 50μL.

A.1.2 Concentration and analysis of pesticides and hormones

Concentration of pesticides and hormones prior to analysis was carried out for the permeate samples from nanofiltration (Chapters 3 and 5) and combined treatment experiments (Chapter 5). The same analytical methods were also used to determine the concentration of pesticides and hormones in the feed, retentate, and control samples of nanofiltration experiments described in Chapter 3. These analyses were carried out by EPAL in the context of a collaboration established in the scope of this thesis and the analytical methodologies applied are described below.

A.1.2.1 Pesticides

Solid phase extraction using an Autotrace workstation system (Caliper Life Sciences, UK) and Waters OASIS HLB cartridges (6 mL, 200 mg) were used to concentrate

---

atrazine, alachlor, and chlorfenvinphos. The conditioning step was carried out with 6 mL of a mixture of n-hexane/dichloromethane (1:1) and 6 mL of methanol, followed by 3 mL of water at a flow rate of 10 mL min^{-1}. 500 mL samples were processed at 30 mL min^{-1} and the elution step was conducted with 6 mL of n-hexane/dichloromethane (1:1) at 10 mL min^{-1}. The detection of these analytes was accomplished by gas chromatography with mass spectrometry in selected ion monitoring mode using a HP-5MS column with 60 m x 0.25 mm x 0.25 μm (Agilent Technologies, CA, US). In the chromatographic analysis, the oven temperature programme starts with 30 °C, which is held during 1 min. A heating rate of 50 °C min^{-1} is performed from 30 to 170 °C and then, 170 °C is held during 1 min. The following heating rate of 1 °C min^{-1} from 170 to 190 °C is performed and the temperature of 190 °C is held for 3 min. The last heating rate is 50 °C min^{-1} from 190 °C to 250 °C, which is held during 10 min. The detection limits of this method are 0.06 μg L^{-1} (atrazine and chlorfenvinphos) and 0.07 μg L^{-1} (alachlor).

The chromatographic analysis of diuron and isoproturon was conducted using a Waters Alliance 2795 Separations Module HPLC, equipped with a quaternary pump, an automatic injector, a thermostatic column compartment, and an Atlantis dC18 (2.1 x 150 mm, 5 μm) column from Waters. Gradient conditions were used to analyse diuron and isoproturon: 10% methanol/90% water with 5 mM ammonium acetate (0 min); 90% methanol/10% water with 5 mM ammonium acetate (15-25 min); 10% methanol/90% water with 5 mM ammonium acetate (25.1-30 min). The flow rate of mobile phases was 0.3 mL min^{-1}, the oven temperature was set at 30 °C, and an injection volume of 20 μL was used in the analysis. A mass spectrometer Quattro micro API triple quadrupole, equipped with a Z-spray electrospray ionisation source was used. Electrospray ionisation source operating conditions were set using a capillary voltage of 3.5 kV, a source temperature of 150 °C, an extractor voltage of 2.0

V, desolvation temperature and gas flow of 300 °C and 850 L h^{-1}, respectively, a RF lens of 0.5 V, and a cone gas flow of 50 L h^{-1}.

Table A.4 shows the monitoring conditions used for the detection of isoproturon and diuron.

Table A.4 *Monitoring conditions – Multiple Reaction Monitoring (MRM) used in the detection of isoproturon and diuron.*

Pesticide	Ionisation mode	Precursor ion	Cone Voltage (V)	Product ion quantification (MRM1)	Collision energy (eV)	Product ion qualification (MRM2)	Collision energy (eV)
Isoproturon	ES +	207.3	26	71.5	17	165.2	14
Diuron	ES +	233.2	28	71.5	16	159.8	25

Nitrogen was used as nebulising, desolvation, and cone gas while argon was used as collision gas with a pressure of 2.83×10^{-3} mbar. The detection limit of the method for diuron and isoproturon is 0.045 μg L^{-1}.

For the detection of pentachlorophenol, 10 μL of chloride acid (15%) and 2 g of sodium chloride were added to the samples prior to the concentration by solid phase microextraction using 85 μm polyacrilate fibre. Gas chromatography with electron capture detection was used for the analysis of pentachlorophenol, using a HP-5MS column with 30 m x 0.32 mm x 0.25 μm (Agilent Technologies, CA, US). The temperature programme starts with a period of 5 min at 40 °C, followed by a heating rate of 5 °C min^{-1} until 210 °C, which is held during 3 min. The detection limit of this method is 0.1 μg L^{-1}.

A.1.2.2 Hormones

Hormones were concentrated by solid-phase extraction and analysed by Ultra performance liquid chromatography. The solid-phase extraction procedure was conducted using the Autotrace workstation system and Waters Oasis HLB cartridges (6 mL, 200 mg). The conditioning step was performed with 6 mL of a mixture of methanol and acetone (3:2), followed by 3 mL of methanol and 3 mL of ultra-pure water at a flow rate of 10 mL min^{-1}. Then, 500 mL samples were loaded at a flow rate of 30 mL min^{-1}. In the elution step, 6 mL of the same mixture of solvents applied in the activation step were used. The final extract was concentrated to a volume of 0.5 mL using a Turbovap evaporation system (Zymark, USA) with a nitrogen stream at 0.2 bar and at a temperature of approximately 35 °C. The chromatographic analysis of the hormones was conducted using an Ultra performance liquid chromatography Acquity System (Waters) and an Acquity BEH C_{18} (2.1 x 50 mm, 1.7 μm) column from Waters. Gradient conditions were used to analyse the hormones: 30% methanol/70% water with 0.05% ammonia (starting at 0min); 95% methanol/5% water with 0.05% ammonia (3-4.2 min); 30% methanol/70% water with 0.05% ammonia (5-6 min). The flow rate of mobile phases was 0.5 mL min^{-1}, the oven temperature was set at 40 °C, and an injection volume of 20 μL was used in the analysis. A mass spectrometer triple quadrupole Acquity TQD, equipped with a Z-spray electrospray ionisation source was used. Electrospray ionisation source operating conditions were set using a capillary voltage of 3.0 kV, a source temperature of 150 °C, an extractor voltage of 2.0 V, desolvation temperature and gas flow of 500 °C and 900 L h^{-1}, respectively, a RF lens of 0.1 V, and a cone gas flow of 20 L h^{-1}. Table A.5 shows the mass spectrometry conditions used for the detection of the selected hormones. The detection limit of the method for all the selected hormones is 0.05 μg L^{-1}.

Table A.5 *Optimised mass spectrometry conditions used for the detection of the target hormones.*

Hormones	**Time (min)**	**Cone voltage (V)**		**MRM transition (m/z) precursor ion → product ion**	**Collision energy (eV)**	**Dwell time (s)**
17β-Estradiol	1.97–2.50	MRM1	65 (ES-)	271.4 → 145.3	40	0.025
		MRM2	65 (ES-)	271.4 → 143.0	65	
17α-Ethinylestradiol	1.97–2.50	MRM1	50 (ES-)	295.4 → 145.0	39	0.025
		MRM2	50 (ES-)	295.4 → 159.0	34	
Estrone	1.97– 2.50	MRM1	60 (ES-)	269.3 → 145.2	40	0.025
		MRM2	60 (ES-)	269.3 → 143.0	55	
Estriol	0.00–1.70	MRM1	60 (ES-)	287.4 → 145.4	40	0.078
		MRM2	60 (ES-)	287.4 → 171.3	35	
Progesterone	2.40–2.80	MRM1	50 (ES+)	315.4 → 96.9	20	0.025
		MRM2	50 (ES+)	315.4 → 108.9	25	

MRM – Multiple Reaction Monitoring; m/z – mass to charge ratio.

A.1.3 Analysis of by-products

A concentration step prior to the identification of by-products from the degradation of atrazine, alachlor, and chlorfenvinphos was carried out under the same conditions previously described for the concentration of the parent compounds (Appendix A1.2.1). The identification of these by-products was carried out in full scan mode (50 to 500 m/z) using a gas chromatographer equipped with a quadropole mass spectrometer in electronic impact ionisation mode. The injection was performed at splitless mode with an injector temperature of 250 °C, a split flux of 25 mL min^{-1}, and a splitless time of 1.5 min. Helium was used as carrier gas with a constant flux of 1.0 mL min^{-1}. The oven temperature programme starts with 40 °C, which is held during 1 minute. A heating rate of 50 °C min^{-1} is performed from 40 to 170 °C and then, 170 °C is held during 1 min. The following heating rate of 1 °C min^{-1} from 170 to 190 °C is performed and the temperature of 190 °C is held for 3 min. The last heating rate is 50 °C min^{-1} from 190 °C to 250 °C, which is held during 20 min.

A Waters Alliance 2795 Separations Module HPLC with a mass spectrometer Quattro micro API triple quadrupole equipped with a Z-spray electrospray ionisation source

---

was used for the identification of by-products from the degradation of isoproturon and diuron. A full scan monitoring was conducted with a cone voltage ramp of 5 to 80 V in the absence of collision gas. The conditions of the method were previously described for the quantification of the parent compounds diuron and isoproturon (Appendix A1.2.1). The same pre-concentration step carried out for the parent compounds was also conducted prior to the analysis to identify the respective by-products.

The method described in Appendix A1.2.2 for the analysis of hormones was also employed using full scan monitoring analysis to detect the formation of by-products.

A.2 LP/UV PHOTOLYSIS

A.2.1 Characterisation of water matrices

The characterisation of surface water and groundwater used in the photolysis experiments described in Chapter 2 are presented in Table A.6.

Table A.6 *Characterisation of the source waters used in the UV photolysis experiments described in Chapter 2.*

Parameter	Surface water	Groundwater
pH	8.05±0.25	7.42±0.24
Total organic carbon (mg L^{-1} C)	4.31±0.34	<0.4
Turbidity (NTU)	6.64±0.12	<0.4
Alkalinity (mg L^{-1} $CaCO_3$)	87.5±3.5	233±19
Total hardness (mg L^{-1} $CaCO_3$)	240	274

A.2.2 Time-based rate constants

The time-based rate constants obtained for the target pesticides by direct and indirect photolysis (Chapter 2) in different water matrices when the compounds were spiked individually and as mixtures are detailed in Table A.7.

Table A.7 *Time-based direct (LP/UV) and indirect (LP/UV/H_2O_2 and LP/UV/TiO_2) photolysis rate constants (k'_t) obtained for the selected pesticides in different water matrices: Laboratory grade water (LGW), surface water (SW), and groundwater (GW) as individual compounds (ind) and mixtures (mix); standard errors are given in parenthesis.*

Pesticide	**k'_t x 10^5 (s^{-1})**								
	LP/UV				**LP/UV/H_2O_2 – 40 mg L^{-1}**			**LP/UV/TiO_2 – 2.5 mg L^{-1}**	
	LGW_{ind}	**GW_{ind}**	**SW_{ind}**	**SW_{mix}**	**LGW_{ind}**	**SW_{ind}**	**SW_{mix}**	**LGW_{ind}**	**SW_{mix}**
ATR	13.89 (0.15) R^2=0.999	13.17 (0.04) R^2=0.999	12.16 (0.22) R^2=0.996	6.23 (0.04) R^2=0.999	12.10 (0.19) R^2=0.997	11.28 (0.07) R^2=0.999	6.03 (0.09) R^2=0.997	13.70 (0.08) R^2=0.999	8.81 (0.09) R^2=0.999
ISO	0.93 (0.01) R^2=0.850	0.82 ($3.13x10^{-3}$) R^2=0.983	1.41 (0.02) R^2=0.769	0.13 (0.02) R^2=0.963	1.82 (0.06) R^2=0.987	0.19 (0.02) R^2=0.880	0.116 (0.03) R^2=0.843	0.71 (0.11) R^2=0.780	0.22 (0.05) R^2=0.920
DIU	20.68 (0.32) R^2=0.997	20.77 (0.21) R^2=0.999	16.64 (0.18) R^2=0.999	12.94 (0.09) R^2=0.999	18.85 (0.18) R^2=0.999	16.37 (0.10) R^2=0.999	12.70 (0.12) R^2=0.999	22.13 (0.35) R^2=0.997	12.65 (0.13) R^2=0.999
ALA	9.53 (0.28) R^2=0.991	11.52 (0.13) R^2=0.998	8.80 (0.28) R^2=0.988	7.15 (0.09) R^2=0.998	10.22 (0.18) R^2=0.996	8.67 (0.08) R^2=0.999	5.12 (0.07) R^2=0.998	10.52 (0.26) R^2=0.993	6.33 (0.15) R^2=0.993
PCP	12.95 (0.10) R^2=0.999	11.90 (0.37) R^2=0.989	9.48 (0.18) R^2=0.996	nd	13.97 (0.31) R^2=0.994	10.21 (0.39) R^2=0.983	nd	nd	nd
CFVP	37.48 (1.01) R^2=0.993	22.26 (1.40) R^2=0.955	19.10 (1.07) R^2=0.964	17.37 (0.50) R^2=0.990	31.68 (1.24) R^2=0.985	20.98 (0.89) R^2=0.979	16.62 (0.44) R^2=0.992	23.20 (0.86) R^2=0.984	16.07 (0.31) R^2=0.996

nd – not determined; ATR – atrazine; ISO – isoproturon; DIU – diuron; ALA – alachlor; PCP – pentachlorophenol; CFVP – chlorfenvinphos.

A.2.3 Modelling

The degradation kinetics of the micropollutants (M) by LP/UV direct photolysis was modelled according to Equations A.1 to A.4 (Sharpless and Linden 2003, Schwarzenbach *et al*. 1993):

$$a_{254nm} = \varepsilon_{254nm} [M] z \qquad \text{(A.1)}$$

with a being the absorbance measured at 254 nm, ε the decadic molar absorption coefficient, $[M]$ the micropollutants concentration (that ranged approximately from 0.3 to 30 μM), and z the 1 cm pathlength.

$$-\frac{d[M]}{dt} = k'_d [M] = \left(\sum_{\lambda} K_s(\lambda)\right)\phi[M] \qquad \text{(A.2)}$$

$$K_s(\lambda) = \frac{E^o{}_p(\lambda)\varepsilon(\lambda)\left[1 - 10^{-a(\lambda)z}\right]}{a(\lambda)z} \qquad \text{(A.3)}$$

$$-\frac{d[M]}{dt} = k'_d [M] \Rightarrow \int_{M_0}^{M} \frac{1}{x}dx = -k'_d \int_{t_0}^{t} ds \Rightarrow ln\frac{[M]}{[M_0]} = -k'_d \times t \qquad \text{(A.4)}$$

where k'_d represents the time-based pseudo-first-order direct rate constant for the individual pesticides by LP direct photolysis in LGW, which was obtained from the slope of the linear regression described by Equation A.4. $K_s(\lambda)$ represents the specific rate of light absorption by the compound; $E^{\circ}_p(\lambda)$ the incident photon irradiance determined taking into account a radiometer reading as well as petri, reflection, water, and divergence factors; $\varepsilon(\lambda)$ the decadic molar absorption coefficient obtained using Equation A.1; $a(\lambda)$ the solution absorbance; z the solution depth in the petri dish (2.1 cm); and ϕ the quantum yield. Since LP lamps emit mainly monochromatic light, all the parameters described above were experimentally obtained at 254 nm.

The degradation of organic compounds during AOPs is the result of direct and indirect photolysis, described by Equation A.5.

$$-\frac{d[M]}{dt}=(k'_d+k'_i)[M] \tag{A.5}$$

with k'_i being the pseudo-first-order rate constant for indirect photolysis. This constant is a function of the second-order reaction rate constant ($k_{OH/M}$), determined experimentally using pCBA as a probe compound, and the steady-state concentration of OH radicals ($[^\bullet OH]_{ss}$) as follows:

$$k'_i=k_{OH/M}\left[^\bullet OH\right]_{ss} \tag{A.6}$$

$[^\bullet OH]_{ss}$ is a function of the quantum yield for photolysis of H_2O_2 into two OH radicals, the sum of the pseudo-first-order rates of reaction of $^\bullet OH$ with scavengers ($k_{OH/S}$; e.g. HCO_3^-, CO_3^{2-}, dissolved organic carbon – DOC, and H_2O_2), and all the other parameters described above in the direct photolysis expressions:

$$\left[^\bullet OH\right]_{ss}=\frac{\sum_\lambda k_{a,H_2O_2}(\lambda)\phi_{OH}(\lambda)[H_2O_2]}{\sum_i k_{OH/S}[S]_i} \tag{A.7}$$

$$K_{a,H_2O_2}(\lambda)=\sum_\lambda\frac{E^o{}_p(\lambda)\varepsilon_{H_2O_2}(\lambda)\left[1-10^{-\left(a(\lambda)+\varepsilon_{H_2O_2}(\lambda)[H_2O_2]\right)z}\right]}{\left(a(\lambda)+\varepsilon_{H_2O_2}(\lambda)[H_2O_2]\right)z} \tag{A.8}$$

The pseudo-first-order rates of reaction of OH radicals with scavengers were taken as: k_{OH/HCO_3^-} = 8.5 × 10^6 L mol^{-1} s^{-1} (Buxton *et al*. 1988), $k_{OH/CO_3^{2-}}$ = 3.9 × 10^8 L mol^{-1} s^{-1} (Buxton *et al*. 1988), $k_{OH/DOC}$ = 2.5 × 10^4 L mg^{-1} s^{-1} (Larson and Zepp 1988), and k_{OH/H_2O_2} = 2.7 × 10^7 L mol^{-1} s^{-1} (Buxton *et al*. 1988). The H_2O_2 concentration was determined in each experiment (Klassen *et al*. 1994) and the DOC concentration of the filtered surface water was 4 mg L^{-1} C. Bicarbonate and carbonate concentrations were calculated according to Equation A.9, using the alkalinity and pH values of the filtered surface water:

$$\mathrm{Alk} = [\mathrm{HCO_3^-}]+2[\mathrm{CO_3^{2-}}]+[\mathrm{OH^-}]-[\mathrm{H^+}] = (\alpha_1+2\alpha_2)\times[\mathrm{TOTCO_3}]+[\mathrm{OH^-}]-[\mathrm{H^+}] \qquad \text{(A.9)}$$

The second-order rate constants for reaction of the pesticides with OH radicals were determined by competition kinetics using pCBA as a reference compound (Huber *et al*. 2003), after rearrangement of Equations A.5 and A.10:

$$-\frac{d[pCBA]}{dt} = k_{OH/pCBA}[{}^{\bullet}OH][pCBA] \qquad \text{(A.10)}$$

After substituting $\int {}^{\bullet}OHdt$ from Equation A.10 into Equation A.5 and rearranging, the expressions allow the determination of the second-order rate constants ($k_{OH/M}$), using Equation A.11 as the slope of a plot of $ln([M]/[M_0]) + k_d^{'}t$ vs $ln([pCBA]/[pCBA_0])(1/k_{OH/pCBA})$, assuming a very fast reaction rate between the OH radicals and pCBA of 5×10^9 M^{-1} s^{-1} (Neta and Dorfman 1968):

$$ln\left(\frac{[M]}{[M_0]} + k_d^{'}t\right) = k_{OH/M}\left[ln\left(\frac{[pCBA]}{[pCBA_0]}\right)\frac{1}{k_{OH/pCBA}}\right] \qquad \text{(A.11)}$$

Before conducting the indirect photolysis experiments, direct photolysis of pCBA was tested and found negligible.

A.3 SAMPLING EVENTS USED FOR MULTIVARIATE STATISTICAL ANALYSIS

The sampling events (rejection and adsorption values) used to develop the models presented in Chapter 4 are depicted in Table A.8.

Table A.8 *Rejection and adsorption values used in multivariate statistical analysis.*

Description of the experiment	**Water matrix**	**Compound**	**Adsorption (%)**	**Apparent rejection (%)**
Experiments without pre-adsorption	Groundwater	Atrazine	90.8	96.2
		Alachlor	98.8	99.9
		Pentachlorophenol	16.4	70.5
		17β-Estradiol	59.4	97.2
		17α-Ethinylestradiol	37.3	92.2
		Estrone	49.3	95.3
		Estriol	39.2	98.3
		Progesterone	na	96.3
	Surface Water	Atrazine	96.9	99.9
		Alachlor	54.5	99.9
		Pentachlorophenol	54.2	75.4
Experiments with static pre-adsorption	Groundwater	Atrazine	73.3	99.0
		Alachlor	97.2	99.8
		Pentachlorophenol	18.1	57.5
		17β-Estradiol	37.2	91.7
		17α-Ethinylestradiol	47.8	94.3
		Estrone	94.3	94.3
		Estriol	na	93.8
		Progesterone	na	94.8

Table A.8 *Rejection and adsorption values used in multivariate statistical analysis (continuation).*

Description of the experiment	Water matrix	Compound	Adsorption (%)	Apparent rejection (%)
Experiments with static pre-adsorption	Surface Water	Atrazine	na	97.1
		Alachlor	98.8	98.9
		Pentachlorophenol	48.1	83.5
		17β-Estradiol	42.3	96.3
		17α-Ethinylestradiol	20.4	93.8
		Estrone	52.0	98.7
		Estriol	32.9	97.4
		Progesterone	na	98.6
Experiments with static and dynamic pre-adsorption	Groundwater	17β-Estradiol	25.8	91.9
		17α-Ethinylestradiol	9.1	90.0
		Estrone	18.1	93.1
		Estriol	9.0	93.7
		Progesterone	na	96.0
	Surface Water	17β-Estradiol	30.8	97
		17α-Ethinylestradiol	23.1	96.0
		Estrone	37.3	97.6
		Estriol	24.4	98.6
		Progesterone	na	99.5

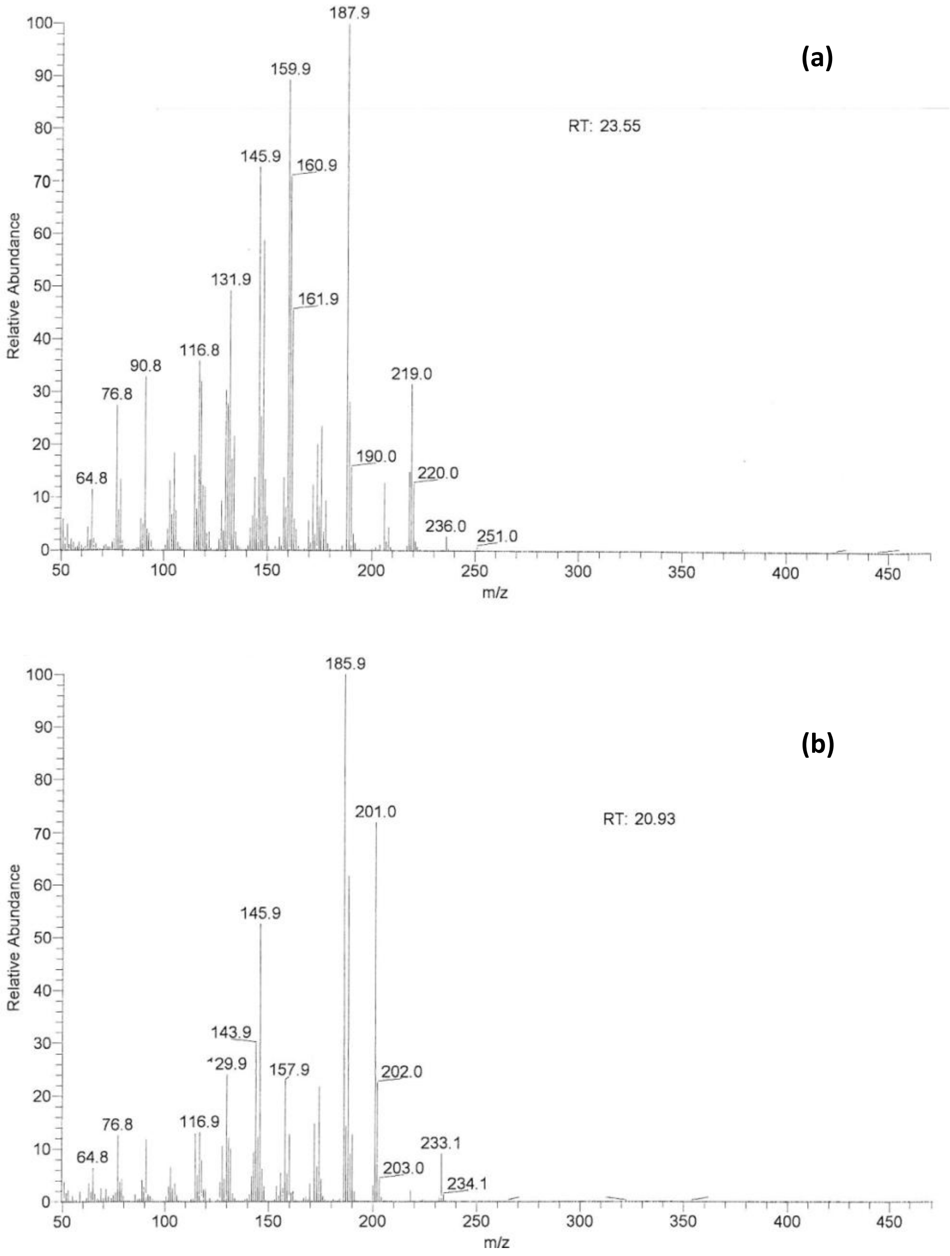
na – not available

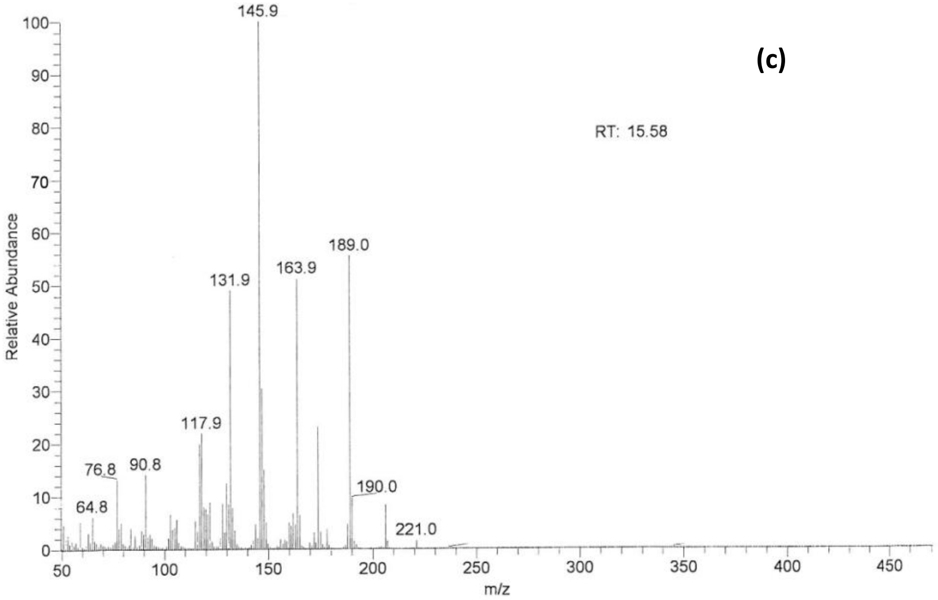
A.4 YEAST ESTROGEN SCREEN ASSAY

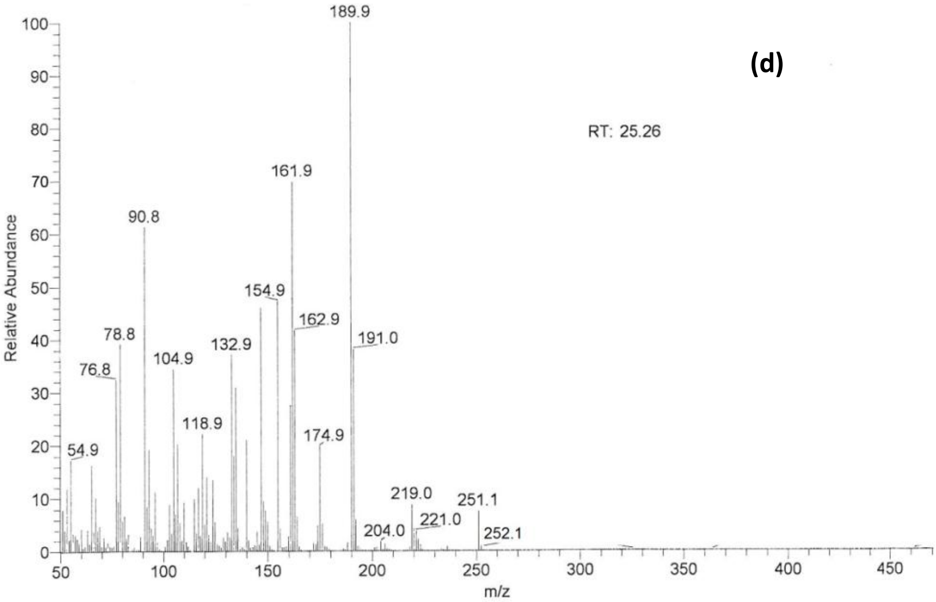
The yeast colonies were propagated using a single colony every 3 weeks on plates containing Sabouraud dextrose agar supplemented with chloramphenicol (60 g L^{-1} of agar and 3 mL of chloramphenicol solution 100 mg L^{-1}) to avoid growth of bacteria. The plates were incubated at 30 °C during 72 to 96 h and then stored at 4 °C. A single colony of a recent plate was used to inoculate liquid growth medium containing several salts, aminoacids, glucose, and vitamins. This growth medium was then incubated at 30 °C in a shaker table (100 rpm) (Innova 2100) placed in a dark room, during 18 to 24 h, until an optical density at 640 nm of approximately 1 was reached. Then, the inoculated growth medium (230 μL) was added to 96-well microplates containing the samples or the respective dilutions and the substrate chlorophenol red-β-D-galactopyranoside (20 μL). 17β-estradiol was also plated as a reference sample and used as a standard reference compound since it presents a very high endocrine disrupting activity. The 96-well microplates were incubated in the dark at 30 °C in a shaker plate (200 rpm) during 96 h to observe colour development (change from yellow to red), which is a measure of the estrogenic activity of the sample. The absorbance of the wells was measured at 562 nm (change of CPRG colour) and 640 nm (turbidity correction) using a microplate spectrophotometer reading. The corrected absorbance was determined by subtracting the absorbance measured at 640nm to the one measured at 562 nm. Then, the software "*R*" v 2.13.0, created by Ritz and Streibig, was used to determine the EC_{50} of 17β-estradiol and samples. For that, the package add-on dose-response-curve was downloaded to the program and used in combination with comma separated values format files containing the absorbance data obtained and the respective concentration factors.

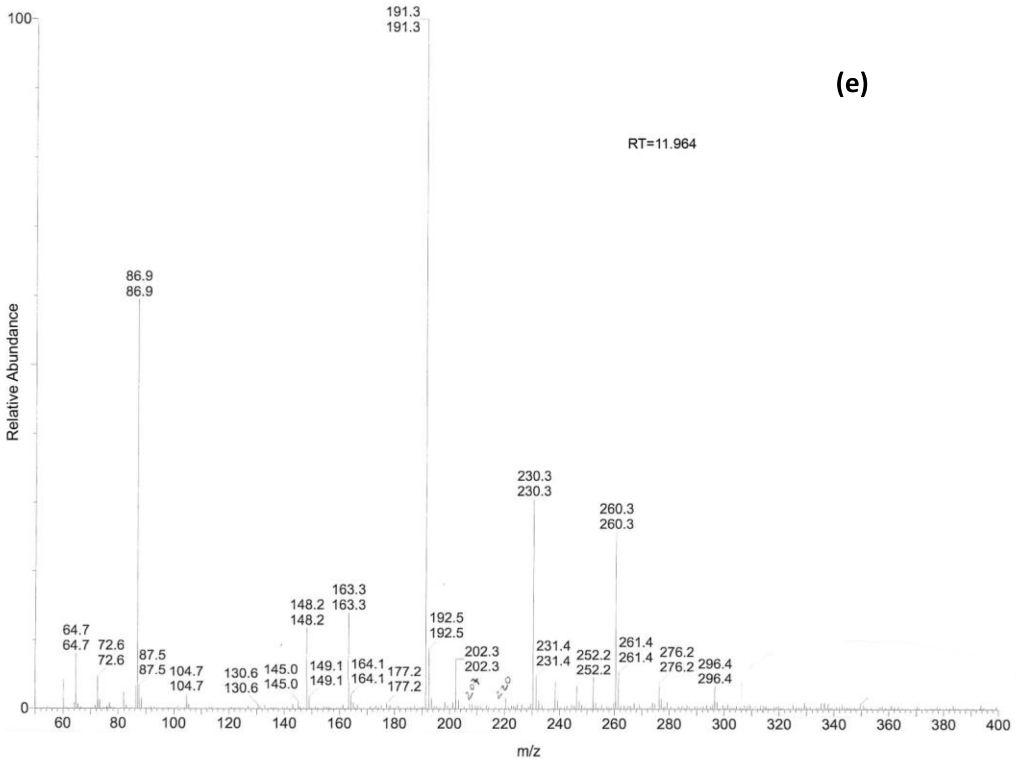
A.5 BY-PRODUCTS DETECTED DURING THE INTEGRATED TREATMENT

The by-products produced during the integrated treatment experiments (Chapter 5) were identified based on the respective mass spectra depicted in Figure A.1.




(c)
RT: 15.58
Relative Abundance
m/z
145.9
189.0
163.9
131.9
117.9
76.8
90.8
64.8
190.0
221.0
0
10
20
30
40
50
60
70
80
90
100
50
100
150
200
250
300
350
400
450


(d)
RT: 25.26
Relative Abundance
m/z
189.9
161.9
90.8
154.9
162.9
78.8
191.0
104.9
132.9
76.8
118.9
174.9
54.9
219.0
251.1
221.0
204.0
252.1
0
10
20
30
40
50
60
70
80
90
100
50
100
150
200
250
300
350
400
450


(e)
RT=11.964
Relative Abundance
m/z
100
0
191.3
86.9
230.3
260.3
163.3
148.2
192.5
64.7
72.6
87.5
104.7
130.6
145.0
149.1
164.1
177.2
202.3
231.4
252.2
261.4
276.2
296.4
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400

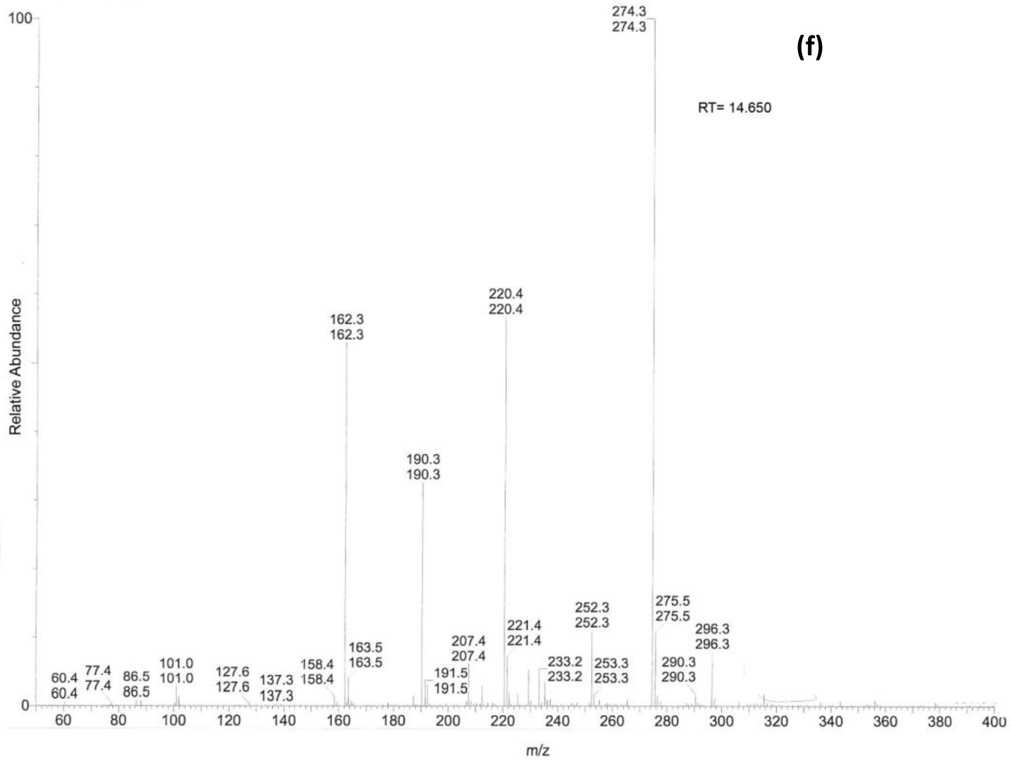
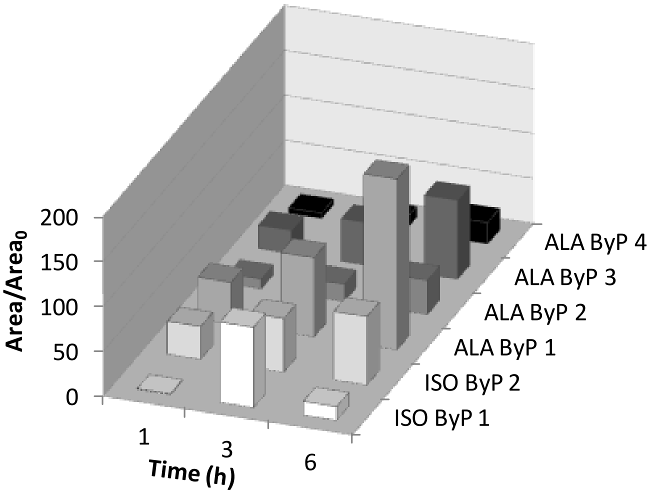


Figure A.1 Mass spectra of major by-products detected.

The relative abundance of alachlor and isoproturon by-products produced throughout the 6h integrated treatment (Chapter 5) is illustrated in Figure A.2.



	1h	3h	6h
□ ISO ByP 1	1	89	15
▨ ISO ByP 2	37	60	76
▨ ALA ByP 1	46	88	190
▨ ALA ByP 2	11	20	38
▨ ALA ByP 3	26	47	88
■ ALA ByP 4	6	12	24

Figure A.2 *Relative abundance of isoproturon (ISO) and alachlor (ALA) by-products (ByP) area in the retentate as a function of operation time.*

REFERENCES

Buxton GV, Greenstock CL, Helman WP, Ross AB (1988) Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals (OH/O^-) in aqueous-solution. *J Phys Chem Ref Data* 17: 513-886.

Huber MM, Canonica S, Park GY, Von Gunten U (2003) Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environ Sci Technol* 37: 1016-1024.

Klassen NV, Marchington D, McGowan HCE (1994) H_2O_2 determination by the I^-_3 method and by $KMNO_4$ titration. *Anal Chem* 66: 2921-2925.

Larson RA, Zepp RG (1988) Reactivity of the carbonate radical with aniline derivatives. *Environ Toxicol Chem* 7: 265-274.

Neta P, Dorfman LM (1968) Pulse radiolysis studies XIII rate constants for reaction of hydroxyl radicals with aromatic compounds in aqueous solutions. *Adv Chem Ser* 81: 222-230.

Schwarzenbach RP, Gschwend PM, Imboden DM, In environmental organic chemistry. John Wiley & Sons, Inc., New York (1993).

Sharpless C, Linden K (2003) Experimental and model comparisons of low- and medium-pressure Hg lamps for the direct and H_2O_2 assisted UV photodegradation of N-nitrosodimethylamine in simulated drinking water. *Environ Sci Technol* 37: 1933-1940.

ITQB-UNL | Av. da República, 2780-157 Oeiras, Portugal
Tel (+351) 214 469 100 | Fax (+351) 214 411 277

www.itqb.unl.pt

"Patience and perseverance have a magical effect before which difficulties disappear and obstacles vanish."
John Quincy Adams (1767 –1848)