TESIS DOCTORAL

Aplicación de tratamientos físicos y de oxidación química a la eliminación de contaminantes emergentes en diferentes matrices acuosas.

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A mi gran familia y amigos

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1. RESUMEN

1. RESUMEN

La presente Memoria de Tesis Doctoral expone y discute de forma detallada los resultados obtenidos en el trabajo realizado, cuyo objetivo global es el estudio de la eliminación mediante procesos físicos y químicos de un grupo de contaminantes emergentes seleccionados que están presentes en diversas matrices acuosas. Estos contaminantes se caracterizan por tres aspectos: baja concentración en aguas superficiales y residuales; desconocimiento de los efectos sobre los procesos de depuración de aguas, los cauces de vertido y, en general, el medio ambiente y la salud humana; y porque no es necesario que persistan en el medio para causar efectos negativos, ya que su eliminación o transformación es compensada por su continua introducción en el mismo. El presente estudio se enmarca y forma parte de una amplia línea de trabajo que se viene desarrollando en el área de Ingeniería Química de la Universidad de Extremadura desde hace ya más de 20 años, y que consiste fundamentalmente en el tratamiento y eliminación de diferentes tipos de contaminantes que están presentes en aguas superficiales y residuales, empleando para ello métodos físicos, químicos y biológicos.

La presente investigación ha sido desarrollada a través de los proyectos CTQ2010-14823 y CTM2013-41354-R, financiados por el Ministerio de Ciencia e Innovación de España. Asimismo, el trabajo se ha enmarcado y recibido financiación parcial por parte del Gobierno Regional a través de recursos cofinanciados por el Fondo Europeo de Desarrollo Regional, y dentro de sus “Planes de Actuación para el Apoyo a Grupos de Investigación Catalogados de la Junta de Extremadura”. Concretamente, tales ayudas han sido concedidas al Grupo “Tecnología del Medio Ambiente e Ingeniería Química, Grupo RNM021”, en el seno del cual se ha desarrollado el trabajo, y dentro de los Programas plurianuales 2011-2014 (referencia GR10026) y 2015-2017 (referencia GR150679). El autor de este trabajo, que conduce a la realización de su Tesis Doctoral, ha formado parte del equipo investigador que ha llevado a cabo dichos proyectos durante los últimos años.

En dicho contexto general, el presente trabajo se ha centrado en la eliminación de tres contaminantes disueltos en diferentes matrices acuosas, que han sido seleccionados

como contaminantes modelo de este grupo genérico de sustancias conocidas como “Contaminantes Emergentes” (ECs). Tales compuestos son: clorhidrato de amitriptilina (AH), salicilato de metilo (MS) y 2-fenoxietanol (PE). Una vez presentes en diferentes tipos de aguas, fueron expuestos individualmente o de forma simultánea a diversos tratamientos de oxidación química, y procesos físicos, como adsorción y tecnologías de membrana. Las aguas reales seleccionadas para analizar la influencia de su matriz orgánica sobre la eliminación de contaminantes fueron las siguientes: un agua superficial de pantano y dos efluentes secundarios procedentes de las EDARs de La Albuera y de Badajoz Todos estos procesos experimentales aplicados se resumen a continuación.

En una primera etapa se llevó a cabo la degradación de los contaminantes seleccionados mediante procesos de oxidación química, los cuales son muy adecuados para la eliminación en general de microcontaminantes orgánicos de las aguas superficiales y residuales. Para este propósito se utilizaron diferentes reactivos oxidantes y combinaciones de los mismos. Se diseñaron experimentos de degradación química para la eliminación de los contaminantes tanto en agua ultrapura (UP) como en las tres aguas reales citadas previamente. Algunas de las variables de operación fueron modificadas con el objetivo de establecer las condiciones óptimas para cada proceso químico. Asimismo, se determinaron los parámetros cinéticos básicos, los cuales son útiles para el posterior diseño de reactores y equipos que están presentes en las estaciones de tratamiento de agua.

El primer agente oxidante utilizado para la degradación individual en agua ultrapura fue la radiación UV, utilizando una lámpara de vapor de mercurio a baja presión. La aplicación del Modelo de Fuente Lineal de Emisión Esférica permitió la determinación de los rendimientos cuánticos de cada compuesto, valores que mostraron el siguiente orden de reactividad: AH > PE > MS. A su vez se determinaron para cada uno de los ECs las constantes de velocidad de primer orden de las reacciones fotoquímicas y los niveles de degradación alcanzados, lo que permitió establecer la influencia de variables de operación tales como pH, temperatura, naturaleza de los contaminantes emergentes seleccionados y presencia de diferentes concentraciones iniciales de H_2O_2.

En la siguiente etapa se llevó a cabo el estudio de la degradación individual de los ECs seleccionados, nuevamente en agua UP, mediante el uso de Procesos de Oxidación Avanzada (POA) basados en el sistema Fe/H_2O_2; concretamente utilizando el reactivo de Fenton (Fe^{2+}/H_2O_2), Fenton-Like (Fe^{3+}/H_2O_2) y el sistema foto-Fenton ($UV/Fe^{2+}/H_2O_2$). Dicho estudio permitió establecer el efecto ejercido tanto por la concentración inicial de Fe^{2+} como por la concentración de H_2O_2. El sistema foto-Fenton resultó ser más efectivo, como era de esperar, debido a la generación adicional de radicales hidroxilo y a la fotodegradación directa de los compuestos orgánicos. Por otra parte, el sistema Fenton-Like fue el menos efectivo en la eliminación de estos compuestos.

Por otro lado, las constantes de velocidad de segundo orden para la reacción directa entre cada uno de los ECs seleccionados y los radicales hidroxilo ($k_{OH\text{-}EC}$) fueron asimismo evaluadas mediante un método competitivo, empleando ácido p-clorobenzoico (p-CBA) como compuesto de referencia.

Por último en esta etapa, se llevaron a cabo experimentos con las sustancias presentes en aguas reales para evaluar el efecto de la presencia de la materia orgánica en tales efluentes sobre los niveles de degradación de los compuestos seleccionados. Finalmente, se propone un modelo cinético para predecir la eliminación de los ECs en cualquier tipo de agua, el cual muestra resultados que se ajustan satisfactoriamente a los valores experimentales obtenidos.

Dado que el proceso de cloración es muy común en los tratamientos de desinfección de agua potable, se eligió dicho agente para realizar su estudio en el presente trabajo. En la primera etapa, el objetivo fue determinar por un lado las constantes de velocidad de segundo orden aparentes para la reacción de cada EC con el oxidante cloro en el intervalo de pH 3-10. Los valores de dichas constantes establecen que tanto la concentración inicial de cloro como la temperatura ejercen un efecto positivo en la degradación de estos contaminantes. Además, dichos valores permiten establecer el siguiente orden de reactividad: AH > MS > PE, orden que coincide con el obtenido previamente para la reacción entre los radicales OH y los ECs. A continuación se determinaron las constantes intrínsecas de velocidad (k_1, k_2 y k_c) para las reacciones específicas entre HOCl y las especies iónicas de cada contaminante. Para ello se propuso un modelo cinético que tenía en cuenta tanto a dichas constantes aparentes como los equilibrios de disociación de cada contaminante y de las especies cloradas. Como se discutirá en los siguientes Capítulos, los valores de k_2 obtenidos son sensiblemente mayores que los de k_1, lo que indica un aumento en la velocidad de reacción con HOCl de las especies disociadas de los contaminantes seleccionados.

En una etapa posterior, se empleó ozono como agente oxidante. Dos tipos de experimentos se realizaron con diferentes propósitos. El primer grupo de experimentos consistió en el proceso de ozonización de cada EC disuelto en agua ultrapura, a diferente pH y en presencia de terc-butanol, con el objetivo de determinar las constantes cinéticas para la reacción directa entre el ozono y cada compuesto. Para aquellos compuestos que muestran constante de disociación también se evaluaron las constantes intrínsecas de velocidad de las especies disociadas y no disociadas. Considerando los valores obtenidos para las constantes de velocidad de cada EC, puede concluirse el siguiente orden de reactividad a pH 7: MS > AH > PE, aunque AH se ha mostrado como el compuesto más reactivo con ozono a pH 3. La comparación entre los valores de las constantes intrínsecas de velocidad deducidos para la cloración y las obtenidas para la ozonización, pone de manifiesto que las reacciones de ozonización son alrededor de tres órdenes de magnitud superiores a las de cloración, lo que sugiere una mayor eficacia de dicho proceso de ozonización.

Con el fin de completar el estudio comparativo de ambos procesos de oxidación (cloración y ozonización), se llevaron a cabo varios experimentos de oxidación simultánea de los contaminantes en las aguas reales ya descritas en procesos de fotooxidación. Los agentes oxidantes utilizados fueron cloro, ozono y la combinación de este último con peróxido de hidrógeno, siendo este último proceso combinado el más efectivo en la eliminación de los contaminantes seleccionados.

El siguiente sistema agente oxidante ensayado fue la combinación de radiación UV con el ión persulfato ($UV/S_2O_8^{2-}$). En primer lugar, se propuso un modelo de cinético de primer orden, en el que se evaluaron las correspondientes constantes de velocidad, y se obtuvieron correlaciones muy satisfactorias que indican la bondad del modelo propuesto.

Estos valores de constantes ponen de manifiesto la influencia positiva que ejerce la concentración inicial de $S_2O_8^{2-}$ y la temperatura. Con respecto al efecto del pH, ejerce un efecto positivo para los casos de AH y MS y no influyó en la degradación de PE. Finalmente, se evaluó la contribución de cada especie radicalaria y se determinaron las constantes de segundo orden de cada EC con el radical sulfato.

Con el fin de completar los experimentos de oxidación química, se realizó un bloque experimental de eliminación de los contaminantes seleccionados mediante el sistema UV/Cloro. Para ello se realizaron experimentos de degradación individuales con el objeto de determinar la influencia de las variables operativas. El estudio cinético llevado a cabo con la determinación de los valores de las constantes de velocidad de primer orden muestra los siguientes aspectos relevantes: el efecto positivo que ejerce la concentración inicial de cloro; la mejora del sistema UV/Cloro con respecto a la fotodegradación simple de los contaminantes; y el efecto negativo que ejerce el pH en la eliminación de los contaminantes seleccionados.

Para finalizar el estudio de este POA se llevaron a cabo experimentos con los tres compuestos modelo disueltos en cuatro matrices de aguas diferentes: agua ultrapura y tres aguas reales ya utilizadas en procesos anteriores (un agua superficial de pantano y dos efluentes secundarios procedentes de las EDAR de La Albuera y de Badajoz) mediante varios sistemas de oxidación de forma individual y combinada (UV, UV/H_2O_2, UV/$S_2O_8^{2-}$ y UV/Cl_2), con el objetivo de comparar el grado de eliminación de los compuestos seleccionados en dichas matrices acuosas. Los resultados obtenidos en los experimentos realizados con similares concentraciones iniciales de oxidantes indican que el proceso de oxidación más eficaz es el sistema UV/Cl_2. Por lo tanto, el POA UV/Cl_2 es una alternativa prometedora para la eliminación de contaminantes emergentes en aguas superficiales y en efluentes de EDARs.

Tras el análisis de los resultados obtenidos en los diferentes procesos químicos estudiados, se puede llegar a la conclusión de que tales métodos de oxidación química resultan adecuados para la eliminación de los contaminantes emergentes presentes en aguas, siendo apta su aplicación en plantas reales de tratamiento de aguas. La elección del proceso más adecuado dependerá de las condiciones operativas y del coste calculado a partir de un estudio económico aplicado a cada caso concreto.

El segundo bloque de tratamientos dentro de este trabajo fue la eliminación de los tres contaminantes emergentes seleccionados mediante técnicas físicas, empezando por tecnologías de membrana. Específicamente, se utilizaron membranas de ultrafiltración (UF) y de nanofiltración (NF). En la bibliografía está ampliamente descrito que estos procesos de membrana son en general adecuados para retener moléculas orgánicas de diferentes tamaños. Los experimentos se llevaron a cabo en un equipo de membrana de laboratorio en modo de concentración y con flujo transversal.

El estudio se centró en evaluar la influencia de algunas variables de operación (naturaleza y MWCO (tamaño de corte de peso molecular) de las membranas, pH, presencia de materia orgánica, etc.) sobre el flujo de permeado y la retención de los compuestos seleccionados. Para ello, se emplearon las matrices acuosas habituales (agua UP, un agua superficial y dos efluentes secundarios) y diferentes membranas: tres membranas de UF (MWCO de 20000, 5000 y 2000 Da) y tres membranas de NF (MWCO en el rango 150-300 Da). Teniendo en cuenta tanto los coeficientes de retención de los ECs como la eliminación de materia orgánica, la membrana de nanofiltración HL resultó ser la más adecuada para la eliminación de estos contaminantes.

El último tratamiento del presente Trabajo se centró en el estudio de la eliminación de los ECs seleccionados disueltos en aguas mediante procesos de adsorción con carbón activo, utilizando dos soportes adsorbentes: carbón activo en polvo (PAC) y carbón activo granular (GAC). Los experimentos se centraron en primer lugar en la determinación de las isotermas de adsorción y el estudio cinético del proceso de adsorción. Los resultados experimentales para los contaminantes seleccionados se ajustan de forma más satisfactoria a la isoterma de Langmuir en la mayoría de los casos. Asimismo, la evaluación de la cinética de adsorción a través de diferentes modelos conduce a la conclusión de que el modelo de pseudo-segundo orden es el que mejor se ajusta a los datos experimentales. Además, tales datos experimentales muestran una eficiencia superior de la adsorción sobre el PAC, mientras que el GAC muestra una menor y más lenta capacidad de adsorción, en concordancia con la menor mesoporosidad del adsorbente.

Para finalizar el estudio de la eliminación de estos contaminantes mediante procesos de adsorción, se realizó un bloque experimental consistente en experimentos de adsorción con PAC de los contaminantes disueltos de forma simultánea en las tres matrices acuosas habituales: agua superficial de pantano y los dos efluentes secundarios procedentes de las EDAR de La Albuera y de Badajoz. Los resultados muestran una importante eliminación de DQO y TOC. Por ello, se concluye que el uso de PAC resulta ser una tecnología eficaz, tanto para eliminación de microcontaminantes como para la reducción de la materia orgánica presente en aguas reales.

2. Introducción

2. INTRODUCCIÓN.

2.1. LA PROBLEMÁTICA GLOBAL DEL AGUA.

El agua es un recurso abundante e imprescindible en el momento presente pues se utiliza para beber, para aseo personal, para producir alimentos y otros bienes de consumo y para generar energía. Al analizar un mapamundi, se observa que las dos terceras partes de nuestro planeta están cubiertas de agua. Sin embargo no toda el agua del planeta es adecuada para el consumo humano, y no toda la población mundial tiene las mismas posibilidades de acceso a este preciado bien, lo que impide el desarrollo de muchas zonas de la tierra.

El 97.5% del agua se encuentra en mares y océanos en forma salada, lo que la hace inútil para la alimentación, la agricultura y la mayor parte de los usos industriales. El 2.5% del agua restante del planeta es agua dulce, pero está confinada en los glaciares, en la nieve, en depósitos subterráneos o en otros lugares de difícil utilización (Figura 2.1). Por todo esto, sólo un 0.26% de la masa total de agua es aprovechable para el consumo humano.

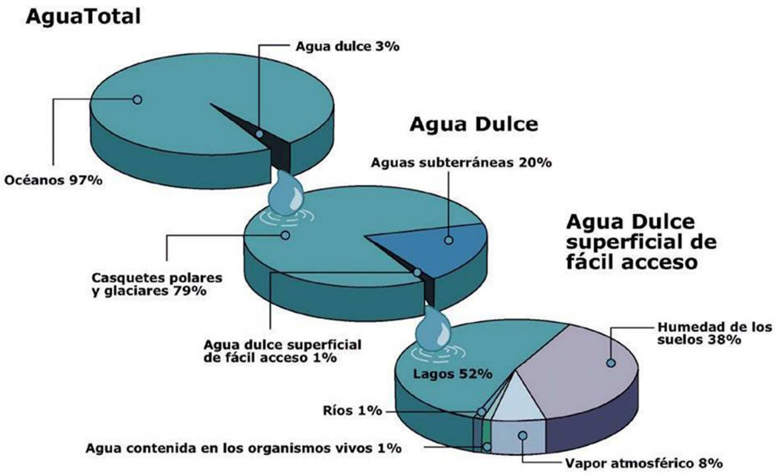


Figura 2.1. Distribución del agua en la Tierra.

Por ello, el agua como recurso natural es un bien muy escaso, ya que, tanto los ecosistemas, como la sociedad y la economía que mueven el planeta necesitan agua (Vanneuville et al., 2012). Además, debido a la presión a la que está sometida este recurso, no sólo provocada por el rápido desarrollo económico y humano, sino también por la mala gestión de los recursos hídricos del planeta, ha sufrido un alarmante deterioro. En gran medida, ello ha sido debido a que durante décadas se ha empleado el agua como medio de eliminación, vertiendo sobre ella toneladas de sustancias biológicamente activas (tales como pesticidas, fármacos, disolventes etc.), lo que ha originado un desgaste del medio ambiente sin reparar en las graves consecuencias que ello conlleva. Adicionalmente, al problema de la contaminación hay que añadirle el problema de la escasez, aspecto que está adquiriendo proporciones alarmantes debido al cambio climático y la creciente desertización que está sufriendo el planeta.

Según el informe de Naciones Unidas de los recursos hídricos del año 2016, se prevé que para el año 2025 más de 2800 millones de habitantes se verán afectados por la escasez del agua; y en 2050 la demanda mundial de agua habrá aumentado un 55%, debido principalmente a demandas relacionadas con la creciente urbanización en los países en desarrollo (OECD, 2012a). Las ciudades tendrán que ir más lejos o perforar más hondo para encontrar agua, o tendrán que depender de soluciones innovadoras o de tecnologías avanzadas para satisfacer sus necesidades hídricas.

Las medidas legislativas que se han ido adoptando a lo largo de estos años para evitar la contaminación química de las aguas y los peligros que se derivan de ella, han contribuido a mitigar parcialmente esta situación. En el año 2000, en el marco de la política medioambiental europea, la WFD (Water Framework Directive) 2000/60/EC fue la primera directiva en integrar la protección de ecosistemas acuáticos en términos de calidad de agua, cantidad de agua y su correspondiente papel para la población. En 2012, la Agencia Europea de Medioambiente (EEA, European Environment Agency) publicó la directiva “A Blueprint to Safeguard Europe’s Water Resources” (COM (2012) 673), que se centra en una política de acciones para la mejora de la implementación de la actual legislación del agua, y en la integración de los objetivos de la política del agua en otras políticas europeas. Todo ello enfocado hacia la gestión sostenible de los recursos hídricos en el marco temporal de la Estrategia UE 2020. Sin embargo, la aparición de nuevos contaminantes potencialmente peligrosos y la creciente demanda de agua ha puesto de manifiesto la necesidad de investigar técnicas y soluciones que contribuyan a proteger tanto la salud humana como el medio ambiente, y así conseguir un uso sostenible de dicho elemento.

2.2. CONTAMINANTES EMERGENTES.

Durante décadas, la comunidad científica ha centrado sus esfuerzos en el estudio de contaminantes químicos cuya presencia en el medio ambiente ha estado o está regulada en las distintas legislaciones, contaminantes que en su mayoría son apolares, tóxicos, persistentes y bioacumulables, como los hidrocarburos aromáticos policíclicos, los policlorobifenilos (PCBs) o las dioxinas, entre otros.

Sin embargo, en los últimos años, el avance tecnológico ha desarrollado nuevos y más sensibles métodos de análisis, los cuales han permitido descubrir y cuantificar la presencia de otros contaminantes potencialmente peligrosos y que están aún sin regular, los cuales son genéricamente denominados **contaminantes emergentes**.

En la actualidad, el estudio de los contaminantes emergentes se encuentra entre las líneas principales de investigación de la Organización Mundial de la Salud (OMS), la Agencia para la Protección del Medio Ambiente (EPA) y la Comisión Europea. Estas organizaciones definen a estos contaminantes como compuestos que penetran en el medio ambiente y que se caracterizan por tres aspectos: baja concentración en el caudal total de aguas residuales; desconocimiento de los efectos sobre los procesos de depuración de aguas, los cauces de vertido y, en general, el medio ambiente y la salud humana y porque no es necesario que persistan en el medio para causar efectos negativos, ya que su eliminación o transformación es compensada por su continua introducción en el mismo (Stuart et al., 2012).

2.3. PROBLEMÁTICA AMBIENTAL DE LOS CONTAMINANTES EMERGENTES.

La existencia de los contaminantes emergentes en las aguas es conocida desde hace décadas, pero es en la actualidad cuando se ha empezado a cuantificar sus niveles en el medio ambiente, reconociéndose como contaminantes potencialmente peligrosos que pueden producir daños en el ecosistema (Fent et al., 2006; Jjemba, 2006). Estas nuevas especies pertenecen a diferentes clases de compuestos y se detectan en concentraciones muy bajas, del orden de partes por billón y partes por trillón (ng-µg L^{-1}), aunque en algunos casos se han detectado en niveles superiores, como concentraciones de 100 mg L^{-1} (Pal et al., 2014).

La lista de contaminantes de interés emergente incluye una amplia variedad de compuestos de diferentes estructuras y usos, así como también sus metabolitos y productos de transformación. En la tabla 2.1 se muestran los contaminantes de interés emergente más representativos (Celano et al., 2014). Muchos de éstos son tóxicos o están clasificados como disruptores endocrinos, lo que implica que una exposición a los mismos puede dar lugar a alteraciones en el crecimiento, desarrollo, reproducción y comportamiento de los organismos vivos.

Tabla 2.1. Principales grupos de contaminantes orgánicos emergentes.

Grupo de contaminantes	Subgrupo	Compuestos de interés emergente
Fármacos	Antibióticos	Lincosamidas, macrólidos, sulfamidas, tetraciclinas, quinolonas
	Analgésicos y antiinflamatorios	Paracetamol, ácido acetil salicílico, ibuprofeno, diclofenac, oxicam.
	Psiquiátricos	Benzodiacepinas, barbitúricos
	β-bloqueantes	Metoprolol, propranolol, timolol
	Medios de contraste de rayos X	Iopromide, iopamidol, diatrizoato

Tabla 2.1. Principales grupos de contaminantes orgánicos emergentes (continuación).

Grupo de contaminantes	**Subgrupo**	**Compuestos de interés emergente**
Fármacos	Esteroides y hormonas	Estradiol, estrona, estriol, dietilestilbestrol
	Citostáticos	Vincristina, etopósido, cisplatino
Productos del cuidado personal	Parabenos	Metilparabeno, etilparabeno, propilparabeno
	Filtros solares	Benzofenonas, cinamato, bencilidenos, derivados del alcanfor
	Perfumes	Fragancias nitro, policíclicas y macrocíclicas
Tensoactivos	Sulfonatos	α-olefin sulfonato de sodio
	Alcanolamidas	Lauril monoetanolamida
	Alquilfenoles	Nonilfenol, octilfenol
Aditivos y agentes industriales	Benzotriazoles	Benzotriazol, toliltriazol
	Agentes quelantes	EDTA
Edulcorantes		Sacarina, sucralosa, aspartamo, ciclamato, stevia, NHDC
Drogas de Abuso	Cocaínicos	Cocaína, benzoilecgonina
	Opiáceos	Morfina, codeína
	Opioides	Heroína, metadona

La aparición de estos elementos no deseables y tóxicos tiene su origen en el denominado ciclo del agua, el cual se esquematiza en la Figura 2.2. De acuerdo con el mismo, las principales vías de entrada de contaminantes en el medio ambiente acuático son las aguas residuales, entre las que se incluyen las urbanas, industriales, y la de origen agrario y ganadero. La prevalencia de una u otra depende en gran medida del tipo de contaminante de que se trate y de la atenuación natural (si existe) que experimentan.

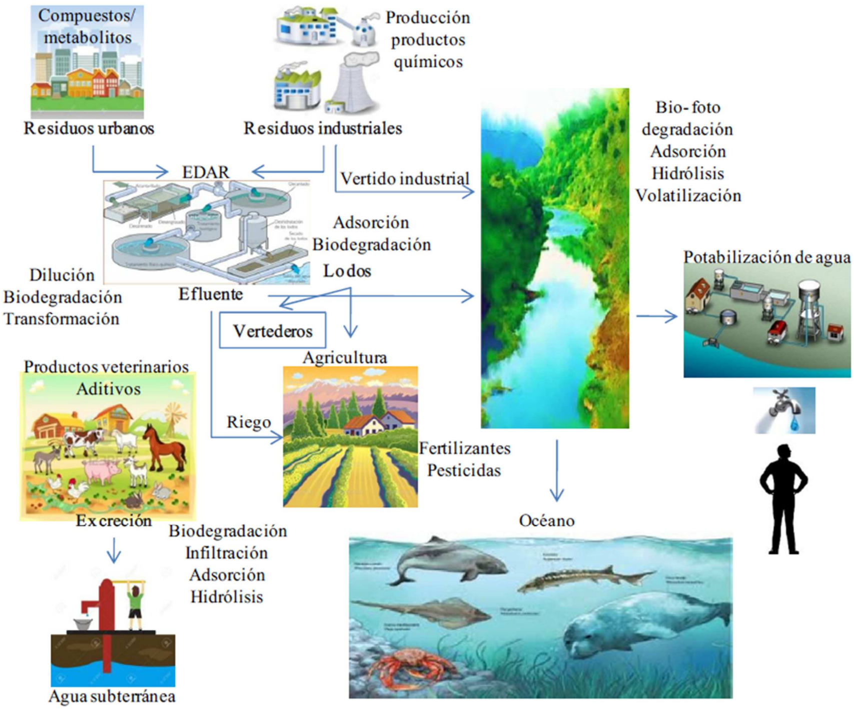


Figura 2.2. Ciclo del agua.

Los efectos que la contaminación química del agua, derivada de los contaminantes emergentes, son múltiples, y entre los más importantes pueden destacarse los siguientes:

- Acción tóxica y cancerígena.
- Incidencia sobre la producción de alimentos.
- Limitación del uso del agua con fines recreativos.
- Reducción de las posibilidades de su uso industrial y agropecuario.

Los riesgos que siguen a la contaminación del agua son difíciles de precisar, ya que no son acumulativos ni volátiles; pero son persistentes, al ser contaminantes liberados al medio ambiente de forma continua, y en algunos casos, varios de estos compuestos son más bioactivos que el precursor metabólico. Esta situación hace que los organismos acuáticos estén expuestos durante todo su ciclo de vida, lo que produce cambios en los procesos fisiológicos, bioquímicos y hormonales que pueden llegar a ser incluso irreversibles. Pero todavía en la actualidad quedan muchas incógnitas por despejar sobre el efecto que estos contaminantes pueden originar sobre los seres humanos, la flora y la fauna (Kent et al., 2006).

Además, el problema de contaminación persiste incluso tras el tratamiento secundario al que se someten las aguas residuales en las estaciones depuradoras, ya que éstas no son capaces de eliminar en su totalidad los contaminantes presentes, siendo aún más complicado por la presencia simultánea de diversos tipos de tales sustancias.

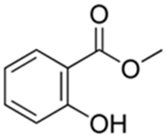
2.3.1. Contaminantes objeto del presente estudio: Salicilato de metilo, 2-fenoxietanol y clorhidrato de amitriptilina.

Teniendo en cuenta las consideraciones anteriores, el presente trabajo fue diseñado para el estudio de la eliminación en sistemas acuáticos de varios de tales conbtaminantes emergentes, concretamente compuestos farmacéuticos y de cuidado personal, que son sustancias características y representativas de este amplio grupo de compuestos. En concreto, se seleccionaron los tres siguientes: **salicilato de metilo, 2-fenoxietanol y clorhidrato de amitriptilina**, cuyas estructuras se muestran en la Figura 2.3.

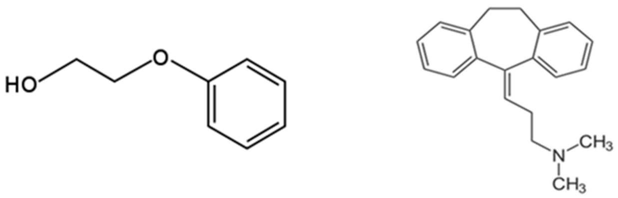
El **salicilato de metilo** es un derivado del ácido salicílico, y constituye un producto natural de muchas especies de plantas, aunque en la actualidad se obtiene por esterificación del ácido salicílico y metanol. Tiene actividad analgésica, antiinflamatoria y rubefaciente, para lo cual se usa una concentración del 10 al 25 %. También se usa en la industria alimentaria para dar sabor, en cuyo caso su concentración no debe ser superior al 0,04%.

El **2-fenoxietanol** se usa en dermatología como producto para cremas cutáneas y solares. Es un bactericida, generalmente usado conjuntamente con amonio cuaternario para soluciones biológicas. Su toxicidad es menor y no reacciona con el cobre o con el plomo. Es también usado como fijador para perfumes, como insecticida y antiséptico tópico. Es asimismo disolvente del acetato de celulosa y algunas tintas y resinas. También se utiliza como ingrediente para ciertas vacunas, y su uso está prohibido en algunos países como es el caso de Japón. Según el Reglamento ECC 2377/90 su administración es ilegal en peces que se destinen a consumo humano.

Por su parte, el **clorhidrato de amitriptilina** es un fármaco antidepresivo, de la familia de los tricíclicos, constituido por un sólido cristalino de color blanco, inodoro y soluble en agua. Tiene la capacidad de inhibir la recaptación de serotonina y de norepinefrina. Es el tricíclico más ampliamente usado, y además es útil en el tratamiento de migrañas, cefaleas por tensión, ataques de ansiedad y algunos síntomas esquizofrénicos.



SALICILATO DE METILO



2-FENOXIETANOL

CLORHIDRATO DE AMITRIPTILINA

Figura 2.3. Estructura química de los contaminantes emergentes objeto de estudio.

2.4. TRATAMIENTO DE AGUAS Y ELIMINACIÓN DE CONTAMINANTES EMERGENTES.

Las estaciones de depuración de aguas residuales y las estaciones de tratamiento de aguas potables han sido diseñadas para eliminar o reducir el nivel de contaminación de las aguas, de modo que pueda ser asimilado de forma natural por el cauce del río sobre el que posteriormente será vertido o bien sean aptas para el consumo humano, cumpliendo los criterios que exige la legislación. Sin embargo, la aparición de nuevos microcontaminantes no regulados requiere un tratamiento más avanzado, empleando nuevas tecnologías. Además, hay que tener en cuenta que los contaminantes emergentes poseen una amplia gama de propiedades químicas y el éxito en la eliminación es muy variable en función de sus propiedades particulares y el grado de contaminación.

Los tratamientos primarios convencionales, que incluyen procesos como la coagulación-floculación, no son capaces de eliminar eficazmente los contaminantes emergentes. El principal mecanismo para la eliminación de microcontaminantes durante este proceso es su asociación o interacción con las superficies de las partículas en suspensión y los flóculos. En general, los compuestos que presentan alta hidrofobicidad (log K_{ow}>6) y baja solubilidad en agua pueden ser eliminados en esta etapa (Snyder et al., 2007b). Por el contrario, la mayoría de pesticidas y productos farmacéuticos polares y semipolares permanecen en la fase acuosa (Stackelberg et al., 2007). Así, la eliminación de microcontaminantes durante los procesos de coagulación-floculación resulta inferior al 20% (Gasperi et al., 2010) y se producen lodos tóxicos, sin olvidar que los contaminantes se transforman de una fase a otra sin necesariamente ser descompuestos (Kasprzyk-Hordern et al., 2009; Maletz et al., 2013).

Los tratamientos biológicos son relativamente baratos y se emplean de forma frecuente en las plantas de tratamiento de aguas residuales para degradar compuestos orgánicos en general, tanto en medio aerobio como anaerobio. Por ejemplo, los procesos de lodos activados y filtros percoladores pueden convertir los contaminantes emergentes presentes en agua en biomasa, que es separada posteriormente (Helbling et al., 2010). Sin embargo, esta degradación microbiológica puede dar lugar a la formación de numerosos productos de degradación o de transformación (Bagnall et al., 2012) y aunque se adopte la mejor tecnología disponible, el tratamiento biológico elimina solo una parte de una amplia gama de contaminantes emergentes. En concreto los compuestos polares se descargan a través del efluente final (Petrovic et al., 2003). Por último, se generan lodos o fangos tóxicos que deben ser tratados.

Por otra parte, la oxidación química mediante tratamientos oxidantes convencionales permite la descomposición de numerosos compuestos orgánicos y se lleva a cabo directamente sobre las aguas a tratar. Para ello, se emplean ciertos agentes químicos que actúan como oxidantes o como catalizadores de la degradación, siendo el cloro el oxidante más común usado en el tratamiento convencional del agua. Así, la cloración permite eliminar más del 90% de los compuestos que presentan estructuras aromáticas con grupos hidróxido. Sin embargo su uso está limitado ya que se forman subproductos de reacción (cloroaminas, trihalometanos, etc.) que deben evitarse.

De forma global por tanto, puede establecerse que los procesos de oxidación química para la eliminación de contaminantes emergentes presentan la ventaja de destruir el contaminante orgánico, frente a los procesos de separación física que transfieren el compuesto de una fase a otra y requieren de un posterior método de recuperación o destrucción del mismo. Además, los tratamientos de oxidación química son aptos para eliminar contaminantes tanto en la obtención de agua potable como en el tratamiento de efluentes industriales altamente contaminados. Sin embargo, las limitaciones más importantes son la cinética del proceso, que puede ser demasiado lenta en muchas ocasiones, y la formación de subproductos de reacción cuya toxicidad o efecto nocivo puede superar al contaminante de partida.

Actualmente, el desarrollo de las tecnologías de oxidación química para degradar contaminantes orgánicos emergentes en medio acuoso se basa en la introducción de uno o varios activadores de la reacción que actúan generando radicales intermedios muy reactivos, tales como los radicales hidroxilo, superóxido e hidroperóxido. Dichos radicales son capaces de atacar con éxito a la mayor parte de las moléculas orgánicas, con constantes de velocidad de reacción muy elevadas que oscilan entre 10^6-10^9 M^{-1} s^{-1}. Estos tratamientos combinados constituyen los denominados Procesos de Oxidación Avanzada (POAs).

Hay que resaltar que en ocasiones la mineralización total mediante oxidación química requiere una gran potencia y dosis de oxidante y, por lo tanto, elevado capital y costes de operación en comparación con otras tecnologías. Por ello es interesante evaluar la eficacia de otras tecnologías y la combinación de estas con los procesos de oxidación química.

Por ello, y como alternativa a los procesos químicos, resulta conveniente estudiar algunos tratamientos físicos para la purificación de aguas naturales y residuales, debido a que generalmente presentan un bajo coste y conllevan poco impacto medioambiental. Estos procesos incluyen, por ejemplo, la adsorción mediante carbón activo o resinas, y la tecnología de membranas.

Recientes estudios han demostrado que procesos de adsorción empleando carbón activo resultan efectivos para la eliminación de algunos contaminantes emergentes, pudiendo alcanzarse hasta el 90% de eliminación (Schafer et al., 2003). Sin embargo, la eficacia del carbón activado se puede ver reducida por la presencia de materia orgánica natural. La capacidad de eliminación de este proceso va a depender de la dosis de carbón activo, el tiempo de contacto, así como de la estructura molecular y comportamiento de los contaminantes (Snyder et al., 2007a).

La aplicación de la tecnología de membranas para el tratamiento de aguas ha aumentado considerablemente en los últimos años. Una de las grandes ventajas que presentan los sistemas de filtración es que son capaces de retener un gran número de sustancias contaminantes en las aguas, entre ellas los contaminantes emergentes; sin embargo, no permiten la degradación de las mismos, por lo que dichos contaminantes se concentran en forma de residuos sólidos o líquido, requiriendo de un tratamiento adicional posterior (Homem y Santos, 2011). Especial interés suscitan los bioreactores de membrana (MBRs), al ser sistemas que combinan la filtración por membranas con la degradación biológica, usando fangos activos (Mutamim et al., 2012), y llevan a cabo tanto la retención física de los contaminantes como su biodegradación.

Tras esta panorámica general de los diversos tratamientos para la eliminación de microcontaminantes en aguas (naturales o residuales), se describen de forma más detallada los fundamentos y características de aquellos tratamientos de oxidación química, de adsorción y de filtración por membranas que han sido específicamente empleados en esta investigación para la eliminación de los contaminantes emergentes seleccionados.

2.5. TRATAMIENTO DE OXIDACIÓN QUÍMICA DE AGUAS.

Como es sabido, la elección del agente oxidante más adecuado depende de diversos factores, como la facilidad de aplicación técnica y económica o la posibilidad de actuar como desinfectante, pero especialmente, de la naturaleza del agua a tratar y de los contaminantes presentes. Los agentes utilizados con más frecuencia son, entre otros: cloro, permanganato potásico, dióxido de cloro, ozono, radiación ultravioleta y peróxido de hidrógeno.

En este trabajo, se han empleado oxidantes individuales como cloro, ozono y radiación ultravioleta, así como las combinaciones de diversos agentes oxidantes que constituyen los denominados Procesos de Oxidación Avanzada (POA). En concreto, las combinaciones utilizadas han sido: Cl_2/UV, O_3/H_2O_2, UV/H_2O_2, Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, UV/H_2O_2/Fe^{2+}, UV/H_2O_2/Fe^{3+}, UV/TiO_2, O_3/UV y UV/$S_2O_8^{2-}$. A continuación se describen de forma breve los fundamentos de tales oxidantes.

2.5.1. Ozono.

El ozono, forma alotrópica del oxígeno, es un oxidante muy enérgico. Es utilizado como tal en la desinfección del agua, dada su eficacia en oxidación de materias orgánicas e inorgánicas (entre éstas últimas destacan el hierro y manganeso). Su poder oxidante y desinfectante, mayor que el del cloro (potencial redox 2.07 V, mientras que el del cloro es 1.36 V), le hace más eficaz que éste en la eliminación del olor, sabor y color del agua, así como en la eliminación de bacterias, virus y otros microorganismos.

La vida media del ozono en el agua es muy variable, dependiendo de diversos factores (temperatura, pH, sustancias presentes en el agua, etc.). En condiciones estándar de temperatura y presión en agua destilada los valores la vida media de ozono varían entre 20 y 160 minutos, aumentando su inestabilidad en medio básico (Rodríguez, 2003).

En el proceso de ozonización hay que considerar dos posibles vías de acción oxidante: la directa debida a la reacción entre el ozono y los compuestos disueltos, donde se produce un ataque selectivo del ozono sobre moléculas orgánicas; y la vía radical derivada de las reacciones entre los radicales generados en la descomposición del ozono (radical hidroxilo, principalmente) y los propios compuestos disueltos. La combinación de ambas vías para la eliminación de compuestos dependerá de la naturaleza de los mismos, del pH del medio y de la dosis de ozono, principalmente.

Las reacciones por vía molecular son procesos más selectivos donde el ozono molecular puede actuar principalmente como dipolo (cicloadición sobre especies insaturadas) o como agente electrófilo (en sitios de alta densidad electrónica, sobre todo en anillos aromáticos activados). Presentan cinéticas de segundo orden y los principales sustratos que reaccionan con el ozono según esta vía son hidrocarburos insaturados e hidrocarburos aromáticos activados con grupos electrón-donadores (OH, NH_2).

La vía radicalaria incluye reacciones en las que las especies reaccionantes son radicales generados en la descomposición del ozono, principalmente el radical hidroxilo (E^o= +2.80 V). Estos radicales libres pueden reaccionar no selectivamente con los compuestos orgánicos (Andreozzi et al., 1999) y constituyen reacciones muy rápidas, presentando cinéticas de segundo orden con valores de constantes $10^8 < k < 10^{10}$ M^{-1} s^{-1}. Algunos sustratos típicos que reaccionan con el ozono según esta vía son hidrocarburos saturados y derivados halogenados, ácidos alifáticos, aldehídos, cetonas, alcoholes, hidrocarburos aromáticos desactivados (con grupos electrón-atractores).

Varios factores favorecen que las reacciones vayan preferentemente por cada una de estas dos vías:

a) Factores que favorecen la vía molecular (inhiben la descomposición del ozono): medio ácido, presencia de secuestradores de radicales ("radical scavengers") como CO_3^{2-}, HCO_3^- (alcalinidad), t-BuOH, etc.
b) Factores que favorecen la vía radicalaria (promueven la descomposición del ozono): medio básico (OH^-), presencia de H_2O_2, radiación UV (253.7 nm), ácido fórmico, Fe^{2+}, etc. La descomposición del ozono puede asimismo ser adicionalmente acelerada por una reacción en cadena típicamente radicalaria en la cual los radicales libres producidos $^{\bullet}OH$ y $HO_2^{\bullet}$ son los que actúan como propagadores de la cadena. Las reacciones que intervienen en el mecanismo de la descomposición del ozono en radicales hidroxilo se muestran en la siguiente Tabla (Acero y von Gunten, 2000).

Tabla 2.2. Mecanismo de descomposición del ozono en radicales hidroxilo.

N°	Reacción			$k; k_f, k_r, K_a$
1	$O_3 + OH^-$	$\rightarrow$	$HO_2^- + O_2$	70 $M^{-1}\,s^{-1}$
2	$O_3 + HO_2^-$	$\rightarrow$	$O_3^{\bullet-} + HO_2^{\bullet}$	$2.8\times10^6\ M^{-1}\,s^{-1}$
3	$O_3 + O_2^{\bullet-}$	$\rightarrow$	$O_3^{\bullet-} + O_2$	$1.6\times10^9\ M^{-1}\,s^{-1}$
4	$O_3^{\bullet-} + H^+$	$\leftrightarrow$	$HO_3^{\bullet}$	$5\times10^{10}\ M^{-1}\,s^{-1}$; $3.3\times10^2\ s^{-1}$
5	$HO_3^{\bullet}$	$\rightarrow$	$^{\bullet}OH + O_2$	$1.4\times10^5\ s^{-1}$
6	$O_3 + {}^{\bullet}OH$	$\rightarrow$	$HO_2^{\bullet} + O_2$	$2\times10^9\ M^{-1}\,s^{-1}$
7	$H_2O_2 + {}^{\bullet}OH$	$\rightarrow$	$HO_2^{\bullet} + H_2O$	$2.7\times10^7\ M^{-1}\,s^{-1}$
8	$HO_2^- + {}^{\bullet}OH$	$\rightarrow$	$O_2^{\bullet-} + H_2O$	$7.5\times10^9\ M^{-1}\,s^{-1}$
9	$HO_2^{\bullet}$	$\leftrightarrow$	$O_2^{\bullet-} + H^+$	1.6×10^{-5}
10	H_2O_2	$\leftrightarrow$	$O_2^- + H^+$	2.5×10^{-12}

Con respecto a la ozonización de compuestos orgánicos en aguas naturales, parece más probable que el mecanismo radicalario juegue un papel dominante en las reacciones de ozonización; incluso en condiciones que favorecen la vía directa de actuación del ozono se generan radicales (orgánicos e inorgánicos) que provocan la aparición de la vía indirecta de actuación del ozono (Rodríguez, 2003).

Las principales ventajas del empleo de ozono en el tratamiento de aguas son:

- El proceso de ozonización utiliza un período corto de contacto (aproximadamente de 10 a 30 minutos).
- No necesita ser eliminado después del proceso de ozonización dado que el ozono se descompone rápidamente.
- El ozono es generado in situ, minimizando problemas de seguridad y costes asociados con el envío y el transporte.
- El proceso de ozonización eleva la concentración de oxígeno disuelto del efluente, pudiendo eliminar la necesidad de aireación.
- Es más eficaz que el cloro para la desinfección o destrucción de virus y bacterias: los microorganismos no crecen nuevamente, a excepción de aquellos que están protegidos por las partículas en la corriente de agua residual.
- No produce trihalometanos y además elimina sus precursores.
- No altera el pH del agua.
- Mejora la coagulación.
- Facilita la eliminación del hierro y manganeso y reduce en gran medida el olor, sabor y color del agua.

Como desventajas se pueden mencionar:

- Su mayor coste, tanto en los equipos como en coste de operación (energía eléctrica).
- Puede formar otros subproductos tóxicos o nocivos, como el ion bromato.
- No mantiene una concentración residual persistente, lo que obliga a emplear cloro u otro desinfectante si se desea mantener un desinfectante residual.
- Puede formar óxido nítrico o ácido nítrico, que causan corrosión en los equipos.
- No resulta viable en aguas con altas concentraciones de sólidos en suspensión, demanda bioquímica de oxígeno, demanda química de oxígeno, o carbono orgánico total.
- Baja solubilidad en agua y relativamente inestable en disolución acuosa, motivo que obliga a generarle in situ.

2.5.2. Radiación UV.

El proceso de degradación de contaminantes disueltos en agua mediante radiación UV se basa en proporcionar energía a los compuestos químicos en forma de radiación, que es absorbida por las distintas moléculas para alcanzar estados excitados el tiempo necesario para experimentar reacciones. La energía radiante es absorbida por las moléculas en forma de unidades cuantizadas denominadas fotones, los cuales contienen las cantidades de energía requeridas para excitar electrones específicos y formar radicales libres que experimentan una serie de reacciones en cadena para dar los productos de reacción. Estos radicales libres pueden generarse por homólisis de enlaces débiles, o bien por transferencia electrónica desde el estado excitado de la molécula orgánica hacia el oxígeno molecular, originándose el radical superóxido ($O_2^{\bullet -}$), o hacia otros reactivos químicos como el ozono o el peróxido de hidrógeno en cuyo caso se producen radicales hidroxilo ($^{\bullet}OH$).

El éxito de un método fotolítico radica en la capacidad de absorber radiación de la longitud de onda incidente por parte de los compuestos a degradar, en el rendimiento cuántico de los mismos y en la estabilidad y simplicidad de los productos de fotodegradación (Lemaire et al., 1982). De estos tres factores, el rendimiento cuántico (ϕ) es el factor más interesante a estudiar, el cual se define como la relación entre el número de moléculas que reaccionan y el número de fotones absorbidos. El rendimiento cuántico hace una función similar a la de la constante cinética en una reacción ordinaria, e incluso matemáticamente se puede relacionar con las distintas constantes de velocidad de las reacciones que intervienen en el mecanismo para explicar el proceso fotoquímico global. En bibliografía se han propuesto diferentes métodos de competición y métodos basados en diversos modelos de radiación para el cálculo de rendimientos cuánticos (Esplugas et al., 1983).

En sistemas fotoquímicos convencionales, el rendimiento cuántico es < 1 y suele ocurrir que solamente alrededor del 15% de la energía total de entrada se encuentra en la banda de absorción de la molécula. Por ello, para que un determinado proceso fotoquímico sea rentable, se requiere bien un alto precio del producto final, o bien un muy elevado rendimiento cuántico. La eficacia del proceso, por tanto, depende fundamentalmente de la capacidad de absorción de radiación del sustrato y de la presencia de otros compuestos que absorben a la misma longitud de onda.

Las ventajas e inconvenientes del empleo de radiación UV en el tratamiento de aguas se muestran en la siguiente Tabla 3.2.

Tabla 2.3. Degradación mediante radiación UV. Ventajas e inconvenientes.

Ventajas
Al no introducirse reactivo ni materia extraña en la disolución, el carácter físico-químico no se ve modificado.
No se producen olores ni sabores desagradables.
No se generan lodos.
Metodología económica si se utiliza energía solar.
La sobredosificación no produce efectos perjudiciales
Inconvenientes
Baja eficiencia y procesos relativamente lentos.
La eficiencia de las lámparas disminuye con el tiempo por lo que es necesario un mantenimiento adecuado y continuo de las mismas.
Se precisa un preacondicionamiento del agua debido a que la radiación UV es absorbida por la materia orgánica y por las sustancias que originan turbidez.
Necesidad de capas finas de agua a tratar.
Aplicación limitada por factores climatológicos cuando utilizamos energía solar.

Puede concluirse, de forma general, que la radiación ultravioleta presenta baja eficacia en la degradación de compuestos orgánicos disueltos en agua en comparación con otros procesos que implican la generación de radicales hidroxilo, si bien la fotólisis puede resultar interesante en aquellos casos en que tanto el poder absorbente (coeficiente de extinción) como el rendimiento cuántico de los contaminantes tratados sea elevado. Además, resulta de gran interés la capacidad de desinfección de la radiación ultravioleta.

Para la generación de la radiación ultravioleta se dispone de lámparas de mercurio de baja y media presión o arcos de Xe/Hg, dependiendo de las longitudes de onda de la radiación deseada. La radiación de 254 nm es la más estudiada según refleja la bibliografía disponible. A continuación se describen los fundamentos de las lámparas de vapor de mercurio, por ser el tipo utilizado en el presente estudio.

Fuentes de radiación UV: lámparas de mercurio.

Una fuente de radiación, para su utilidad en reacciones fotoquímicas, debe tener las siguientes características: alta intensidad en la longitud de onda deseada, larga vida, dimensiones geométricas adecuadas para el proceso considerado, mínimo coste del equipo auxiliar necesario y facilidad de operación. Las fuentes actuales de radiación más importantes que cumplen tales condiciones, y por tanto las más utilizadas, son las lámparas de vapor de mercurio y la luz solar, especialmente las primeras.

De forma general, al hacer pasar una corriente eléctrica entre dos electrodos separados por un gas o vapor, se genera radiación ultravioleta. La intensidad y distribución de longitudes de onda de esta radiación dependerá de la naturaleza y presión del gas o vapor. Generalmente, ésta suele ser vapor de mercurio a diferentes presiones, ya que dicho vapor posee un espectro amplio en la zona ultravioleta y además no reacciona con los electrodos ni ataca al vidrio. A su vez, las lámparas de mercurio se subdividen en arcos de baja, media y alta presión.

Las lámparas de mercurio de baja presión operan a temperatura ambiente y a 0.001 atmósferas, emitiendo dos líneas principales de radiación a 253.6 y 184.9 nm, líneas que son interesantes para llevar a cabo reacciones fotosensibilizadas. Suelen refrigerarse por aire y su vida media es relativamente elevada, de 9500 a 12000 horas.

Por otra parte, las lámparas de mercurio de media presión operan a alrededor de 1 atmósfera. Tienen diversas líneas principales de radiación (253.7, 313, 365, 404.7, 435.8, 546.1 y 570.8 nm), y su vida media es de aproximadamente 1000 horas.

Finalmente, las lámparas de mercurio de alta presión son quizás las más importantes desde el punto de vista industrial, debido a su mayor potencia lumínica. Operan a presiones de entre 2 y 110 atmósferas, por lo que generalmente constan de un tubo de cuarzo de pequeño diámetro y pared gruesa que está rodeado de otro tubo de vidrio que hace las funciones de filtro de radiación, aislante de calor y protector en caso de rotura del tubo de cuarzo. Su espectro es más completo, y según sea la presión de la lámpara, la refrigeración será por aire o por agua, siendo su duración bastante más corta (de 100 a 200 horas).

Diseño de reactores fotoquímicos: modelos de radiación.

En el modelo matemático de un reactor convencional deben tenerse en cuenta los balances de materia y de energía y la ecuación cinética de la reacción o reacciones que tengan lugar. En el caso de un reactor fotoquímico hay que considerar además un balance de radiación, que depende del modelo que se proponga para describir la emisión y distribución de radiación en el reactor. En efecto, esta distribución de energía radiante en la masa de reacción no es uniforme debido a varias causas, como la atenuación debida a la absorción de luz por las especies del sistema, las propiedades físico-químicas del mismo sistema de reacción y las características geométricas del reactor y de la lámpara. En consecuencia, la energía radiante y por tanto la reacción de iniciación fotoquímica, no está distribuida homogéneamente en el reactor.

En la bibliografía se han propuesto una gran diversidad de modelos para describir la distribución de la energía radiante en el reactor. Éstos pueden clasificarse en dos grupos principales: a) modelos de incidencia, que suponen la existencia de una distribución de energía radiante dada en las proximidades del reactor; y b) modelos de emisión, que suponen una forma determinada de emisión de radiación por la lámpara, a partir de la cual se deduce la energía absorbida por la masa de reacción.

De todos los modelos mencionados, los que reproducen con mayor precisión los resultados experimentales son los modelos de emisión (Spadoni et al., 1980); y de éstos, los que consideran una fuente de radiación con emisión esférica resultan ser los más apropiados para el diseño de reactores fotoquímicos debido a su relativa simplicidad matemática. Entre ellos destaca el desarrollado por Jacob y Dranoff (1966, 1968, 1970) el cual ha sido empleado en el presente trabajo. El mismo también ha sido utilizado en diversos trabajos anteriores con resultados muy satisfactorios en la determinación de rendimientos cuánticos de reacciones individuales de degradación de compuestos orgánicos diversos mediante la acción oxidante de la radiación ultravioleta (Benítez et al., 2005; Real et al., 2010). Básicamente, supone una naturaleza tridimensional del proceso de emisión de energía, emitiendo la lámpara una radiación en todas las direcciones y de forma isotrópica.

La aplicación del modelo de emisión esférica a un sistema de estas características geométricas está ya ampliamente descrita (Benitez et al., 2009a; 2013; Real et al., 2012) y como resultado final, permite deducir la expresión para el cálculo de la energía absorbida por la masa de reacción. De forma general, el caudal de energía radiante absorbida por un medio de reacción viene dado por la expresión:

$$W_{abs} = \Sigma\, W_{abs} = \Sigma \int_V \mu_i\ I_i\ dV \tag{11}$$

donde μ_i es la absorbancia del medio de reacción para cada longitud de onda de la radiación policromática, e I_i la intensidad de radiación para cada longitud de onda y en cada punto del reactor.

Teniendo en cuenta que la lámpara utilizada puede considerarse monocromática en la longitud de onda de 254 nm, la expresión (11) puede escribirse de la siguiente forma:

$$W_{abs} = \int_V \mu\, I\, dV \tag{12}$$

donde μ es la absorbancia del medio de reacción por unidad de longitud, e I la intensidad de radiación en cada punto del reactor.

Con objeto de evaluar W_{abs}, resulta necesario establecer y resolver el balance de radiación. De acuerdo con las características geométricas del reactor y con las hipótesis del modelo de emisión esférica (Jacob y Dranoff, 1968, 1970), y si μ es constante con la posición, resulta:

$$W_{abs} = 2\,\pi\,\mu \int_0^H \int_{R1}^{R0} I(r, z)\, r\, dr\, dz \tag{13}$$

donde I(r,z) es la intensidad de radiación en cada punto del reactor e igual a:

$$I(r, z) = \frac{W_L}{4 \pi L} \int_{L0}^{L0+L} \frac{\exp\left[-\mu (r - R_1)\cdot c\right]}{r^2 + (z - l)^2} \, dl \tag{14}$$

siendo el parámetro c igual a:

$$c = \frac{[r^2 + (z - l)^2]^{1/2}}{r} \tag{15}$$

En estas expresiones, r y z son las coordenadas radial y axial de un punto genérico considerado, y l la coordenada axial de la lámpara; L y L_0 son la longitud de la lámpara y la distancia de la base de la lámpara a la base del reactor; R_1 y R_0, los radios externo e interno del reactor fotoquímico, y H es la altura del reactor. Finalmente, W_L es el caudal total de radiación emitido por la lámpara.

Con objeto de simplificar, en lo sucesivo la integral triple que engloba a todos los términos geométricos se expresa mediante el parámetro N:

$$N = \int_0^H \int_{R1}^{R0} \int_{L0}^{L0+L} \frac{\exp[-\mu (r - R_1)\cdot c]}{r^2 + (z - l)^2} \, r \, dl \, dr \, dz \tag{16}$$

Por tanto, teniendo en cuenta las expresiones (13) a (16), el caudal de energía radiante absorbida puede evaluarse por la expresión reducida:

$$W_{abs} = W_L \frac{\mu N}{2 L} \tag{17}$$

que permitirá determinar el caudal total de radiación absorbida, W_{abs}, para cada tiempo de reacción fotoquímica en la longitud de onda a la que las disoluciones del compuesto orgánico estudiado absorben.

2.5.3. Cloro.

El cloro es el desinfectante más utilizado para el tratamiento del agua potable y su uso extendido se debe al alto potencial de oxidación y a que provee el nivel adecuado de concentración residual en el agua tratada, necesaria para evitar que se produzca una contaminación microbiológica dentro del sistema de distribución (Sadiq y Rodríguez, 2004).

Además, se ha encontrado que el cloro también es útil para otros propósitos distintos al de la desinfección (USEPA, 1999), tales como:

- Control del olor y el sabor en el agua.
- Evita el crecimiento de algas y mantiene limpios los sistemas de tratamiento.
- Eliminación de hierro y manganeso por precipitación.
- Oxidación de sulfuro de hidrógeno.
- Mejora la eficiencia de la coagulación y la filtración.

El cloro adicionado al agua se transforma en varias formas diferentes a la especie elemental, como el ácido hipocloroso (HOCl) y el ión hipoclorito (OCl^-). En la actualidad su uso más frecuente es como gas, Cl_2 (g), generado por vaporización de cloro líquido almacenado bajo presión; y como sales, tanto hipoclorito de sodio, NaOCl, como hipoclorito de calcio, $Ca(OCl)_2$.

La forma en la que se adiciona el cloro al agua influye sobre ciertas propiedades químicas de ésta. La adición de cloro gaseoso a un agua disminuirá su alcalinidad:

$$\mathrm{Cl_{2(g)} + H_2O \leftrightarrow HOCl + H^+ + Cl^-} \tag{18}$$

Sin embargo, si el cloro se dosifica como sal de ácido hipocloroso se tendrá:

$$\mathrm{NaOCl \leftrightarrow Na^+ + OCl^-} \tag{19}$$

$$\mathrm{OCl^- + H_2O \leftrightarrow HOCl + OH^-} \tag{20}$$

y provocará un aumento de la alcalinidad de acuerdo con el grado en el que el OCl^- reaccione con el H_2O.

Por otro lado, el valor de pK_a del equilibrio de disociación $HOCl/OCl^-$ (ec. 21) a 20 °C es 7.5. Por tanto, la cantidad relativa de las distintas especies cloradas oxidadas varía en función del pH del agua.

$$\mathrm{HOCl \leftrightarrow H^+ + OCl^-} \tag{21}$$

El ácido hipocloroso y el ión hipoclorito representan el “cloro libre residual” que es el desinfectante primario empleado. Así, se tiene que para valores 3 < pH < 6 predomina el ácido hipocloroso y para pH > 9 predomina el ión hipoclorito. El ácido hipocloroso no disociado es alrededor de 80 a 100 veces más efectivo en la eliminación de bacterias indicadoras de contaminación fecal que el ión hipoclorito (Snoeyink y Jenkins, 2000). Por ello, el intervalo óptimo de pH para la aplicación como desinfectante está en el rango de 6 a 8 tal y como se puede observar en la Figura 2.5.

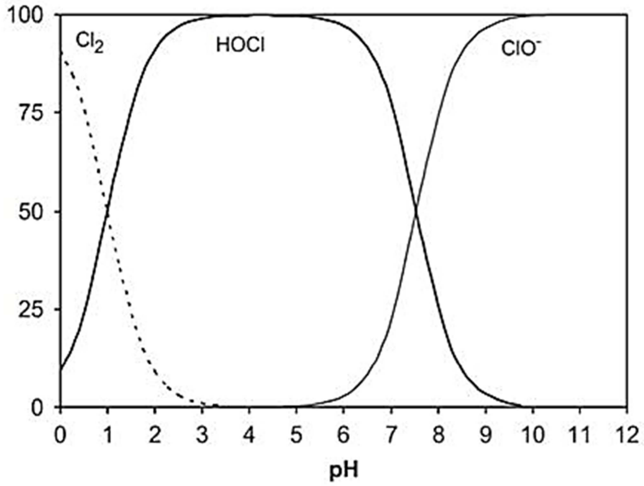


Figura 2.4. Porcentaje de especies de cloro presentes en el agua en función del pH.

El cloro participa en diferentes reacciones de oxidación-reducción con compuestos inorgánicos reducidos (Mn^{2+}, Fe^{2+}, S^{2-}, etc., en general se trata de reacciones muy rápidas) y con compuestos orgánicos (reacciona con el nitrógeno orgánico y con ciertas sustancias químicas perdiendo su poder oxidante para producir cloruro, ácido clorhídrico, óxidos de nitrógeno, cloro-orgánicos...). Pero sin duda las reacciones de oxidación-reducción con nitrógeno amoniacal son las más interesantes, al formarse una serie de compuestos denominados cloraminas, con cierto poder desinfectante.

El principal inconveniente del uso de cloro en el tratamiento de aguas recae en la formación de sustancias o subproductos de la desinfección que presentan posibles efectos genotóxicos para la salud de las personas. La naturaleza y la concentración de los compuestos formados son dependientes de variables físicoquímicas de la materia orgánica, las cuales reaccionan originándose productos que son compuestos de diferente toxicidad, entre ellos mutagénicos y carcinogénicos; a todos en conjunto se les conoce como productos secundarios de cloración, que incluyen compuestos llamados trihalometanos (THM) y ácidos haloacéticos (HAA). Los THM originados durante este proceso de cloración incluyen cloroformo ($CHCl_3$), bromodiclorometano ($CHCl_2Br$), clorodibromometano ($CHClBr_2$) y bromoformo ($CHBr_3$), entre otros compuestos volátiles. Se ha descrito que el cloroformo en altas dosis es cancerígeno y que los otros THM son mutagénicos. Entre los HAAs, el tricloroacético y dicloroacético son las especies encontradas en mayores concentraciones.

2.5.4. Procesos de Oxidación Avanzada.

Tal y como se ha señalado en el Apartado 2.4, los Procesos de Oxidación Avanzada (POAs) constituyen uno de los recursos tecnológicos más prometedores en el tratamiento de aguas contaminadas con productos orgánicos de vertidos industriales, urbanos o simplemente aguas superficiales o subterráneas contaminadas. Los POAs están especialmente indicados para tratar compuestos orgánicos que son especialmente resistentes y refractarios a la acción directa de los agentes oxidantes más frecuentes utilizados individualmente, siendo necesario el uso de otros oxidantes más fuertes, o bien la aplicación de nuevos procesos basados en combinaciones simultáneas de algunos de los oxidantes habituales.

Estas técnicas han demostrado ser muy efectivas en la destrucción de compuestos no biodegradables y refractarios (Glaze et al., 1982; Vallejo et al., 2015) y se caracterizan por generar principalmente radicales muy reactivos como son los radicales hidroxilo ($^{\bullet}OH$) que tras el flúor son los oxidantes más enérgicos. Existen diferentes alternativas para la formación de estos radicales, unas más eficaces que otras dependiendo del compuesto, como: UV/O_3, UV/H_2O_2, O_3/H_2O_2, Fe^{2+}/H_2O_2 (denominado reactivo de Fenton), UV/TiO_2, además de posibles combinaciones ternarias o cuaternarias de estos agentes.

Los POAs pueden clasificarse como fotoquímicos o no fotoquímicos dependiendo de si se irradia o no la muestra para la obtención del radical $^{\bullet}OH$ (ver Tabla 2.4). Los procesos fotoquímicos a su vez, pueden clasificarse en procesos fotocatalíticos o no fotocatalíticos, dependiendo de si utilizan o no un semiconductor o fotocatalizador para la absorción directa o indirecta de energía UV-Visible.

Tabla 2.4. Algunos de los POAs más conocidos.

Procesos fotoquímicos	Procesos no fotoquímicos
Fotólisis directa	Ozonación en medio alcalino (O_3/OH^-)
Fotólisis en el ultravioleta de vacío (UVV)	Ozonación con H_2O_2 (O_3/H_2O_2)
UV/H_2O_2	Reacción de Fenton ($Fe^{+2/+3}/H_2O_2$)
UV/O_3	Oxidación electroquímica
Foto-Fenton ($Fe^{+2/+3}/H_2O_2/UV$)	Radiolisis y tratamiento con haces de electrones
Fotocatálisis Heterogénea (TiO_2/UV)	Plasma no térmico
Oxidación en agua sub/ y supercrítica	Descarga electrohidráulica-ultrasonidos

En general, las ventajas que presentan los POAs incluyen:

- El contaminante se destruye, no se concentra ni cambia de medio.
- No generan lodos que a su vez requieren de un proceso de tratamiento posterior.
- Es una tecnología limpia y segura, y en algunos procesos como los fotocatalíticos se puede emplear la radiación solar.
- Sirven para tratar contaminantes a muy bajas concentraciones.
- Generalmente se puede conseguir la mineralización completa del contaminante orgánico, en especial de compuestos no biodegradables, y transformación de compuestos inorgánicos hasta CO_2, H_2O e iones simples como cloruros, nitratos y otras sustancias más fácilmente tratables por otros métodos más económicos.
- Eliminan los efectos perjudiciales sobre la salud, que presentan algunos desinfectantes y oxidantes residuales como el cloro.

El inconveniente principal de estos procesos es que los radicales $^{\bullet}OH$ son fácilmente atrapados por iones HCO_3^- y CO_3^{2-} abundantes en sistemas de tratamiento de aguas y/o residuos:

$$^{\bullet}\mathrm{OH} + \mathrm{HCO_3^-} \rightarrow \mathrm{H_2O} + \mathrm{CO_3^{\bullet -}} \quad (22)$$

$$^{\bullet}\mathrm{OH} + \mathrm{CO_3^{2-}} \rightarrow \mathrm{HO^-} + \mathrm{CO_3^{\bullet -}} \quad (23)$$

Se describen a continuación de forma más extensa los mecanismos de reacción y las etapas que tienen lugar en la oxidación general de compuestos orgánicos mediante los siguientes Procesos de Oxidación Avanzada: O_3/H_2O_2, UV/H_2O_2, Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, UV/H_2O_2/Fe^{2+}, UV/H_2O_2/Fe^{3+}, UV/TiO_2, Cl_2/UV y UV/O_3, los cuales han sido empleados en el presente estudio.

2.5.4.1. Proceso de Oxidación Avanzada O_3/H_2O_2.

El H_2O_2 es un ácido débil (pK_a=11.6), poderoso oxidante y un compuesto inestable, que dismuta con una velocidad máxima al pH correspondiente al valor de su pK_a:

$$\mathrm{H_2O} + \mathrm{H_2O_2} \rightarrow \mathrm{HO_2^-} + \mathrm{H_3O^+} \quad (24)$$

El mecanismo de reacción del Proceso de Oxidación Avanzada constituido por la combinación de O_3/H_2O_2 es similar al descrito en el Apartado 2.5.1 para ozono individual. Existe una vía directa de ataque de ozono a la materia orgánica y una vía radicalaria mediante la cual el ozono se descompone formando radicales hidroxilos que actuarían como oxidantes secundarios (Tabla 2.2 y Figura 2.6). La vía radicalaria se encuentra favorecida en el presente sistema de oxidación respecto al proceso de ozonación simple por la presencia de peróxido de hidrógeno, el cual acelera la descomposición de ozono hacia la formación de radicales hidroxilo según se muestra en la Tabla 2.2 (reacción 2 y siguientes). Por tanto, la principal diferencia entre los procesos de ozonación simple y la combinación O_3/H_2O_2 es la reacción de iniciación de la descomposición de ozono; esto es, iones hidroxilo en ozonación simple y el anión peróxido en el proceso combinado (Staehelin y Hoigné, 1982).

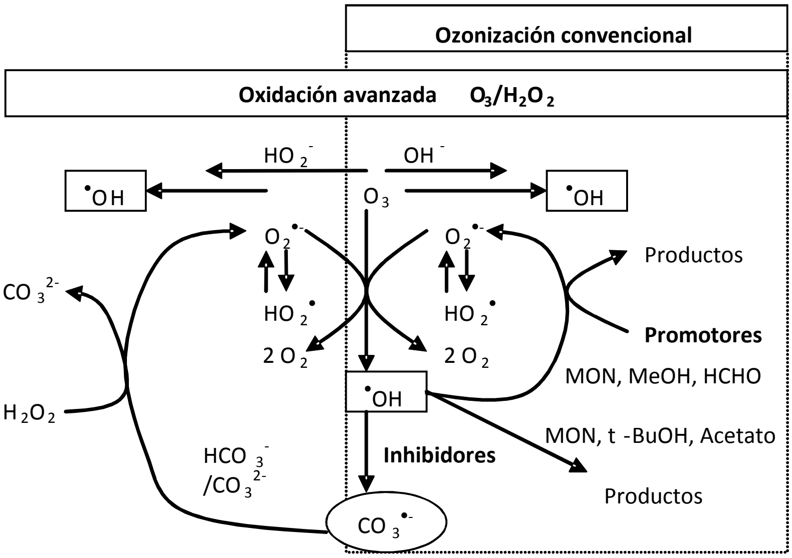


Figura 2.5. Esquema de las reacciones de descomposición de ozono en los sistemas de ozonización simple o del Proceso de Oxidación Avanzada O_3/H_2O_2.

Este POA conlleva un coste más elevado que la ozonización simple pero es más eficiente, pudiéndose tratar contaminantes orgánicos presentes en muy bajas concentraciones (ppb).

2.5.4.2. Proceso de Oxidación Avanzada UV/H_2O_2.

Entre los distintos procesos de aplicación para el tratamiento de aguas la combinación de la radiación ultravioleta y el peróxido de hidrógeno resulta ser muy interesante cuando se desea un agua con alto grado de pureza. Este POA implica la formación de radicales hidroxilo por fotólisis del peróxido de hidrógeno y consiguientes reacciones de propagación. El mecanismo más comúnmente aceptado para la fotólisis del peróxido de hidrógeno es la ruptura del enlace O-O por la acción de la radiación ultravioleta para formar dos radicales hidroxilo (presenta un rendimiento cuántico casi unitario ($\phi_{HO\bullet}$= 0.98 a 254 nm)):

$$H_2O_2 + h\upsilon \rightarrow 2\ {}^{\bullet}OH \qquad (25)$$

La fotolisis de un compuesto orgánico en disolución acuosa catalizada por la presencia de peróxido de hidrógeno es un proceso muy complejo que, de forma resumida, se esquematiza en la Figura 2.7, la cual muestra el mecanismo de reacciones más comúnmente aceptado para la misma (Legrini et al., 1993).

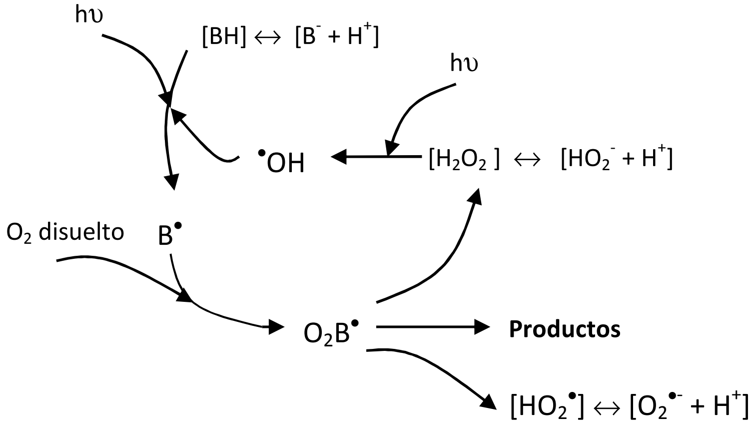


Figura 2.6. Mecanismo de reacción de la combinación UV/H_2O_2 sobre la materia orgánica.

Este mecanismo considera que en la primera etapa tiene lugar la degradación fotolítica de peróxido de hidrógeno que, mediante la escisión del mismo, produce dos radicales libres hidroxilo por cada molécula descompuesta (expresión (25)).

Una vez formados estos radicales altamente reactivos, reaccionan a continuación con el compuesto orgánico mediante abstracción de un átomo de hidrógeno, adición a dobles enlaces C-C o transferencia de electrones, dependiendo de la naturaleza y grupos funcionales del compuesto orgánico. La vía de reacción más general es la abstracción de un átomo de hidrógeno y producción del consiguiente radical orgánico $B^\bullet$, que a su vez reacciona rápidamente con O_2 disuelto para formar el radical orgánico peróxido $O_2B^\bullet$ (Legrini et al., 1993). Estos radicales orgánicos descomponen mediante reacciones bimoleculares dando lugar a los diferentes productos de degradación del compuesto de partida junto con otros subproductos tales como peróxido de hidrógeno, radicales hidroperóxido, formaldehído, etc. (Von Sonntag y Schuchmann, 1997).

Los radicales ${}^{\bullet}OH$ generados, pueden actuar sobre el H_2O_2 remanente o adicionado a la solución, haciendo que se regenere y mantenga el ciclo de oxidación de los contaminantes orgánicos. En exceso de H_2O_2 y con elevadas concentraciones de radicales ${}^{\bullet}OH$, tienen lugar reacciones competitivas que producen un efecto inhibidor para la degradación de la materia orgánica (reacciones (26) a (29)) por lo que se debe determinar en cada caso la cantidad óptima de H_2O_2, para evitar un exceso que podría retardar la degradación (Baxendale et al., 1957). De la misma forma, se debe considerar el equilibrio ácido-base del peróxido de hidrógeno (ecuación (24)), que está favorecido en medio básico, mientras que en medio ácido apenas tiene lugar.

$$\mathrm{H_2O_2} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{HO_2^{\bullet}} + \mathrm{H_2O} \qquad (26)$$

$$\mathrm{H_2O_2} + \mathrm{HO_2^{\bullet}} \rightarrow {}^{\bullet}\mathrm{OH} + \mathrm{H_2O} + \mathrm{O_2} \qquad (27)$$

$$2\,\mathrm{HO_2^{\bullet}} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \qquad (28)$$

$$\mathrm{HO_2^{\bullet}} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{H_2O} + \mathrm{O_2} \qquad (29)$$

En resumen, existe un ciclo de descomposición y formación simultánea de peróxido de hidrógeno cuyo resultado global dependerá de diversas variables, como la intensidad de la radiación ultravioleta, la temperatura, el pH y la naturaleza de los compuestos orgánicos.

2.5.4.3. Procesos de Oxidación Avanzada Fe^{2+}/H_2O_2 (reactivo de Fenton) y Fe^{3+}/H_2O_2 (reactivo de Fenton-like).

El POA de catálisis homogénea Fenton (Fe^{2+}/H_2O_2) data de 1894, cuando Henry J. Fenton demostró que el peróxido de hidrógeno podía ser activado en presencia de sales de Fe(II) para oxidar ácido tartárico en rangos ácidos de pH (Fenton, 1894). En 1934 Haber y Weiss propusieron que el oxidante activo generado mediante la reacción de Fenton es el radical hidroxilo. Más tarde, Barb et al. (1949), revisaron el mecanismo original propuesto por Haber y Weiss para dar lugar a lo que actualmente se conoce como la reacción en cadena “clásica” o “vía radicales libres” de Fenton, en la que se considera como etapa clave del proceso la producción de radicales (${}^{\bullet}OH$). La aplicación de la reacción de Fenton como proceso oxidante para la destrucción de sustancias orgánicas tóxicas comenzó a desarrollarse a mediados de los años 60 por Brown et al. (1964). Aunque el mecanismo exacto de la oxidación de un compuesto orgánico por dicho reactivo es complejo y no conocido de forma absoluta, diversos autores coinciden en las principales etapas del mismo:

$$\mathrm{H_2O_2 + Fe^{2+} \rightarrow\ ^{\bullet}OH + OH^- + Fe^{3+}} \tag{30}$$

Los radicales $^{\bullet}$OH así formados pueden reaccionar luego por varias vías: oxidando a Fe(II) o H_2O_2 (reacciones improductivas) y atacando a la materia orgánica:

$$\mathrm{^{\bullet}OH + Fe^{2+} \rightarrow OH^- + Fe^{3+}} \tag{31}$$

$$\mathrm{^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}} \tag{32}$$

$$\mathrm{RH +\ ^{\bullet}OH + H_2O \rightarrow ROH + H_3O^+} \tag{33}$$

A pH < 3, la reacción de Fenton es autocatalítica, ya que el ión hierro (III) formado puede reducirse por reacción con H_2O_2 y formar de nuevo el ión hierro (II):

$$\mathrm{H_2O_2 + Fe^{3+} \leftrightarrow FeOOH^{2+} + H^+} \tag{34}$$

$$\mathrm{FeOOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+}} \tag{35}$$

$$\mathrm{HO_2^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2} \tag{36}$$

En el caso que inicialmente solo esté presente el ión hierro (III), el proceso se denomina comúnmente como “Fenton-like” (Fe^{3+}/H_2O_2). Ambos sistemas (Fenton y Fenton-like) resultan potencialmente útiles para destruir contaminantes, ya que son muy efectivos para la generación de $^{\bullet}$OH. No obstante, un exceso de iones Fe^{2+}, H_2O_2, o halógenos si están presentes, pueden actuar como secuestradores de estos radicales (expresiones (31) y (32)).

En presencia de exceso de peróxido, la concentración de Fe^{2+} es pequeña en relación a la de Fe^{3+}, ya que la reacción (35) es más lenta que la (31). Se cree por ello que la destrucción de contaminantes por reactivo de Fenton es debida al ciclo catalítico de descomposición de H_2O_2, y que el reactivo de Fenton con exceso de H_2O_2 es esencialmente el proceso Fe^{3+}/H_2O_2.

Como se ha señalado anteriormente, la actividad catalítica máxima del sistema Fe^{2+}-Fe^{3+}/H_2O_2 ocurre a pH 2.8-3.0. A pH > 5 se genera precipitado de Fe^{3+}; si bien se generan así barros que obligan a su posterior gestión, es frecuente alcalinizar las aguas al final del proceso con el agregado simultáneo de un floculante para eliminar el hierro remanente.

2.5.4.4. Procesos de Oxidación Avanzada $UV/H_2O_2/Fe^{2+}$ (sistema foto-Fenton) y $UV/H_2O_2/Fe^{3+}$ (sistema foto Fenton-like).

La velocidad de degradación de los contaminantes orgánicos se ve considerablemente aumentada cuando el reactivo Fenton se combina con la radiación UV visible debido a la regeneración continua del Fe^{2+}, como consecuencia del mecanismo de fotorreducción del Fe^{3+}, y a la generación adicional de nuevos radicales hidroxilo a partir de la fotólisis del H_2O_2 (Pignatello, 1992). Este proceso se conoce como foto-Fenton, y en él los complejos de Fe^{3+} sufren una transferencia de carga ligando-metal, dando lugar a su disociación en Fe^{2+} y el ligando oxidado (Pignatello et al., 2006).

Los complejos de Fe^{3+} que se suelen formar en solución ácida son el $Fe(OH)^{2+}$ y $Fe_2(OH)_2^{4+}$, que absorben luz UV y visible, siendo la especie más importante el complejo $Fe(OH)^{2+}$ debido a la combinación entre su alto coeficiente de absorción y su alta concentración relativa con respecto a otras especies de Fe^{3+}:

$$\mathrm{Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + {}^{\bullet}OH} \qquad (37)$$

Por su parte, la adición de luz al sistema Fenton-like constituye el sistema foto Fenton-like, en el cual se acelera considerablemente la reducción del Fe^{3+} (Amigó et al., 2008). Este sistema requiere la presencia de radiación de hasta 410 nm, por lo que se puede producir con la participación de la luz solar (Pignatello et al., 2006).

2.5.4.5. Proceso de Oxidación Avanzada $UV/S_2O_8^{2-}$.

El ión persulfato o peroxodisulfato ($S_2O_8^{2-}$) es un poderoso oxidante (Eº = 2.43 V) que se emplea para degradar algunos contaminantes orgánicos con una selectividad ligeramente superior a la del radical hidroxilo. Debido a que las reacciones con $S_2O_8^{2-}$ son muy lentas, se han propuesto diversas técnicas para activar o acelerar su descomposición. El método más frecuente consiste en generar radicales sulfato $SO_4^{\cdot -}$ por descomposición fotoquímica, térmica o química de $S_2O_8^{2-}$. En concreto, la fotólisis de $S_2O_8^{2-}$ da lugar a la formación del radical $SO_4^{\cdot -}$ (reacción (38)). A su vez, el radical sulfato puede generar radicales hidroxilo según la reacción (39) (He et al., 2013).

$$\mathrm{S_2O_8^{2-} + h\nu \rightarrow 2\,SO_4^{\bullet -}} \qquad (38)$$

$$\mathrm{SO_4^{\bullet -} + H_2O \rightarrow SO_4^{2-} + {}^{\bullet}OH + H^+} \qquad (39)$$

La distribución de los dos radicales libres depende del pH de la disolución. En una disolución a pH<7 el radical libre dominante es $SO_4^{\cdot -}$, mientras que a pH>9 predomina el radical $^{\bullet}OH$. Ambos radicales son importantes en el rango de pH 7-9 (Xie et al., 2012).

2.5.4.6. Proceso de Oxidación Avanzada Cl_2/UV.

La combinación de cloro y radiación UV es un Proceso de Oxidación Avanzada que ha sido estudiado recientemente (Jing et al., 2011). Dicho proceso se basa en la fotólisis del cloro libre, el cual en presencia de radiación UV con longitudes de onda inferiores a 400 nm produce radicales hidroxilo y cloro de acuerdo con las siguientes reacciones (Carlin et al., 1990):

$$\mathrm{HOCl + h\upsilon \rightarrow HO^{\cdot} + }Cl^{\cdot} \qquad (40)$$

$$\mathrm{OCl^- + h\upsilon \rightarrow O^- + }Cl^{\cdot} \qquad (41)$$

$$\mathrm{O^{\bullet} + H_2O \rightarrow {}^{\bullet}OH + HO^-} \qquad (42)$$

Además, este POA es más eficiente generando especies $HO^{\bullet}$, $Cl^{\bullet}$ y $Cl_2^{\bullet -}$ a pH ácido y neutro (Fang et al., 2014). Incluso se ha demostrado que este preoceso es más eficiente en la eliminación de contaminantes emergentes que le proceso constituido por radiación UV y peróxido de hidrógeno (Sichel et al., 2011). Por lo tanto, el proceso de UV / Cl_2 puede ser considerado como alternativa al POA basado en UV para la eliminación de los microcontaminantes en el agua potable y aguas residuales.

2.6. PROCESOS DE SEPARACIÓN MEDIANTE MEMBRANAS.

Las primeras referencias que existen sobre investigaciones relacionadas con el campo de las membranas datan de mediados del siglo XVIII, cuando Abbé Nolet, utilizó la palabra “ósmosis” para describir la permeación de agua a través de una membrana natural (Baker, 2004). A lo largo del siglo XIX, las membranas fueron utilizadas como herramientas de laboratorio para desarrollar teorías físico-químicas, pero no existían aplicaciones industriales ni comerciales.

El descubrimiento que permitió la transformación de una técnica de laboratorio en un proceso industrial se produjo en el comienzo de la década de 1960, con el desarrollo del proceso Loeb-Sourirajan para la fabricación de membranas de ósmosis inversa formadas por una capa selectiva ultrafina depositada sobre un soporte micro-poroso mucho más grueso pero a su vez mucho más permeable. El siguiente avance significativo se obtuvo en los métodos de empaquetado de las membranas (desarrollo de módulos de fibras huecas, enrollamientos en espiral o configuración de placas y marcos, entre otros), consiguiéndose en 1980 que microfiltración (MF), ultrafiltración (UF), osmosis inversa (OI) y electrodiálisis (ED) estuvieran establecidas como procesos a escala industrial (Urtiaga et al., 2010).

Actualmente, los avances basados en nuevos materiales y mejora de las técnicas de fabricación han generado un grado de durabilidad que hace que los procesos de membranas se encuentran ampliamente extendidos en multitud de procesos de separación industrial.

Con respecto al consumo de agua, las membranas semipermeables permiten hoy el suministro de agua potable para millones de personas en el mundo gracias a la purificación y desalación. Los avances en este campo han sido posibles gracias al bajo coste (menos de 1 USD m^{-3} de agua potable), bajo consumo energético y al alto rendimiento de esta tecnología.

Las operaciones de separación mediante membranas presentan una serie de ventajas que se enumeran a continuación:

- Bajo consumo de energía, puesto que la energía que hay que aportar habitualmente es la necesaria para conseguir el desplazamiento de las diferentes corrientes de fluido, ya que no suele ser necesario producir un cambio de estado de las fases implicadas.
- Condiciones de operación suaves, ya que con frecuencia la separación se lleva a cabo a temperatura ambiente.
- Posibilidad de obtener elevadas selectividades y eficacias en la separación mediante una correcta elección del tipo y características de la membrana a utilizar.
- Los equipos de membranas son compactos y modulares, por lo que ocupan poco espacio y se pueden acoplar fácilmente en instalaciones ya existentes. Asimismo, las inversiones de capital a realizar en la adquisición de estos equipos no son elevadas.
- Facilidad de montaje, desmontaje y operación.

La principal limitación de este tipo de separaciones reside en la sensibilidad de la membrana, ya que tiende a deteriorarse y/o ensuciarse con el paso del tiempo, siendo necesario reemplazarla con una cierta periodicidad. Además, estas membranas suelen presentar un coste elevado.

2.6.1. Operaciones de membrana.

Las operaciones de separación con membranas se pueden clasificar en tres grupos, dependiendo del objetivo perseguido en cada caso:

- *Operaciones de concentración de disoluciones:* se elimina parte del disolvente presente en la misma haciéndolo pasar a través de la membrana. El producto de interés en la separación es la disolución concentrada, que queda retenida por la membrana. A veces, se trata en realidad de una preconcentración, eliminándose el resto de disolvente mediante otra operación de separación posterior.
- *Operaciones de purificación o clarificación:* la separación tiene como objeto la eliminación de componentes no deseados, que habitualmente son rechazados y retenidos por la membrana, por lo que el producto con valor suele ser la fase que

atraviesa la membrana. Este es el objetivo perseguido en el caso de sus aplicaciones para la purificación de aguas.

- *Operaciones de fraccionamiento:* en este caso se pretende conseguir la separación de determinados componentes presentes en el medio, resultando de interés tanto los retenidos por la membrana como los que pueden atravesarla.

Las diversas operaciones basadas en membranas se diferencian entre sí en el estado físico de las fases en contacto con la membrana, la fuerza impulsora del transporte de materia, el tipo de componentes que pueden atravesar la membrana y el tamaño de las especies que son rechazadas. En la Tabla 2.4 se resumen las características más relevantes de los procesos de separación con membranas empleados en el tratamiento de agua.

Tabla 2.4. Características de las operaciones de separación con membranas.

Operación	Fuerza impulsora	Fases implicadas	Composición permeado	Estructura membrana
Diálisis	ΔC_i	L/M/L	Solutos	Porosa (0.1-10µm)
Electrodiálisis	ΔV	L/M/L	Iones	Intercambio iónico
Microfiltración	ΔP	L/M/L	Disolvente	Porosa (0.1-10µm)
Ultrafiltración	ΔP	L/M/L	Disolvente	Porosa (2-100nm)
Nanofiltración	ΔP	L/M/L	Disolvente	Porosa (<2nm)
Ósmosis inversa	ΔP	L/M/L	Disolvente	Densa (<1nm)

Además, mientras que las operaciones convencionales de separación suelen estar controladas por el equilibrio entre las fases, en las operaciones mediante membranas existe un control cinético, ya que la clave de la separación reside en las diferentes velocidades de transporte de los componentes a través de la membrana. La solubilidad es una variable de equilibrio que permite calcular la concentración de soluto en la interfase y depende de la afinidad química entre el soluto y la membrana. El equilibrio que se establece en la interfase se suele describir por analogía con el equilibrio de otras operaciones: ley de Henry (destilación), isoterma de Langmuir (adsorción), etc. Por otro lado, la difusividad del soluto es un parámetro cinético relacionado con su movilidad en la membrana, por lo que depende de variables como el tamaño molecular y naturaleza del soluto, así como de la estructura de la membrana.

A continuación se explican brevemente las operaciones de membrana de más interés en el tratamiento de aguas, con especial énfasis en las dos operaciones empleadas en el presente trabajo: ultrafiltración y nanofiltración.

En microfiltración (MF) la fuerza impulsora es una diferencia de presiones hidrostáticas de hasta 2 bar, a través de membranas microporosas con tamaño de poro entre 0.1 µm y 10 µm, para la separación de coloides y partículas suspendidas. Se fabrican con materiales orgánicos (polímeros tales como el teflón (PTFE), fluoruro de polivinilideno (PVDF), polipropileno (PP9, etc.) o inorgánicos (cerámicas, metales, vidrios, etc.). La microfiltración puede emplearse en cualquier escala (fermentaciones, clarificación y recuperación de biomasa, etc.). Se puede emplear para eliminar turbidez, bacterias y protozoos de aguas residuales, ya sea totalmente o de manera significativa.

En ultrafiltración (UF) la fuerza electromotriz es una diferencia de presiones hidrostáticas de 1 hasta 6 bar. El mecanismo de transporte es el mismo que el de MF, variando únicamente el tamaño de poro de las membranas que ahora se encuentra entre 2 nm y 0.1 µm. Se utilizan para eliminar partículas (clarificar) y desinfectar el agua. Estas membranas son porosas y eliminan bacterias, virus, sólidos en suspensión y partículas de hierro y manganeso, pero en general no son eficaces en la eliminación de compuestos orgánicos naturales o sintéticos. La UF es similar a la coagulación y la filtración con arena, en cuanto que se usa como pretratamiento para las aguas potables.

Las membranas más utilizadas en ultrafiltración son las anisótropas de tipo Loeb-Sourijan, donde una delgada capa de poros de pequeño diámetro se encuentra unida, sin discontinuidad, a otra capa más gruesa y microporosa. Los materiales habitualmente empleados en la fabricación de este tipo de membranas son: poliacrilonitrilo, polímeros de polivinilcloruro/poliacrilonitrilo, polisulfonas, fluoruro de polivinilideno, poliamidas aromáticas, acetato de celulosa y materiales cerámicos (óxidos de titanio, aluminio y silicio).

Los costes de capital y de operación en los tratamientos por UF son todavía demasiado altos para que pueda aplicarse como única tecnología de tratamiento de grandes caudales de agua residual, pero sí tiene ya un importante campo de aplicación, en combinación con otras tecnologías, como es el caso de los reactores biológicos de membrana o como pre-tratamiento en los procesos de OI. Como única tecnología se utiliza en el tratamiento de efluentes de aguas residuales de 2.5-25 m^3 $día^{-1}$, sobre todo en aquellos casos como el tratamiento del agua caliente y recuperación de proteínas en la industria de la alimentación; recuperación de partículas de pintura del agua de los procesos de pintado de piezas industriales; recuperación de polímeros sintéticos en la industria textil; recuperación de aceites presentes en las aguas de proceso de la industria metalúrgica, etc.; donde se plantea el doble objetivo de recuperar un producto valioso y/o reutilizar el agua.

En nanofiltración (NF) se emplean membranas con un tamaño de poro inferior a 2 nm y las presiones que se les aplica se encuentran entre 5-25 bar. Resulta adecuada para eliminar dureza, metales pesados, materia orgánica natural, partículas y un gran número de compuestos orgánicos e inorgánicos. Presenta una elevada retención de iones divalentes y multivalentes, donde su retención es prácticamente total. Sin embargo, no es una tecnología adecuada para retener iones monovalentes, ofreciendo retenciones de NaCl moderadas o bajas, siendo mejores para este propósito las membranas de ósmosis inversa. De este modo, el proceso de nanofiltración es útil para el tratamiento de aguas subterráneas y superficiales con una elevada concentración de sólidos disueltos, pero con un bajo contenido en NaCl. Se utilizan membranas poliméricas con MWCO en el rango 150-1000 Da y coeficientes de retención de cloruro sódico de 0.2–0.8%.

En definitiva, la NF se utiliza principalmente en el tratamiento de aguas de consumo en pequeñas comunidades, en eliminación de la dureza del agua y como pre-tratamiento para la obtención de agua ultrapura. Recientes estudios han demostrado la viabilidad de empleo de este proceso; por ejemplo, García-Vaquero et al. (2014) estudiaron la eliminación de carbono orgánico disuelto (93%), iones (97%), metales (80-100%), color y turbidez (100%), THMs (53%) y microcontaminantes (15-100%) en una planta piloto de nanofiltración.

Por su parte, la ósmosis inversa (OI) es un proceso de filtración y difusión generalmente utilizado para aguas salobres y de mar. En este proceso la clave se encuentra en la gran diferencia de presiones que se utilizan, con valores de hasta 80 bar, en el sentido contrario al que está actuando la presión osmótica. Las membranas de OI deben ser altamente selectivas, con gran afinidad y permeabilidad para el agua y gran tolerancia hacia los agentes oxidantes como el cloro, para permitir que las membranas puedan ser desinfectadas y limpiadas. La OI también se utiliza para purificar las aguas potables; en dicho caso se trabaja a baja presión (7 bar) y se consigue un 85-90% de rendimiento. Las unidades de OI eliminan contaminantes de hasta 0.0001 µm; esto incluye bacterias, virus y todos los compuestos orgánicos y de desinfección. Por todo lo anterior, la ósmosis inversa resulta también una técnica altamente eficaz para tratamientos de deshidratación, concentración/separación de sustancias de bajo peso molecular en solución, o tratamiento de desechos.

A la vista de las principales aplicaciones de OI/NF, puede deducirse que las calidades del agua obtenida son suficientes para poder ser reutilizadas en las condiciones más exigentes. Además, el nivel de desarrollo alcanzado en los últimos años, como lo demuestra la aplicación de las membranas en nuevos procesos de separación (pervaporación, reactores de membranas, aplicaciones médicas, etc.), junto con la aparición de nuevos materiales que permitan, además de la depuración del agua, la recuperación de sustancias valiosas, hacen prever unas buenas perspectivas de futuro para estos procesos. Los aspectos más importantes a tener en cuenta para el diseño en plantas reales de NF son los caudales de agua potable requeridos y el nivel de retención de ciertos compuestos presentes en el agua bruta (van der Bruggen et al., 2001). La elección de la membrana más adecuada dependerá en gran medida de estas consideraciones, así como el cálculo de la superficie de la misma, que supone un coste importante.

2.6.1.1. Clasificación de las membranas según el mecanismo de separación

La clasificación de las membranas basada en mecanismos de separación, se reduce a tres clases principales:

- *Membranas porosas*. Poseen poros finos de diferentes tamaños y realizan la filtración por medio del efecto criba: se distinguen macroporos, mayores de 50 nm (MF), mesoporos, en el rango de 2 a 50 nm (UF) y microporos, menores de 2 nm (NF).
- *Membranas no porosa*s. Estas membranas pueden considerarse como medios densos. La difusión de especies tiene lugar en el volumen libre que esté presente entre las cadenas macromoleculares del material de la membrana. La OI, entre otras, utilizan este tipo de membrana.
- *Membranas de intercambio iónico*. Son un tipo especial de membranas no porosas, de separación electroquímica, en la que los iones se transfieren a través de la membrana por medio de una tensión o corriente eléctrica continua.

2.6.1.2. Formas de operar en procesos de membranas

En el tratamiento de aguas por operaciones de membrana se puede operar de dos formas (Figura 2.8):

- Filtración en línea o flujo final ciego. Las membranas se disponen en la línea de flujo del efluente que se desea tratar (alimentación), quedando las partículas contaminantes retenidas en el interior de las membranas y generándose una corriente depurada o permeado. Las membranas utilizadas son de tipo filtro profundo, dispuestas en cartuchos.
- *Filtración tangencial*. El efluente que se desea tratar se hace circular tangencialmente a la membrana. Los contaminantes quedarán en la superficie de la membrana, siendo arrastrados por el flujo tangencial, evitándose en gran medida el ensuciamiento de la membrana. Esta forma de operar genera a partir de la alimentación dos corrientes o flujos: concentrado o rechazo, con una concentración de contaminantes mayor que en la alimentación, y permeado, con

una baja concentración de contaminantes que hace posible su vertido o reutilización. Las membranas utilizadas son de tipo tamiz o densas.

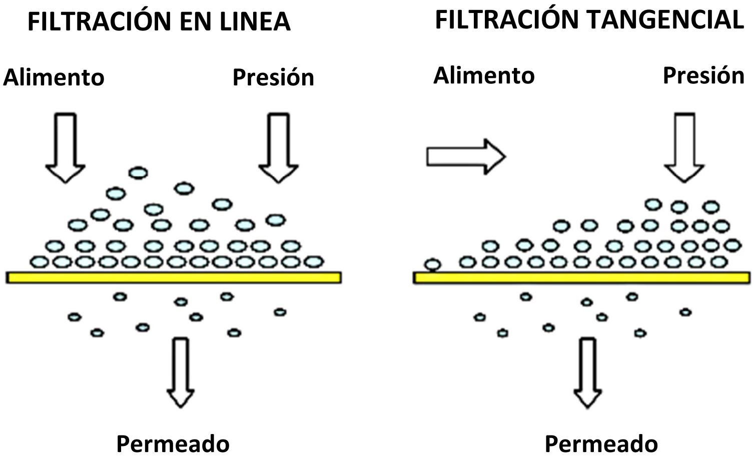


Figura 2.8. Esquema de filtración lineal y tangencial.

2.6.1.3. Factores que reducen las prestaciones de las membranas

El buen funcionamiento de una membrana se consigue cuando se mantiene el flujo de permeado y los factores de retención dentro de las condiciones de diseño de la operación, esto es, sin grandes modificaciones en la diferencia de propiedad (presión, potencial eléctrico) que genera el flujo de permeado (Rodríguez et al., 2006). El flujo de permeado (J_v) es el flujo de la solución que cruza la membrana, mientras que el coeficiente de retención (R) de un componente i que se desea excluir del permeado es una forma de estimar el grado de separación conseguido por la membrana. A continuación se describe brevemente los dos principales factores que reducen las prestaciones de las membranas.

❖ Polarización de la concentración

Tiene lugar en aquellos procesos que operan en filtración tangencial. En las condiciones de trabajo de estos procesos es difícil evitar que los componentes de la alimentación que son rechazados por la membrana se acumulen en su superficie. El resultado es la creación de gradientes de concentración (polarización de la concentración) en el lado de la alimentación, que pueden disminuir la eficacia de separación de la membrana y el flujo de permeado (Thorsen, 2004). La Figura 2.9 representa la situación en la que un componente i de la alimentación, que es rechazado por la membrana, se acumula en su superficie, creándose un gradiente de concentración localizado en una película de espesor δ, próximo a la membrana.

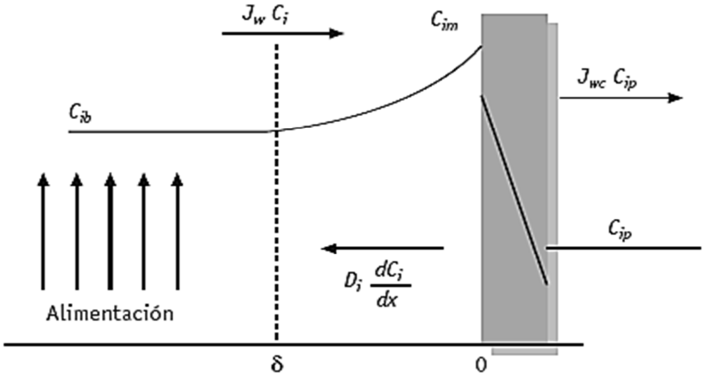


Figura 2.9. Creación de gradientes de concentración.

❖ **Ensuciamiento de las membranas**

El ensuciamiento de la membrana es debido a la presencia en la alimentación de sustancias que pueden interaccionar con ella, adsorbiéndose y/o precipitando en su superficie o penetrando en su interior. Los diferentes tipos de ensuciamiento se muestran en la Figura 2.10.

- La formación de la capa de gel se produce cuando la concentración de ciertos componentes de naturaleza macromolecular se eleva demasiado, de manera que se alcanza su límite de solubilidad. Se forma así un depósito sobre la membrana que ejerce una resistencia hidráulica extra. Esto provoca una disminución del flujo de permeado. En principio, el ensuciamiento es reversible (limpieza con agua) pero puede ser irreversible si los componentes de la capa de gel reaccionan con otros formando una capa densa sobre la membrana que no es fácil de eliminar.
- Bloqueo de los poros, que generalmente es irreversible. Para eliminarlo se puede llevar a cabo la inversión del sentido del flujo a través de la membrana, aunque no es aplicable a cualquier tipo de membranas. Además se debe considerar las incrustaciones inorgánicas debido a la precipitación de sales pocos solubles y metales, generalmente

debidas a carbonato cálcico y sulfatos de bario, de calcio o de estroncio. Este tipo de ensuciamiento es especialmente importante en nanofiltracion y osmosis inversa.

- Adsorción de componentes, debido a lo cual se estrecha el radio del poro y se incrementa la resistencia hidráulica con la consecuente disminución del flujo. Se puede intentar la limpieza con productos específicos como sustancias fuertemente alcalinas o agentes ácidos a elevadas temperaturas.

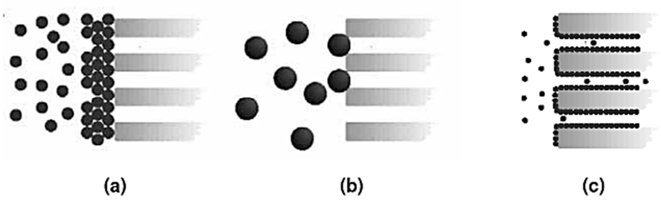


Figura 2.10. a) Formación de la capa de gel; b) Bloqueo de poros; c) Adsorción.

La consecuencia del ensuciamiento es una disminución del flujo de permeado, debido a una mayor resistencia de la membrana. Un aumento progresivo de la presión transmembrana, con el fin de mantener el flujo de permeado, acelera el proceso de ensuciamiento, pudiéndose llegar a una situación irreversible de taponamiento de la membrana que haría necesaria su sustitución (Al-Amoudi y Lowitt, 2007).

2.7. PROCESOS DE ADSORCIÓN

La adsorción es definida por la IUPAC como el enriquecimiento, en uno o más componentes, de la región entre dos fases, conocida como interfase o superficie interfacial (IUPAC, 1997). La sustancia que se concentra en la superficie o se adsorbe se llama adsorbato mientras que en la fase donde se produce dicho fenómeno se denomina adsorbente.

Las fuerzas intermoleculares implicadas en el proceso de adsorción son de la misma naturaleza que las fuerzas existentes en el seno de un líquido o sólido. En el interior de una fase, las fuerzas que mantienen unidas las diferentes partes de la misma se encuentran compensadas en todas direcciones. Este equilibrio de fuerzas se altera en la superficie del adsorbente, como consecuencia del acercamiento de las moléculas de adsorbato. Cuando el balance de fuerzas en la superficie no está compensado, aparece una fuerza atractiva neta normal a la superficie, responsable del fenómeno de adsorción. La energía de adsorción determina el tiempo que permanecen en la superficie del adsorbente las distintas especies.

El enlace que une los átomos de la sustancia con menor grado de ordenación con los enlaces de los átomos de la materia de mayor grado de ordenación depende de ambos materiales. Según este enlace, pueden darse dos tipos de adsorción: fisisorción y quimisorción.

En el caso de la fisisorción, el adsorbato se encuentra unido débilmente a la superficie del sólido por fuerzas de van der Waals. Por esta razón la adsorción física es totalmente reversible., pudiendo producirse la desorción a la misma temperatura. Este tipo de adsorción no es específica, y por lo tanto las moléculas de adsorbato pueden llegar a cubrir toda la superficie del adsorbente. En cambio, la quimisorción involucra un intercambio o una compartición de electrones entre las moléculas de adsorbato y la superficie del adsorbente dando como resultado una reacción química. Tiene lugar sólo en determinadas zonas del sólido (los centros activos), siendo normalmente un proceso irreversible. En la Tabla 2.4 se muestran las diferencias entre fisisorción y quimisorción (Bansal et al, 2005; Barrow, 1975).

La adsorción sólido-líquido es más compleja que la sólido-gas, puesto que las fuerzas de interacción no son sólo adsorbente-adsorbato, sino que también intervienen fuerzas de interacción adsorbente-disolvente, adsorbato-disolvente y adsorbato-adsorbato. Este hecho motiva que la afinidad de un adsorbente por un adsorbato no dependa solamente de la naturaleza de las interacciones entre ambos, sino también de la naturaleza del disolvente en el que el adsorbato se encuentra disuelto. El carácter polar o no polar (Guadayol et al., 1997; Park et al., 2009) define la afinidad del soluto por el disolvente, de manera que la adsorción se ve favorecida cuanto menor es la afinidad del adsorbato por el disolvente y mayor lo es por el adsorbato.

Tabla 2.4. Características principales de la adsorción física y química

Fisisorción	Quimisorción
Enlaces débiles. Interacciones de van der Waals.	Enlaces fuertes de corto alcance (verdaderos enlaces químicos)
Entalpía de adsorción está entre los 10 y 20 kJ/mol.	Entalpía de adsorción se encuentra entre 40 y 400 kJ/mol.
Al incrementar la temperatura, se reduce la adsorción. Es un proceso reversible.	Un incremento en la temperatura puede favorecer la adsorción. Es un proceso irreversible.
La adsorción toma lugar en cualquier punto del adsorbente.	La adsorción se lleva a cabo en puntos específicos en la superficie.
Se lleva a cabo en una monocapa o en multicapa.	Se realiza la adsorción en una monocapa.
No existen reacciones superficiales tales como de neutralización, descomposición, etc.	Pueden darse reacciones superficiales (disociación, catálisis, reconstrucción, etc.)
El adsorbato mantiene su identidad.	El adsorbato cambia su estructura química respecto al precursor.

2.7.1. Factores que influyen en la adsorción en fase líquida.

Los factores que influyen en la adsorción en fase líquida son muy diversos. A continuación se enumeran los más significativos:

Superficie específica. Dado que la adsorción es un fenómeno superficial, cuanto mayor sea la superficie del adsorbente, mayor será la retención del adsorbato. Por ello, los sólidos que se emplean mayoritariamente son sólidos porosos (carbón activado, zeolitas, etc.) y el cálculo de la superficie específica de los materiales adsorbentes es una de las características texturales más importantes a determinar.

Naturaleza del adsorbente. En la adsorción en fase líquida pueden ser tan importantes las propiedades químicas superficiales del adsorbente como sus características estructurales. Por un lado, la naturaleza química de la superficie del adsorbente influirá en los enlaces que se formen entre éste y el adsorbato y, por otro, sus propiedades texturales, como son la superficie específica, el volumen de poros y tamaño de partícula, influirán tanto en la cantidad total de adsorbato retenida en el equilibrio, como en la cinética del proceso (Walker et al., 1988).

Naturaleza del adsorbato. Factores como la solubilidad del adsorbato, su estructura química, o su naturaleza iónica son parámetros a tener en cuenta en el proceso de adsorción. Así, cuanto mayor sea la solubilidad del mismo, menor será el grado de adsorción (regla de Lundelius) (Lundelius, 1920). La presencia de grupos funcionales es también de gran importancia ya que pueden interaccionar con otros grupos polares del adsorbente dando lugar a una adsorción específica. Por otro lado, la carga superficial asociada a algunos adsorbentes (i.e., carbones activados, zeolitas) puede asimismo determinar la capacidad de retención en función del grado de ionización del adsorbato (Bean et al., 1964).

pH. El pH de la fase líquida afecta tanto al sólido adsorbente como al adsorbato. Por una parte, los iones hidroxonio e hidronio se adsorben fuertemente sobre algunos adsorbentes, estableciéndose una competencia con la retención del adsorbato. Por otra parte, el pH determina también el grado de disociación del adsorbato, de manera que se puede aumentar la solubilidad en la fase líquida (especies en forma iónica) o su retención en la fase sólida (especies en forma neutra) (Costa et al., 1988). No obstante, este factor no afecta por igual a todos los sistemas adsorbato-adsorbente, por lo que debe determinarse experimentalmente.

Temperatura. La adsorción es un fenómeno exotérmico, por lo que un aumento en la temperatura da lugar a una disminución en la capacidad de adsorción. Sin embargo, la entalpía de adsorción suele ser muy baja, con lo que las variaciones con la temperatura no son muy significativas. Pese a que la adsorción disminuye con el aumento de la temperatura, algunos autores han observado que en algunos casos (adsorción de fenoles sobre carbones muy microporosos) se produce el fenómeno contrario (Seidel et al., 1985).

Competencia entre adsorbatos. En la práctica se suele trabajar con fases líquidas multicomponentes, donde la competencia entre los distintos adsorbatos adquiere gran importancia. Esta competencia no solo puede afectar a la capacidad de adsorción, sino también a la velocidad del proceso global de adsorción (Fritz et al, 1981). Generalmente, el compuesto con mayor capacidad de retención cuando es el único adsorbato, es también el que se adsorbe con preferencia en una mezcla binaria equimolecular de dos adsorbatos. Cuando la naturaleza de los adsorbatos es similar, los efectos competitivos suelen ser mucho menores, comportándose la mezcla como un sistema de un solo componente (Yonge et al., 1986; Álvarez, 1989).

Naturaleza del disolvente. La naturaleza química del disolvente influye en las interacciones con el adsorbato. El grado de adsorción de un adsorbato variará dependiendo del disolvente en el que se encuentre disuelto.

Otro factor importante es la tensión superficial del disolvente, que influye en el contacto entre el sólido y el líquido, y determinará la superficie eficaz para la adsorción. En el caso de sólidos microporosos, la mayor parte de la superficie es interna, por lo que el líquido tiene que llenar estos poros para que el adsorbato quede retenido.

2.7.2. Cinética de adsorción.

En un proceso de adsorción de un soluto disuelto en fase líquida, se pueden distinguir las siguientes etapas consecutivas (Figura 2.11):

- Difusión externa del adsorbato desde el seno de la disolución hasta la superficie externa de las partículas de adsorbente.
- Difusión interna, debido a que la superficie externa expuesta por las partículas tiende a ser menor al 1% del total, el adsorbato migra a través de la red porosa del sólido desde la superficie externa del adsorbente hasta los centros activos de adsorción.
- Adsorción de las moléculas sobre la superficie de los poros internos del adsorbente (etapa de adsorción).

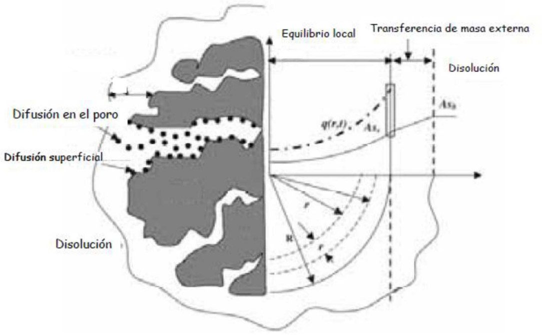


Figura 2.11. Etapas del proceso de adsorción.

Desde el punto de vista cinético, la etapa de adsorción es la más rápida de todas, de hecho se considera que se alcanza el equilibrio de forma instantánea. En estas condiciones, el transporte externo y/o la difusión intraparticular serán los factores limitantes que condicionarán la velocidad global del proceso de adsorción.

El transporte por el interior de las partículas es tratado generalmente como un proceso de difusión. Hay que destacar la existencia de dos mecanismos de difusión del adsorbato por el interior de los poros:

- Difusión molecular ordinaria a través del fluido que llena los poros de las partículas, denominada difusión de poro.
- Difusión superficial, migración de las moléculas, previamente adsorbidas, a lo largo de las paredes del poro sin producirse una desorción completa.

La diferencia esencial entre las etapas de difusión de poro y difusión superficial es que están separadas por la etapa de adsorción propiamente dicha y por tanto ocurren en fases diferentes.

2.7.2.1. Modelos cinéticos.

En la bibliografía existen numerosos modelos ampliamente utilizados para analizar la cinética de los procesos de adsorción, algunos de los cuales destacan por su sencillez en la aplicación y su fácil interpretación.

A continuación se hace una breve descripción de los modelos teóricos más empleados a la hora de realizar estudios cinéticos.

Modelo cinético de pseudo-primer orden o de Lagergren.

Este modelo considera que la fuerza impulsora es la diferencia entre la concentración del soluto adsorbido en el equilibrio y la concentración del soluto adsorbido a un tiempo determinado, de modo que la velocidad de adsorción viene determinada por la siguiente ecuación (43):

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{43}$$

Donde k_1 (min^{-1}) es la velocidad de pseudo-primer orden, q_e y q_t ($mg \cdot g^{-1}$) se corresponden con la cantidad de soluto adsorbido en el equilibrio y en un tiempo t, respectivamente. Integrando la ecuación (43) entre las condiciones límites $q_t = 0$ cuando $t = 0$ y $q_t = q_t$ cuando $t = t$, se obtiene la ecuación (44):

$$\ln(q_e - q_t) = lnq_e - k_1 t \tag{44}$$

De esta forma, representando los valores de $\ln(q_e-q_t)$ frente a t, se puede obtener el valor de la constante de la velocidad del proceso de adsorción k_1 y la concentración del soluto en el equilibrio (q_e) a partir de la pendiente y la ordenada.

Modelo de pseudo-segundo orden o modelo de Ho.

El modelo de pseudo-segundo orden asume que la capacidad de adsorción es proporcional al número de centros activos del adsorbente y que la velocidad de adsorción se encuentra controlada por adsorción química. La ecuación de este modelo se muestra a continuación (Vinod et al., 2003):

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{45}$$

Donde k_2 ($g \cdot mg^{-1} \cdot min^{-1}$) es la constante de velocidad de pseudo-segundo orden. Integrando la ecuación (45) entre las condiciones límites $q_t = 0$ cuando $t = 0$ y $q_t = q_t$ en el instante t = t se obtiene la ecuación:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{46}$$

Si se representa t/q_t frente a t se puede obtener, a partir de la pendiente y de la ordenada en el origen, los valores de q_e y k_2, respectivamente.

Modelo de Elovich

Se utiliza generalmente para determinar cinéticas de quimisorción de gases sobre sólidos, aunque también es adecuado para describir la cinética de adsorción de contaminantes en disoluciones acuosas. La ecuación de Elovich generalmente se expresa como:

$$\frac{dq_t}{dt} = \alpha exp(-\beta q_t) \tag{47}$$

Donde α y β' son parámetros de la ecuación de velocidad de Elovich; α ($g \cdot mg^{-1} \cdot min^{-1}$) es la velocidad inicial de adsorción y β ($g \cdot mg^{-1}$) es la constante de desorción, la cual se relaciona con el número de centros activos de adsorción disponibles. Una forma simplificada de esta ecuación se introdujo en 1980 (Chien et al., 1980), asumiendo αβt>>1 y aplicando las condiciones $q_t = 0$ cuando t = 0, y $q_t = q_t$ cuando t = t, se puede expresar como:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} lnt \tag{48}$$

Ambos parámetros se pueden obtener por regresión lineal de la representación gráfica de q_t en función del tiempo.

2.7.2.2. Equilibrio de adsorción.

En el equilibrio de adsorción existe una proporción definida de soluto repartida entre las dos fases, líquida y sólida. La forma habitual de expresar esta distribución es la capacidad de equilibrio, definida como:

$$q_e = \frac{C_0 - C_e}{W} V \tag{49}$$

Siendo q_e la capacidad de equilibrio, que informa de la concentración de adsorbato en fase sólida, C_0 es la concentración inicial de adsorbible en fase líquida, C_e es la concentración de adsorbible en fase líquida en el equilibrio, V es el volumen de disolución y W es la masa de adsorbente. Las isotermas de adsorción son curvas construidas a partir de pares (C_e,q_e) a una temperatura constante.

Existen diversos modelos teóricos para la descripción de las isotermas de adsorción, que difieren entre sí en las hipótesis de partida y en el número de parámetros característicos de cada uno de ellos. Los modelos más empleados en estudios de adsorción en sistemas sólido-líquido de un solo componente se basan tanto en modelos termodinámicos como semiempíricos. Los primeros están obtenidos a partir de modelos teóricos de adsorción en función de las propiedades termodinámicas del adsorbente y la fase fluida; los semiempíricos son el resultado de un ajuste de datos experimentales a determinadas funciones, si bien en ocasiones pueden presentar una base termodinámica. A continuación se detallan los modelos más comúnmente empleados para el ajuste e interpretación de los datos experimentales obtenidos en estudios de adsorción en sistemas sólido-líquido de un solo componente.

Isoterma de Langmuir

Langmuir fue el primer autor en proponer una teoría coherente de adsorción sobre una superficie plana desde un punto de vista cinético (Do, 1988), explicando el fenómeno como un continuo “bombardeo” de moléculas adsorbiéndose sobre la superficie mientras otras se desorben a la misma velocidad. Las suposiciones básicas de la teoría de Langmuir son las siguientes:

- La superficie del sólido es homogénea, por lo que la energía de adsorción es constante en todos los centros.
- La adsorción sobre la superficie se produce únicamente sobre los centros activos.
- Cada centro activo puede acumular solamente una molécula de adsorbato.

La ecuación que describe el modelo de Langmuir es la siguiente:

$$q_e = \frac{q_{sat} \cdot C_e}{1 + k_L C_e} \tag{50}$$

En la que q_e es la cantidad de soluto adsorbido por unidad de masa de adsorbente en equilibrio con una disolución de concentración C_e, q_{sat} es la cantidad de adsorbato por unidad de masa de adsorbente que forma una monocapa, (que por lo tanto deber ser independiente de la temperatura) y k_L es una constante de equilibrio que varía con la temperatura.

Isoterma de Freundlich

Se utiliza en sistemas en los que la superficie de adsorción es energéticamente heterogénea. La ecuación empírica que describe el modelo de Freundlich tiene por expresión:

$$q_e = k_F \, C_e^{\frac{1}{n_F}} \tag{51}$$

k_F y n_F son los parámetros propios del modelo. Al observar la Ecuación (Matsui et al., 2009) se puede comprobar que no conduce a una capacidad finita de adsorción: conforme aumente C_e, lo hará q_e sin límite.

2.7.3 Carbón activo.

El carbón activado puede definirse como un material carbonoso poroso carbonizado, activado mediante la reacción con gases o por la adición de productos químicos, antes, durante o después del proceso de carbonización. Estos procesos confieren al material una elevada porosidad y extensa área superficial. El alcance de la activación condiciona la porosidad final del carbón, si bien, habitualmente presenta tres tipos de poros: microporo (diámetro <2nm), mesoporo (diámetro en el rango 2-50nm) y macroporo (diámetro >50nm). Aunque la mayor parte de la adsorción tiene lugar en los microporos, los mesoporos y macroporos juegan un papel crucial, dado que sirven de camino al adsorbato hacia el interior de los microporos, los cuales apenas se encuentran en la superficie exterior del material.

La eficiencia de adsorción está condiciona por diversos factores, tales como: superficie específica, tamaño y estructura de los poros, volumen del poro y reactividad de los diferentes componentes del material. Dentro de las características del adsorbato, que influyen en el proceso de adsorción, se incluyen: solubilidad, hidrofobicidad, estructura molecular, peso molecular, polaridad y grupos funcionales. Además de estos factores, las características del agua (conductividad, pH, temperatura, carbono orgánico disuelto, turbidez, metales disueltos etc.) también influyen en el proceso (Di Bernardo y Dantas, 2005).

Los adsorción con carbón activado es ampliamente empleada en el tratamiento de aguas, siendo su principal ventaja que no genera productos tóxicos y posee una elevada capacidad de adsorción (Estevinho et al., 2007). Por ello, numerosos estudios evalúan la adsorción de contaminantes emergentes (individuales o mezclas binarias) sobre carbones activados en agua ultrapura y en competencia con materia orgánica natural; sin embargo, se encuentran muy pocos estudios sobre la eliminación de mezclas de contaminantes (Rossner et al., 2009).

2.8. ESTUDIOS PREVIOS SOBRE ELIMINACIÓN DE CONTAMINANTES EMERGENTES MEDIANTE OXIDACIÓN QUÍMICA Y OPERACIONES DE MEMBRANA.

Aproximadamente, miles de toneladas de fármacos se liberan en el agua anualmente. Se ha estimado que existen unos 6 millones de PPCPs comerciales disponibles en el mundo y que el uso de estos compuestos está incrementándose de forma preocupante cada año (Kümmener, 2003). Esto ha dado lugar a la creación de nuevas y complejas sustancias químicas que entran en el medio ambiente y se desconoce tanto su comportamiento como su impacto ambiental. Esta preocupación hace que la comunidad científica realice un gran esfuerzo en investigar este problema e intentar paliar sus efectos; prueba de ello, es la publicación en los últimos años de numerosos artículos y revisiones bibliográficas.

En primer lugar, surgió la necesidad de crear técnicas que permitieran detectar y cuantificar estos contaminantes. Así Richardson, en el año 2006, publicó un artículo que pone de manifiesto que se han detectado unos 3.000 compuestos químicos en el medio ambiente.

Por desgracia, algunos de estos compuestos no son completamente eliminados en las estaciones depuradoras de aguas residuales (Ternes, 1998; Ternes et al., 1999; Boyd et al., 2003). Estudios recientes han puesto de manifiesto que los sistemas tradicionales, basados en microorganismos, son ineficaces para destruir de una forma efectiva estos contaminantes, debido a su compleja estructura química y las bajas concentraciones en las que se encuentran. En algunos casos, el porcentaje que se elimina puede ser inferior al 10% (Ternes et al., 2002; Stackelberg et al., 2004; Jones et al., 2005).

Estos compuestos terminan en las aguas superficiales y subterráneas de muchos países como: Alemania (Ternes, 1998; Hirsch et al., 1999), Holanda (Belfroid et al., 1998), España (Rodríguez et al., 2003; Carballa et al., 2005), EEUU (Drewes et al., 2001; Kolpin et al., 2002; Xia et al., 2003) etc. Pero no sólo se han identificado en esta agua, sino que la presencia de estos contaminantes pueden alcanzar incluso las aguas potables (Ternes et al., 2002; Lin et al., 2005).

Es por ello que surge la necesidad de aplicar nuevas tecnologías que permitan una eliminación efectiva de estos compuestos. Así, tratamientos tales como la ozonación, procesos de oxidación avanzada, o filtración a través de membranas, deben ser utilizados para lograr la total eliminación de estos compuestos durante los tratamientos tanto de aguas residuales como de potabilización.

En vista de todo ello, son numerosos los trabajos que se encuentran en la bibliografía sobre la degradación de productos farmacéuticos y de cuidado personal mediante procesos de oxidación química. Muchos de estos trabajos han sido recopilados en revisiones publicadas recientemente. Así Ikehata et al. (2006) han realizado una revisión sobre el ozono, tanto de forma individual como combinada con peróxido de hidrógeno y el reactivo de Fenton, en el tratamiento de potabilización del agua. En el año 2007, Esplugas et al. realizaron una revisión sobre la ozonación y la aplicación de POAs en la eliminación de PPCPs presentes en efluentes acuosos. Del mismo modo, Rosal et al. (2009) han publicado una revisión sobre la eliminación de productos farmacéuticos en aguas residuales municipales mediante la combinación de O_3/H_2O_2 y ozono alcalino. Paralelamente a esta investigación, en ese mismo año, Klavarioti et al. (2009) elaboraron una exhaustiva revisión sobre la eliminación de productos farmacéuticos en aguas residuales mediante procesos de oxidación avanzada.

Dentro de los Procesos de Oxidación Avanzada (POAs), la ozonación es una técnica efectiva para lograr la eliminación de ciertos compuestos farmacéuticos en cualquier matriz de agua (Huber et al., 2003; 2005). Estos trabajos se han centrado en el estudio detallado de la ozonación de nueve compuestos farmacéuticos (bezafibrato, carbamazepina, diazepam, diclofenaco, 17α-etinilestradiol, ibuprofeno, iopromida, sulfametoxazol y roxitromicina) incluyendo un estudio cinético de la degradación, así como la evaluación del grado de eliminación de los mismos durante la ozonación de aguas potables y residuales. Otros estudios sólo se interesan por mostrar el porcentaje de eliminación de compuestos farmacéuticos alcanzado tras la aplicación de ozono en aguas contaminadas con estos compuestos (Ternes et al., 2003). Por otro lado, con el fin de mejorar la eficacia de esta técnica, se han realizado estudios donde se aplica ozono en combinación con carbón activo u otros catalizadores con el fin de eliminar compuestos farmacéuticos de las aguas

(Pocostales et al., 2010; Beltrán et al., 2009). También, Nakada et al., publicaron en el año 2007, un artículo que trataba sobre la eliminación de contaminantes mediante filtración con arena y ozonación en plantas de tratamiento de aguas.

Huber et al. (2003) estudiaron la combinación O_3/H_2O_2 y determinaron las constantes cinéticas de las reacciones entre los radicales OH y los nueve compuestos farmacéuticos mencionados anteriormente. En otros artículos, se ha estudiado la combinación de radiación UV con otros agentes oxidantes para oxidar ciertos compuestos farmacéuticos y de cuidado personal (Andreozzi et al., 2003; Doll y Frimmel, 2004; Shemer et al., 2006), determinando los rendimientos cuánticos y analizando los subproductos de oxidación para ciertos casos.

También cabe destacar los trabajos relacionados con el sistema Fenton y Foto-Fenton. Así, Packer et al. (2003) llevaron a cabo la eliminación de cuatro productos farmacéuticos: naproxeno, diclofenaco, ácido clofíbrico e ibuprofeno mediante radicales hidroxilo. También para la amoxicilina se ha realizado un detallado estudio sobre la oxidación avanzada mediante dichos sistemas (Ay, 2010). Así mismo, Benítez et al. (2009b) estudiaron la eliminación de otros cuatro productos farmacéuticos (amoxicilina, naproxeno, metoprolol y fenacetina) mediante los sistemas Fenton y Foto-Fenton, estableciendo su secuencia de reactividades y determinando las constantes cinéticas de segundo orden.

Con respecto a dicha problemática, en España se ha detectado una gran cantidad de contaminantes emergentes en aguas en los últimos años. Así, López-Roldán et al. (2010) detectaron 28 contaminantes en el río Llobregat determinando una concentración máxima de 8042 ng L^{-1} para el fármaco metoprolol; un año más tarde, en el mismo río los contaminantes emergentes detectados ascendieron a 47 (Calderón-Preciado et al., 2011). López-Serna et al. (2013) encontraron 95 contaminantes cuando estudiaron tres aguas superficiales en el distrito de la ciudad de Barcelona. En 2014, numerosos estudios han sido publicados en relación a la presencia de contaminantes emergentes en agua; a modo de ejemplo, Köck-Schulmeyer et al. (2014) han identificado 22 pesticidas en aguas subterráneas de Cataluña; Robles-Molina et al. (2014) detectaron diversos contaminantes en varias localizaciones de la provincia de Jaén: 53 contaminantes en agua de pantano (entre los cuales se encontraba DEET en concentraciones de hasta 43.5 ng L^{-1}), 26 contaminantes en humedales y 44 en el río Guadalquivir (entre ellos DEET, en concentraciones de hasta 5.7 ng L^{-1}); Esteban et al. (2014) han encontrado 31 disruptores endocrinos al analizar aguas de los ríos Jarama y Manzanares (Madrid); y en Valencia, Carmona et al. (2014) han encontrado un total de 21 contaminantes al analizar muestras procedentes de agua potable, agua superficial y efluentes de estaciones depuradoras de aguas residuales.

En lo referente a estudios en los que se ha investigado sobre los contaminantes emergentes objeto de estudio en el presente trabajo, hay que decir que el número de publicaciones es muy escaso. Únicamente, en lo referente a la presencia de algunos de los contaminantes en diversas aguas, Simonich y colaboradores (2002) han advertido de la persistencia del salicilato de metilo en aguas residuales de Europa y Estados Unidos, para el caso del 2-fenoxietanol, en la tesis elaborada por la Doctora Patricia Bautista y presentada en el año 2008, indica la presencia de este contaminante en las aguas residuales procedentes de la industria cosmética. Mientras que, en el artículo publicado en el año 2011 por Puyol y colaboradores, se muestra que hay una eficacia mayor del 99% en la eliminación del 2-fenoxietanol en las aguas residuales procedentes de la industria cosmética mediante el uso de un reactor UASB. Para el caso del clorhidrato de amitriptilina, se detectó su presencia de este contaminante en aguas residuales y subterráneas con una concentración superior a 1 µg/L en el Bajo LLobregat (Barcelona), tal y como muestra la publicación realizada por Teijón y colaboradores en el año 2010.

2.9. OBJETO Y ALCANCE DE LA PRESENTE INVESTIGACIÓN.

De acuerdo a todo lo expuesto en los Apartados precedentes del presente Capítulo, y en vista de la escasez de estudios referentes a la eliminación de estos contaminantes emergentes en general, y de los compuestos concretos seleccionados en particular, se consideró de interés plantear el presente trabajo de investigación, con el objetivo global de aportar información acerca del comportamiento de los mismos al ser sometidos a los distintos procesos de eliminación aplicados en este estudio, tanto los de naturaleza química como física.

Además, el trabajo se enmarca dentro de una amplia línea de investigación que se viene desarrollando desde hace varios años, en el Área de Ingeniería Química de la UEx sobre la eliminación de contaminantes orgánicos en aguas naturales y residuales, mediante el empleo de tratamientos físicos, químicos y biológicos a escala de laboratorio. Entre los múltiples contaminantes ensayados en estos trabajos pueden mencionarse: colorantes textiles, fenoles y polifenoles, ácidos, pesticidas, productos farmacéuticos, etc.

Los objetivos genéricos de todos estos estudios precedentes se centraron fundamentalmente en medir los niveles de eliminación de los contaminantes estudiados que se alcanzan en los diversos tratamientos, así como en la determinación de las condiciones operativas óptimas y la evaluación de una serie de parámetros cinéticos específicos. Como se ha comentado previamente, la importancia de estas determinaciones reside en que tales parámetros permiten llevar a cabo el diseño y la optimización de los dispositivos, equipos y reactores reales que se han de utilizar posteriormente en las plantas de tratamiento de aguas.

Dentro de este contexto general se enmarca la presente Tesis Doctoral, que se ha desarrollado a través de los Proyectos de referencia CTQ2010-14823 financiado por el Ministerio de Ciencia e Innovación y titulado “Utilización de tecnologías avanzadas en aguas superficiales y tratadas para la eliminación de contaminantes resistentes a métodos convencionales”; y CTM2013-41354-R financiado por el Ministerio de Ciencia e Innovación y titulado “Tratamientos avanzados de efluentes de EDARs para la eliminación de contaminantes emergentes y su posterior reutilización”. Asimismo, el trabajo se ha enmarcado y recibido financiación parcial por parte del Gobierno Regional a través de recursos cofinanciados por el Fondo Europeo de Desarrollo Regional, y dentro de sus “Planes de Actuación para el Apoyo a Grupos de Investigación Catalogados de la Junta de Extremadura”. Concretamente tales ayudas han sido concedidas al Grupo “Tecnología del Medio Ambiente e Ingeniería Química, Grupo RNM021”, en el seno del cual se ha desarrollado el trabajo, y dentro de los Programas plurianuales 2011-2014 (referencia GR10026) y 2015-2017 (referencia GR150679).

De forma específica, en esta Tesis se decidió investigar la eliminación de varios contaminantes frecuentes pertenecientes al grupo genérico de "Contaminantes Emergentes", planteándose los siguientes tratamientos adecuados para llevar a cabo su eliminación, tanto en agua ultrapura como en aguas reales:

- Degradación de los contaminantes emergentes seleccionados mediante procesos de oxidación química, empleando los sistemas oxidantes: cloro, ozono, radiación UV, O_3/H_2O_2, UV/H_2O_2, $UV/S_2O_8^{2-}$, Fe^{2+}/H_2O_2, $UV/Fe^{2+}/H_2O_2$, Fe^{3+}/H_2O_2, $UV/Fe^{3+}/H_2O_2$ y UV/Cl_2.
- Separación de los contaminantes emergentes seleccionados del medio acuoso mediante operaciones de filtración con membranas: procesos de ultrafiltración y nanofiltración.
- Estudio de la adsorción de los compuestos objeto de estudio mediante carbón activo, en dos soportes diferentes: carbón granular y carbón en polvo.

Los objetivos generales planteados se pueden a su vez concretar en los siguientes objetivos específicos:

1) En la oxidación química individual de los contaminantes presentes en agua ultra-pura:

    a) En el tratamiento con radiación UV, establecimiento de la influencia de las variables operativas sobre la fotodegradación, obtención de las constantes de primer orden de reacción, y determinación de los rendimientos cuánticos.
    b) En el tratamiento de oxidación química con radicales hidroxilo generados mediante reactivo de Fenton, evaluación de las constantes específicas de velocidad de la reacción entre cada contaminante emergente y el radical hidroxilo.
    c) En el tratamiento con ozono, determinación de la constante aparente de velocidad de la reacción directa de cada contaminante con ozono, así como de las constantes intrínsecas de reacción de las especies disociadas y neutras.
    d) En los tratamientos de oxidación química con cloro, determinación de las constantes aparentes y las constantes intrínsecas de velocidad para las

reacciones elementales de cloro con las especies ionizadas y no ionizadas de los contaminantes seleccionados.

e) En los tratamientos de eliminación con el sistema UV/$S_2O_8^{2-}$, establecimiento de la influencia de las variables operativas sobre la degradación, obtención de las constantes de primer orden de reacción, y evaluación de las constantes de velocidad de la reacción entre cada contaminante emergente y el radical persulfato.

f) En la oxidación química de los contaminantes seleccionados con el sistema UV/Cl_2, estudio cinético y establecimiento de la influencia de las variables operativas sobre la eliminación de estos contaminantes con este sistema oxidante. Asimismo, comparación de la eficacia de diversos sistemas fotoquímicos empleados: radiación UV, UV/H_2O_2, UV/Cl_2 y UV/$S_2O_8^{2-}$, en base a sus constantes de reacción.

2) En la oxidación química simultánea de los contaminantes emergentes disueltos en aguas reales, habiéndose seleccionado para tal fin un agua superficial de pantano y dos efluentes secundarios de EDARs:

   a) Realización de un estudio cinético en el proceso de fotodegradación mediante radiación UV simple y desarrollo de un modelo para la predicción de la eliminación de los compuestos en sistemas reales. Además, comparación de la eficacia de todos los sistemas oxidantes ensayados en tales aguas: ozono, radiación UV, UV/H_2O_2, Fe^{2+}/H_2O_2, UV/Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2 y UV/Fe^{3+}/H_2O_2, basándose en los valores de las constantes aparentes de reacción de primer orden.
   b) Comparación entre los procesos de cloración y ozonización de los ECs, basándose en los grados de eliminación alcanzados.
   c) En la oxidación simultánea de los ECs mediante los sistemas combinados UV/$S_2O_8^{2-}$ y UV/Cl_2, comparación de la eficacia de eliminación basándose asimismo en sus constantes de reacción de primer orden.

3) En la eliminación de contaminantes emergentes mediante procesos de filtración mediante membranas (UF y NF), tanto en agua ultra-pura como en aguas reales:

a) Determinación de flujos de permeado y coeficientes de retención de contaminantes, y establecimiento de la influencia del tamaño de poro y de la naturaleza de las membranas utilizadas sobre ambos parámetros.

b) Análisis y evaluación de las distintas resistencias presentes en tales procesos de filtración y proposición de los principales mecanismos de ensuciamiento.

c) Determinación del efecto de la materia orgánica presente en las matrices acuosas sobre los parámetros anteriores.

4) En los tratamientos de adsorción con carbón activo mediante PAC y GAC:
   a) Determinación de las isotermas de adsorción de los ECs seleccionados sobre ambos soportes.
   b) Estudio de la influencia de las variables operativas en tales procesos de adsorción.
   c) Estudio cinético de los procesos de adsorción de cada contaminante seleccionado.
   d) Eficacia de la eliminación simultánea de los ECs cuando están presentes en las aguas reales seleccionadas y análisis de la influencia de la materia orgánica presente sobre la adsorción de los contaminantes.

2.10. BIBLIOGRAFÍA

Acero, J.L.; von Gunten, U. Influence of carbonate on the ozone/hydrogen peroxide based advanced oxidation process for drinking water treatment. Ozone Sci. Eng. **2000**, 22, 305-328.

Al-Amoudi, A.; Lowitt, R.W. Fouling strategies and the cleaning system of NF membranes factors affecting cleaning efficiency J. Membr. Sci. **2007**, 303, 4-28.

Álvarez J. Adsorción de compuestos fenólicos en fase líquida sobre carbón activado. Equilibrio de mezclas multicomponentes. Tesis Doctoral, Universidad Complutense de Madrid, 1989.

Amigó, J.; Buhigas, G.; Ortega, E. Caracterización de la degradación de Sulfametazina mediante Foto-Fenton (POA's). Departamento de Ingeniería Química. Universidad Politécnica de Catalunya (**2008**).

Andreozzi, R.; Caprio, V.; Insola, A.; Marotta, R. Advanced Oxidation Processes (AOP) for water purification and recovery. Catal. Today **1999**, 53, 51-59.

Andreozzi R.; Caprio V.; Marotta R y Radovnikovic A. Ozonation and H_2O_2/UV treatment of clofibric acid in water: a kinetic investigation. J. Hazard. Mater. **2003**, B103, p233-246.

Ay F. y Kargi F. Advanced oxidation of Amoxicillin by Fenton's reagent treatment. J. Hazard. Mater. 2010, 179, 622-627.

Bagnall, J.P.; Evans, S.E.; Wort, M.T.; Lubben, A.T.; Kasprzyk-Hordern, B. Using chiral liquid chromatography quadrupole time-of-flight mass spectrometry for the analysis of pharmaceuticals and illicit drugs in surface and wastewater at the enantiomeric level. J. Chromatogr. A **2012**, 1249, 115-129.

Baker, R. Membrane technology and applications, 2nd edition. Ed. John Wiley &Sons. 2004.

Bansal. R.C; Goyal, M. Activated Carbon Adsorption. United States of America, 2005.

Barb, W.G.; Baxendale, J.H.; George, P.; Hargrave, K.R. Reactions of ferrous and ferric ions with hydrogen peroxide. Nature **1949**, 163, 692-694.

Barrow, G. Química Física, tercera edición. España: Editorial Reverté. 1975.

Bautista Carmona P. Tratamiento de aguas residuales de la industria cosmética mediante el proceso Fenton y con el sistema Fe/γ-Al_2O_3/H_2O_2. Tesis Doctoral. Sección Dept. Ing. Química, Universidad Autónoma de Madrid, 2008.

Baxendale, J.H.; Wilson, J.A. Photolysis of hydrogen peroxide at high light intensities. Trans. Faraday. Soc. **1957**, 53, 344-356.

Bean E.L.; Campbell S.J.; Anspach F.R. Zeta Potential measurements in the control of coagulation chemical doses. Journal of American Water Works Association, 1964, 56, 214-224.

Belfroid A.C.; Van Der Horst A.; Vethaak A.D.; Schäfer A.J.; Rijs G.B.J.; Wegener J. y Cofino W.P. Analysis and occurrence of estrogenic hormones and their glucuronides in surface water and waste water in The Netherlands. Sci. Total Environ. 1999, 225, 101-108.

Beltrán F.J.; Pocostales P.; Álvarez P.M. y López-Piñero F. Catalyts to improve the abatement of sulfamethoxazole and the resulting organic carbon in water during ozonation. Applied Catalysis B: Environmental 2009. 92, 262-270.

Benitez, F.J.; Real, F.J.; Acero, J.L.; Leal, A.I.; Garcia, C. Gallic acid degradation in aqueous solutions by UV/H_2O_2 treatment, Fenton's reagent and the photo-Fenton system. J. Hazard. Mater. **2005**, 126, 31-39.

Benitez F.J.; Real F.J.; Acero J.L. y Roldán G. Removal of selected pharmaceuticals in waters by photochemical processes. J. Chem. Technol. Biotechnol **2009a**, 84, 1186–1195.

Benitez F.J.; Real F.J.; Acero J.L. y Roldán G. Ozonation of pharmaceutical compounds: Rate constants and elimination in various water matrices. Chemosphere **2009b**, 77, 53-59.

Benítez, F.J.; Acero, J.L.; Real, F.J.; Roldán, G.; Rodríguez, E. Modeling the photodegradation of emerging contaminants in waters by UV radiation and UV/H2O2 system. J. Environ. Sci. Health A. 2013, 48, 120-128.

Boyd G.R.; Reemtsma H.; Grimm D.A. y Miltra S. Pharmaceuticals and personal care products (PPCPs) in surface and treated waters of Louisiana, USA and Ontario, Canada. Sci. Total Environ. 2003, 311, 135-149.

Calderón-Preciado, D.; Matamoros, V.; Bayona, J.M. Occurrence and potential crop uptake of emerging contaminants and related compounds in an agricultural irrigation network. Sci. Total Environ. **2011**, 412, 14-19.

Carballa M.; Omil F. y Lema J.M. Removal of cosmetic ingredients and pharmaceuticals in sewage primary treatmentcarlin. Water Res. 2005, 39, 4790-4796.

Carlin V.; Minero C.; Pelizzetti E. Effect of chlorine on photocatalytic degradation of organic contaminants, Environ. Technol. **1990**; 11, 919-926 .

Carmona, E.; Andreu, V.; Picó, Y. Occurrence of acidic pharmaceuticals and personal care products in Turia River Basin: From waste to drinking water. Sci. Total Environ. **2014**, 484, 53-63.

Celano R.; Piccinelli.; Campone L.; Rastrelli L. Ultra-preconcetration and determination of selected personal care products in different water matrices by solid-phase extraction combined with dispersive liquid-liquid microextraction prior to ultra high pressure liquid chromatography tandem mass spectrometry amalysis. J. Chromatogr. A. **2014**, 1355, 26-35.

Chien S.H.; Clayton W.R. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. Soil Science Society of America Journal, **1980**, 44, 265-268.

Costa C.; Calleja G.; Marijuán L. Comparative adsorption of phenol, p-nitrophenol and hydroxybenzoic acid on activated carbon. Adsorption Science and Technology, **1988**, 5, 213.

Di Bernardo, L.; Dantas, A.D.B. Métodos e técnicas de tratamento de água. Ed. São Carlos: Rima Editora. Vol. 2, **2005**.

Doll T.E. y Frimmel F.H. Kinetic study of photocatalytic degradation of carbamazepine, clofibric acid, iomeprol and iopromide assisted by different TiO_2 materials-determination of intermediates and reaction pathways. Water Res. **2004**, 38, 955-964.

Drewes J.E.; Fox P. y Jekel M. Occurrence of iodinated x-ray contrast media in domestic effluents and their fate during indirect potable reuse. J. Environ. Sci. Health, Part A 2001, 36, 1633-1645.

Esplugas, S.; Ibarz, A.; Vicente, M. Influence of lamp position on the performance of the annular photoreactor. Chem. Eng. J. **1983**, 27, 107-111.

Esplugas S.; Bila D.M.; Krause L.G.T. y Dezotti M. Ozonation and advanced oxidation Technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. J. Hazard. Mater. **2007**, 149, 631-642.

Esteban, S.; Gorga, M.; Petrovic, M.; González-Alonso, S.; Barceló, D.; Valcárcel, Y. Analysis and occurrence of endocrine-disrupting compounds and estrogenic activity in the surface waters of Central Spain. Sci. Total Environ. **2014**, 466, 939-951.

Estevinho, B.N.; Martins, I.; Ratola, N.; Alves, A.; Santos, L. Removal of 2,4.dichlorophenol and pentachlorophenol from waters by sorption using coal fly ash froma Portuguese thermal power plant. J. Hazard. Mater. **2007**, 143, 533-540.

Fent K.; Weston A.A.; Caminada D. Ecotoxicology of Human Pharmaceuticals. Aquatic Toxicology 2006, 76, 122-159.

Fenton, H.J.H. Oxidation of tartaric acid in presence of iron. J. Chem. Soc. **1894**, 65, 899-910.

Fritz W.; Schlünder E.U. Competitive adsorption of two dissolved organics onto activated carbon-I. Chemical Engineering Science, 1981, 3636, 721-723.

García-Vaquero, N.; Lee E., Jiménez Castañeda, R.; Cho J., López-Ramírez, J.A. Comparison of drinking water pollutant removal using a nanofiltration pilot plant powered by renewable energy and a conventional treatment facility. Desalination **2014**, 347, 94-10.

Glaze, W.H.; Peyton, G.R.; Lin, S.; Huang, R.Y.; Burleson, K. Destruction of pollutants in water with ozone in combination with ultraviolet radiation. 2. Natural trihalomethane precursors. Environ. Sci. Technol. **1982**, 16, 454-458..

Guadayol, J.M.; Caixach, J.; Ribé, J.; Cabanas, J.; Rivera. Extraction, Separation and Identification of Volatile Organic Compounds from Paprika Oleoresin (Spanish Type). Journal Agriculture Food Chemistry, **1997**, 45 (5), 1868-1872.

Haber, F.; Weiss, J. The catalytic decomposition of hydrogen peroxide by iron salts. R. Soc. London Ser. **1934**, 147, 332-351.

He, X.; de la Cruz, A.A.; Dionysiou, D.D. Destruction of cyanobacterial toxin cylindrospermopsin by hydroxyl radicals and sulfate radicals using UV-254 nm activation of hydrogen peroxide, persulfate and peroxymonosulfate. J. Photochem. Photobiol. A **2013**, 251, 160-166.

Helbling, D.E.; Hollender, J.; Kohler, H.P.E.; Singer, H.; Fenner, K. High-throughput identification of microbial transformation products of organic micropollutants. Environ. Sci. Technol. **2010**, 44, 6621-6627.

Hirsch R.; Ternes T.; Haberer K. y Kratz K.L. Occurrence of antibiotics in the aquatic environment. Sci. Total Environ. 1999, 225, 109-118.

Homem, V.; Santos, L. Degradation and removal methods of antibiotics form aqueous matrices. A review. J. Environ. Manag. **2011**, 92, 2304-2347.

Huber M.; Canonica M.; Park G.Y y von Gunten U. Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. Environ. Sci. Technol. **2003**, 7(5), 1016-1024.

Huber M.M.; Gobel A.; Joss A.; Hermann N.; Loffler D.; McArdell C.S.; Ried A.; Siegrist H.; Ternes T.A y von Gunten U. Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study. Environ. Sci. Technol. **2005**, 39, 4290-4299.

Ikehata K. y Gamal El-Din M. Aqueous pesticide degradation by hydrogen peroxide/ultraviolet irradiation and Fenton-Type Advanced Oxidation Processes: A Review. J. Environ. Eng. Sci. **2006**, 5 (2), 81-135.

Ikehata K.; Naimeh J.N. y Mohamed G.E. Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: A review; Ozone Sci. Eng. **2006**, 28, 353-414.

Jacob, S.M.; Dranoff, J.S. Radial scale-up of perfectly mixed photochemical reactors. Chem. Eng. Prog. Symp. Ser. **1966**, 62, 47-55.

Jacob, S.M.; Dranoff, J.S. Design and analysis of perfectly mixed photochemical reactors. Chem. Eng. Prog. Sym. Ser. **1968**, 64, 54-63.

Jacob, S.M.; Dranoff, J.S. Light intensity profiles in a perfectly mixed photoreactor. AIChE J. **1970**, 16, 359-363.

Jin J.; El-Din MG.; Bolton JR. Assesment of the UV/chlorine process as an advanced oxidation process, Water Res. **2011**; 45, 1890-1896.

Jjemba P.K. Excretion and Ecotoxicity of Pharmaceuticals and Personal Care Products in the Environment. Ecotoxicol. Environ. Safety 2006, 63, 113-159.

Jones O.A.; Lester J.N. y Voulvoulis N. Pharmaceuticals: a threat to drinking water?. Trends Biotechnol. **2005**, 23, 163-167.

Kasprzyk-Hordern, B.; Dinsdale, R.M.; Guwy, A.J. The removal of pharmaceuticals, personal cares products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters. Water Res. **2009**, 43, 363-380.

Kent K.; Weston A.A. y Caminada D. Review ecotoxicology of human pharmaceuticals. Aquatic Toxicology. **2006**, 76, 122-159.

Klavarioti M.; Mantzavinos D. y Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. Environ. Internat. 2009, 35, 402-407.

Köck-Schulmeyer, M.; Ginebreda, A.; Postigo, C.; Garrido, T.; Fraile, J.; López de Alda, M.; Barceló, D. “Four-year advanced monitoring program of polar pesticides in groundwater of Catalonia (NE-Spain)”. Sci. Total Environ. **2014**, 470, 1087-1098.

Kolpin D.W.; Furlong E.T.; Meyer M.T.; Thurman E.M.; Zaugg S.D.; Barber L.B. y Buxton H.T. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. Environ. Sci. Technol. 2002, 36 (6), 1202-1211.

Kümmener K. Significance of Antibiotics in the Environment. J. Antimicrobial Chemotherapy 2003, 52, 5-7.

Legrini, O.; Oliveros, E.; Braun, A.M. Photochemical processes for water treatment. Chem. Rev. **1993**, 93, 671-698.

Lemaire, J.; Campbell, I.; Hulpke, H.; Guth, J.A.; Merz, W.; Philip, J.; Von Waldow, C. An assessment of test methods for photodegradation of chemicals in the environment. Chemosphere **1982**, 11, 119-164.

Lin W.C.; Chen H.C. y Ding W.H. “Determination of pharmaceuticals residues in waters by solid-phase extraction and large-volume on-line derivatization with gas chromatography-mass spectrometry”. J. Chromatography A. **2005**, 1065, 279-285.

López-Roldán, R.; López de Alda, M.; Gros, M.; Petrovic, M.; Martín-Alonso, J.; Barceló, D. “Advanced monitoring of pharmaceuticals and estrogens in the Llobregat River basin (Spain) by liquid chromatography–triple quadrupole-tandem mass spectrometry in combination with ultra-performance liquid chromatography-time of flight-mass spectrometry”. Chemosphere **2010**, 80, 1337-1344.

López-Serna, R.; Jurado, A.; Vázquez-Suñé, E.; Carrera, J.; Petrović, M.; Barceló, D. “Occurrence of 95 pharmaceuticals and transformation products in urban groundwaters underlying the metropolis of Barcelona”. Environ. Pollut. **2013**, 174, 305-315.

Lundelius E.F. Adsorption and solubility. Kolloid Zeitschrift, **1920**, 26, 145-151.

Maletz, S.; Floehr, T.; Beier, S.; Klumper, C.; Brouwer, A.; Behnisch, P.; Higley, E.; Giesy, J.P.; Hecker, M.; Gebhardt, L.V.; Pinnekamp, J.; Hollert, H. In vitro characterization of the effectiveness of enhanced sewage treatment processes to eliminate endocrine activity of hospital effluents. Water Res. **2013**, 47, 1545-1557.

Matsui, Y. Branched pore kinetic model analysis of geosmin adsorption on super-powdered activated carbon. Water Research, **2009**, 43(12), 3095-3103.

Mutamim, N.S.A.; Noor, Z.Z.; Hassan, M.A.A.; Olsson G. Application of membrane bioreactor technology in treating high strength industrial wastewater: a performance review. Desalination **2012**. 305, 1-11.

Nakada N.; Shinohara H.; Murata A.; Kiri K.; Managaki S.; Sato N. y Takada H. "Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant". Water Res. **2007**, 41, 4373-4382.

OECD Envirommental Outlock 2050. The consequences of Inaction. OECD Publishing, Paris, http://dx.doi.org/10.1787/9789264122246-en. 2012a.

Oscik J. Adsorption. Ed. Ellis Horqood Limited, Chichester, **1983**.

Packer J.L.; Werner J.J.; Latch D.E.; McNeill K. y Arnold W.A. Photochemical fate of pharmaceuticals in the environmental: naproxen, diclofenac, clofibric acid, and ibuprofen. Aquat. Sci. 2003, 65, 342-351.

Pal, A.; He, Y.; Jekel, M.; Reinhard, M.; Yew-Hoong Gin, K. Emerging contaminants of public health significance as water quality indicator compounds in the urban water cycle. Environ. Int. **2014**, 71, 46-62.

Park, H.; Vecitis, C.; Hoffmann, M. R. Electrochemical Water Splitting Coupled with Organic Compound Oxidation: The Role of Active Chlorine Species,Journal of Physical Chemistry C, 2009, 113, 7935-7945.

Parfitt G.D.; Rochester C.H. Adsorption from solution in the solid liquid interface. Ed. Academic Press, London, **1983**.

Petrovic, M.; Gonzales, S.; Barcelo, D. Analysis and removal of emerging contaminants in wastewater and drinking water. Trends Anal. Chem. **2003**, 22, 685-696.

Pignatello, J.J. Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environ. Sci. Technol. **1992**, 26, 944-951.

Pignatello, J.J.; Oliveros, E.; Mackay, A. Advanced Oxidation Processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Environ. Sci. Techol. **2006,** 35, 1-84**.**

Pocostales J.P.; Álvarez P.M. y Beltrán F.J. "Kinetic modeling of powdered activated carbon ozonation of sulfamethoxazole in water". Chem. Eng. J. 2010, 164, 70-76.

Puyol D.; Monsalvo V.M.; Mohedano A.F.; Sanz J.L. y Rodríguez J.J. Cosmetic wastewater treatment by upflow anaerobic sludge blanket reactor. J. Hazard. Mater. 2011, 185, 1059-1065.

Real F.J.; Benitez F.J.; Acero J.L.; Roldan G. and Casas F. Elimination of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in ultrapure water and secondary effluents by photolytic and radicalary pathways. Ind. Eng. Chem. Res. **2012**, 51, 16209-16215.

Robles-Molina, J.; Gilbert-López, B.; García-Reyes, J.F.; Molina-Díaz, A. Monitoring of selected priority and emerging contaminants in the Guadalquivir River and other related surface waters in the province of Jaén, South East Spain. Sci. Total Environ. **2014**, 479, 247-257.

Rodríguez, A.; Letón, P.; Rosal, R.; Dorado, M.; Villar, S.; Sanz, J.M. Tratamientos avanzados de aguas residuales industriales. Informe de Vigilancia Ambiental. Universidad de Alcalá. Círculo de Innovación en Tecnologías Medioambientales y Energía (CITME): 1-136. **2006**.

Rodríguez, F.J. Potabilización del agua e influencia del tratamiento de ozonación. Ed. Díaz de Santos, S.A. **2003**.

Rossner, A.; Snyder, S.; Knappe, D. Removal of emerging contaminants of concern by alternative adsorbents. Water Res. **2009**, 43, 3787-3796.

Rosal R.; Rodriguez A.; Perdigón-Melón J.A.; Mezcua M.; Hernando M.D.; Letón P.; García-Calvo E.; Agüera A. y Fernández-Alba A.R. Removal of pharmaceuticals and kinetics of mineralization by O_3/H_2O_2 in a biotreated municipal wastewater”. Water Research. **2009**, 42, 3719-3728.

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

Shemer H.; Kunukcu K. y Linden K.G. Degradation of the pharmaceutical Metronidazole via UV, Fenton and photo-Fenton processes. Chemosphere. 2006, 269-276.

Simonich S.L.; Federle T.W.; Eckhoff W.S.; Rottiers A.; Webb S.; Sabaliunas D. y de Wolf W. Removal of fragrance materials during U.s. and European wastewater treatment. Environ. Sci. Technol. 2002, 36, 2839-2847.

Snyder, S.A.; Adham, S.; Redding, A.M.; Cannon, F.S.; De Carolis, J.; Oppenheimer, J.; Wert, E.C.; Yoon, Y. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. Desalination **2007a**, 202, 8156-181.

Snyder, S.A.; Wert, E.C.; Lei, H.; Westerhoff, P.; Yoon, Y. Removal of EDCs and pharmaceuticals in drinking and reuse treatment processes. American Water Works Association Research Foundation. Report 91188. **2007b.**

Snyder, S.A.; Wert, E.C.; Rexing, D.J.; Zegers, R.E.; Drury, D.D. Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. Ozone Sci. Eng. **2006**, 28, 445-460.

Spadoni, G.; Stramigioli, C.; Santarelli, F. Rigorous and simplified approach to the modelling of continuous photoreactors. Chem. Eng. Sci. **1980**, 35, 925-931.

Stackelberg P.E.; Furlong E.T.; Meyer M.T.; Zaugg S.D.; Henderson A.K. y Reissman D.B. Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water treatment plant. Sci. Total Environ. **2004**, 329, 99-113.

Stackelberg, P.E.; Gibs, J.; Furlong, E.T.; Meyer, M.T.; Zaugg, S.D.; Lippincot, R.L. Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. Sci. Total Environ. **2007**, 377, 255-272.

Staehelin, J.; Hoigné, J. Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. Environ. Sci. Technol. **1982**, 16, 676-681.

Stuart, M.; Lapworth, D.; Crane, E.; Hart, A. Review of risk from potential emerging contaminants in UK groundwater. Sci. Total Environ. **2012**, 416, 1-21.

Teijon G.; Candela L.; Cabeza Y. y Yamoh K. Emerging contaminants in treated wastewater and groundwater alter a three years monitoring period. The Baux Llobregat (Barcelona, Spain). The 12th Internat. Confer. Environ. Sci. Technol. 2011.

Ternes T.A. Occurrence of drugs in German sewage. Treatment plants and rivers. Water Research. 1998, 32, 3245-3260.

Ternes T.A.; Stumpf M.; Mueller J.; Haberer K.; WilkenR.D. y Servos M. Behavior and occurrence of estrogens in municipal sewage treatment plants-I. Investigations in Germany, Canada and Brazil. Sci. Total Environ. 1999, 225, 81-90.

Ternes T.A.; Meisenheimer M.; McDowell D.; Sacher F.; Brauch H.J.; Haist-Culde B.; Preuss G.; Wilme U. y Zulei-Seibert N. Removal of pharmaceuticals during drinking water treatment. Environ. Sci. Technol. **2002**, 36, 3855-3863.

Ternes T.A.; Stuber J.; Herrmann N.; McDowell D.; Ried A.; Kampmann M. y Teiser B. “Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? “. Water Res. 2003, 1976-1982.

Thorsen, T. Concentration polarisation by natural organic matter (NOM) in NF and UF. J. Membr. Sci. **2004**, 233, 79-91.

Urtiaga, A.M.; Ibáñez, R.; Ortiz, I.; Acero, J.L.; Teva, F.; Benítez, F.J. Tecnología de membranas: ultrafiltración, nanofiltración, ósmosis inversa. Tecnologías de tratamiento de agua para su reutilización. Programa Consolider Tragua. Cap. 7. **2010**.

USEPA Office of Pesticide Programs, Health Effects Division, Science Information Management Branch: Chemicals Evaluated for Carcinogenic Potential. **2006**.

USEPA., Office of Water, Guidance Manual. Alternative Disinfectantes and Oxidants 815-R-99-014. Cap. 8, 1-25. **1999**.

Vallejo, M.; Fresnedo San Román, M.; Ortiz, I.; Irabien, A. Overview of the PCDD/Fs degradation potential and formation risk in the application of advanced oxidation processes (AOPs) to wastewater treatment. Chemosphere **2015**, 118, 44-56.

van der Bruggen, B.; Everaert, K.; Wilms, D.; Vandecasteele, C. Application of nanofiltration for removal of pesticides, nitrate and hardness from ground water: rejection properties and economic evaluation. J. Membr. Sci. **2001**, 193, 239-248.

Vanneuville W.; Werner B.; Uhel R. Water resources in Europe in the context of vulnerability. EEA Report 11/**2012**.

von Sonntag, C.; Schuchmann, H.P. The Chemistry of free radicals: Peroxyl radicals in aqueous solutions. Ed. Z.B. Alfassi. **1997**.

Vinod V.P.; Anirudhan T. S. Adsorption behaviour of basic dyes on the humic acid immobilized pillared clay. Water Air and Soil Pollution, **2003**, 150, 193-217.

Walker P.L.; J. Shyam J.; Verma K.; Rivera-Utrilla J.; Davis A. Densities, porosities and surface areas of coal macerals as measured by their interaction with gases, vapours and liquids. Fuel, **1988**, 67, 1615-1623.

West W.; Carroll B.H.; Whitcomb D.H. The adsorption of sensitizing dyes in photographic emulsions. Journal of Physical Chemistry, **1952**, 56, 1054-1067.

Xia K.; Bhandari A.; Das K. y Pillar G. Ocurrence and fate of pharmaceuticals and personal care products (PPCPs) in biosolids. J. Environ. Qual. **2005**, 34, 91-104.

Yonge D.R.; Keinath T. M. The effects of non-ideal competition on multi-component adsorption equilibria. Journal of Water Pollution Control Federation, **1986**, 58, 77-81.

3. RESULTADOS Y DISCUSIÓN

3. RESULTADOS Y DISCUSIÓN.

3.1. RESUMEN.

En este Apartado se resumen los principales resultados obtenidos en el trabajo realizado en esta Tesis Doctoral, el cual tiene como objetivo global el estudio de la eliminación de una selección de tres contaminantes emergentes ("ECs", por sus siglas en inglés; clorhidrato de amitriptilina (AH), salicilato de metilo (MS) y 2-fenoxietanol (PE)), elegidos como modelos de dicho grupo, mediante la aplicación de procesos químicos y físicos, algunos de ellos tradicionalmente empleados en el tratamiento de aguas, tanto residuales como superficiales. En los restantes apartados del presente Capítulo se exponen de forma detallada tales resultados y la consiguiente discusión de los mismos mediante la transcripción literal de las publicaciones científicas a las que han dado lugar.

Entre los procesos químicos desarrollados cabe destacar el empleo de distintos agentes oxidantes utilizados de forma individual, así como diversas combinaciones de los mismos en lo que constituyen los Procesos de Oxidación Avanzada (POA). Por su parte, entre los procedimientos físicos se encuentra la adsorción sobre carbón activo, tanto en polvo (PAC) como granular (GAC), y la filtración mediante membranas. A continuación se describen brevemente los diversos procesos de tratamientos aplicados y los principales resultados obtenidos.

En una fase inicial de los tratamientos químicos, el primer agente empleado fue la radiación UVC, la cual promueve la fotólisis de un gran número de compuestos orgánicos. Esta radiación es considerada como un proceso muy eficaz en la eliminación de contaminantes y asimismo se emplea como desinfectante en el tratamiento de aguas. Este estudio ha dado lugar a la publicación que se detalla en el Apartado 3.2 de la presente Memoria. En el mismo, se han realizado experimentos de degradación individual de los contaminantes seleccionados mediante radiación UVC (254 nm) en agua ultrapura a diferentes pHs (3, 5, 7 , 9 y 11) y temperaturas (10ºC, 20ºC y 40ºC), utilizando una lámpara de vapor de mercurio a baja presión, en ausencia y presencia de terc-butanol (t-BuOH). La aplicación del Modelo de Fuente Lineal de Emisión Esférica en los ensayos realizados en presencia de t-BuOH (agente que garantiza que la única vía de degradación significativa es la fotólisis directa) permitió la determinación de los valores de los rendimientos cuánticos para cada compuesto a 20°C en el intervalo de pH 3-11, obteniéndose para tales rendimientos cuánticos los siguientes rangos de valores: (8.0-29.1)x10^{-3} mol E^{-1} para clorhidrato de amitripitilina, (1.9-32.9)x10^{-3} mol E^{-1} para salicilato de metilo y (8.8-10.5)x10^{-3} mol E^{-1} para 2-fenoxietanol. Estos valores de rendimientos cuánticos permiten deducir el siguiente orden de reactividad: AH > PE > MS.

Además de los mencionados rendimientos cuánticos, en estos experimentos de degradación fotolítica se determinaron también las constantes de velocidad de primer orden, así como los niveles de degradación alcanzados para cada uno de los contaminantes emergentes en presencia y ausencia de t-BuOH a diferentes pHs (3, 5, 7, 9 y 11). Así, en presencia de este secuestrador de radicales, el orden de reactividad de los contaminantes coincide con el orden de los rendimientos cuánticos. La comparación de los valores de estas constantes de reacción para los experimentos realizados en presencia y ausencia del t-BuOH ponen de manifiesto que la principal vía de degradación de los contaminantes seleccionados mediante radiación UV es la vía radicalaria. También se observa que tanto la variación de pH como de temperatura ejerce un efecto positivo en el proceso de degradación; y que la adición de diferentes concentraciones iniciales de H_2O_2 ejerce asimismo una influencia positiva en la eliminación de los contaminantes al favorecer aún más la degradación por vía radicalaria, debido a la presencia adicional de radicales hidroxilo procedentes de la fotólisis del H_2O_2.

En la siguiente etapa se llevó a cabo el estudio de la degradación individual de los ECs seleccionados mediante el uso de los POA basados en el sistema Fe/H_2O_2, concretamente utilizando el reactivo de Fenton (Fe^{2+}/H_2O_2), Fenton-Like (Fe^{3+}/H_2O_2) y el sistema foto-Fenton (UV/Fe^{2+}/H_2O_2). Los resultados obtenidos están recogidos de forma más detallada en el Apartado 3.2 del presente Capítulo y ponen de manifiesto diversos aspectos tales como: el efecto positivo que ejerce tanto la concentración inicial de Fe^{2+} como de H_2O_2; que el sistema foto-Fenton es más efectivo, como era de esperar, debido a la generación adicional de radicales hidroxilo y a la fotodegradación directa de los compuestos orgánicos; y que el sistema Fenton-Like es el menos efectivo en la eliminación de estos contaminantes, de acuerdo con los valores de conversión alcanzados a 1.5 minutos de reacción.

Por otro lado, se llevaron a cabo experimentos con reactivo de Fenton con el objeto de determinar la constante de velocidad de segundo orden para la reacción directa entre cada uno de los ECs seleccionados y los radicales hidroxilo (k_{OH}). Para ello se utilizó un método competitivo, empleando ácido paraclorobenzoico (p-CBA) como compuesto de referencia, a pH 3 y con dos concentraciones iniciales de H_2O_2 diferentes. Este método proporcionó los valores para la constante de reacción directa de los ECs con los radicales OH, los cuales fueron: $(10.3\pm0.1)x10^{9}$ $M^{-1}S^{-1}$ para AH, $(7.1\pm0.1)x10^{9}$ M^{-1} s^{-1} para MS y $(4.3\pm0.1)x10^{9}$ M^{-1} s^{-1} para PE.

Para finalizar el estudio de la aplicación de UVC se llevaron a cabo experimentos con los compuestos modelo presentes en tres aguas reales diferentes: un agua superficial de pantano, y dos efluentes secundarios procedentes de las EDAR de La Albuera y de Badajoz, con el objetivo de evaluar el efecto de la presencia de materia orgánica en tales matrices acuosas sobre los niveles de degradación. Los resultados obtenidos están asimismo detallados en el Apartado 3.2, y reflejan que en concordancia con sus contenidos en materia orgánica, se alcanzó una eliminación similar en las dos primeras matrices acuosas (agua de pantano y efluente de la EDAR La Albuera), y se consiguió una menor degradación al emplear el efluente secundario de la EDAR de Badajoz.

A partir de tales resultados se realizó una propuesta de un modelo cinético que permitía predecir la eliminación de los contaminantes emergentes en cualquiera de las matrices acuosas, y la aplicación del mismo proporcionó resultados que coinciden satisfactoriamente con los valores experimentales obtenidos. Estos resultados permiten concluir que en aguas reales el proceso de fotodegradación de AH presenta una mayor reactividad, seguido de MS y PE. La diferencia en la reactividad entre los dos últimos ECs es más evidente en los sistemas UV/H_2O_2, indicando una mayor reactividad de MS hacia los radicales hidroxilo.

La siguiente etapa del presente trabajo se centró en el estudio de la degradación de los tres ECs seleccionados en diferentes matrices acuosas mediante dos nuevos agentes oxidantes, concretamente cloro y ozono, que son agentes comunes en el tratamiento de aguas, y con el objetivo inicial del establecimiento de la cinética de la degradación de los ECs con cada uno de estos sistemas oxidantes por separado.

La cloración es un tratamiento ampliamente aplicado en la desinfección de agua potable y de efluentes secundarios procedentes de EDAR. Los resultados obtenidos se encuentran ampliamente detallados en el Apartado 3.3. En primer lugar, se llevaron a cabo ensayos de reacción entre cloro y cada contaminante individual en el intervalo de pH 3-10, y en el rango de temperaturas entre 10 y 40ºC, con dichas sustancias disueltas en agua ultrapura. Se determinaron las constantes aparentes de velocidad de reacción de segundo orden, constantes que ponen de manifiesto el efecto positivo que ejerce la concentración inicial de cloro y la temperatura. Estos valores de constantes aparentes se encuentran detallados en el mencionado Apartado 3.3 del presente Capitulo, y permiten establecer el siguiente orden de reactividad: clorhidrato de AH > MS > PE, orden que coincide con el obtenido previamente para la reacción entre los radicales OH y los ECs.

Adicionalmente a estas constantes aparentes, se evaluaron las constantes intrínsecas de velocidad (k_1, k_2 y k_c) para las reacciones específicas entre HOCl y las especies iónicas de cada contaminante. Para ello se propuso un modelo cinético que tenía en cuenta tanto a dichas constantes aparentes como los equilibrios de disociación de cada contaminante y de las especies cloradas. Tras aplicar dicho procedimiento, se deduce que los valores de k_2 obtenidos son sensiblemente mayores que los de k_1, lo que indica un aumento en la velocidad de reacción con HOCl de las especies disociadas de los contaminantes seleccionados. Además, los valores más elevados de k_c con respecto a k_1 para AH y PE permiten explicar el aumento de la constante de velocidad aparente a pH 3-4, donde se mejora la reacción catalizada por ácido. Por el contrario, este efecto no se muestra para MS que presenta un valor muy inferior de k_c. La bondad del modelo propuesto quedó corroborada al encontrarse una satisfactoria concordancia entre los valores experimentales de dichas constantes aparentes y los valores teóricos calculados a partir de las constantes intrínsecas para cada especie.

Por su parte, el ozono es un agente oxidante reconocido por su alta eficacia para la eliminación de numerosos microcontaminantes orgánicos, motivo por el cual también fue seleccionado en este trabajo. Por ello, se llevó a cabo un estudio de ozonización de los contaminantes seleccionados que dio lugar a la publicación conjunta con el estudio de cloración que se muestra en el Apartado 3.3 ya referido.

En primer lugar se realizó el estudio de la ozonización individual de cada contaminante en agua ultrapura y en presencia de t-BuOH, con el objetivo de determinar las constantes cinéticas aparentes de reacción directa entre el ozono y cada compuesto para cada pH. Y después, se determinaron las constantes de velocidad específicas de las especies disociada y no disociada de aquellos compuestos que presentan constante de disociación en el rango de pH estudiado (valores que se detallan en el Apartado 3.3). A partir de los resultados obtenidos, se puede observar una influencia positiva del pH sobre la eliminación de clorhidrato de AH y de MS, ya que ambos presentan constante de disociación ácida. Por último, no hay influencia del pH sobre la eliminación de PE, y por ello se propone un valor medio de 150 ± 5 $M^{-1}s^{-1}$, válido para el rango de pH de 3-9. Por lo tanto, teniendo en cuenta los valores de las constantes de velocidad de cada EC, se obtiene el siguiente orden de reactividad a pH 7: MS > AH > PE, aunque cabe señalar que AH fue el compuesto más reactivo en el caso concreto de pH 3. La comparación entre los valores de las constantes intrínsecas de velocidad obtenidos para la cloración y las obtenidas para la ozonización, pone de manifiesto que las reacciones de ozonización son alrededor de tres órdenes de magnitud superiores a las de cloración, lo que sugiere una mayor eficacia de este proceso de ozonización.

Para completar el estudio comparativo de ambos procesos de oxidación (cloración y ozonización), se llevaron a cabo varios experimentos de oxidación simultánea de los contaminantes en las aguas reales ya descritas en proceso de fotooxidación. Los agentes oxidantes utilizados fueron ácido hipocloroso, ozono y la combinación de éste último con peróxido de hidrógeno. La secuencia de reactividad coincidió con la establecida previamente para la degradación de los contaminantes disueltos en agua ultrapura, tanto en el caso de los experimentos de cloración como los de ozonización por separado. En cuanto a la influencia de la matriz acuosa empleada, se consiguió una mayor eliminación en el efluente secundario de la EDAR de La Albuera, intermedia cuando se empleó agua de pantano y aún menor eliminación al emplear el efluente de la EDAR de Badajoz, lo cual está en concordancia con el mencionado contenido en materia orgánica presente en cada una de estas aguas. Además, la elevada eliminación de ECs alcanzada en la cloración del efluente de la EDAR de La Albuera se atribuye en gran medida a la presencia natural de una baja concentración de bromuro, el cual se transforma en ácido hipobromoso, favoreciendo así la eliminación de contaminantes.

En una fase siguiente de oxidación química avanzada, el sistema combinado UV/persulfato (UV/$S_2O_8^{2-}$) fue seleccionado, cuyo estudio dio lugar a la publicación recogida en el Apartado 3.4 del presente Capítulo. Para llevar a cabo dicho estudio, se realizaron experimentos individuales de eliminación de estos contaminantes en agua ultrapura con valores de pH entre 3 y 9. Inicialmente se plantearon como objetivos el establecimiento del efecto de la temperatura (en el rango de 10 a 30ºC) sobre MS, la influencia de la dosis inicial de $S_2O_8^{2-}$ (de 25 a 100 µM) sobre PE y el tipo de tampón y la presencia de bicarbonato en el medio de reacción (este último solo en el caso de AH). Para ello, se propuso un modelo de cinético de pseudo-primer orden, en el que se evaluaron las correspondientes constantes de velocidad, y se obtuvieron correlaciones muy satisfactorias que indican la bondad del modelo propuesto.

Estos valores de constantes ponen de manifiesto la influencia positiva que ejerce la concentración inicial de $S_2O_8^{2-}$, ya que dichas constantes aumentaron desde $8.6x10^{-3}$ s^{-1} para una concentración inicial de 25 µM, hasta $3.05x10^{-2}$ s^{-1} para una concentración de 100 µM (en el caso de PE). Respecto a la influencia de la temperatura, los valores de la constante se incrementan desde $3.06x10^{-3}$ s^{-1} a 10ºC a $1.94x10^{-2}$ s^{-1} para 30ºC y obteniéndose un valor de energía de activación de 60.0 KJ/mol (en el caso de MS). Finalmente, el efecto del pH fue diferente para cada EC estudiado: así mientras que para los casos de AH y MS este efecto resultó ser positivo, tal variable operativa no influyó en la degradación de PE.

Por su parte, la naturaleza del tampón ensayado afecta ligeramente a este proceso de oxidación, siendo sin embargo tal efecto menor que lo encontrado en otros procesos de oxidación avanzada cuando están catalizados por iones metálicos. Además, la presencia de iones carbonato y bicarbonato produce un efecto negativo en la eliminación de ECs debido a que los radicales sulfato pueden reaccionar con ambos, HCO_3^- y CO_3^{2-}. Y finalmente, el uso de agentes secuestrantes de radicales adecuados permitió determinar el papel de las especies reactivas de oxígeno que intervienen en la reacción, HO· y SO_4^-·, poniendo de manifiesto dicho estudio que ambas especies son importantes en la eliminación de los contaminantes seleccionados. La contribución de los radicales hidroxilo es más importante en la oxidación de AH, y menos significativa para la eliminación de MS y PE.

La comparación del sistema UV/persulfato con el sistema persulfato activado térmicamente permite concluir que este sistema de oxidación es alrededor de 15-50 veces menos reactivo que el proceso activado con radiación UV.

Por último, se determinaron las constantes de segundo orden para la reacción directa entre los radicales sulfato y cada EC mediante un método cinético competitivo, en el que se utilizó isoproturon como compuesto de referencia. Los valores obtenidos fueron: $(4.8 \pm 0.6)x10^9$ $M^{-1}·s^{-1}$ para AH, $(9.2 \pm 0.9)x10^8$ $M^{-1}·s^{-1}$ para MS, y $(1.38 \pm 0.02)x10^9$ $M^{-1}·s^{-1}$ para PE.

En una fase posterior, y con el objetivo de mejorar el proceso de cloración simple para la eliminación de estos contaminantes, se introdujo un nuevo sistema de oxidación formado por la combinación de la radiación UV y Cl_2. Los datos obtenidos se recogen en el Apartado 3.5 del presente Capítulo, donde se transcribe la publicación a la que ha dado lugar este estudio. El uso de este sistema conjunto de oxidación produce una mejora en la eliminación de estos ECs con respecto al uso de la radiación UV y Cl_2 como agentes oxidantes individuales, debido a una generación mayor de radicales (HO· y Cl·).

Los valores de las constantes cinéticas deducidas permiten establecer el siguiente orden de reactividad: clorhidrato de AH > MS > PE. Además, dichos valores ponen de manifiesto el efecto positivo que ejerce la concentración inicial de cloro: así para PE, el valor de la constate se incrementa desde 0.30 min^{-1} para $[Cl_2]_0$ = 5 μM, hasta 0.41 min^{-1} para $[Cl_2]_0$ = 15 μM. Sin embargo, este aumento en los valores de las constates es más significativo cuando se comparan los experimento con la presencia y ausencia de cloro. En efecto, la adición al medio de reacción de una concentración 5 μM de cloro produce un aumento entre tres y cinco veces en los valores de las constantes de velocidad en comparación con los experimentos realizados en ausencia de cloro. Con respecto al efecto del pH se deduce que tal variable operativa ejerce un efecto negativo en la eliminación de los ECs seleccionados. Así, en el intervalo de pH entre 3 y 9, los valores de las constantes disminuyen desde 0.42 min^{-1} a 0.21 min^{-1} para PE; 0.60 a 0.42 min^{-1} para MS, y 0.82 a 0.46 min^{-1} para AH.

Para finalizar el estudio de este POA se llevaron a cabo experimentos con los tres compuestos modelo disueltos en cuatro matrices de aguas diferentes: agua ultrapura y tres aguas reales ya utilizadas en procesos anteriores (un agua superficial de pantano y dos efluentes secundarios procedentes de las EDAR de La Albuera y de Badajoz). Nuevamente, el objetivo perseguido consistía en evaluar el efecto de la presencia de materia orgánica en dichas matrices acuosas sobre los niveles de degradación. De forma global cualitativa se observa el mismo orden de reactividad que el obtenido en los experimentos realizados con los compuestos disueltos individualmente en agua ultrapura. Además, y en concordancia plena con el contenido en materia orgánica de las diferentes aguas ensayadas, se alcanzó una rápida eliminación de los contaminantes en agua ultrapura y una menor degradación al emplear el efluente secundario de la EDAR de Badajoz, como consecuencia de la materia orgánica disuelta en la misma que consume agente oxidante. Finalmente, de forma menos exhaustiva y solo con fines comparativos, se ensayaron varios sistemas de oxidación que utilizan estos agentes oxidantes, de forma individual y combinada (UV, UV/H_2O_2, $UV/S_2O_8^{2-}$ y UV/Cl_2), con el objetivo de eliminar estos contaminantes en dichas matrices acuosas. Los resultados más favorables se obtuvieron al aplicar el sistema UV/Cl_2. Los resultados obtenidos en los experimentos realizados con similares concentraciones iniciales de oxidantes indican que el proceso de oxidación más eficaz es el sistema UV/Cl_2. Por lo tanto, el POA UV/Cl_2 es una alternativa prometedora para la eliminación de contaminantes emergentes en aguas superficiales y en efluentes de EDARs.

Una vez estudiados todos los procesos de oxidación química descritos, se continuó con una nueva etapa centrada en la aplicación de procesos físicos, la cual se inició con un estudio basado en el uso de tecnologías de membrana, concretamente utilizando membranas de ultrafiltración (UF) y nanofiltración (NF). Los principales objetivos planteados en este estudio fueron la evaluación del flujo de permeado y del ensuciamiento de las membranas, así como la determinación de los coeficientes de retención de los contaminantes. Una vez obtenida dicha información, se propusieron los mecanismos de ensuciamiento de las membranas y de la propia retención de los contaminantes. Para ello se empleó un equipo de filtración de laboratorio que operaba en modo concentración y con flujo tangencial.

Inicialmente se realizó un estudio centrado en la evaluación de la influencia sobre el flujo de permeado y sobre la retención de los compuestos seleccionados de algunas variables de operación, tales como naturaleza y MWCO (tamaño de corte de peso molecular) de las membranas, pH, y presencia de materia orgánica y Ca^{2+}. Para este fin, se emplearon las diferentes matrices acuosas ya descritas (agua ultrapura, agua superficial de pantano y los dos efluentes secundarios procedentes de la EDAR de Badajoz y de La Albuera). En este proceso se ensayaron diversas membranas: tres membranas de ultrafiltración (PW, PT y GK, con MWCO de 20000, 5000 y 2000 Da, respectivamente); y tres membranas de nanofiltración (DK, CK y HL, con MWCO en el rango 150-300 Da). Los resultados obtenidos en se recogen y discuten de forma detallada en la publicación que se muestra en el Apartado 3.6 del presente Capítulo.

Al comienzo del proceso de filtración, el flujo de permeado (J_v) disminuye como consecuencia del ensuciamiento creciente de la membrana, que puede deberse a diferentes causas, como el bloqueo de poros o la adsorción de solutos en las membranas. Los valores de flujo de permeado en estado estacionario (J_{vss}) se ven afectados por las variables operativas estudiadas. Se observa una influencia directa del MWCO sobre el J_{vss}. Así, en el proceso de UF (pH = 7 y TMP = 0.3 MPa) se produce un aumento del flujo de permeado al aumentar el MWCO de las membranas seleccionadas, con valores de 16.5, 56.7 y 185.8 $dm^3\ h^{-1}\ m^{-2}$ para las membranas GK, PT y PW, respectivamente. Estos resultados se deben al hecho de que una membrana con menor MWCO presenta una mayor resistencia para que la solución atraviese la membrana. En el proceso de NF las tres membranas testadas tenían el mismo tamaño de poro (en el intervalo de 150-300 Da). Sin embargo, los resultados indican que en condiciones operativas similares, la membrana HL presentó un flujo de permeado más alto que las membranas CK o DL: 138.1 frente a 41.6 y

54.9 dm^3 h^{-1} m^{-2}. Estas diferencias son consecuencia de la diferente naturaleza de las membranas y coinciden con resultados previamente publicados sobre la permeabilidad hidráulica de las mismas. Por otro lado, y con respecto a la influencia del pH, la membrana PT (UF) presentó una ligera disminución de J_{vss} con el aumento del mismo. Sin embargo, este efecto es casi insignificante en la membrana HL (NF).

El compuesto que presenta mayor coeficiente de retención para los experimentos de nanofiltración fue AH, cuyos valores están próximos al 100%, lo que indica que este contaminante fue prácticamente retenido en su totalidad por estas membranas. Por su parte, en los procesos de ultrafiltración este compuesto también presentó coeficientes de retención elevados, aunque decrecientes con el aumento del MWCO, como cabe esperar. En el caso de MS, se deducen valores intermedios para dichos coeficientes (de 80 a 100% en nanofiltración; y 65-78% para ultrafiltración); y finalmente, para PE se obtuvieron bajos valores para tales coeficientes (30-60% en nanofiltración y 25-38% en ultrafiltración). En los procesos de ultrafiltración la membrana más eficaz fue la GK, siendo la adsorción el mecanismo de retención preferente. Por su parte, en el proceso de NF, la diferencia entre los coeficientes de retención obtenida permite establecer que para AH, al tener un peso molecular en el rango del MWCO de las membranas, el mecanismo de exclusión de tamaño es el principal responsable de la retención del compuesto, mientras que para MS y PE el principal mecanismo de retención vuelve a ser la adsorción, al igual que ocurría en experiencias de UF. Por su parte, en el proceso de NF, la membrana más eficaz fue la HL.

Para finalizar el estudio de la eliminación de estos contaminantes mediante filtración por membranas, y siguiendo el mismo protocolo que en anteriores procesos, se realizaron experimentos con los tres ECs disueltos en las tres matrices acuosas habituales, usando la membrana HL para NF y la membrana PT para UF. Los resultados muestran que se produce una disminución en el flujo de permeado (J_{vss}) por ensuciamiento de las membranas de acuerdo a la secuencia siguiente: LA < PA < BA. Esta disminución está en concordancia plena con el aumento de materia orgánica presente en las aguas seleccionadas. Dicho aumento de materia orgánica induce varios efectos, como la mayor adsorción de especies en la membrana, el bloqueo de los poros y la formación de una torta en la superficie de la membrana, que explica la disminución de J_{vss}. Por otro lado, se obtienen mayores coeficientes de retención en el proceso de NF que en el proceso de UF como cabía esperar. Y además la secuencia de retención es la misma que la obtenida cuando los contaminantes se encontraban disueltos en agua ultrapura: AH > MS > PE.

Finalmente, y con respecto a la eliminación de materia orgánica, se obtuvieron mejores resultados en el proceso de nanofiltración (74-92% para TOC, 52-59% para DQO y del 74-100% en absorbancia), que en el proceso de ultrafiltración (40-71% para TOC, 28-53% para DQO y 52-67% en la absorbancia). A partir de estos resultados se puede concluir que la membrana HL es adecuada para la eliminación de ECs en aguas reales con los objetivos de producir agua potable y de purificación de efluentes secundarios no muy contaminados para su posterior reutilización. Sin embargo, el retenido producido presenta un alto contenido en compuestos contaminantes y necesitaría tratamientos adicionales para una satisfactoria purificación.

En la última fase del presente Trabajo se realizó el estudio de la eliminación de los ECs seleccionados disueltos en aguas mediante procesos de adsorción con carbón activo, utilizando dos adsorbentes: carbón activo en polvo (PAC) y carbón activo granular (GAC). Dicho estudio dio lugar a la publicación que se recoge en el Apartado 3.7 del presente Capítulo. En primer lugar se determinaron las isotermas de adsorción de los ECs seleccionados y disueltos en agua UP, a 20ºC y pH 7. Para evaluar las características del equilibrio de adsorción, los datos experimentales fueron ajustados a dos modelos clásicos de isotermas de adsorción: modelos de Langmuir y de Freundlich. Los datos experimentales obtenidos para los contaminantes seleccionados se ajustan de forma más satisfactoria a la ecuación del modelo de Langmuir en la mayoría de los casos. Además, tales datos experimentales muestran una eficiencia superior en la adsorción sobre el PAC, mientras que el GAC muestra una menor capacidad de adsorción, aspectos que quedan confirmados por los valores de los parámetros q_s para el modelo de Langmuir, y K_f para el modelo de Freundlich. Este hecho puede explicarse a partir del menor volumen de macroporos y mesoporos del GAC, lo que dificulta la difusión de cada contaminante hacia los sitios activos localizados en la superficie microporosa. De esos valores experimentales se deduce asimismo que el orden en la capacidad de adsorción para ambos adsorbentes fue el siguiente: AH > MS ≥ PE.

A continuación se realizó el estudio cinético del proceso de adsorción de cada contaminante individual asimismo disuelto en agua ultrapura. Los resultados obtenidos muestran que entre los modelos cinéticos probados para reproducir este proceso, el modelo de pseudo-segundo orden se ajusta satisfactoriamente a los datos experimentales, con coeficientes de correlación lineal (R^2) superiores a 0.999 en todos los experimentos. Adicionalmente, la adsorción con PAC muestra altas tasas de adsorción inicial y menores tiempos de vida media que con GAC. El estudio de las variables operativas muestra un efecto positivo en la dosis inicial de adsorbente, mientras que el pH no ejerce efectos significativos sobre la eliminación de los ECs. Los valores de constantes obtenidos confirman la secuencia de velocidad de eliminación anteriormente señalada: AH > MS > PE.

Para finalizar el estudio de la eliminación de estos contaminantes mediante procesos de adsorción, y con el objetivo de simular condiciones más realistas, se llevaron a cabo experimentos con PAC, estando los contaminantes modelo presentes de forma simultánea en las tres matrices de aguas habituales: un agua superficial de pantano y dos efluentes secundarios procedentes de las EDAR de La Albuera y de Badajoz. Los resultados muestran una eficacia menor para los niveles de eliminación en tales aguas con respecto a los obtenidos en agua UP, lo que sugiere que la materia orgánica disuelta en las mismas compite con los ECs por los centros activos del adsorbente, causando una disminución en la capacidad de adsorción del PAC. Esto queda confirmado por el hecho de que este contenido de materia orgánica presente en las matrices acuosas se reduce considerablemente, obteniéndose una eliminación de TOC superior al 50% con dosis de PAC de alrededor de 100 mg L^{-1}, así como una eliminación de DQO superior al 65%. Por lo tanto, se demuestra que el uso de PAC resulta ser una tecnología eficaz, tanto para eliminación de microcontaminantes como para la reducción de materia orgánica en aguas reales.

3.2. Elimination of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in ultrapure water and secondary effluents by photolytic and radicalary pathways.

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3.2. ELIMINATION OF THE EMERGING CONTAMINANTS AMITRIPTYLINE HYDROCHLORIDE, METHYL SALICYLATE AND 2-PHENOXYETHANOL IN ULTRAPURE WATER AND SECONDARY EFFLUENTS BY PHOTOLYTIC AND RADICALARY PATHWAYS.

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Chemical degradation of the pharmaceuticals and personal care products (PPCPs) amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol by means of several advanced oxidation processes, including 254 nm UV radiation and Fenton's reagent has been studied in different water matrices, such as ultrapure and surface waters and two secondary effluents from wastewater treatment plants. Influence of the operating variables on the elimination of these compounds in UP water was established, and kinetic parameters for their degradation, such as quantum yields along a pH range of 3-11 and second-order rate constants for their oxidation by hydroxyl radicals were determined. Specifically, for the reactions of oxidation of the three PPCPs with hydroxyl radicals, the use of a competition kinetic model in Fenton's reagent experiments allowed to evaluate their rate constants, whose values were: $(10.3\pm0.3)\mathrm{x}10^{9}$ $M^{-1}\cdot s^{-1}$ for amitriptyline hydrochloride, $(7.1\pm0.1)\mathrm{x}10^{9}$ $M^{-1}\cdot s^{-1}$ for methyl salicylate and $(4.3\pm0.1)\mathrm{x}10^{9}$ $M^{-1}\cdot s^{-1}$ for 2-phenoxyethanol. Furthermore, the simultaneous oxidation of these selected PPCPs in three different water systems (surface water from a reservoir and two secondary effluents) was studied, and the influence of the operating conditions on the removal efficiency was established. Finally, a kinetic model was proposed for the prediction of the elimination of these compounds by

UV radiation and UV/H_2O_2 system in these water matrices, with theoretical results that agreed well with the experimental ones.

Keywords: Pharmaceuticals and personal care products, PPCPs, amitriptyline, methyl salicylate, 2-phenoxyethanol, UV radiation, Fenton's reagent, rate constants, quantum yields.

1. INTRODUCTION.

The presence of emerging contaminants in waters is known for decades, but it is now, at the present times, when their levels in the environment are just being quantified, and being recognized themselves as pollutants potentially dangerous that can produce damages in the ecosystem (Fent et al., 2006; Jjemba, 2006). Among them, pharmaceuticals and personal care products (PPCPs) constitute an increasing group, since they are widely consumed all over the world and not completely eliminated by conventional water treatment processes. Consequently, they have been found in effluents exiting the treatment plants (Ternes et al., 2002). These effluents are characterized by the low concentrations of these emerging contaminants and the lack of knowledge of their effect on the processes of purification of waters, the environment and the human health.

Different advanced treatment technologies have recently been assayed with the aim of achieving high levels of elimination of these pollutants. Among them, chemical oxidation by photodegradation and advanced oxidation processes, such as UV/H_2O_2 or Fenton's reagent, have demonstrated their effectiveness in the elimination of this group of substances (Canonica et al., 2008; Li et al., 2012). Photodegradation process involves both, direct and indirect pathways by the action of photons emitted by the lamp or radicals generated in the mass reaction, respectively (Legrini et al., 1993). On the other hand, advanced oxidation processes are essentially based on the generation of free radicals, such as hydroxyl radicals.

The purpose of the present work is to study the degradation of three selected PPCPs in different water matrices by several chemical oxidation systems including UV radiation and advanced oxidation processes. Specifically, the antidepressant amitriptyline hydrochloride, the rubefacient methyl salicylate and the bactericide 2-phenoxyethanol, were selected to be eliminated by UV radiation and by the systems UV/H_2O_2, Fenton's reagent, Fenton-like and photo-Fenton.

Amitriptyline hydrochloride is the most widely used tricyclic antidepressant. Its mechanism of action involves the inhibition of reuptake of norepinephrine and serotonin. Methyl salicylate is a salicylic acid derivative, naturally produced by many species of plants, although nowadays is industrially produced by esterification of the acid with methanol. At high concentrations, this drug acts as rubefacient, analgesic and anti-inflammatory. Finally, 2-phenoxyethanol is a bactericide generally combined with quaternary ammonium compounds. It is often used in dermatological products, such as skin creams and sunscreens, and also as fixative for perfumes, insecticide and topical antiseptic.

Although rather information on the elimination of PPCPs, including very interesting reviews about pharmaceutical compounds (Ikehata et al., 2006; Eplugas et al., 2007), has been published, very scarce studies on the elimination of the specific emerging contaminants selected in this work were found (Puyol et al., 2011; Canosa-Mas, 2002), and no kinetic parameters have been reported. Therefore, the first step of the present study is focused on the determination of the quantum yields and rate constants for the individual reactions between each one of these PPCPs with UV radiation and OH radicals individually in ultrapure water, as well as the establishment of the influence of the main operating conditions. Additionally, a study of the oxidation of these compounds during photodegradation processes in several water systems was also conducted.

2. EXPERIMENTAL SECTION.

2.1. Reagents.

Amitriptyline hydrochloride (A, $C_{20}H_{23}N{\cdot}HCl$, ≥99%), methyl salicylate (S, $C_8H_8O_3$, ≥98%) and 2-phenoxyethanol (P, $C_8H_{10}O_2$, ≥99%) were purchased from Sigma-Aldrich Spain.

p-Chlorobenzoic acid (p-CBA) and general reagents used in this work were obtained from Panreac Spain, with pure component quality.

2.2. Experimental procedures.

The photodegradation experiments were carried out in a 500 cm^3 thermostated cylindrical glass reactor, equipped with a radiation lamp located in axial position and a quartz sleeve housing the lamp. This lamp consisted in a low pressure mercury vapor lamp (TNN 15/32 nominal electrical power 15 W; Heraeus, Spain) which emitted a monochromatic radiation at 254 nm. A solution of 350 mL of the corresponding PPCP (1 µM) buffered at the selected pH by adding phosphoric acid/phosphate solution (0.01 M) was inserted into the reactor. In these experiments, an upward nitrogen gas stream was used in order to homogeneize the solution. At regular reaction times, samples were taken from the reactor. The experiments using the UV/H_2O_2 system were conducted by adding H_2O_2 to the solution just before switching on the lamp.

The photodegradation experiments focused on the determination of the quantum yields were conducted in UP water in presence of tert-butylalcohol (t-BuOH, 0.01 M) as OH radical scavenger, due to the positive influence of the radicalary pathway on the overall photodegradation, which was stated in previous experiments carried out with and without t-BuOH.

In the experiments carried out in natural water and secondary effluents, a solution of the three compounds at concentrations of 1 µM for each one was used at 20 ºC and at the proper pH of the water (around pH 7).

The experiments of oxidation by Fenton’s reagent and Fenton-like were carried out in 250 mL Erlenmeyer flasks, where the temperature was kept constant at 20 ºC, and the solutions were homogenized by means of a magnetic stirrer. For every experiment conducted, each flask was filled with the aqueous solution containing the selected PPCP (1 µM), and buffered at the selected pH by adding a perchloric acid/perchlorate solution (0.01 M), which has been confirmed as the most appropriate pH regulator in a previous research (Benitez et al., 2007). The required amounts of hydrogen peroxide and ferrous or ferric ion were also added to the reactor. The experiments using the photo-Fenton reagent were conducted in the same reactor as the photodegradation ones. In both cases, at regular reaction times, samples were withdrawn from the reactor and quenched by adding sodium thiosulfate, which reacts quickly with the remaining hydrogen peroxide.

Fenton's reagent experiments were also performed for the determination of the second-order rate constants of the reaction between each compound and hydroxyl radicals. For this purpose, the well known competition kinetic model widely described in the literature (Benitez et al., 2007) was used. The reference compound selected in these experiments was p-chlorobenzoic acid (p-CBA), whose rate constant with OH radicals is known in advance (Buxton et al., 1988).

2.3. Analytical methods.

The three selected PPCPs, as well as p-CBA (used as reference compound), were analysed by HPLC in a Waters Chromatograph equipped with a 996 Photodiode Array Detector and a Waters Nova-Pak C18 Column (5 µm 150x3.9 mm). The detection was performed at 238 nm for amitriptyline hydrochloride, methyl salicylate and p-CBA and 220 nm for 2-phenoxyethanol. The mobile phase was a mixture of methanol and 0.01 M aqueous phosphoric acid solution in different proportions, depending on the mixture analysed. The elution flow rate was 1 mL min^{-1} and the injection volume was 100 µL in all samples.

2.4. Natural water systems.

Three different water systems were used in the present study for the oxidation of the selected PPCPs under realistic water treatment conditions. The first one was surface water (SW) collected from the public reservoir "Peña del Aguila", in the Extremadura Community (southwest Spain). The other water systems were two secondary effluents collected from the municipal wastewater treatment plants of the cities of Badajoz (SEB) and La Albuera (SEA), respectively. These water systems were filtered within the first 24 hours after collected and stored at 4 ºC until used. Quality parameters for these waters, such as pH, absorbance at 254 nm, TOC content and alkalinity are listed in Table S1. Specifically, the parameters UV absorbance and TOC content constitute a significant indication of the total dissolved organic matter (DOM) present in these waters, stuff of great influence in the performance of the different oxidation pathways involved.

Table S1, Quality parameters of the water system used.

Water matrix	pH	TOC ($mg \cdot L^{-1}$)	COD ($mg \cdot L^{-1}$)	A254nm (cm^{-1})	Alkalinity x103 ($mg \cdot L^{-1}$ $CaCO_3$)	Conductivity x10^3 (µS)
SW	7.4	5.2	18	0.187	30	80
SEB	8.3	11.1	56	0.245	325	550
SEA	7.9	2.9	7	0.041	335	570

3. RESULTS AND DISCUSSION.

3.1. Oxidation of the PPCPs individually in ultrapure water.

The oxidation of the three target pharmaceuticals and personal care products amitriptyline hydrochloride (denoted A), methyl salicylate (denoted S) and 2-phenoxyethanol (denoted P) was carried out in a first stage in ultrapure water by using different oxidizing systems on each compound individually: UV radiation, UV/H_2O_2 system, Fenton’s reagent, Fenton-like and photo-Fenton systems. The influence of the main operating variables for every set of experiments was established and the main kinetic parameters, quantum yields for the direct photodegradation and second-order rate constant for the degradation by hydroxyl radicals, were evaluated.

3.1.1. Degradation of the PPCPs by UV radiation and UV/H_2O_2 system.

The photodegradation of the three selected PPCPs was studied in experiments carried out individually by using a 254 nm monochromatic radiation at 20 ºC, varying the pH from 3 to 11 and in presence and absence of t-butylalcohol (t-BuOH), used as radical scavenger. In the case of amitriptyline hydrochloride, additional experiments at 10 and 40 ºC were conducted with the aim to establish the effect of the temperature. Table S2 summarizes the operating conditions for these experiments, including two experiments carried out by using the UV/H_2O_2 system with different initial H_2O_2 doses (experiments PH-1 and PH-2).

Table S2. Photodegradation experiments in ultrapure water.

Expt.	T (ºC)	pH	[t-BuOH] (mM)	[H_2O_2] (µM)	k_{UV-A} x10^3 (min^{-1})	k_{UV-S} x10^3 (min^{-1})	k_{UV-P} x10^3 (min^{-1})	ϕ_A x10^3 (mol/Eins)	ϕ_S x10^3 (mol/EIns)	ϕ_P x10^3 (mol/EIns)
Pt-1	20	3	10	0	41	1.6	4.4	8.0	1.9	8.8
Pt-2	20	5	10	0	46	3.2	6.0	8.3	4.1	11.9
Pt-3	20	7	10	0	53	4.5	6.1	9.2	5.7	12.3
Pt-4	20	9	10	0	79	14	7.2	14.4	13.2	14.3
Pt-5	20	11	10	0	163	61	5.3	29.1	32.9	10.5
Pt-6	10	7	10	0	37			7.0		
Pt-7	40	7	10	0	57			10.8		
P-1	20	3	0	0	109	58	69			
P-2	20	5	0	0	118	54	71			
P-3	20	7	0	0	133	52	91			
P-4	20	9	0	0	207	55	120			
P-5	20	11	0	0	341	37	39			
P-6	10	7	0	0	105					
P-7	40	7	0	0	218					
PH-1	20	7	0	10	192	136	203			
PH-2	20	7	0	50	578	408	497			

Pt-n: Experiments with the presence of t-BuOH

P-n: Experiments without the presence of t-BuOH

Figure 1 shows the evolution of the concentration of each compound R, (being R = A, S or P) for the photodegradation experiments conducted at 20 ºC and pH 7, by varying the presence of t-BuOH and hydrogen peroxide. It can be observed the negative effect of the presence of a scavenger on the degradation of every PPCP (experiments Pt-3 versus P-3), as well as the positive effect of the presence of a radical promoter such as H_2O_2 (experiments PH-2). These results show clearly the greater contribution of the radicalary pathways on the overall photodegradation of these compounds. Moreover, it can also be deduced from the comparison of reactivities among every compound that amitriptyline hydrochloride is more reactive than 2-phenoxyethanol and methyl salicylate, in both presence and absence of t-BuOH.

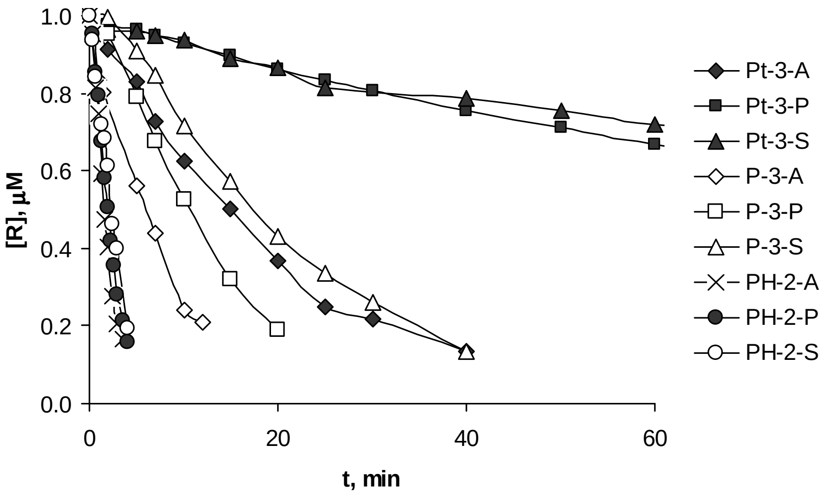

Figure 1. Oxidation curves of the selected PPCPs with reaction time in the photodegradation experiments in ultrapure water. Experimental conditions: T=20 ºC; pH=7; Experiment Pt-3: $[t\text{-BuOH}]_0$=10 mM; Experiment PH-2: $[H_2O_2]_0$=50 µM; PPCP initial concentration: 1 µM. A: amitriptyline; P: 2-phenoxyethanol; S: methyl salicylate.

Table S2 also reports the pseudo-first order rate constants for the photodegradation of each organic compound, k_{UV-R}, obtained for every experiment. A first glance at these values confirms the importance of the radicalary pathway contribution on the overall photodegradation, since lower values of these rate constants were obtained in all cases when the radical scavenger t-BuOH was added into the reaction mass (experiments Pt-n versus P-n). These differences in the rate constant values between experiments with and without t-BuOH ranged from 50% smaller in amitriptyline experiments to over 90% smaller for methyl salicylate and 2-phenoxyethanol, confirming the indirect photodegradation along radicalary pathways as the main contribution in the photodegradation of these compounds in ultrapure water. This effect is mainly due to the very low reactivity of the selected compounds towards the direct UV radiation, which leads to first-order rate constants values under 0.1 min^{-1} in most of the experiments carried out in presence of t-BuOH, fact that will be confirmed further with the evaluation of the quantum yields. Finally, from the results exposed in Table S2 it can be again deduced that 2-phenoxyethanol and methyl salicylate are very less reactive than amitriptyline hydrochloride, trend in agreement with the radicalary pathway contribution percentage previously stated.

Therefore, the direct photodegradation of the emerging contaminants, represented as Equation 1, constitutes their minor degradation way; while the indirect photodegradation, involving radicalary pathways across the formation of superoxide and hydroxyl radicals (Equations 2 to 6) (Legrini et al., 1993), becomes the major way of photodegradation of the selected PPCPs, especially when hydrogen peroxide is added into the reactor and Equations 5 and 6 are favoured (experiments PH-1 and PH-2).

$$R + h\upsilon \xrightarrow{\phi\,\mu\,I} P \qquad [1]$$

$$R + h\,\upsilon \rightarrow R^{\bullet} \qquad [2]$$

$$R^{\bullet} + O_2 \rightarrow R^{\bullet+} + O_2^{\bullet-} \qquad [3]$$

$$2\,O_2^{\bullet-} + 2\,H_2O \rightarrow O_2 + H_2O_2 + 2\,OH^{-} \qquad [4]$$

$$H_2O_2 + h\upsilon \rightarrow 2\,{}^{\bullet}OH \qquad [5]$$

$$R + {}^{\bullet}OH \rightarrow P \qquad [6]$$

It can also be established from the results listed in Table S2 the positive influence of the pH on the degradation rate of each compound, as in direct photolysis (experiments Pt-

n) as in overall photolysis including radicalary way (experiments P-n). The only exception to this fact occurred for the methyl salicylate experiments in absence of t-BuOH, which showed no significant influence of the pH and the direct photodegradation of 2-phenoxyethanol (experiments Pt-n) whose rate constant values hardly show a light increase. The trend observed in the direct photodegradation experiments of the three compounds can be attributed to the different reactivity showed by the un-dissociated and dissociated species of each PPCP. In effect, amitriptyline hydrochloride and methyl salicylate present pKa values of 9.4 and 9.9 (Blessel et al., 1974; Sergeant and Dempsey, 1979) respectively, justifying the great step in reactivity observed at high pH. On the other hand, the absence of acid dissociation constant in the case of 2-phenoxyethanol agrees with its slight pH-dependence. This effect was observed in previous photodegradation works (Benitez et al., 2005), as well as the minor pH-dependence of the radical pathway in relation with the direct photodegradation (Shen et al., 1995), which could explain that this effect is more notorious in experiments in presence of t-BuOH.

Temperature also shows a clear positive influence in the case of the photodegradation of amitriptyline hydrochloride, the only compound in which the effect of this variable has been studied, as can be seen in experiments Pt-6, Pt-3 and Pt-7 of Table S2 of the Supporting Information, as well as in experiments P-6, P-3 and P-7, in presence and absence of t-BuOH, respectively. This effect is well expected, since the kinetic parameters of both, photodegradation and radical pathways usually fulfill the Arrhenius law.

Finally, in order to determine the kinetics of the reactions of direct and indirect phododegradation of the selected PPCPs, two parameters can be evaluated: quantum yields (ϕ), defined as the number of molecules decomposed per photon absorbed (Chu, 2001), which governs the reaction exposed in Equation 1; and second-order rate constants of the reaction with hydroxyl radicals, Equation 6, which will be evaluated later by using Fenton’s reagent experiments.

For the determination of ϕ, only results of experiments in presence of t-BuOH must be considered, due to the exclusion of the indirect pathway that they cause. Quantum yields values have been evaluated by assuming the Line Source Spherical Emission Model, initially proposed by Jacob and Dranoff (Jacob and Dranoff, 1970), and previously used in similar studies on the photooxidation of organic substances (Esplugas et al., 2007; Yue, 1993; Benitez et al., 2005). This model provides the following final equation for the disappearance rate of the selected compound, R:

$$-\frac{d[R]}{dt}=\frac{\phi}{V}W_{abs} \qquad [7]$$

where V is the volume of reaction, 350 mL in all the experiments and W_{abs} represents the absorbed radiation flow rate. The integration of Equation 7 leads to:

$$[R]=[R]_0-\frac{\phi}{V}\int_0^t W_{abs}dt \qquad [8]$$

The determination of W_{abs} is carried out by using the referred LSSEM, previously known the molar extinction coefficients of each compound at 254 nm, ε, measured at the pH of the experiment; and the radiation intensity emitted by the lamp into the reactor, I, whose value is $1.73\text{x}10^{-6}$ Einstein·s^{-1}. Once W_{abs} is determined, the quantum yields for every experiment can be evaluated according to Equation 8 and following the procedure described in a previous paper (Benitez et al., 2005). The ϕ values for every PPCP determined are listed in Table S2 for every experiment. It can be observed the very low values obtained for these quantum yields, which usually range between 0.01 and 0.3 mol·Einstein^{-1} for organic compounds, while in this case only reached a tenth of these values, which agrees with the scarce contribution of the direct photodegradation previously discussed. Besides, the positive influence of the pH on the ϕ values can also be observed, as well as the effect of the temperature on the direct photodegradation of amitriptyline hydrochloride.

3.1.2. Oxidation of the PPCPs by Fe/H_2O_2 systems.

In a second step of the study of degradation of the selected PPCPs, individual oxidation experiments of each compound by using several Fe/H_2O_2 systems, such as Fenton's reagent (Fe^{2+}/H_2O_2), Fenton-like (Fe^{3+}/H_2O_2) and photo-Fenton (Fe^{2+}/H_2O_2/UV) systems were performed in ultrapure water at 20 ºC. All these oxidation systems are based on the formation of the very reactive hydroxyl radicals, whereas Fe^{2+} is being regenerated, according to the reactions described by Walling (Walling, 1975) for Fenton's reagent:

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-}} \qquad [9]$$

$$\mathrm{R + {}^{\bullet}OH \rightarrow P} \qquad [10]$$

$$\mathrm{H_2O_2 + HO_2^{\cdot} \rightarrow HO_2^{\cdot} + H_2O} \qquad [11]$$

$$\mathrm{Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^{+} + O_2} \qquad [12]$$

Additionally, in the case of Fenton-like system, Equations 13 and 14 must also be considered for the generation of Fe^{2+} ion; and Equations 15 and 16 in the photo-Fenton system:

$$\mathrm{Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^{+}} \qquad [13]$$

$$\mathrm{FeOOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+}} \qquad [14]$$

$$\mathrm{H_2O_2 + h\upsilon \rightarrow 2\ {}^{\bullet}OH} \qquad [15]$$

$$\mathrm{Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + {}^{\bullet}OH} \qquad [16]$$

Several experiments by using the three mentioned oxidation systems were carried out at 20 ºC and pH 3 by varying the dose of ferrous/ferric ion and hydrogen peroxide, with the aim to establish the efficiency of each system and the influence of the initial concentration of some of the reagents. Besides, amitriptyline oxidation experiments by Fenton's reagent at pH 2 and 5, usual pH limits for this oxidation system, were conducted in order to investigate its effect. Table S3 depicts the conditions and initial doses used for each experiment, as well as the removals reached for each compound at 1.5 min of reaction for comparison purposes.

According to the removals, X_R, shown in this Table, the positive influence of the initial concentrations of Fe^{2+} and H_2O_2 on the degradation by Fenton's reagent of the three selected PPCPs can be deduced (experiments F-1, F-2 and F-3; and experiments F-5, F-4 and

F-3, respectively), since both species promote the main generation of hydroxyl radicals through Equation 9. Once again, amitriptyline hydrochloride has shown as the most reactive compound towards hydroxyl radicals, followed by methyl salicylate; and finally, 2-phenoxyethanol, according to their removals reached at 1.5 min of reaction. Also, in the study of the influence of the pH on the degradation of amitriptyline, the optimum value of pH 3 for Fenton's reagent has been proved (experiments F-6, F-3 and F-7). The decrease in degradation at pH 5 can be attributed to the precipitation of ferric oxyhydroxides; while the decrease at pH 2 is probably due to the inhibition of the formation Fe (III)-peroxy complexes ($FeOOH^{2+}$), precursors of Fe^{2+} regeneration (Equations 13 and 14) (Laat et al., 1999).

Table S3. Fe/H_2O_2 systems experiments in ultrapure water.

Expt.	pH	$[Fe^{2+}]_0$ (μM)	$[Fe^{3+}]0$ (μM)	$[H_2O_2]$ (μM)	UV radiation	X_A, % (1.5 min)	X_S, % (1.5 min)	X_P, % (1.5 min)
F-1	3	10		50		77.7	65.6	55.9
F-2	3	25		50		87.0	85.2	60.4
F-3	3	50		50		100	93.0	78.5
F-4	3	50		25		90.7	83.2	60.4
F-5	3	50		10		64.3	50.1	34.5
F-6	2	50		50		81.3		
F-7	5	50		50		73.3		
FL-1	3		50	50		24.7	20.8	9.8
PF-1	3	10		50	254 nm	95.4	80.2	61.6
FC-1	3	50		10		51.3	51.7	30.0
FC-2	3	50		50		100	92.6	75.8

Moreover, the efficiency of the three oxidation systems can be compared from the removals exposed in Table S3. Thus, results of experiments using Fenton-like and photo-Fenton systems (experiments FL-1 and PF-1, respectively) can be contrasted with the corresponding Fenton's reagent reaction using equal initial concentrations (experiments F-3 and F-1, respectively). As can be seen, Fenton-like experiment is the less efficient one, leading to removals below 25% in spite of using higher reagent doses. On the other hand, photo-Fenton system generate greater removals of the PPCPs than in Fenton's reagent (experiment PF-1 versus F-1), as could be expected, due to the additional generation of hydroxyl radicals (Equations 15 and 16) plus the direct photodegradation of the organic compounds (Equation 1). Nevertheless, the overall improvement of using the photo-Fenton system is unusually low, probably due to the scarce photodegradability of the selected compounds stated in Section 3.1.1. Additionally, Figure 2 shows the influence of the three Fe/H_2O_2 oxidation systems on the degradation of methyl salicylate, taken as example. It can be again observed the effects previously commented: the poor degradation obtained by using the Fenton-like system and the improvement achieved when using photo-Fenton system (experiments F-1 and PF-1).

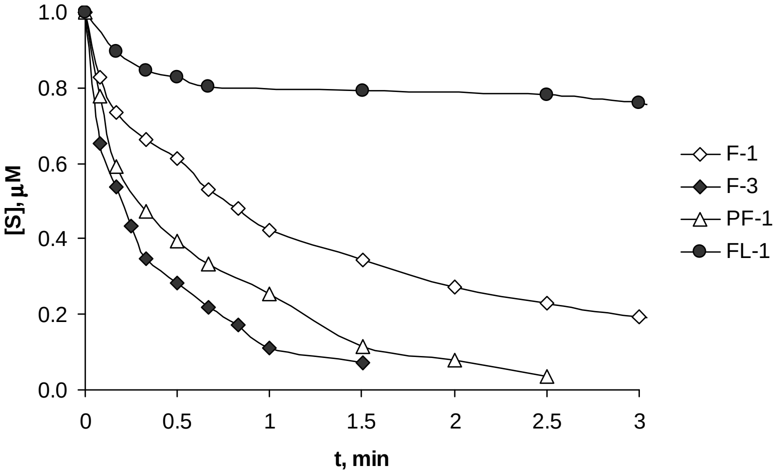

Figure 2. Oxidation curves of methyl salicylate by Fe/H2O2 systems in ultrapure water. Experimental conditions: T=20 ºC; pH=3; PPCP initial concentration: 1 µM; $[H_2O_2]_0$=50 µM. Experiments F-1 and PF-1: $[Fe^{2+}]_0$=10 µM. Experiment F-3: $[Fe^{2+}]_0$=50 µM. Experiment FL-1: $[Fe^{3+}]_0$=50 µM.

Finally, in order to determine the second-order rate constants for the oxidation of each PPCP with hydroxyl radicals, Fenton's reagent experiments were carried out by using a competition kinetic model (Haag and Yao, 1992; Benitez et al., 2007), due to the impossibility to measure the $^{\cdot}$OH concentration accurately. For this study, p-chlorobenzoic acid (p-CBA) has been selected as reference compound, since its rate constant with hydroxyl radicals is well known (k_{pCBA} = 5x10^{9} M^{-1}·s^{-1}) (Buxton et al., 1988). The model proposes a competition towards hydroxyl radicals of both compounds, the selected PPCP and p-CBA, according to the reaction represented in Equation 6 for each compound. From the kinetic equation of each reaction, the following relationship can be deduced:

$$\ln\frac{[\mathrm{R}]_0}{[\mathrm{R}]}=\frac{k_R}{k_{pCBA}}\ln\frac{[\text{p-CBA}]_0}{[\text{p-CBA}]} \qquad [17]$$

According to this competition kinetic model, two experiments at 20 ºC and pH 3 of the simultaneous oxidation of each PPCP and p-CBA by Fenton's reagent were performed, denoted FC-1 and FC-2, whose experimental conditions and removals reached at 1.5 min of reaction are also listed in Table S3. With the experimental results obtained along every reaction time and according to Equation 17, plots of the logarithmic terms led to straight lines with very similar slope k_R/k_{pCBA} in both experiments for each compound, from which the rate constants for their reaction with hydroxyl radicals can be evaluated. The values obtained were (10.3±0.3)x10^{9} M^{-1}s^{-1} for amitriptyline hydrochloride, (7.1±0.1)x10^{9} M^{-1}s^{-1} for methyl salicylate and (4.3±0.1)x10^{9} M^{-1}s^{-1} for 2-phenoxyethanol. As can be seen, the order obtained for these rate constant values matches with the order of reactivity observed among each compound in Fenton's reagent experiments (experiments F-1 to F-5). Calculation data of these rate constants are provided in Table S4.

Table S4. Calculation data of the rate constants for the oxidation of each emerging contaminant with hydroxyl radicals by using the competition kinetic model

Compound	Expt.	Slope k_P/k_R	k_R x10^{-9}, M^{-1} s^{-1}	k_R x10^{-9}, M^{-1} s^{-1}
Amitriptyline hydrochloride	FC-1-A	2.13	10.67	10.3±0.3
	FC-2-A	2.00	10.01	
Methyl salicylate	FC-1-S	1.43	7.17	7.1±0.1
	FC-2-S	1.42	7.11	
2-phenoxiethanol	FC-1-P	0.88	4.42	4.3±0.1
	FC-2-P	0.85	4.23	

3.2. Oxidation of the PPCPs in water systems.

In order to study the overall oxidation processes in real aqueous systems, several experiments on the simultaneous oxidation of the selected PPCPs in different water matrices were carried out at 20 ºC and at the specific pH of each water matrix (7.4-8.3). The oxidation system used was UV radiation, alone and combined with hydrogen peroxide to promote the generation of hydroxyl radicals. Table S5 shows the H_2O_2 dose applied for every experiment (0, 10 and 50 µM for the experiments numbered 1, 2 and 3, respectively). The water systems used were described in the Experimental Section: surface water (SW) from a public reservoir and two secondary effluents from the municipal wastewater treatment plants of the cities of Badajoz (SEB) and La Albuera (SEA). The experimental procedures for the photodegradation of the mixture of PPCPs in these water matrices were the same as the individual UV radiation in ultrapure water.

Table S5 also lists the removals reached for each PPCP at 15 min of reaction taken as example. Obviously, an increase in the removals of each compound is observed from experiment 1 to 3, due to the positive effect that exerts the initial hydrogen peroxide concentration on the indirect photodegradation by radicalary pathway. From the comparison of the data shown in Table S5, the higher reactivity of amitriptyline hydrochloride can be assumed once again, followed by methyl salicylate and 2-phenoxyethanol. The difference in reactivity between the last two PPCPs is more evident in UV/H_2O_2 systems (experiments 2 and 3), indicating a greater reactivity of methyl salicylate toward hydroxyl radicals, as stated in Section 3.1.2. In the same way, Figure 3 shows the evolution in the concentration of the three compounds in every experiment conducted in surface water. Again, it can be deduced the order of reactivity: amitriptyline hydrochloride > methyl salicylate > 2-phenoxyethanol, as well as the increase in the degradation when increasing the initial hydrogen peroxide concentration, especially in the experiment SW-3 with maximum initial concentration of H_2O_2.

Table S5. Photodegradation experiments in real water matrices

Expt.	$[H_2O_2]$ (µM)	X_A, % (15 min)	X_M, % (15 min)	X_P, % (15 min)
SW-1	0	52.1	27.9	22.5
SEB-1	0	66.0	16.0	23.9
SEA-1	0	71.3	47.5	24.9
SW-2	10	59.9	33.9	24.5
SEB-2	10	62.0	35.4	25.2
SEA-2	10	84.6	71.4	28.3
SW-3	50	99.0	58.4	49.1
SEB-3	50	83.3	57.0	31.7
SEA-3	50	91.9	88.9	39.1

Finally, the effect of the water matrix used on the efficiency of the degradation of the selected PPCPs can be also studied from their removals depicted in Table S5. According to these removals, the general sequence of efficiency in most of the compounds and experiments carried out in the water systems used is: SEA > SW > SEB. This trend can be explained by considering the content in total dissolved organic matter (DOM) present in these waters, mentioned in Section 2.4 and shown in Table S1. In effect, from this Table S1, one observes that the water matrix SEA presents lower content in TOC, COD and absorbance at 254 nm, followed by SW and finally SEB. Therefore, it can be concluded that the presence of organic matter dissolved in the water matrix may have a negative effect on the degradation of the PPCPs due to the competition of this DOM for both, photons and mainly hydroxyl radicals generated in the oxidizing system.

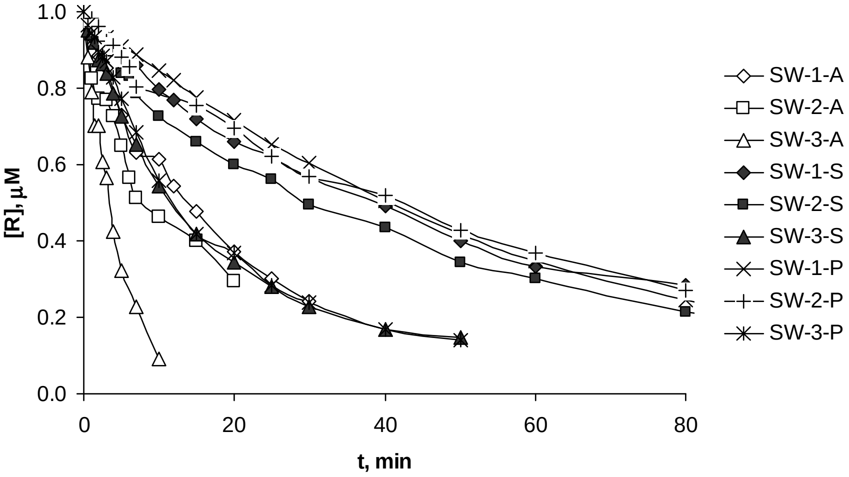

Figure 3. Oxidation curves of the selected PPCPs with reaction time in photodegradation experiments in surface water. Experimental conditions: T=20 ºC; pH=7.4; PPCPs initial concentration: 1 µM each one. Experiment SW-1: $[H_2O_2]_0$=0 µM. Experiment SW-2: $[H_2O_2]_0$=10 µM. Experiment SW-3: $[H_2O_2]_0$=50 µM.

In a final study of the simultaneous degradation of the PPCPs in different water matrices by UV and UV/H_2O_2 systems, a kinetic model previously applied successfully (Benitez et al., 2009) has been proposed in order to predict and model the photodegradation rate of these emerging contaminants in each water system. In this study, the quantum yields and second-order rate constants determined in Section 3.1 have been used to evaluate theoretically the removal of each compound with reaction time. For this purpose, a compound must be selected as reference compound (denoted R) and the evolution of its concentration in each experiment can be used to determine the first-order rate constants of both, direct photodegradation and radical pathway promoted by the presence of hydrogen peroxide, according to the following expression:

$$\ln\frac{[R]_o}{[R]} = k'_R\, t = \ln\frac{[R]_0}{[R]}\bigg|_d + \ln\frac{[R]_0}{[R]}\bigg|_r = (k'_{\phi-R} + k'_{OH-R})\, t \qquad [18]$$

where k'_R, $k'_{\phi\text{-}R}$ and $k'_{OH\text{-}R}$ represent the first-order rate constants for the overall photodecomposition, the direct photochemical decomposition (subscript d) and the radical decomposition (subscript r) reactions, respectively. These rate constants must be evaluated for the selected reference compound. In this work, 2-phenoxyethanol has been selected as reference compound, due to its intermediate reactivity in the experiments of degradation of the mixture of emerging contaminants in the three water systems used. Additional experiments of degradation of this mixture by UV radiation in presence of t-BuOH were carried out in order to determine the direct photochemical decomposition rate constant values $k'_{\phi\text{-}R}$, and subsequently, $k'_{OH\text{-}R}$ values. The corresponding values of these first-order rate constants are listed in Table S6 for every experiment carried out.

Table S6. First-order rate constants obtained for the reference compound (2-phenoxyethanol) in water systems.

Water Matrix	k'_R (1) x10^3 min^{-1}	k'_R (2) x10^3 min^{-1}	$k'_{OH\text{-}R}$ (2) x10^3 min^{-1}	k'_R (3) x10^3 min^{-1}	$k'_{OH\text{-}R}$ (3) x10^3 min^{-1}	k'_R (4) x10^3 min^{-1}	$k'_{OH\text{-}R}$ (4) x10^3 min^{-1}
SW	3.2	17.0	13.8	15.7	12.5	59.2	56.0
SEB	3.8	19.2	15.3	17.2	13.4	17.4	13.6
SEA	5.2	15.1	9.9	16.5	11.3	32.6	27.5

Thus, the evolution of the remaining compounds, amitriptyline hydrochloride and methyl salicylate (target compounds, denoted P) will be estimated along the reaction time from Equation (19), by using the data reported in Table S6:

$$\ln\frac{[P]_o}{[P]} = k'_P\, t = \frac{\phi_P\ \varepsilon_P}{\phi_R\ \varepsilon_R} k'_{\phi-R}\, t \ + \frac{k_{OH-P}}{k_{OH-R}} k'_{OH-R}\, t \qquad [19]$$

where k'_P represents the first-order rate constant for the overall decomposition reaction of the target compound. It can be evaluated as a function of ϕ_P and ε_P, and ϕ_R and ε_R, i.e. quantum yields and molar extinction coefficients for the target and reference compounds, respectively. Moreover, k_{OH-P} and k_{OH-R} are the second-order rate constants for the reaction between OH radicals and the target and the reference compounds, respectively; and $k'_{\phi-R}$ and k'_{OH-R} are the first-order rate constants for the reference compound. All these parameters, quantum yields, molar extinction coefficients and rate constants, were previously determined in this work, which permits to evaluate the overall first-order rate constants for the target compounds, being shown in Table S7.

Table S7. First-order rate constants obtained for the target compounds in water systems.

PPCPs	Water Matrix	k'_P (1) x10^3 min^{-1}	k'_P (2) x10^3 min^{-1}	k'_P (3) x10^3 min^{-1}	k'_R (4) x10^3 min^{-1}
Amitriptyline hydrochloride	SW	27.4	60.5	57.2	161.1
	SEB	32.2	68.9	64.1	64.8
	SEA	43.8	67.5	70.7	109.4
Methyl salycilate	SW	3.5	26.3	24.1	95.9
	SEB	4.1	29.4	26.1	26.6
	SEA	5.6	22.0	24.2	50.9

Experimental conditions: T=20 ºC; pH=7.4-8.3; PPCPs initial concentration: 1 µM each one.

(1) Experiments with UV/t-BuOH.
(2) Experiments 1, with UV radiation alone.
(3) Experiments 2, with UV/H_2O_2 system: $[H_2O_2]_0$ = 10 µM.
(4) Experiments 3, with UV/H_2O_2 system: $[H_2O_2]_0$ = 50 µM.

Finally, from those first-order rate constant values, the remaining concentration of each target compound can be determined theoretically in the experiments performed, and compared with the experimental results. Figure 4 presents this comparison, for both target compounds in the experiments SW-1 and SEB-2 taken as examples, where the symbols represent the experimental results, and the lines represent the predicted values by means of Equation 19. The fair agreement between predictions and experiments confirms the goodness of this kinetic approach. Moreover, Table S8 reports the relative errors obtained between predicted values and experimental results for each experiment. Once again, little deviations between theoretical and experimental curves can be observed in most of the experiments. Therefore, it can be concluded that the application of the present model can be of great interest in predicting the oxidation of these compounds during drinking water treatments.

Table S8. Relative errors between the model predictions and the experimental values in photodegradation experiments

PPCPs	Water Matrix	Error (1) (%)	Error (2) (%)	Error (3) (%)	Error (4) (%)
Amitriptyline hydrochloride	SW	7.7	1.3	1.5	5.7
	SEB	7.7	6.3	1.5	14.6
	SEA	13.8	9.1	16.2	8.0
Methyl salycilate	SW	2.2	-3.0	3.4	-9.0
	SEB	6.7	-14.8	3.6	14.4
	SEA	16.9	10.2	10.8	8.8

Experimental conditions: T=20 ºC; pH=7.4-8.3; PPCPs initial concentration: 1 µM each one.

(1) Experiments with UV/t-BuOH.

(2) Experiments 1, with UV radiation alone.

(3) Experiments 2, with UV/H_2O_2 system: $[H_2O_2]_0$ = 10 µM.

(4) Experiments 3, with UV/H_2O_2 system: $[H_2O_2]_0$ = 50 µM.

Negative errors mean that the predicted concentrations are lower than the experimental ones.

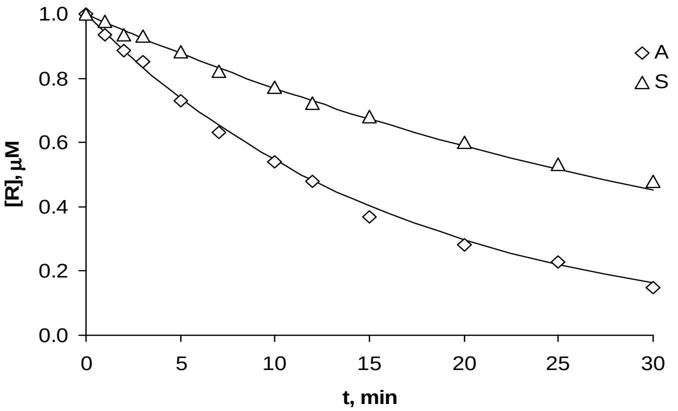

Figure 4a. Comparison of the predicted (lines) and experimental (symbols) concentrations of the PPCPs in experiment SW-1. Experimental conditions: T=20 ºC; PPCPs initial concentration: 1 μM, pH=7.4; $[H_2O_2]_0$=0 μM.

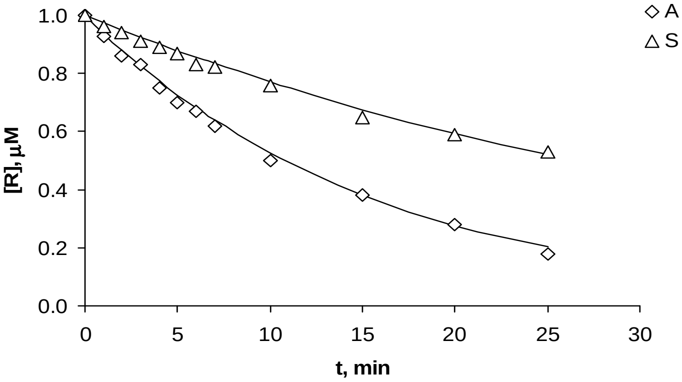

Figure 4b. Comparison of the predicted (lines) and experimental (symbols) concentrations of the PPCPs in experiment SEB-2. Experimental conditions: T=20 ºC; PPCPs initial concentration: 1 μM, pH= 8.3; $[H_2O_2]_0$= 10 μM.

4. CONCLUSIONS.

Three pharmaceuticals and personal care products were selected to be individually photooxidized in ultrapure water, by monochromatic UV radiation and UV/H_2O_2. Amitriptyline hydrochloride was shown more reactive towards photodegradation than methyl salicylate and 2-phenoxyethanol. Indirect photodegradation involving radicalary reactions was established as the main oxidation pathway of the three emerging contaminants. Quantum yields were determined in experiments of photodegradation at different pH using a radical scavenger.

Fenton's reagent experiments of the individual PPCPs were also carried out. The use of a competition kinetic model allowed to evaluate their rate constants with hydroxyl radicals. The following values were obtained: $(10.3\pm0.3)x10^9$ $M^{-1}\cdot s^{-1}$ for amitriptyline hydrochloride, $(7.1\pm0.1)x10^9$ $M^{-1}\cdot s^{-1}$ for methyl salicylate and $(4.3\pm0.1)x10^9$ $M^{-1}\cdot s^{-1}$ for 2-phenoxyethanol. Influence of different Fe/H_2O_2 systems used, initial reagent dose and pH was also evaluated.

Simultaneous oxidation experiments of these pharmaceuticals by UV radiation and by UV/H_2O_2 system were performed in three water systems: a surface water from a reservoir and two effluents from wastewater treatment plants. The influence of the operating conditions (presence of hydrogen peroxide, nature of the compounds and water matrix) on the PPCPs removal efficiency were established. Finally, a kinetic model was proposed for the prediction of the elimination of these emerging contaminants in these water matrices, using the kinetic parameters determined previously (rate constants and quantum yields), with theoretical results that agree well with the experimental ones.

REFERENCES

Benitez, F. J.; Real, F. J.; Acero, J. L.; Leal, A. I.; Garcia, C. Gallic acid degradation in aqueous solutions by UV/H_2O_2 treatment, Fenton's reagent and the photo-Fenton system. J. Hazard. Matet. **2005**, B126, 31-39.

Benitez, F. J.; Real, F. J.; Acero, J. L.; Roldan, G. Removal of selected pharmaceuticals in waters by photochemical processes. J. Chem. Technol. Biotechnol. **2009**, 84, 1186-1195.

Benitez, F. J.; Real, F. J.; Acero, J. L.; Garcia, C.; Llanos, E. M. Kinetics of phenyl-ureas oxidation by Fenton and photo-Fenton processes. J. Chem. Tech. Biotech. **2007**, 82, 65-73.

Blessel, K.W.; Rudy, B. C.; Senkowsky, B. Z. Analytical profiles of drug substances, Vol. 3; K. Florey, Editor, Academic Press: London, **1974**.

Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical review of rate constants for oxidation of hydrated electrons, hydrogen atoms and hydroxyl radicals (AOH/AO^-) in aqueous solutions. J. Phys. Chem. Ref. Data **1988**, 17, 513-886.

Canonica, S.; Meunier, L.; von Gunten, U. Phototransformation of selected pharmaceuticals during UV treatment of drinking water. Water Res. **2008**, 42, 121-128.

Canosa-Mas, C. E.; Duffy, J. M.; King, M. D.; Thompson, K. C.; Wayne, R. P. The atmospheric chemistry of methyl salicylate-reactions with atomic chlorine and with ozone. Atmospheric Environ. **2002**, 36, 2201-2205.

Chu, W. Modeling the quantum yields of herbicide 2,4-D decay in UV/H_2O_2 process, Chemosphere **2001**, 44, 935-941.

De Laat, J.; Gallard, H. Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: Mechanism and kinetic modelling. Environ. Sci. Technol. **1999**, 33, 2726-2732.

Esplugas, S.; Bila, D. M.; Krause, L. G. T.; Dezotti, M. Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. J. Hazard. Mater. **2007**, 149, 631-642.

Fent, K.; Weston, A. A.; Caminada, D. Ecotoxicology of human pharmaceuticals. Aquatic Toxicology **2006**, 76, 122-159.

Haag, W. R.; Yao, D. C. C. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. Environ. Sci. Technol. **1992**, 26, 1005 1013.

Ikehata, K; Nagashkar, N. J.; El-Din, M. G. Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: a review. Ozone Sci. Eng. **2006**, 28, 353-414.

Jacob, S. M.; Dranoff, J. S. Light intensity profiles in a perfectly mixed photoreactor. AIChE J. **1970**, 16, 359-363.

Jjemba P. K. Excretion and Ecotoxicity of pharmaceuticals and personal care products in the environment. Ecotoxicol. Environ. Safety **2006**, 63, 113-159.

Legrini, O.; Oliveros, E.; Braun, A. M. Photochemical processes for water treatment, Chem. Rev. **1993**, 93, 671 698.

Li, W.; Nanaboina, V.; Zhou, Q.; Korshin, G. V. Effects of Fenton treatment on the properties of effluent organic matter and their relationships with the degradation of pharmaceuticals and personal care products, Water Res. **2012**, 46, 403-412.

Puyol, D.; Monsalvo, V. M.; Mohedano, A. F.; Sanz, J. L.; Rodriguez, J. J. Cosmetic wastewater treatment by upflow anaerobic sludge blanket reactor. J. Hazard. Mater. **2011**, 185, 1059-1065.

Serjeant, E. P.; Dempsey, B. 1979. Ionisation constants of organic acids in aqueous solution. International Union of Pure and Applied Chemistry (IUPAC) Chemical Data Series No. 23; Pergamon Press: New York, **1979**.

Shen, Y. S.; Ku, Y.; Lee, K. C. The effect of light absorbance on the decomposition of chlorophenols by UV radiation and UV/H_2O_2 processes. Water Res. **1995**, 29, 907-914.

Ternes, T. A.; Meisenheimer, M.; McDowell, D.; Sacher, F.; Brauch, H. J.; Gulde, B. H.; Preuss, G.; Wilme, U.; Seibert, N. Z. Removal of pharmaceuticals during drinking water treatment. Environ. Sci. Technol. **2002**, 36 (17), 3855-3863.

Walling, C. Fenton’s reagent revisited. Acc. Chem. Res. **1975**, 8, 125-131.

Yue, L. Modelling of kinetics and reactors for water purification by photo-oxidation. Chem. Eng. Sci. **1993**, 48, 1-11.

3.3. Comparison between chlorination and ozonation treatments for the elimination of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in surface waters and secondary effluents.

Journal of Chemical Technology and Biotechnology 90 (8), 1357-1544 (2015).

3.3. COMPARISON BETWEEN CHLORINATION AND OZONATION TREATMENTS FOR THE ELIMINATION OF THE EMERGING CONTAMINANTS AMITRIPTYLINE HYDROCHLORIDE, METHYL SALICYLATE AND 2-PHENOXYETHANOL IN SURFACE WATERS AND SECONDARY EFFLUENTS.

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Journal of Chemical Technology and Biotechnology 90 (8), 1357-1544 (2015).

BACKGROUND: A new class of micropollutants, generally called as emerging contaminants (ECs), is increasingly found in surface waters and wastewaters. Due to their potential ecologic and health risks, ECs must be removed by using different procedures, such as chemical oxidation processes.

RESULTS: The oxidation of the selected ECs amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol has been investigated by means of two known oxidizing agents: chlorine and ozone. The efficiencies of elimination of each system have been compared, and apparent second-order rate constants of the reactions involved are determined. The variation of these kinetic parameters with the pH of work is also evaluated, which provides the determination of the intrinsic rate constant values for the oxidation reactions of the neutral and dissociated species. Additionally, the simultaneous oxidation of these selected ECs in different water systems (ultrapure water, surface water from a reservoir and two secondary effluents) is studied, and the influence of the operating conditions on the removal efficiency is established.

CONCLUSION: The reaction rates between chlorine or ozone and neutral and dissociated species revealed that ozonation process is around three orders of magnitude higher than chlorination.

Keywords: emerging contaminants; amitriptyline; methyl salicylate, 2-phenoxyethanol; chlorination; ozonation; rate constants.

1. INTRODUCTION.

The presence of a wide variety of emerging contaminants (ECs) in waters has been frequently reported in the last decade (Lapworth et al., 2012). Within this denomination it can be included compounds such as pharmaceuticals and personal care products (PPCPs), hormones, pesticides, dyes, etc. These ECs had not been considered before as contaminants because of their very small concentration in natural water and wastewater. However, recent studies show the potential ecologic and health risks derived from their bioactivity and toxicity, being now recognized themselves as micropollutants potentially dangerous that can produce damages in the ecosystem (Jjemba, 2006). Also, the fate of ECs through the environment is scarcely known, but several researchers reported that they are not completely eliminated by conventional water treatment processes; and consequently, they have been found in effluents exiting the treatment plants (Fatta-Kassinos et al., 2011).

In this way, several treatment technologies have recently been assayed with the aim of achieving high levels of elimination of these pollutants. Among them, chemical oxidation by advanced oxidation processes (AOPs), such as ozonation, photolytic degradation or Fenton‘s reagent, have demonstrated their effectiveness in the elimination of this group of substances, frequently based on the generation of very reactive radical species (Rivera-Utrilla et al., 2013; Prieto-Rodríguez et al., 2013). These AOPs can become a more efficient alternative to conventional treatments, such as oxidation processes by using chlorine or permanganate ion.

The purpose of the present work is to study the degradation of three selected ECs in different water matrices by two common oxidizing agents, with the aim to compare the efficiency of conventional and advanced treatments by establishing the kinetics of degradation with each system. In this case, the ECs amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol, were selected to be eliminated, and the oxidation systems chosen were chlorination and ozonation.

Amitriptyline hydrochloride is the most widely used tricyclic antidepressant. Methyl salicylate is a salicylic acid derivative, produced by esterification with methanol, and used as rubefacient, analgesic and anti-inflammatory. Finally, 2-phenoxyethanol is a bactericide often used in dermatological products, such as skin creams and sunscreens; and also, as fixative for perfumes, insecticide and topical antiseptic. These ECs have been found in surface waters and treated wastewaters in concentrations ranging from ng·L^{-1} to µg·L^{-1}. Specifically, 2-phenoxyethanol was found in surface waters at concentrations up to 14 µg·L^{-1} (Kimura et al., 2014), while amitriptyline was detected among other anxiolytics in both raw and treated wastewater, at concentration levels <900 ng·L^{-1} (Martínez Bueno et al. 2012), and also methyl salicylate was found in surface water at concentrations of 0.18 µg·L^{-1} (Kolpin et al., 2013). These ECs were already selected in a previous work (Real et al., 2012), in which their degradation by UV radiation and Fenton’s reagent was also studied.

Although some information on the elimination of ECs has been published (Rivera-Utrilla et al., 2013; Esplugas et al., 2007), very scarce studies on the elimination of these specific emerging contaminants have been found (Puyol et al., 2011; Canosa-Mas et al., 2002), and no kinetic parameters have been reported, with exception of that prior work (Real et al., 2012) in which quantum yields and rate constants for their reaction with OH radicals were provided. Therefore, the first step of the present study is focused on the determination of the efficiencies and rate constants for the individual reactions between each one of these ECs and chlorine or ozone separately in ultrapure water, as well as the establishment of the influence of the main operating conditions. Additionally, a study of the oxidation of a mixture of these compounds in several natural waters and secondary effluents by both oxidation procedures was also conducted.

2. EXPERIMENTAL.

2.1. Reagents.

Amitriptyline hydrochloride (A, $C_{20}H_{23}N{\cdot}HCl$, ≥99%), methyl salicylate (S, $C_8H_8O_3$, ≥98%) and 2-phenoxyethanol (P, $C_8H_{10}O_2$, ≥99%) were purchased from Sigma-Aldrich (Spain). Isoproturon, metoprolol, naproxen, amoxicillin and fenuron, used as reference compounds, were also purchased from Sigma-Aldrich. General reagents were obtained from Panreac (Spain), with pure component quality.

2.2. Experimental procedures.

In a first step, experiments for the determination of rate constants of the reactions between each EC and chlorine or ozone were conducted. The chlorination experiments were carried out under pseudo-first-order conditions, where chlorine, according to its hydrolysis reaction (Equation 1), was applied as hypochlorous acid at least 50 folds in excess with respect to the EC initial concentration (1 µM in all cases).

$$Cl_2 + H_2O \rightleftarrows HOCl + Cl^- + H^+ \qquad [1]$$

In these experiments, a 200 mL volume of a buffered solution of each EC was individually prepared in a batch reactor, located in a thermostatic bath at the desired temperature (20±0.2 ºC in most experiments), and at the designed pH by means of phosphoric acid/phosphate buffer 0.01 M. The experiments were started after addition of a volume of the chlorine stock solution into the reactor while stirring (for 5 seconds). At fixed time intervals, 2 mL of sample were retired and rapidly transferred with a syringe into a HPLC vial containing 10 µL of thiosulfate (0.1 M) to stop the reaction. The residual EC concentrations were analyzed directly by HPLC.

The ozonation experiments were carried out in semi-batch conditions with respect to ozone (which was fed in a gas stream) by using competition kinetics. The ozone was produced from a bottled purified synthetic air stream in a laboratory ozone generator (Sander, mod. 300.5; Ingetecsa, Barcelona, Spain). The ozone-air gas flow in every experiment was set at 40 $L{\cdot}h^{-1}$, and the inlet ozone concentration was adjusted to the desired value of $7x10^{-4}$ $g{\cdot}L^{-1}$ in the gas mixture. The gas stream was introduced through a porous plate into the reactor containing a solution of 350 mL of the corresponding EC and its adequate reference compound (10 µM, each one). The reacting mass was thermostated at 20±0.2 ºC and buffered at the selected pH by adding phosphoric acid/phosphate solution (0.01 M). The experiments were conducted in ultrapure water in presence of tert-butylalcohol (t-BuOH, 0.01 M) as OH radical scavenger, in order to scavenge the radicalary pathway, and to ensure that only direct ozonation is involved in the oxidation of each compound. At regular reaction times, samples were taken from the reactor in order to determine the concentrations of the EC and the reference compound.

In a second step, experiments for the chlorination and ozonation of ECs in natural waters and secondary effluents were performed with the aim to study the effect of the water matrix on the oxidation of the selected ECs. In these experiments, a mixture of the three compounds at concentrations of 1 µM for each one was used, at 20 ºC and at the natural pH of the water (around pH 7). The procedures followed were the same as described above. Nevertheless, neither reference compounds nor radical scavenger were used in these ozonation experiments. Besides, some ozonation plus hydrogen peroxide experiments were also conducted.

2.3. Analytical methods.

The three selected ECs, as well as the reference compounds used, were analysed by HPLC in a Waters Chromatograph equipped with a 996 Photodiode Array Detector and a Waters Nova-Pak C18 Column (5 µm 150x3.9 mm). The detection was performed at 238 nm for amitriptyline hydrochloride and methyl salicylate; and 220 nm for 2-phenoxyethanol and the reference compound amoxicillin. The remaining reference compounds were also detected at 238 nm. The mobile phase was a mixture of methanol and 0.01 M aqueous phosphoric acid solution in different proportions, depending on the mixture analysed. The elution flow rate was 1 mL min^{-1} and the injection volume was 100 µL in all samples.

2.4. Water systems.

Four different water systems were used in the present study for the oxidation of the selected ECs under realistic water treatment conditions. They were ultrapure water (UP) obtained from a Milipore Milli-Q system; surface water (SW), collected from the public reservoir “Peña del Aguila”, located in the Extremadura Community (southwest Spain); and two secondary effluents from municipal wastewater treatment plants, located in Badajoz (SEB) and La Albuera (SEA). These water systems were filtered through a 0.45 µm cellulose nitrate filter within the first 24 hours after collected and stored at 4 ºC until used. The main quality parameters of these water matrices are compiled in Table 1. Specifically, UV absorbance and TOC content constitute a significant indication of the total dissolved organic matter (DOM) present in these effluents, stuff of great influence in the performance of the different oxidation pathways involved.

Table 1. Quality parameters of the water matrices used.

Water matrix	pH	TOC ($mg \cdot L^{-1}$)	COD ($mg \cdot L^{-1}$)	$A_{254\,nm}$ (cm^{-1})	Alkalinity x10^3 ($mg \cdot L^{-1}$ $CaCO_3$)	Conductivity ($\mu S \cdot cm^{-1}$)	Bromide ($mg \cdot L^{-1}$)
UP	7.0	< 1.0	< 5	< 0.001	< 5	4	n.d.
SW	7.4	5.2	18	0.187	30	80	n.d.
SEB	8.3	11.1	56	0.245	325	550	n.d.
SEA	7.9	2.9	7	0.041	335	570	0.33

3. RESULTS AND DISCUSSION.

The oxidation of the three selected emerging contaminants amitriptyline hydrochloride (denoted A), methyl salicylate (denoted S) and 2-phenoxyethanol (denoted P) was carried out in a first stage in ultrapure water by using two oxidizing agents: hypochlorous acid and ozone. In a second stage, the oxidation of a mixture of the three compounds in different effluents was conducted with the aim to investigate the efficiencies of elimination of each compound with each oxidizing agent in more realistic conditions.

3.1. Chlorination of the ECs in ultrapure water.

The chlorination of the three selected ECs was studied in experiments carried out individually by using different initial concentrations of hypochlorous acid between 1x10^{-4} and 1x10^{-3} M; and also, by varying the pH from 3 to 10, and the temperature between 10 and 40 ºC. Table 2 summarizes the operating conditions for these experiments, as well as the removal values reached after 20 min of reaction, time taken as example.

Table 2. Individual chlorination of the selected ECs in ultrapure water: removal percentages obtained after 20 min of reaction and apparent second-order rate constants (k_{app}) for the chlorination process ($[EC]_0$ = 1 µM)

				Removals at 20 min, %			k_{app}, $M^{-1}s^{-1}$		
Expt.	$[Cl_2]_0$, Mx10^4	pH	T, ºC	X_A	X_S	X_P	k_{app-A}	k_{app-S}	k_{app-P}
1	1	3	20	80.0	11.6	37.6	13.9	0.18	2.9
2	1	4	20	45.1	12.6	9.4	4.2	0.21	0.33
3	1	5	20	51.7	24.0	2.6	5.0	0.39	0.204
4	1	6	20	56.0	25.5	2.4	6.6	1.5	0.14
5	1	7	20	87.8	59.8	8.1	22.7	7.0	0.15
6	1	8	20	> 95	86.7	10.6	48.3	20.4	0.17
7	1	9	20	> 99	> 95	11.0	50.4	24.5	0.15
8	1	10	20	78.1	89.7	5.7	12.2	19.2	0.17
9	1	7	10	54.8	48.8	1.0	6.9	4.7	0.07
10	1	7	30	> 95	79.2	10.9	48.5	12.2	0.21
11	1	7	40	> 99	87.9	11.8	81.6	17.0	0.27
12	5	7	20	> 95	> 95	4.2	5.4	7.0	0.03
13	10	7	20	> 99	> 99	7.0	3.1	5.7	0.03

As can be observed in Table 2, the removals at 20 min of reaction increased when increasing the initial concentration of chlorine (Experiments 5, 12 and 13) and temperature (Experiments 9, 5, 10 and 11), as could be expected. The effect of pH (Experiments 1-8), although apparently positive on the removal values reached for amitriptyline and methyl salicylate, needs a deeper consideration. Besides, a comparison of the data obtained for each EC allows to establish the following sequence of reactivity towards chlorine among these selected ECs: amitriptyline > methyl salicylate > 2-phenoxyethanol. The same sequence of reactivity was already observed towards other reactants such as UV radiation and OH radicals (Kimura et al., 2014), which probably indicates similar mechanisms of molecular breakage. Figure 1 depicts the oxidation curves of the three compounds with chlorine at pH 3 and 7, showing some of the influences previously described from Table 2, as a sequence of the reactivity of the selected ECs and the effect of the pH.

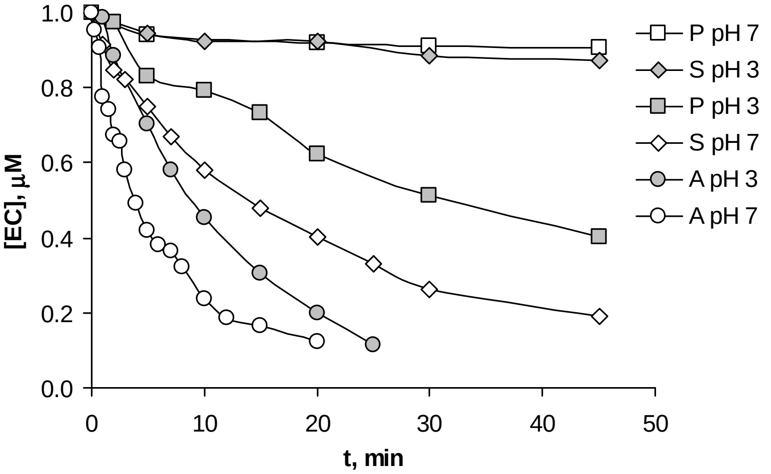

Figure 1. Oxidation curves of the selected ECs with reaction time in the chlorination experiments in ultrapure water. Experimental conditions: $[Cl_2]_0=10^{-4}$ M; $[EC]_0=1$ μM; pH=3 (Expt. 1) and pH=7 (Expt. 5). A: amitriptyline; P: 2-phenoxyethanol; S: methyl salicylate.

As it was pointed out, the effect of the pH is a more complex issue and it must be taken into account the different reactions involved within the chlorination mechanism. Thus, the decrease of the removal efficiency for the three ECs at higher pH values (pH 9-10; experiments 7 and 8) can be explained by considering the dissociation equilibrium of HOCl (Equation (2), pKa = 7.5) (Albert and Serjeant et al., 1984); as well as the very low reactivity of the deprotonated species OCl^- towards organic compounds, which must be considered as negligible (Deborde and von Gunten, 2008). Therefore, among the different species of chlorine present, only the reaction with HOCl might be taken into account.

$$HOCl \xrightleftharpoons{K_a} OCl^- + H^+ \qquad [2]$$

$$EC + HOCl \xrightarrow{k_1} Products \qquad [3]$$

$$EC + OCl^- \xrightarrow{k_1^{'}} Products \qquad [4]$$

Moreover, the acid dissociation of each EC must also be considered (Equation (5)). In effect, amitriptyline hydrochloride and methyl salicylate present pKa values of 9.4 and 9.9 (Blessel et al., 1974; Serjeant and Dempsey, 1979), respectively; whereas for 2-phenoxyethanol, no acid dissociation constant can be considered since its reported value is 15.1 (Serjeant and Dempsey, 1979).

$$EC \xrightleftharpoons{K_{a1}} EC^- + H^+ \qquad [5]$$

Therefore, the elimination of each EC by chlorine can take place on the neutral species, according to Equation (3); or the dissociated one EC^-, according to:

$$EC^- + HOCl \xrightarrow{k_2} Products \qquad [6]$$

Also, the acid-catalyzed reaction of HOCl with the EC in its neutral form must be taken into account at low pH values, as Equation (7) shows:

$$EC + HOCl + H^+ \xrightarrow{k_c} Products \qquad [7]$$

From Equations (3), (6) and (7), the overall elimination of each EC by chlorine can be represented by the following rate equation:

$$-\frac{d[EC]}{dt} = k_1[EC][HOCl] + k_2[EC^-][HOCl] + k_c[EC][HOCl][H^+] \qquad [8]$$

Taking into account that the chlorination experiments were performed under pseudo-first-order conditions, Equation (8) can be reduced to:

$$-\frac{d[EC]}{dt} = k_{app}[EC]_t[Cl_2]_t = k'[EC]_t \qquad [9]$$

In this Equation (9) k_{app} represents the apparent second-order rate constant, k' the pseudo-first-order rate constant, $[EC]_t$ the total concentration of each emerging contaminant, and $[Cl_2]_t$ the total concentration of chlorine species, equal to the sum of HOCl and ClO^- concentrations, according to reactions (1) and (2). Under this assumption, the rate constant values k' can be easily determined from the results of each experiment; and also the apparent rate constants k_{app}, because the chlorine concentration was kept constant throughout each experiment. Following this procedure, the determined apparent rate constants k_{app} for each experiment and EC are also listed in Table 2. Once again, it can be observed the positive effect of temperature (Experiments 9, 5, 10 and 11) and initial concentration of chlorine (Experiments 5, 12 and 13) for the three selected ECs, as well as the variation with the pH. Besides, Figure 2 depicts the evolution of these experimental apparent rate constant values in the studied pH range 3-10: it is observed that the sequence of reactivity with chlorine of the selected ECs previously established is confirmed. pK_a values of amitriptyline and methyl salicylate are also shown in Figure 2, which give an idea of the pH range of predominance of neutral and dissociated species.

Finally, by equaling Equations (9) and (8), and also, by introducing the equilibrium constants of reactions (2) and (5), the following expression can be deduced:

$$k_{app} = \frac{\left\{k_1[H^+] + k_2K_{a1} + k_c[H^+]^2\right\}\left\{\dfrac{[H^+]}{[H^+]+K_a}\right\}}{[H^+] + K_{a1}} \qquad [10]$$

where k_1, and k_2 and k_c are the intrinsic rate constants for the elementary reactions (3), (6) and (7) and K_{a1} and K_a the dissociation constants for each EC and HOCl, respectively. Whereas k_{app} and the dissociation constants are already known, the use of a non-linear least-squares regression analysis led to the evaluation of the intrinsic rate constant values, being compiled for the three selected ECs in Table 3.

The introduction of the calculated values into Equation (10) allows to determine theoretically the k_{app} rate constants for each compound at any selected pH value. Thus, Figure 2 shows these theoretical apparent rate constants for the selected ECs in the whole pH range, as well as the experimental values. The excellent agreement shown among them confirms the goodness of the proposed reaction mechanism. One can observe in Table 3 the much higher values of k_2 with respect to k_1, indicating an increase in the reaction rate with HOCl of the dissociated species EC^-. Also, the higher values of k_c with respect to k_1 for amitriptyline hydrochloride and 2-phenoxyethanol may explain the increase of the apparent rate constant at pH 3-4, where the acid-catalyzed reaction is enhanced, as Figure 2 shows. On the contrary, this effect is not shown for methyl salicylate which presents a very low k_c value. Obviously, due to the higher value of pK_a in the case of 2-phenoxyethanol (15.1), far outside the pH range studied, k_2 is not relevant for this EC.

Table 3. Intrinsic rate constants for the reactions of HOCl with EC species

ECs	k_1, $M^{-1}\cdot s^{-1}$	k_2, $M^{-1}\cdot s^{-1}$	k_c, $M^{-2}\cdot s^{-1}$
Amitriptyline·HCl	4.2 ± 0.3	5500 ± 350	8100 ± 650
Methyl salicylate	0.21 ± 0.01	8200 ± 400	< 1
2-Phenoxyethanol	0.15 ± 0.02		2700 ± 400

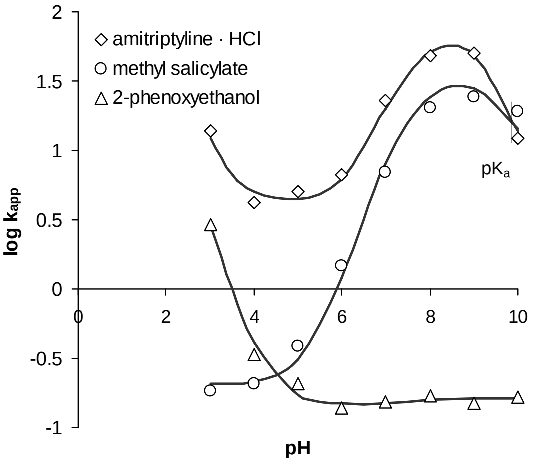

Figure 2. Apparent rate constants for the chlorination of selected ECs with the variation of pH: comparison of experimental (symbols) and calculated values from Equation (10).

3.2. Ozonation of the ECs in ultrapure water.

Individual ozonation experiments of the selected ECs were performed in ultrapure water at 20 ºC by feeding an ozone-air gas stream as stated in the Experimental Section. Competition kinetics was used with the aim to determine the second-order rate constants for the direct reaction between each EC and ozone at different pH values between 3 and 9. In these experiments t-BuOH was added to scavenge radical pathways, being the only reaction involved in the ozonation process the one represented by Equation (11). Competition kinetics model proposes a competition towards ozone of a target compound, in this case each EC, and a reference compound (R) whose ozonation rate constant k_R is previously known and presents similar reactivity towards ozone than the target compound, according to reactions (11) and (12).

$$EC + O_3 \xrightarrow{k_{O3}} Products \qquad [11]$$

$$R + O_3 \xrightarrow{k_R} Products \qquad [12]$$

According to these reactions, by dividing their corresponding kinetic equations, the following relationship can be deduced:

$$\ln\frac{[EC]_0}{[EC]} = \frac{k_{O3}}{k_R}\ln\frac{[R]_0}{[R]} \qquad [13]$$

This model has been satisfactorily used in heterogeneous conditions (Xiong and Graham, 1992; Benitez et al., 1998), but it is only applicable for situations in which the concentration of the organic compounds remain undepleted in the liquid film. In the present study, several adequate reference compounds were selected, each of them should exhibit similar reactivity to ozone that its corresponding target compound. Specific reference compounds used were: for amitriptyline, isoproturon at pH 3-7 and metoprolol at pH 8-9 (Benitez et al., 2007; 2009) ; for methyl salicylate, metoprolol at pH 3, isoproturon at pH 5, naproxen at pH 6-8 and amoxicillin pH 9 (Benitez et al., 2007; 2009); and for 2-phenoxyethanol, fenuron (Acero et al., 2001). According to Equation (13), plots of the logarithmic terms must lead to straight lines from whose slope the target rate constant value k_{O3} can be determined. Figure 3 shows this plot for some experiments taken as examples. As can be seen, experimental points lie satisfactory around straight lines passing through the origin, and confirming the goodness of the model used. Similar plots were obtained for the rest of the experiments.

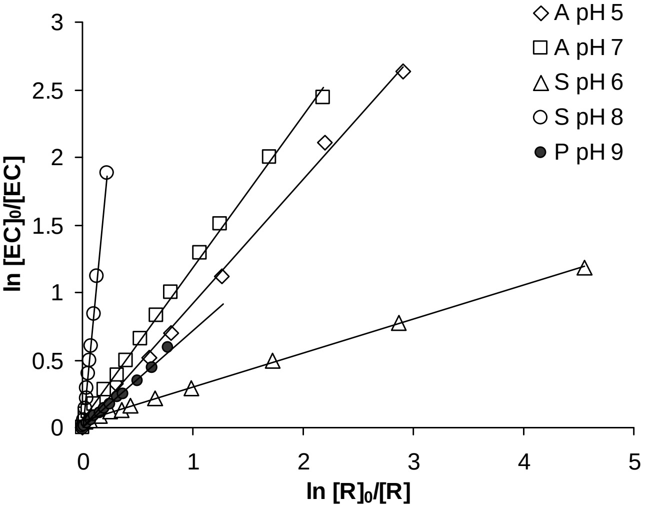

Figure 3. Determination of the apparent rate constants for the ozonation of selected ECs by the competition kinetics. Amitriptyline at pH 5 and 7 (R: isoproturon); methyl salicylate at pH 6 and 8 (R: naproxen) and 2-phenoxyethanol at pH 9 (R: fenuron). Experimental conditions: T=20 ºC; pH=7. ECs and reference compounds initial concentration: 10 μM each one.

Figure 4 depicts the variation with the pH of the k_{O3} rate constant values obtained for each ozonation experiment of amitriptyline hydrochloride and methyl salicylate conducted by applying this procedure. From the results shown in this Figure, it can be observed a positive influence of the pH on the elimination of these two ECs, since both present acid dissociation constant. Thus, in the ozonation of amitriptyline it can be noted a great leap of this rate constant between pH 7 and 9, near its reported pK_a value of 9.4. In the case of methyl salicylate (pK_a = 9.9) there is a steady increase of the rate constant with the pH from 190 $M^{-1}s^{-1}$ at pH 3 to $8.3x10^6$ $M^{-1}s^{-1}$ at pH 9. Finally, there is not influence of the pH on the removal of 2-phenoxyethanol by ozonation being proposed an average value of 150±5 $M^{-1}s^{-1}$, valid for the pH range of 3-9. Therefore, by considering the rate constant values of each EC, the following order of reactivity at pH 7 can be concluded: methyl salicylate > amitriptyline > 2-phenoxyethanol, although amitriptyline showed itself as the most reactive compound towards ozone at pH 3.

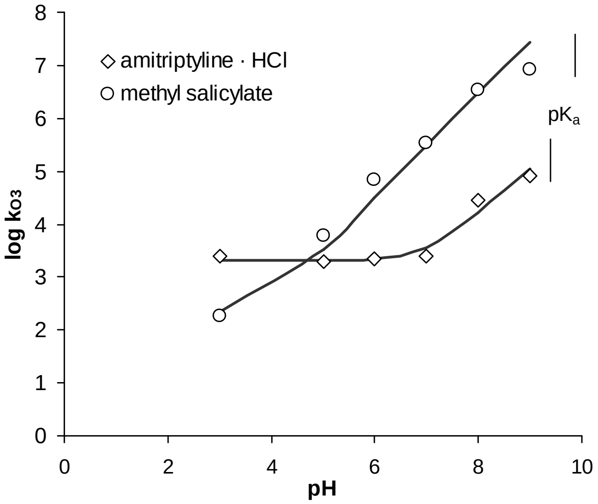

Figure 4. Apparent rate constants for the ozonation of amitriptyline and methyl salicylate with the variation of pH: comparison of experimental (symbols) and calculated values from Equation (15).

The variations of k_{O3} with the pH allow us again to determine the intrinsic rate constants k_1 and k_2 of the elementary reactions of each species with ozone in a similar way as in the chlorination study, being represented the direct ozonation of each EC by the expression:

$$-\frac{d[EC]}{dt}=k_1[EC][O_3]+k_2[EC^-][O_3]=k_{O3}[EC]_t[O_3] \qquad [14]$$

These intrinsic rate constants can be determined by applying the model initially proposed by Hoigné and Bader and later widely used by other authors (Benitez et al., 2003; Benner et al., 2008), which is based on the calculation of the respective fractions α_1 and α_2 for each one of the species. These parameters can be evaluated at each pH from the corresponding concentration of H^+ and pK$_a$ value. Thus, the apparent second-order rate constant, k_{O3}, can be expressed by Equation (15):

$$k_{O3}=\alpha_1 k_1+\alpha_2 k_2 \qquad [15]$$

As in the chlorination study, the use of a non-linear least-squares regression analysis allows us to evaluate the intrinsic rate constants, which are summarized in Table 4. As could be expected, the rate constant values for the dissociated species k_2 is much greater in both cases, indicating a higher reactivity of the dissociated species, which favour the electrophilic attack of ozone.

Finally, Figure 4 shows also the variation of the experimental (symbols) and theoretical (lines) apparent rate constant values for the ozonation of amitriptyline hydrochloride and methyl salicylate. The satisfactory agreement between both sets of rate constants for the two ECs again confirms the goodness of the intrinsic rate constants listed in Table 4. Furthermore, the comparison between the intrinsic rate constant values of Table 3 and 4 reveals that those for the ozonation reactions are of around three orders of magnitude higher than those of the chlorination reactions, suggesting a much greater efficiency of the ozonation process.

Table 4. Intrinsic rate constants for the reactions of ozone with EC species.

ECs	k_1, $M^{-1}\cdot s^{-1}$	k_2, $M^{-1}\cdot s^{-1}$
Amitriptyline·HCl	2040 ± 200	$(3.8 \pm 0.5)x10^5$
Methyl salicylate	184 ± 40	$(2.3 \pm 0.5)x10^8$
2-Phenoxyethanol	150 ± 5	

3.3 . Chlorination and ozonation of the selected ECs in water systems.

Once the individual chlorination and ozonation of the selected ECs in UP water was studied, the oxidation processes were performed in four different aqueous systems, with the aim of studying the efficiency of the overall process under more realistic water treatment conditions; and also, to investigate the effect of the water matrix. Thus, several experiments of simultaneous oxidation of the selected ECs dissolved together in the selected water matrices were carried out at 20 ºC and at the specific pH of each water matrix (7.0-8.3). The oxidation systems used were hypochlorous acid, ozone and ozone combined with hydrogen peroxide, with similar doses as the ones used in the preceding sections ($[Cl_2]_0=10^{-4}$ M for chlorination experiments; and 40 $L·h^{-1}$ of a $7x10^{-4}$ $g·L^{-1}$ of ozone gas stream for ozonation ones). The water systems used were described in the Experimental Section: ultrapure water of milli-Q quality (UP), surface water (SW) from a public reservoir, and two secondary effluents from the municipal wastewater treatment plants of the cities of Badajoz (SEB) and La Albuera (SEA). Tables 5 and 6 report the experiments carried out, as well as the removals obtained after 20 and 5 min of reaction for chlorination and ozonation experiments, respectively.

Table 5. Chlorination experiments of the selected ECs in different water matrices: removals obtained after 20 min (experimental conditions: T = 20 ºC; $[Cl_2]_0$ = 10^{-4} M; $[EC]_0$ = 1 µM each one).

Water matrix	pH	X_A, % (20 min)	X_S, % (20 min)	X_P, % (20 min)
UP	7.0	81.2	78.8	15.5
SW	7.4	77.9	47.5	16.2
SEB	8.3	41.8	22.0	8.4
SEA	7.9	> 99	93.9	10.2

[UP] = ultrapure water; [SW] = surface water from reservoir
[SEB] = secondary effluent from wastewater treatment plant of Badajoz
[SEA] = secondary effluent from wastewater treatment plant of La Albuera

According to the results compiled in Table 5 and 6, the trends observed in the individual chlorination and ozonation reactions of the three ECs are confirmed. That is, among the ECs the sequence of reactivity towards chlorine is again amitriptyline > methyl salicylate > 2-phenoxyethanol for the four waters tested. This trend is in agreement with the apparent rate constant values at pH 7, which are compiled in Table 2: that is, 22.7 $M^{-1}·s^{-1}$ for amitriptyline hydrochloride, 7.0 $M^{-1}·s^{-1}$ for methyl salicylate and 0.15 $M^{-1}·s^{-1}$ for 2-

phenoxyethanol. The same trend of apparent rate constants is fulfilled at pH 8, average pH value of the secondary effluents used (SEB and SEA).

Table 6. Ozonation experiments of the selected ECs in different water matrices: removals obtained after 5 min (experimental conditions: T = 20 ºC; $[EC]_0$ = 1 μM each one).

Water matrix	pH	$[H_2O_2]_0$ x10^4 (M)	X_A, % (5 min)	X_S, % (5 min)	X_P, % (5 min)
UP-1	7.0	0	> 95	> 99	76.3
SW-1	7.4	0	42.6	93.4	33.3
SEB-1	8.3	0	51.6	37.2	16.3
SEA-1	7.9	0	39.8	> 95	14.3
UP-2	7.0	1	> 99	100	> 95
SW-2	7.4	1	64.0	> 95	56.1
SEB-2	8.3	1	74.3	77.9	20.5
SEA-2	7.9	1	> 99	> 99	24.3

[UP] = ultrapure water; [SW] = surface water from reservoir
[SEB] = secondary effluent from wastewater treatment plant of Badajoz
[SEA] = secondary effluent from wastewater treatment plant of La Albuera

In the case of the ozonation process, the trend observed in Table 6 is again methyl salicylate > amitriptyline > 2-phenoxyethanol in most experiments. It must be noted that in this set of experiments no scavenger substance was used. Therefore, the removals observed in Table 6 correspond to both, direct ozonation and radical reactions. On the one hand, the rate constants of the direct ozonation at pH 7 are depicted mostly in Figure 4, that is: $2.5x10^3$ $M^{-1}\cdot s^{-1}$ for amitriptyline hydrochloride, $3.4x10^5$ $M^{-1}\cdot s^{-1}$ for methyl salicylate and 150 $M^{-1}\cdot s^{-1}$ for 2-phenoxyethanol, accordingly with the trend observed. On the other hand, the rate constants for the reactions of the selected ECs with the most reactive hydroxyl radicals has been recently reported in a previous work (Real et al., 2012), being their values 1.0×10^{10} $M^{-1} \cdot s^{-1}$ for amitriptyline hydrochloride, 7.1×10^{9} $M^{-1} \cdot s^{-1}$ for methyl salicylate and 4.3×10^{9} $M^{-1} \cdot s^{-1}$ for 2-phenoxyethanol. Therefore, for both oxidants, 2-phenoxyethanol is the least reactive EC, while methyl salicylate shows the highest value for the direct reaction with ozone and amitriptyline hydrochloride was the most reactive towards OH radicals.

Additionally, the presence of hydrogen peroxide provided higher efficiency towards ozonation. In this way, Figure 5 shows the oxidation curves of the three ECs for the three experiments carried out in the secondary effluent from Badajoz, SEB for chlorination, SEB-1 for ozonation, and SEB-2 for ozonation plus H_2O_2. It can be clearly observed the different reactivity of each EC and the effect of each oxidizing system used, in agreement with the influences previously described.

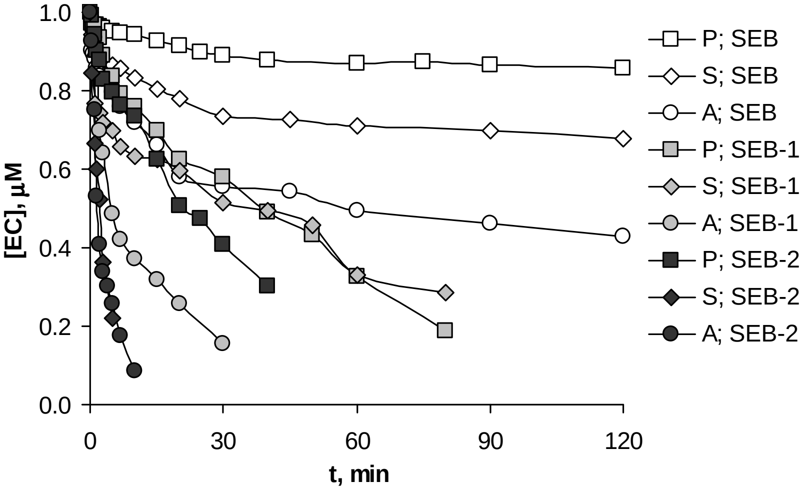

Figure 5. Oxidation curves of the selected ECs with reaction time in chlorination and ozonation experiments in the secondary effluent of municipal wastewater treatment plant of Badajoz. Experimental conditions: T=20 ºC; ECs initial concentration: 1 μM each one. Experiment SEB: chlorination; Experiment SEB-1: ozonation; Experiment SEB-2: ozonation plus hydrogen peroxide ($[H_2O_2]_0 = 1 \times 10^{-4}$ M).

With regard to the water matrix used, lower removals of every compound were obtained when increasing the organic matter content of the water, measured as TOC, COD or absorbance at 254 nm, according to the data collected in Table 1. Therefore, it can be concluded that the organic matter present in the water matrices competes with ECs for the oxidizing agents. Also, alkalinity content of the water matrix plays and important role on the indirect ozonation process, since carbonate or bicarbonate anions scavenge radical pathways. As a result, experiments carried out in secondary effluents present lower removals due to their higher alkalinity, especially for 2-phenoxyethanol, whose direct ozonation rate constant was clearly lower and is more dependent on the indirect pathway. Specifically, in the case of chlorination experiments, very high removals were observed in the experiment carried out in the effluent from the treatment plant of La Albuera (SEA). This fact can be explained by taking into account the presence of bromide ion, as reported in Table 1. In effect, this ion can be responsible of secondary reactions involving the formation of hypobromous acid according to Equation (16) (Deborde and von Gunten, 2008), which may enhance the elimination of organic compounds (Acero et al, 2013).

$$\mathrm{HOCl} + \mathrm{Br}^- \leftrightarrow \mathrm{HOBr} + \mathrm{Cl}^- \qquad [16]$$

In the remaining chlorination experiments, the negative effect on the removals reached by the organic matter content in the water matrix can be clearly observed.

4. CONCLUSIONS.

Three emerging contaminants were selected to be oxidized in different water matrices, by chlorine and ozone, leading to the following conclusions:

- Amitriptyline hydrochloride was shown the most reactive compound towards chlorine and methyl salicylate towards ozone, while 2-phenoxyethanol was clearly found as the least reactive one in both treatments. Chlorination removals were increased with increasing temperatures and initial concentrations of chlorine.

- Apparent second-order rate constants for chlorination and ozonation were determined at different pH, allowing to determine the intrinsic rate constants for neutral and dissociated species. Results confirm that ozonation provided rate constant values of around three orders of magnitude higher than those of chlorination.

- Simultaneous oxidation experiments of these EC by chlorination and ozonation performed in four water systems confirmed the trends previously stated: sequence of degradation among the selected ECs and efficiency of each treatment. Also, the effect on the ECs removal efficiency of the water matrices used and the presence of hydrogen peroxide was established.

REFERENCES

Acero J.L.; Benitez F.J.; Gonzalez M. and Benitez R. Kinetics of fenuron decomposition by single-chemical oxidants and combined systems. Ind. Eng. Chem. Res. **2002**, 41, 4225-4232.

Acero J.L.; Benitez F.J.; Real F.J.; Roldan G. and Rodriguez E. Chlorination and bromination kinetics of emerging contaminants in aqueous systems. Chem. Eng. J. **2013**, 219, 43-50.

Albert A. and Serjeant E.P. The determination of ionization constants: a laboratory manual. 3rd Ed Chapman and Hall, London and New York **1984**.

Benitez F.J.; Beltran-Heredia J.; Gonzalez T. and Real F.J.; Kinetics of the direct reaction between ozone and phenolic aldehydes. J. Chem. Technol. Biotechnol. **1998**, 72, 235-244.

Benitez F.J.; Acero J.L.; Real F.J. and Garcia J. Kinetics of photodegradation and ozonation of pentachlorophenol. Chemosphere **2003**, 51, 651-662.

Benitez F.J.; Real F.J.; Acero J.L. and Garcia C. Kinetics of the transformation of phenyl-urea herbicides during ozonation of natural waters: rate constants and model predictions. Water Res. **2007**, 41, 4073-4084.

Benitez F.J.; Acero J.L. Real F.J. and Roldan G. Ozonation of pharmaceutical compounds: Rate constants and elimination in various water matrices. Chemosphere **2009**, 77, 53-59.

Benner J.; Salhi E.; Ternes T. and von Gunten U. Ozonation of reverse osmosis concentrate: kinetics and efficiency of beta blocker oxidation. Water Res. **2008**, 42, 3003-3012.

Blessel K.W.; Rudy B.C. and Senkowsky B.Z. Analytical profiles of drug substances. Vol. 3, K. Florey, Editor, Academic Press, London **1974**.

Canosa-Mas C.E., Duffy J.M.; King M.D.; Thompson K.C. and Wayne R.P. The atmospheric chemistry of methyl salicylate-reactions with atomic chlorine and with ozone. Atmospheric Environ. **2002**, 36, 2201-2205.

Deborde M. and von Gunten U. Reactions of chlorine with inorganic and organic compounds during water treatment-Kinetics and mechanism: A critical review. Water Res. **2008**, 42, 13-51.

Esplugas S.; Bila D.M.; Krause L.G.T. and Dezotti M. Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. J. Hazard Mater. **2007**, 149, 631-642.

Fatta-Kassinos D.; Meric S. and Nikolaou A. Pharmaceutical residues in environmental waters and wastewater: current state of knowledge and future research. Anal. Bioanal. Chem. **2011**, 399, 251-275.

Hoigné J. and Bader H. Rate constants of reactions of ozone with organic and inorganic compounds in water-II. Dissociating organic compounds. Water Res. **1983**, 17,185-194.

Jjemba P.K. Excretion and ecotoxicity of pharmaceuticals and personal care products in the environment. Ecotoxicol. Environ. Safety. **2006**, 63, 113-159.

Kimura K.; Kameda Y.; Yamamoto H.; Nakada N.; Tamura I.; Miyazaki M. and Masunaga S. Occurrence of preservatives and antimicrobials in Japanese rivers. Chemosphere in press, http://dx.doi.org/10.1016/j.chemosphere.2014.01.008 **2014**.

Kolpin D.W.; Blazer V.S.; Gray J.L.; Focazio M.J.; Young J.A.; Alvarez D.A.; Iwanowicz L.R.; Foreman W.T., Furlong E.T., Speiran G.K., Zaugg S.D., Hubbard L.E., Meyer M.T.; Sandstrom M.W. and Barber L.B. Chemical contaminants in water and sediment near fish nesting sites in the Potomac River basin: Determining potential exposures to smallmouth bass (Micropterus dolomieu). Sci. Total. Environ. **2013**, 443, 700-716.

Lapworth D.J.; Baran N., Stuart M.E. and Ward R.S. Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environ. Pollut. **2013**, 163, 287-303.

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

Prieto-Rodríguez L.; Oller I.; Klamerth N.; Agüera A.; Rodríguez E.M. and Malato S. Application of solar AOPs and ozonation for elimination of micropollutants in municipal wastewater treatment plant effluents. Water Res. **2013**, 47, 1521-1528.

Puyol D.; Monsalvo V.M.; Mohedano A.F.; Sanz J.L. and Rodriguez J.J. Cosmetic wastewater treatment by upflow anaerobic sludge blanket reactor. J. Hazard Mater. **2011**, 185:1059-1065.

Real F.J.; Benitez F.J.; Acero J.L.; Roldan G. and Casas F. Elimination of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in ultrapure water and secondary effluents by photolytic and radicalary pathways. Ind. Eng. Chem. Res. **2012**, 51, 16209-16215.

Rivera-Utrilla J.; Sánchez-Polo M.; Ferro-García M.A.; Prados-Joya G. and Ocampo-Pérez R. Pharmaceuticals as emerging contaminants and their removal from water. A review. Chemosphere **2013**, 93, 1268-1287.

Serjeant E.P. and Dempsey B. Ionisation constants of organic acids in aqueous solution. International Union of Pure and Applied Chemistry (IUPAC) Chemical Data Series No 23, Pergamon Press, New York **1979**.

Xiong F. and Graham N.J.D. Rate constants for herbicide degradation by ozone. Ozone Sci. Eng. **1992**, 14, 283-301.

3.4. Oxidation of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol by persulfate activated by UV irradiation.

Journal of Chemical Technology and Biotechnology 91 (4), 1004-1011 (2016).

3.4. OXIDATION OF THE EMERGING CONTAMINANTS AMITRIPTYLINE HYDROCHLORIDE, METHYL SALICYLATE AND 2-PHENOXYETHANOL BY PERSULFATE ACTIVATED BY UV IRRADIATION.

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BACKGROUND: Despite the small concentration of emerging contaminants (ECs) in water systems, in recent years numerous works have reported potential toxicological risks associated to their presence in the environment, being recommendable their elimination by different procedures, such as chemical oxidation processes.

RESULTS: The elimination of three selected emerging contaminants (ECs), amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in aqueous solutions by persulfate photochemically activated has been investigated. Main operating conditions, such as persulfate dose, temperature, pH and buffer used, were varied and efficiencies of elimination and apparent pseudo-first-order rate constants of the oxidation reactions were determined for comparison purposes. The role of reactive oxygen species generated in the system, such as $SO_4{\cdot}^-$ and HO·, in the overall oxidation of the ECs was determined by using suitable scavenger compounds. Moreover, thermally activated persulfate was around 15-50 times less reactive than the UV/persulfate system. Finally, second-order rate constants for the reaction between sulfate radical and each EC were determined by competition kinetics, and the values obtained were $(4.8 \pm 0.6)\times10^{9}$ $M^{-1}{\cdot}s^{-1}$ for amitriptyline hydrochloride, $(9.2 \pm 0.9)\times10^{8}$ $M^{-1}{\cdot}s^{-1}$ for methyl salicylate, and $(1.38 \pm 0.02)\times10^{9}$ $M^{-1}{\cdot}s^{-1}$ for 2-phenoxyethanol.

CONCLUSION: Both radical species $SO_4^{\cdot -}$ and HO· exert an important role on the oxidation of the ECs investigated by the UV/persulfate system, being the contribution of sulfate radicals predominant for those compounds with low reactivity towards HO radicals.

Keywords: emerging contaminants; amitriptyline; methyl salicylate; 2-phenoxyethanol; persulfate; rate constants.

1. INTRODUCTION.

During recent years, the contamination of water resources by micropollutants has become a growing concern. Among them, emerging contaminants (ECs) are particularly relevant, being frequently identified during the last decade in wastewaters and aquatic environments (Lapworth et al., 2012). The term ECs is generally used to cover not only newly developed compounds but also compounds newly discovered in the environment, often due to analytical developments (Richardson and Ternes, 2011). Nevertheless, published results concerning occurrence, and especially potential toxicological effects and treatment of ECs are limited. Due to their large number (ranging in an order of thousands) (Thomaidis et al., 2012; Ibañez et al., 2013; Miranda-García et al., 2011), only few of these compounds have been evaluated.

Several technologies have been assayed successfully with the aim of reaching high levels of elimination of these ECs (Ibañez et al., 2013; Miranda-García et al., 2011; Benitez et al., 2013). Among them, advanced oxidation processes (AOPs) have shown to be very effective towards these compounds, even in the cases of ECs that were very refractory to conventional treatments, such as oxidation processes by using chlorine or permanganate ion (Real et al., 2015).

In this work, the elimination of three selected ECs (amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol) by means of an AOP based on sulfate radicals has been studied in experiments carried out in aqueous solutions. Amitriptyline hydrochloride is the most widely used tricyclic antidepressant; methyl salicylate is a salicylic acid derivative produced by esterification with methanol and used as rubefacient, analgesic and anti-inflammatory; and 2-phenoxyethanol is a bactericide often used in dermatological products, fixative for perfumes, insecticide and topical antiseptic.

Sulfate radical ($SO_4^{\cdot-}$) is a very strong oxidant (E^o = 2.43 V) which can react quickly with aromatic compounds with a selectivity slightly higher than hydroxyl radical (Neta et al., 1977). An advantage of the AOPs based on sulfate radicals is that the final product of the oxidation is sulfate ion, which is practically inert and is not considered to be a pollutant (Chan et al., 2010). Persulfate ion ($S_2O_8^{2-}$) is the most common oxidant used for the generation of sulfate radicals. Persulfate is generally stable under typical water treatment conditions. However, the activation of persulfate can be performed by three main ways, heat, transition metals and UV irradiation. Specifically, formation of sulfate radicals can be induced via thermal and photochemical activation according to Equation (1) (Wilmarth et al., 1962):

$$S_2O_8^{2-} \xrightarrow{\Delta\ /\ h\nu} 2\,SO_4^{\cdot-} \qquad [1]$$

A 254-nm monochromatic UV irradiation was used in this work for the activation of persulfate ion, which has been successfully applied in previous researches (Criquet and Leitner, 2009; He et al., 2013). Previous studies showed that sulfate radicals can subsequently produce hydroxyl radicals ($HO^{\cdot}$) (E^o = 2.7 V) by means of reactions (2) and (3) (Xie et al., 2012; Huang et al., 2002).

$$SO_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + HO\cdot + H^+ \qquad \text{all pH} \quad [2]$$

$$SO_4^{\cdot-} + HO^- \rightarrow SO_4^{2-} + HO\cdot \qquad \text{alkaline pH} \quad [3]$$

Therefore, both reactive oxygen species, sulfate and hydroxyl radicals, are responsible of the oxidizing action of this AOP. At pH below 7, $SO_4\cdot^-$ is the dominant free radical, whereas both radicals are important at pH 7-9, and HO· is the predominant radical at higher pH (Liang and Su, 2009).

Rate constants of selected ECs with hydroxyl radicals were determined in a previous work (Real et al., 2012). However, rate constants for the reactions of these ECs with sulfate radicals are still unknown. The aim of this work was to establish the relative role of both reactive oxygen species in the oxidation of the selected ECs under different aqueous pH, temperature and persulfate concentration conditions. In addition, the impact of activation methods on persulfate oxidation of ECs was evaluated. Finally, the second-order rate constants for the reactions between each EC and sulfate radicals were determined by competition kinetics.

2. EXPERIMENTAL.

2.1. Reagents.

Amitriptyline hydrochloride (AH, $C_{20}H_{23}N \cdot HCl$, ≥99%), methyl salicylate (MS, $C_8H_8O_3$, ≥98%) and 2-phenoxyethanol (PE, $C_8H_{10}O_2$, ≥99%) were purchased from Sigma-Aldrich (Spain). Isoproturon ($C_{12}H_{18}N_2O$, ≥99%), used as reference compound, was also purchased from Sigma-Aldrich. Sodium persulfate ($Na_2S_2O_8$) and other general reagents were obtained from Panreac (Spain), with pure component quality. All the solutions were prepared by dissolved each EC in deionized water provided by a Milli-Q water system (Millipore, USA).

2.2. Experimental procedures.

The experiments of oxidation of the selected ECs by persulfate activated with UV irradiation were carried out in a 500 mL jacketed column reactor thermostatized at the consigned temperature and stirred by a magnetic stirrer. A low pressure vapour mercury lamp (TNN 15/32, nominal electrical power 15W; Heraeus, Madrid, Spain) which emitted monochromatic radiation at 254 nm, was located inside the reactor in axial position and was protected by a quartz sleeve which housed the lamp. Several experiments were performed at different temperature (10-30 ºC) and pH (3-9). For every experiment conducted, the reactor was filled with 350mL of solution containing 1 µM of a single EC at the selected pH (10 mM phosphate or perchlorate buffer). Persulfate was added to reach a molar concentration 25-100 times higher than the EC initial concentration. Once connected the lamp, the reaction started and samples were periodically withdrawn from the reactor to analyze the residual EC concentration by HPLC analysis after quenching the reaction with 0.1 M sodium thiosulfate.

Control experiments using chemical probes were carried out to evaluate the contribution of the reactive oxygen species generated in the system, such as $SO_4\cdot^-$ and HO·, in the overall oxidation of the ECs by persulfate. In that sense, tert-butanol (t-BuOH, 0.01 M) was added as HO· scavenger, and 2-propanol (0.01 M) as HO· and $SO_4\cdot^-$ scavenger. Besides, an experiment in presence of 0.01 M $NaHCO_3$ was conducted with the aim of estimating the scavenging effect of bicarbonate ions. Moreover, oxidation experiments by thermally activated persulfate were conducted at 56 ºC in absence of UV irradiation.

A competition kinetic method was used for determining the second-order rate constant of the reaction of each EC with sulfate radicals. These experiments were carried out in the same conditions at pH 7 but adding a reference compound (isoproturon) whose second-order rate constant with sulfate radical is known. Also, t-BuOH was added as HO radical scavenger, in order to quench the reactions involving hydroxyl radicals and to ensure that $SO_4\cdot^-$ is the only radical species involved in the oxidation of each compound. Control experiments to evaluate the direct photodegradation contribution were also conducted. At regular reaction times, samples were taken from the reactor and residual EC and reference compound concentrations were analyzed.

2.3. Analytical methods.

The three selected ECs, as well as the reference compound used, were analysed by HPLC in a Waters Chromatograph (Waters, Milford, MA, USA) equipped with a 996 Photodiode Array Detector and a Waters Nova-Pak C18 Column (5 μm 150x3.9 mm). The detection was performed at 238 nm for amitriptyline hydrochloride and methyl salicylate; and 220 nm for 2-phenoxyethanol. Reference compound was detected at 248 nm. The mobile phase was a mixture of methanol and 0.01 M aqueous phosphoric acid solution in different proportions, depending on the compounds analysed. The elution flow rate was 1 mL min^{-1} and the injection volume was 100 μL in all samples.

3. RESULTS AND DISCUSSION.

The oxidation by persulfate of the three selected emerging contaminants amitriptyline hydrochloride (denoted AH), methyl salicylate (denoted MS) and 2-

phenoxyethanol (denoted PE) was carried in deionized water. In a first stage, apparent pseudo-first-order rate constants were determined and the influence of the main operating conditions evaluated. In a second stage, the use of competition kinetics led to the determination of the second-order rate constant of the reaction between each EC and sulfate radicals.

3.1. Oxidation of selected ECs by persulfate.

The oxidation of the three selected ECs by persulfate activated with UV irradiation ($UV/S_2O_8^{2-}$) was studied in experiments carried out individually at pH values between 3 and 9. In addition, the effect of temperature (from 10 to 30 ºC, for MS), initial concentration of persulfate (from 25 to 100 μM, for PE), and type of buffer or presence of bicarbonate (for AH) was also investigated. Table 1 summarizes the operating conditions for these experiments, as well as the removal values reached after 90 seconds of reaction, time taken as example. Note that experiments 1, 2, 3, 10, 11 and 12 actually compile three different experiments carried out in the same conditions, each of them with an individual EC. Table 1 also collects the pseudo-first-order rate constants, k, determined for every experiment according to Eq (4), for comparison purposes. Pseudo-first-order kinetics is plausible for this reaction due to the great $Na_2S_2O_8$/EC ratio applied, and consequently because, according to the quasi-steady-state hypothesis, the concentration of the radical intermediates $SO_4\cdot^-$ and $HO\cdot$ should remain almost constant along the reaction (He et al., 2013; Xie et al., 2012). As verification, all the regression coefficients (R^2) estimated for the evaluation of these rate constants presented values ranged between 0.98 and 0.999, indicating a good agreement of the reaction to pseudo-first-order kinetics.

$$\ln\frac{[\mathrm{EC}]_0}{[\mathrm{EC}]} = k\ t \qquad [4]$$

Among the selected ECs for this study, AH was the most reactive compound towards the $UV/S_2O_8^{2-}$ system, followed by PE, and finally MS, according to the pseudo-first-order rate constants for Expts. 1-3 compiled in Table 1. Moreover, Figure 1 depicts a plot of $\ln[EC]_0/[EC]$ versus time, according to Equation (4), for the three ECs for experiments conducted at pH 7 (Expt. 2), showing also this sequence of reactivity. The good agreement of the data points to straight lines indicates the goodness of the assumed pseudo-first-order kinetics.

Table 1. Individual oxidation of the selected ECs by UV/persulfate in deionized water: removal percentages (X) obtained after 90 s of reaction and apparent pseudo-first-order rate constants (k) for the oxidation process ($[EC]_0$ = 1 μM).

					AH		MS		PE	
Expt.	$[S_2O_8^{2-}]_0$, μM	pH	T, ºC	Buffer / scavenger	X_{AH}, % (90 s)	k x10^3, s^{-1}	X_{MS}, % (90 s)	k x10^3, s^{-1}	X_{PE}, % (90 s)	k x10^3, s^{-1}
1	50	3	20	H_3PO_4/HPO_4^{2-}	81.2	24.5	70.4	14.2	80.5	17.8
2	50	7	20	H_3PO_4/HPO_4^{2-}	100	68.5	44.5	7.7	70,3	15.1
3	50	9	20	H_3PO_4/HPO_4^{2-}	100	65.8	39.2	6.5	75.8	14.6
4	50	7	10	H_3PO_4/HPO_4^{2-}			22.5	3.6		
5	50	7	30	H_3PO_4/HPO_4^{2-}			83.9	19.4		
6	25	7	20	H_3PO_4/HPO_4^{2-}					50.3	8.6
7	100	7	20	H_3PO_4/HPO_4^{2-}					100	30.5
8	50	7	20	$HClO_4/ClO_4^-$	100	37.2				
9	50	7	20	HCO_3^-	67.7	11.4				
10	50	7	20	t-BuOH	38.4	6.2	12.4	1.7	31.2	4.9
11	50	7	20	2-propanol	7.4	0.99	3.6	0.27	6.7	0.51
12	50	7	56	No UV lamp	9.9	1.36	5.1	0.50	6.8	0.59

As can be observed in Table 1, removals at 90 s of reaction and pseudo-first-order rate constants increased when increasing the initial concentration of persulfate (Expts. 6, 2 and 7 for PE) indicating a positive influence of this operative variable on the oxidation rate of ECs. Thus, the pseudo-first-order rate constant for the reaction of PE increased from 8.6x10^{-3} s^{-1} with an initial concentration of persulfate of 25 μM to 3.05x10^{-2} s^{-1} with 100 μM. A plot of the natural logarithm of the pseudo-first-order rate constant (ln k) versus the natural logarithm of the initial persulfate concentration yielded a straight line with a slope of 0.91 (R^2=0.996), indicating that the rate of PE degradation was proportional to initial persulfate concentration, at least in the concentration range used in the present investigation. In addition, the reaction was approximately first-order with respect to persulfate, which indicates that an oxidizing species (mostly likely $SO_4^{\cdot-}$) might dominate the reaction with PE although different radical species could exist in the system and react with PE (Anipsitakis and Dionysiou, 2004).

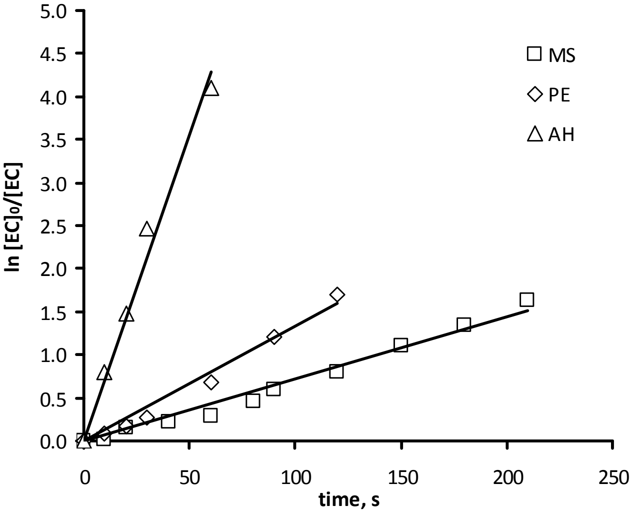

Figure 1. Oxidation of selected ECs using the UV/$S_2O_8^{2-}$ system in deionized water. Experimental conditions: $[S_2O_8^{2-}]_0$=50 μM; $[EC]_0$=1 μM; T=20 ºC; pH=7. MS: methyl salicylate; PE: 2-phenoxyethanol; AH: amitriptyline hydrochloride.

With respect to the effect of temperature (Expts. 4, 2 and 5 for MS), Fig. 2. shows the semi-logarithmic graph of $[MS]_0/[MS]$ under different temperature as a function of reaction time. The excellent linear fits (R^2>0.99) of experimental data confirmed pseudo-first-order kinetics. The rate of MS degradation increased as a function of temperature, as it can be appreciated in Table 1, since MS rate constants increased from $3.6\text{x}10^{-3}$ s^{-1} at 10ºC to $1.94\text{x}10^{-2}$ s^{-1} at 30ºC. Therefore, more active species (sulfate or hydroxyl radicals) may yield at higher temperatures resulting in faster pollutants degradation (Deng et al., 2013). The activation energy (E_a), responsible for sulfate radical generation and, secondarily, hydroxyl radical generation (Equations (1)-(3)) is obtained by fitting the temperature dependent rate constant into an Arrhenius equation (inset of Fig. 2), giving a value of 60.0 kJ/mol. Similar value of 49.97 kJ/mol was obtained for aniline (Xe et al., 2012). As a consequence, changing the system temperature is one of the ways to control the generation of sulfate or hydroxyl radicals.

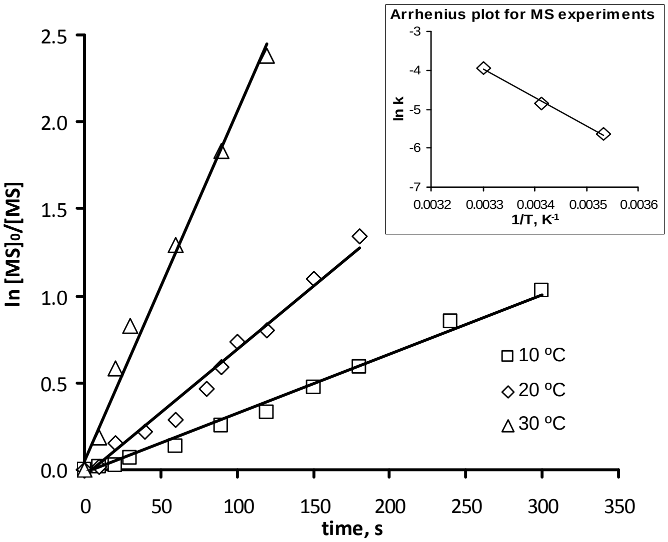

Figure 2. Oxidation of methyl salicylate (MS) using the UV/$S_2O_8^{2-}$ system under different temperatures. Experimental conditions: $[S_2O_8^{2-}]_0$=50 μM; $[MS]_0$=1 μM; pH=7. Inset; Arrhenius plot.

The effect of pH (Expts. 1-3) was different for each EC studied. While oxidation of AH showed a positive effect of pH, its influence on MS degradation was negative, and pseudo-first-order rate constants of the oxidation of PE did not show a significant variation at different pH values. These different trends of reactivity with the pH may be explained, on one hand by the acid dissociation of each EC (pK_a values for AH and MS of 9.4 and 9.9, respectively; no acid dissociation constant is considered for PE since its reported value is 15.1) (Blessel et al., 1974; Serjeant and Dempsey, 1979), and on the other hand, by the predominance of the main radical species involved in the oxidation process. In that sense, Liang and Su (2009), found that $SO_4\cdot^-$ is the predominant radical at pH < 7; both $SO_4\cdot^-$ and HO· are present at pH 9 and HO· is the predominant radical at a more basic pH. In addition, while the transformation of sulfate radicals into HO radicals is favoured at high pH (Eq. (3)), the dissociation of persulfate into sulfate radicals could be acidic-catalyzed, which might accelerate ECs degradation at low pH (House, 1962). Therefore, it is assumed that different reactivity of each EC with each radical species as well as different mechanisms of reaction can affect the overall oxidation capacity of the UV/persulfate process. Thus, if the previously reported second-order rate constants for the reaction of the selected ECs with HO radicals are considered (1.0×10^{10} $M^{-1} \cdot s^{-1}$ for AH, 7.1×10^{9} $M^{-1} \cdot s^{-1}$ for MS and 4.3×10^{9} $M^{-1} \cdot s^{-1}$ for PE) (Real et al., 2016) it can be assumed that the oxidation by means of hydroxyl radicals may occur in greater extent for AH than for MS and PE. This would explain the positive influence of pH on the AH oxidation rate, since HO radicals are promoted at high pH. Similarly to the negative pH effect on MS oxidation, the rate of MTBE removal by persulfate decreased with increasing solution pH (Gu et al., 2013). However, Liang et al. (2007) found that neutral conditions were favourable for TCE degradation. Finally, the presence of anionic species of selected buffers could increase the scavenger capacity due to their higher reaction rate constants with hydroxyl and sulfate radicals, leading to a lower oxidation rate of selected ECs.

The influence of the buffer used was also investigated in experiments carried out with AH. In other advanced oxidation processes, such as Fenton's reagent, the effect of the buffer used has been stated (Benitez et al., 2001), causing complexation of some of the oxidizing agents and compromising the good performance of the process. In order to determine the possible influence of the nature of the buffer on the oxidation by the $UV/S_2O_8^{2-}$ process, two buffer systems were assayed: H_3PO_4/HPO_4^{2-} and $HClO_4/ClO_4^-$ (Expts. 2 and 8, respectively). The results show complete elimination of AH after 90 s of reaction in both cases, although the oxidation rate was slightly slower in the experiment performed with $HClO_4/ClO_4^-$ buffer (pseudo-first-order rate constant of 6.85×10^{-2} and 3.72×10^{-2} s^{-1} for H_3PO_4/HPO_4^{2-} and $HClO_4/ClO_4^-$, respectively). Although the buffer concentration was 0.01 M, buffers had lower scavenger rate than AH, since rate constants of the reactions of $H_2PO_4^-$ with HO and sulfate radicals are 2.0×10^{4} and 7×10^{4}, respectively (Adewuyi and Owusu, 2006; Maruthamuthu and Neta, 1978). In a previous work involving Fenton's reagent (Benitez et al., 2001) phosphoric acid/phosphate led to slower oxidation of organic compounds due to the quenching of iron ions through formation of stable complexes with phosphate ion (Pignatello, 1992). In conclusion, the nature of the buffer may affect slightly on the performance of the oxidation process, although this effect was not as pronounced as in other advanced oxidation processes catalyzed by metallic ions.

The influence of the presence of carbonate/bicarbonate ions, well-known radical scavengers, was also investigated in order to anticipate its negative effect, since carbonate or bicarbonate ions usually can be found in natural water eligible for water treatment. As with hydroxyl radicals, sulfate radicals can also react with HCO_3^- and CO_3^{2-} at different rates (Huang et al., 2002). This effect was again investigated only for AH (Expt. 9 in contrast to Expt. 2), leading to a great decrease in the pseudo-first-order rate constant, from $6.85x10^{-2}$ s^{-1} in absence of HCO_3^- to $1.14x10^{-2}$ s^{-1} when using a concentration of 0.01 M of sodium bicarbonate at pH 7. In a previous work, Deng et al. (2013) found that the inhibition of inorganic anions on the degradation of carbamazepine followed the order $CO_3^{2-} > HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$. Moreover, the scavenging capacity of carbonate/bicarbonate ions increases at higher pH. These results suggest that the presence of carbonate or bicarbonate ions in the water to be treated must be taken into account in order to prevent the scavenging of the reactive oxygen species.

In order to evaluate the contribution of the reactive oxygen species generated in the system, such as $SO_4\cdot^-$ and HO·, in the overall oxidation of the ECs by UV/persulfate, control experiments using two different scavengers were used. Literature reports that alcohols containing an α-hydrogen, such as 2-propanol, react at high rates with both radical species (rate constants for reactions with hydroxyl and sulfate radicals of $1.9x10^9$ and $8.2x10^7$ M^{-1} s^{-1}, respectively) (Clifton and Huie, 1989; Buxton et al., 1988, Xu et al., 2014). However, alcohols without α-hydrogen, such as tert-butanol (t-BuOH), are significantly more reactive with hydroxyl radicals than with sulfate radicals (rate constants for reactions with hydroxyl and sulfate radicals of $5.2x10^8$ and $8.4x10^5$ M^{-1} s^{-1}, respectively) (Buxton et al., 1988, Xu et al., 2014). These properties have been successfully applied to distinguish the predominance between both radical species in a thermally activated persulfate system (Xu et al., 2014). Therefore, oxidation experiments in presence of 0.01 M of t-BuOH and 2-propanol (Expts. 10 and 11) have been performed at pH 7 with each EC individually. Under these conditions, while 2-propanol efficiently scavenged both hydroxyl and sulfate radicals, t-BuOH was able to scavenge HO radicals almost completely and only partially sulfate radicals (Lutze et al., 2015). In this sense, Lutze et al. 2014 determined a scavenging of $SO_4\cdot^-$ by 20-40% in the degradation of atrazine by sulfate radicals when using the same concentration of t-BuOH. Figure 3 depicts the decay of MS, taken as example, for experiments carried out in absence of scavenger, with t-BuOH and with 2-propanol (Expts. 2, 10 and 11, respectively). As can be observed, the presence of t-BuOH and specially of 2-propanol inhibited significantly the degradation rate of MS. Similar plots were obtained from the other ECs studied.

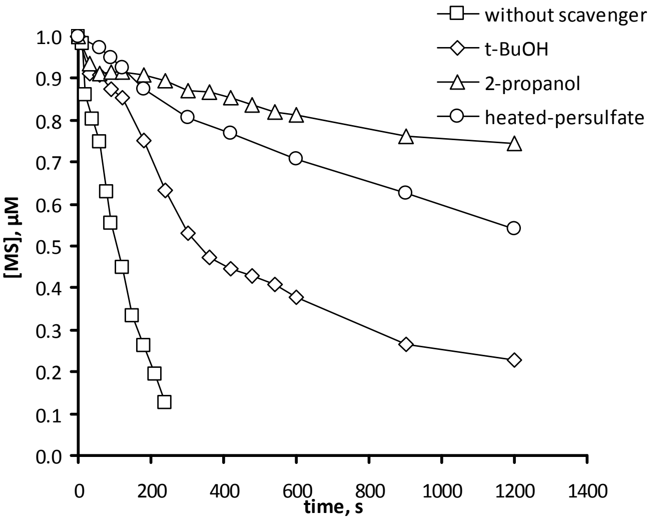

Figure 3. Oxidation curves of MS with reaction time using UV/$S_2O_8^{2-}$ and heated-persulfate systems in deionized water. Effect of the presence of radical scavengers t-BuOH and isopropanol. Experimental conditions: $[S_2O_8^{2-}]_0$=50 µM; $[MS]_0$=1 µM; $[scavenger]_0$= 0.01 M; T=20 ºC except for the heated-persulfate experiment (56 ºC); pH=7.

In order to better quantify the effect of each reactive oxygen species, a complementary study has been carried out, taking into account the contribution of both direct photolysis and radical pathway. These two pathways can be expressed by Equations (5) and (6), respectively (Benitez et al., 2009):

$$EC + h\nu \xrightarrow{k_{UV}} EC_{oxid} \quad [5]$$

$$EC + R \xrightarrow{k_R} EC_{oxid} \quad [6]$$

where k_{UV} and k_R are the pseudo-first-order rate constants of each reaction and R represents all the reactive oxygen species involved in the oxidation of the ECs, although only $SO_4\cdot^-$ and HO· have been considered in this system. In agreement with the proposed mechanism, the global degradation rate of each EC, r_T can be expressed as the sum of both reaction rates, according to:

$$-r_T = \left(-\frac{d[EC]}{dt}\right) = -(r_{UV} + r_R) = (k_{UV} + k_R)[EC] = k_T[EC] \qquad [7]$$

being k_T the total pseudo-first-order rate constant referred in Equation (4) and exposed in Table 1. A comparison of the first-order rate constants k_R and k_{UV} for each experiment conducted should indicate the weight of both pathways on the overall oxidation of each EC. Since the k_{UV} values were determined in a previous research (Real et al., 2012), k_R can be calculated according to Equation (7) by subtraction of k_{UV} from k_T. Table 2 compiles all the pseudo-first-order rate constants determined, as well as the half-lives for each experiment. Therefore, taking into account that in Expt. 10 HO radicals were quenched and in Expt. 11 both $SO_4\cdot^-$ and HO· were quenched, k_R values of each experiment will provide valuable information about the role of each of them in the oxidation of any EC.

Table 2. Pseudo-first-order rate constants (k_T, k_R) and half-lives ($t_{1/2}$) for the oxidation with UV/persulfate and photolysis of selected ECs at pH 7.

EC	AH			MS			PE		
Expt.	k_T x10^4, s^{-1}	k_R x10^4, s^{-1}	$t_{1/2}$, s	k_T x10^4, s^{-1}	k_R x10^4, s^{-1}	$t_{1/2}$, s	k_T x10^4, s^{-1}	k_R x10^4, s^{-1}	$t_{1/2}$, s
2	685	676	10.1	77.3	76.6	89.3	151	150	45.9
10	62.3	53.5	111	17.4	16.6	398	49.0	48.0	141
11	9.93	1.10	698	2.70	1.95	2567	5.10	4.08	1359
k_{UV} (1)	8.83	-	-	0.75	-	-	1.02	-	-

(1) Real et al., 2012.

From the results exposed in Table 2, first of all, an almost negligible contribution of the direct photolysis to the oxidation of these compounds by the UV/persulfate system can be assumed, since its contribution to the total rate constant k_T is less than 1.3%. Also, it can be concluded that the presence of 2-propanol (Expt. 11) led to a greater inhibition of the oxidation of the three ECs, being the values of the pseudo-first-order rate constant comparable to those of direct photolysis. This fact would indicate the almost total inhibition of the radical pathway, ranging the decrease of the rate constant between 96% and 99%. On the other hand, the inhibitory effect of the presence t-BuOH (Expt. 10) was lower in all cases, leading to a decrease of the radical pathway of 94%, 80% and 68% for AH, MS and PE, respectively. The removal of ECs in presence of t-BuOH was due to their reaction with sulfate radicals. Anyway, it must be taken into account that sulfate radicals were also partially scavenged by t-BuOH (20-40%) (Lutze et al., 2015), hence those percentages of inhibition should not be attributed entirely to the quenching of HO radicals. These results give an idea about the role of both reactive oxygen species, in the same way as previously did Figure 3 for MS. Thus, as the decay of the pseudo-first-order rate constants was staggered when quenched completely one or both radicals, it can be deduced that both of them exert an important role in the oxidation of these ECs by persulfate activated by UV irradiation at pH 7. Although it is difficult to quantify these effects, results indicate that the role of HO radicals must be very important in the oxidation of AH, and less significant for MS and PE, which is in agreement with the previously reported second-order rate constants towards hydroxyl radicals (Real et al., 2012) and with the different effects of the pH on the decay of AH and MS observed before. On the contrary, the role of sulfate radicals might be more important when the reactivity of target pollutants with HO radicals is rather low, as occurs with PE.

Finally, an oxidation experiment of each EC was carried out by using thermally activated persulfate in absence of UV irradiation, with the aim of comparing both, UV and thermally activated persulfate processes. Table 1 also collects the conditions (56ºC) and results obtained in Expt. 12. As can be observed in this Table, the pseudo-first-order rate constants were very low, with values of $1.4x10^{-3}$, $5.0x10^{-4}$ and $5.9x10^{-4}$ s^{-1} for AH, MS and PE, respectively. Therefore, heated-persulfate rate constants were between 15 and 50 times lower than those of the UV/persulfate process. Figure 3 also depicts the evolution of MS in this experiment for comparison purposes. In this Figure it is remarkable the poor efficiency of the heated-persulfate system, even worse than that carried out by photochemical activation in presence of HO radical scavengers. These results confirm the

$UV/S_2O_8^{2-}$ system as the best of those tested for the oxidation of the selected ECs, at least with a temperature up to 56 ºC. In addition, it has been shown in previous investigations that the $UV/S_2O_8^{2-}$ system is even more efficient for the removal of micropollutants than the UV/H_2O_2 process at the same molar concentration of the oxidant (He et al., 2013; Mendez-Diaz et al., 2010). Although some components of natural waters, such as NOM and bicarbonate, could act as radical scavengers and thus inhibit the destruction of contaminants, the presence of transition metals, such as Cu^{2+} and Fe^{2+}, in water sources could enhance the transformation of persulfate into sulfate radicals and benefit the removal of micropollutants.

3.2. Determination of the second-order rate constant of the reaction between ECs and sulfate radicals.

Individual experiments of the oxidation of the selected ECs by sulfate radicals were performed in deionized water at 20 ºC by competition kinetics with the aim of determining the second-order rate constant for this reaction. The competition kinetic method allows to remove the unknown concentration of the reactive species $SO_4\cdot^-$ from the kinetic equation by comparing its simultaneous effect on target and reference compounds. This method has already been successfully tested for the determination of rate constants for reactions involving sulfate radicals photochemically generated (He et al., 2013). Isoproturon was selected as reference compound, since its second-order rate constant for the reaction with sulfate radicals is previously known (k_{SO4-R} = 2.90x10^9 M^{-1} s^{-1}) (Canle et al., 2005). t-BuOH was added in all these experiments to quench the hydroxyl radicals generation. In addition, blank experiments in absence of persulfate were carried out in order to confirm that there was not apparent UV direct photolysis of ECs and isoproturon, indicating no direct photolysis adjustment was necessary (Pereira et al., 2007). Therefore, sulfate radicals were responsible for the oxidation of each EC, as was also stated in the previous section.

Competition kinetics model proposes a competition towards sulfate radicals of a target compound, in this case each EC individually, and a reference compound (R) whose rate constant k_{SO4-R} is previously known, according to reactions (8) and (9).

$$EC + SO_4^{\cdot -} \xrightarrow{k_{SO_4^{\cdot -}-EC}} Products \qquad [8]$$

$$R + SO_4^{\cdot -} \xrightarrow{k_{SO_4^{\cdot -}-R}} Products \qquad [9]$$

By dividing their corresponding kinetic equations and integrating, the following equation can be deduced:

$$\ln\frac{[EC]_0}{[EC]} = \frac{k_{SO_4^{\cdot -}-EC}}{k_{SO_4^{\cdot -}-R}} \ln\frac{[R]_0}{[R]} \qquad [10]$$

According to Equation (10), plots of the logarithmic terms must lead to straight lines from whose slope the target rate constant value k_{SO4-EC} can be determined. Figure 4 shows this plot for the experiments carried out (two for every EC at different persulfate initial concentrations). As can be seen, experimental points lie satisfactory around straight lines passing through the origin, confirming the goodness of the model used.

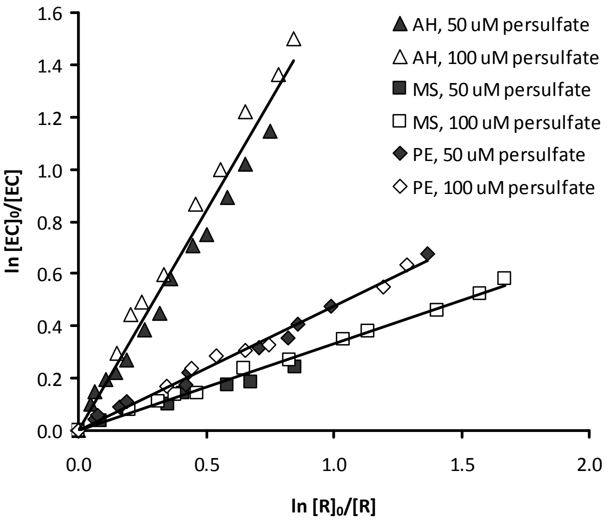

Figure 4. Determination of second-order rate constants for the oxidation of selected ECs with $SO_4^{\cdot -}$ by the competition kinetics. Experimental conditions: T=20 ºC; pH=7; $[EC]_0$=$[isoproturon]_0$=1 μM; $[t\text{-}BuOH]_0$= 0.01 M.

Table 3 shows the results obtained for the experiments conducted. The slopes are shown with their corresponding errors, which were calculated with 95% confidence intervals. The low error values also prove the goodness of competition kinetics. Finally,

Table 3 also shows the average second-order rate constant values proposed for the reaction between sulfate radicals and each EC, as well as the standard deviations for the couple of experiments carried out with each of them, being (4.8 ± 0.6)x10^9 M^{-1}·s^{-1} for AH, (9.2 ± 0.9)x10^8 M^{-1}·s^{-1} for MS and (1.38 ± 0.02)x10^9 M^{-1}·s^{-1} for PE. The results compiled in this Table, and also the previously reported second-order rate constants for the reaction of the selected ECs with HO radicals (1.0x10^{10} M^{-1}·s^{-1} for AH, 7.1x10^9 M^{-1}·s^{-1} for MS and 4.3x10^9 M^{-1}·s^{-1} for PE) (Real et al., 2012), can explain the trends of relative reactivity of the three selected ECs exposed in Figure 1 and through the pseudo-first-order rate constants shown in Table 1 for Expt. 2 (6.8x10^{-2} s^{-1} for AH, 7.7x10^{-3} s^{-1} for MS and 1.7x10^{-2} s^{-1} for PE). In effect, AH is confirmed as the most reactive EC towards both radical species according to the second-order rate constants exposed above. Also, the lowest reactivity of MS observed in the previous section, in agreement with the trend of reactivity for the reaction with sulfate radicals and not with hydroxyl radicals, allows to deduce the important role of sulfate radicals in the overall process.

Table 3. Individual oxidation of the selected ECs by sulfate radicals: determination of second-order rate constants (k_{SO4-EC}) ($[EC]_0$ = $[R]_0$= 1 μM; T = 20 ºC; $[t\text{-}BuOH]_0$ = 0.01 M).

EC	$[S_2O_8^{2-}]_0$, μM	slope	k_{SO4-EC}, x10^{-9} $M^{-1}s^{-1}$	k_{SO4-EC}, x10^{-9} $M^{-1}s^{-1}$
AH	50	1.53 ± 0.02	4.44	4.8 ± 0.6
	100	1.80 ± 0.03	5.23	
MS	50	0.294 ± 0.010	0.853	0.92 ± 0.09
	100	0.337 ± 0.003	0.978	
PE	50	0.474 ± 0.009	1.38	1.38 ± 0.02
	100	0.479 ± 0.010	1.39	

Reference compound: isoproturon (k_{SO4-R} = 2.90x10^9 M^{-1} s^{-1}) (Canle et al., 2005).

4. CONCLUSIONS.

The three emerging contaminants selected were quickly eliminated by using the UV/$S_2O_8^{2-}$ system. AH was removed at 2 min of reaction, PE at 2.5 min and MS needed more than 4 min when using 50 μM of persulfate ion at pH intervals from 3 to 9. The observed pseudo-first-order rate constants increased with initial concentration of persulfate and temperature. While oxidation of AH showed a positive effect of pH, its influence on MS degradation was negative, and the degradation of PE did not show a significant variation at different pH values.

The use of adequate scavenger compounds allowed to determine the role of the reactive oxygen species involved, HO· and $SO_4\cdot^-$ radicals, resulting both species important in the elimination of each EC studied. The results indicate that the role of HO radicals must be very important in the oxidation of AH, and less significant for MS and PE, which is in agreement with the values of second-order rate constants for the reactions with hydroxyl radicals. Meanwhile, the role of sulfate radicals might be more important when the reactivity of target pollutants with HO radicals is rather low, as occurs with PE.

The comparison of the UV/persulfate system with thermally activated persulfate allows to conclude that the heated-persulfate system is around 15-50 times less reactive than the UV/persulfate process, at least for the conditions tested in this work.

Finally, second-order rate constants for the reaction between sulfate radicals and each EC were determined by competition kinetics, being their values $(4.8 \pm 0.6)\text{x}10^9\ M^{-1}\cdot s^{-1}$ for AH, $(9.2 \pm 0.9)\text{x}10^8\ M^{-1}\cdot s^{-1}$ for MS, and $(1.38 \pm 0.02)\text{x}10^9\ M^{-1}\cdot s^{-1}$ for PE.

REFERENCES

Adewuyi Y.G. and Owusu S.O. Ultrasound-induced aqueous removal of nitric oxide from flue gases: effects of sulfur dioxide, chloride, and chemical oxidant. J. Phys. Chem. A. **2006**, 110, 11098-11107.

Anipsitakis G.P. and Dionysiou D.D. Radical generation by the interaction of transition metals with common oxidants. Environ. Sci. Technol. **2004**, 38, 3705-3712.

Benitez F.J.; Acero J.L.; Real F.J.; Rubio F.J. and Leal A.I. The role of hydroxyl radicals for the decomposition of p-hydroxyphenyl acetic acid in aqueous solutions. Water Res. **2001**, 35, 1338-1343.

Benitez F.J.; Real F.J.; Acero J.L. and Roldan G. Removal of selected pharmaceuticals in waters by photochemical processes. J. Chem. Technol. Biotechnol. **2009**, 84, 1186-1195.

Benitez F.J.; Acero J.L.; Real F.J.; Roldan G. and Rodriguez E. Modeling the photodegradation of emerging contaminants in waters by UV radiation and UV/H_2O_2 system. J. Environ. Sci. Health A. **2013**, 48, 120-128.

Blessel K.W.; Rudy B.C. and Senkowsky B.Z. Analytical profiles of drug substances. Vol. 3, Florey K, Editor, Academic Press, London , **1974**.

Buxton G.V.; Greenstock C.L.; Helman W.P. and Ross A.B.; Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals. J. Phys. Chem. Ref. Data**. 1988, 17**, 513-886.

Canle M.; Fernández M.I.; Rodríguez S.; Santaballa J.A.; Steenken S. and Vulliet E. Mechanisms of direct and TiO_2-photocatalysed UV degradation of phenylurea herbicides. *ChemPhysChem.* **2005**, 6, 2064-2074.

Clifton C.L. and Huie R.E. Rate constants for hydrogen abstraction reactions of the sulfate radical, $SO_4^{\cdot-}$. Alcohols. Int. J. Chem. Kinet. **21**:677-687 (1989).

Criquet J. and Leitner N.K.V. Degradation of acetic acid with sulfate radical generated by persulfate ions photolysis. Chemosphere **2009**, 77, 194-200.

Chan T.W., Graham N.J.D. and Chu W. Degradation of iopromide by combined UV irradiation and peroxydisulfate. J. Hazard Mater. **2010, 181**, 508-513.

Deng J.; Shao Y.; Gao N.; Deng Y.; Zhou S. and Hu X. Thermally activated persulfate (TAP) oxidation of antiepileptic drug carbamazepine in water. Chem. Eng. J. **2013**, 228, 765-771.

Gu X.; Lu S.; Qiu Z.; Sui Q.; Banks C.J.; Imai T. Lin K. and Luo Q. Photodegradation performance of 1,1,1-trichloroethane in aqueous solution: In the presence and absence of persulfate. Chem. Eng. J. **2013**, 215-216, 29-35.

He X.; de la Cruz A.A. and Dionysiou D.D. Destruction of cyanobacterial toxin cylindrospermopsin by hydroxyl radicals and sulfate radicals using UV-254 nm activation of hydrogen peroxide, persulfate and peroxymonosulfate. J. Photochem. Photobiol. A. **2013**, 251, 160-166 (2013).

House D.A. Kinetics and mechanism of oxidations by peroxydisulfate. Chem. Rev. **1962**, 62, 185-203.

Huang K.C.; Couttenye R.A. and Hoag G.E.; Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE). Chemosphere **2002**, 49(4), 413-420 (2002).

Ibañez M.; Gracia-Lor E.; Bijlsma L.; Morales E.; Pastor L. and Hernández F. Removal of emerging contaminants in sewage water subjected to advanced oxidation with ozone. J. Hazard Mater. **2013**, 260, 389-398.

Lapworth D.J.; Baran N.; Stuart M.E. and Ward R.S. Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environ. Pollut. **2012**, 163, 287-303.

Liang C.J.; Wang Z. and Bruell C.J. Influence of pH on persulfate oxidation of TCE at ambient temperatures. Chemosphere **2007**, 66, 106-113.

Liang C.J. and Su H.W. Identification of sulfate and hydroxyl radicals in thermally activated persulfate. Ind. Eng. Chem. Res. **2009,** 48(11), 5558-5562.

Lutze H.V.; Bircher S.; Rapp I.; Kerlin N.; Bakkour R.; Geisler M.; von Sonntag C. and Schmidt T.C. Degradation of chlorotriazine pesticides by sulfate radicals and influence of organic matter. Env. Sci. Technol. **2015**, 49, 1673-1680.

Maruthamuthu P. and Neta P. Phosphate radicals. Spectra, acid-base equilibria, and reactions with inorganic compounds. J. Phys. Chem. **1978**, 82, 710-713.

Mendez-Diaz J.; Sanchez-Polo M.; Rivera-Utrilla J.; Canonica S. and von Gunten U. Advanced oxidation of the surfactant SDBS by means of hydroxyl and sulphate radicals. Chem. Eng. J. **2010,** 163, 300-306.

Miranda-García N.; Suárez S.; Sánchez B.; Coronado J.M.; Malato S. and Maldonado M.I. Photocatalytic degradation of emerging contaminants in municipal wastewater treatment plant effluents using immobilized TiO_2 in a solar pilot plant. Appl. Catal. B: Environ. **2011**, 103, 294-301.

Neta P.; Madhavan V.; Zemel H. and Fessenden R.W. Rate Constants and mechanism of reaction of $SO_4{\cdot}^-$ with aromatic compounds. J. Am. Chem. Soc. **1977**, 99(1), 163-164.

Pereira V.J.; Weinberg H.S.; Linden K.G. and Singer P.C. 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. **2007**, 41, 1682-1688.

Pignatello J.J. Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environ. Sci. Technol. **1992**, 26, 944-951.

Real F.J.; Benitez F.J.; Acero J.L.; Roldan G. and Casas F. Elimination of the emerging contaminants amitriptyline hydrochloride, methyl salicylate, and 2-phenoxyethanol in ultrapure water and secondary effluents by photolytic and radicalary pathways. Ind. Eng. Chem. Res. **2012**, 51, 16209-16215.

Real F.J.; Benitez F.J.; Acero J.L.; Roldan G. and Casas F. Comparison between chlorination and ozonation treatments for the elimination of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in surface waters and secondary effluents. J. Chem. Technol. Biotechnol. in press, **2015**, DOI 10.1002/jctb.4441.

Richardson S.D. and Ternes T.A. Water analysis: emerging contaminants and current issues. Anal. Chem. **2011**, 83, 4614-4648.

Serjeant E.P. and Dempsey B. Ionisation constants of organic acids in aqueous solution. International Union of Pure and Applied Chemistry (IUPAC) Chemical Data Series No 23, Pergamon Press, New York **1979.**

Thomaidis N.S.; Asimakopoulos A.G. and Bletsou A.A. Emerging contaminants: A tutorial mini-review (Review). Global Nest J. **2012**, 14(1), 72-79.

Wilmarth WK and Haim A, Mechanisms of oxidation by peroxydisulfate ion. In Peroxide Reaction Mechanisms, 175-225, Edwards JO, Ed. Interscience, New York **1962**.

Xie X, Zhang Y, Huang W and Huang S, Degradation kinetics and mechanism of aniline by heat-assisted persulfate oxidation. J. Environ. Sci. **2012**, 24(5), 821-826.

Xu M.; Gu X.; Lu S.; Qiu Z. and Sui Q. Role of reactive oxygen species for 1,1,1-trichloroethane degradation in a thermally activated persulfate system. Ind. Eng. Chem. Res. **2014**, 53, 1056-1063.

3.5. Assessment of the UV/Cl_2 advanced oxidation process for the degradation of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in water systems.

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3.5. ASSESSMENT OF THE UV/CL_2 ADVANCED OXIDATION PROCESS FOR THE DEGRADATION OF THE EMERGING CONTAMINANTS AMITRIPTYLINE HYDROCHLORIDE, METHYL SALICYLATE AND 2-PHENOXYETHANOL IN WATER SYSTEMS.

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ABSTRACT

Three emerging contaminants (amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol) frequently found in waste-waters were selected to be individually degraded in ultra-pure water by the advanced oxidation process constituted by the combination of UV radiation and chlorine. The influence of pH, initial chlorine concentration and nature of the contaminants was firstly explored. The trend for the reactivity of the selected compounds was deduced: amitriptyline hydrochloride > methyl salicylate > 2-phenoxyethanol. A later kinetic study was carried out focused on the specific evaluation of the first-order rate constants and the determination of the partial contribution to the global reaction of the direct photochemical pathway and the radical pathway. A comparison between the rate constant values of the photochemical experiments without and with the presence of Cl_2 revealed a clear increase in the oxidation efficiency of the combined process with respect to the photochemical reaction alone.

In a second stage, the simultaneous oxidation of mixtures of the selected contaminants in several types of water (ultrapure water, surface water from a reservoir, and two secondary effluents) was also performed by the same combination UV/Cl_2 under more realistic operating conditions. The efficiency of this combined system UV/Cl_2 was compared to other oxidants such as the UV/$S_2O_8^{2-}$ and UV/H_2O_2 AOPs, and the influence of the operating variables was discussed. Results confirmed that the UV/Cl_2 system provides higher elimination efficiencies among the AOPs tested. The presence of dissolved organic matter and bicarbonate ions in the water matrix caused a decrease in the treatment efficiency.

Keywords: emerging contaminants; amitriptyline; methyl salicylate; 2-phenoxyethanol; chlorination; photolysis; rate constants; UV/chlorine advanced oxidation process.

1. INTRODUCTION.

An increasing public health concern has grown recently in relation to a new group of hazardous pollutants that are frequently present in water systems, since little is known about their potential effects in humans and animals. The referred compounds are commonly known as Emerging Contaminants (ECs), because they are still unregulated or in the process of being regulated. Within this denomination, several compounds are included, such as nanomaterials, pesticides, pharmaceuticals and personal care products (PPCPs), hormones, dyes, fragrances water treatment by-products, flame retardants and surfactants, etc. (Lapworth et al., 2012). They had not been considered before as contaminants because of their very small concentration in natural waters and wastewaters. However, recent studies showed the potential ecologic and health risks derived from their bioactivity and toxicity, being now recognized themselves as micropollutants potentially dangerous that can produce damages in the ecosystem (Jjemba, 2006). The main source of ECs is municipal treated wastewaters, because most of the wastewater treatment plants (WWTPs) technologies are frequently unable to entirely degrade such persistent pollutants. Therefore, their elimination from waters, together with other priority pollutants, is currently an important goal to be pursued in environmental issues.

For this purpose, new technologies have recently been assayed with the aim of achieving high levels of elimination of ECs. Among others, chemical oxidation treatments have demonstrated to be effective in degrading organic constituents in waters, including hazardous organic pollutants such as the ECs (Ikehata et al., 2008). Among them, it can be mentioned some single oxidation process, like ozonation, photolytic degradation or Fenton's reagent; or advanced oxidation processes (AOPs) constituted by combinations of oxidants, such as UV/H_2O_2, O_3/UV, $S_2O_8^{2-}$/UV, or photo-Fenton system, which have demonstrated their effectiveness in the elimination of this group of substances (Yamal-Turbay et al., 2014; Noutsopoulos et al., 2014). These AOPs are characterized by the generation of a powerful oxidizing agent, which often is the hydroxyl radical that oxidizes complex compounds to smaller molecules.

A new oxidation technology recently tested with promising results is that constituted by the photolysis of free chlorine. In general terms, the potential of the UV/Cl_2 combined system in the degradation of ECs has been explored (Jin et al., 2011), and compared to the UV/H_2O_2 AOP in terms of treatment efficiency (Carlin et al., 1990). In addition, the applicability of UV/Cl_2 for ECs removal in real surface waters and wastewaters has been examined at a technical scale (Xiang et al., 2016; Sichel et al., 2011).

Specifically, chlorine (Cl_2), as gaseous chlorine or hypochlorite, is commonly applied in water disinfection (Sharma, 2008; Deborde et al., 2008), at one or two points of the process: preoxidation (to induce a primary disinfection at the beginning of the treatment), and post-treatment (to maintain a disinfectant residual in the distribution system). In presence of UV irradiation at wavelengths less than 400 nm, hydroxyl and chlorine radicals are generated from chlorine photolysis according to the following reactions (Carlin et al., 1990):

$$HOCl + h\nu \longrightarrow HO\cdot + Cl\cdot \qquad [3]$$

$$OCl^- + h\nu \longrightarrow O^- + Cl\cdot \qquad [4]$$

$$O^- + H_2O \longrightarrow HO\cdot + OH^- \qquad [5]$$

The UV/Cl_2 AOP is found to be more efficient in producing reactive species (mainly HO· and Cl·; and $Cl_2^{\cdot -}$ to a lesser extent) at acidic and neutral pH (Fang et al., 2014). Even the UV/Cl_2 AOP can be more efficient than the UV/H_2O_2 AOP in the degradation of some emerging contaminants such as benzotriazole, tolytriazole and iopamidole (Sichel et al., 2011). Therefore, the UV/Cl_2 process can be considered to be an alternative of UV-based AOP for the removal of micropollutants in drinking water and wastewater. However, the effectiveness of the UV/Cl_2 process in degrading different groups of recalcitrant ECs, specially in real surface water and municipal wastewater, is still unknown.

With all these considerations in mind, the present work was designed for the study of the degradation of three selected ECs, taken as model compounds, by the UV/Cl_2 AOP, in order to explore its application in water and wastewater treatments. The specific objectives were: 1) to evaluate the effectiveness of the UV/Cl_2 AOP for the degradation of selected ECs in both, UP and real waters (surface water and municipal wastewater), and to investigate the influence of water quality parameters; 2) to compare the efficiency of ECs removal by UV/Cl_2, by single UV photolysis or chlorine, and by other UV-based AOPs such as UV/H_2O_2 and UV/$S_2O_8^{2-}$; and 3) to determine the degradation kinetics (first-order rate constants) of selected ECs under different conditions.

For this purpose, the following three ECs were selected as model compounds: amitriptyline hydrochloride (AH), methyl salicylate (MS), and 2-phenoxyethanol (PE). Specifically, AH is the most widely used tricyclic antidepressant; MS is a salicylic acid derivative produced by esterification with methanol, and used as rubefacient, analgesic and anti-inflammatory; and PE is a bactericide often used in dermatological products, fixatives for perfumes, insecticides and topical antiseptics.

2. MATERIALS AND METHODS.

2.1. Experimental procedures.

In this work, chlorine was fed as hypochlorous acid. For that purpose, previous chlorine stock solutions were prepared by diluting a commercial solution of sodium hypochlorite (Panreac, nominally 10% w/w chlorine) and were standardized iodometrically (Clesceri et al., 1989).

The ECs degradation experiments were carried out in the 500 cm^3 thermostated cylindrical glass reactor, described elsewhere (Real et al., 2012). This reactor was equipped with a low pressure mercury vapor lamp (TNN 15/32 nominal electrical power 15 W; Heraeus, Spain) which emitted a monochromatic radiation at 254 nm.

In the first group of experiments, individual ECs dissolved in ultrapure (UP) water were degraded by chlorine, UV irradiation and the UV/Cl_2 AOP. For this purpose, a solution of 350 mL of the corresponding EC (1 μM in all cases), at the designed pH (3, 5, 7 and 9) by means of phosphoric acid/phosphate buffer (0.01 M), was fed into the reactor. The reactor was located in a thermostatic bath at the desired temperature (20±0.2 ºC). Each run was initiated by injecting into the reactor aliquots of the chlorine stock solution to achieve the desired initial chlorine concentration (from $5x10^{-6}$ to $15x10^{-6}$ M). At regular reaction times, 2 mL samples were retired and rapidly transferred with a syringe into a HPLC vial containing 10 μL of thiosulfate (0.1 M) to stop the reaction. At the same time, a second sample was withdrawn from the reactor to immediately analyze the residual chlorine concentration according to the ABTS method.

In a second step, experiments for the degradation of selected ECs in surface water and municipal wastewater were performed with the aim to study the degradation process under more realistic conditions. In these experiments, the three ECs were spiked to the real water samples at concentrations of 1 μM for each one. These experiments were performed at the natural pH of the water (pH 7-8) and 20 ºC, following the same procedures described above for the individual degradation of the ECs in UP water, and with an initial concentration of chlorine of $10x10^{-6}$ M. Finally, several experiments of ECs degradation in these real waters by the UV/$S_2O_8^{2-}$ and UV/H_2O_2 AOPs were performed with similar oxidant concentration ($10x10^{-6}$ M of $S_2O_8^{2-}$ or H_2O_2) for comparison purposes.

2.2. Emerging contaminants, secondary effluents, and analytical methods.

General reagents were obtained from Panreac (Spain), with pure component quality. Amitriptyline hydrochloride (AH, $C_{20}H_{23}N\cdot HCl$, ≥99%), methyl salicylate (MS, $C_8H_8O_3$, ≥98%) and 2-phenoxyethanol (PE, $C_8H_{10}O_2$, ≥99%) were purchased from Sigma-Aldrich (Spain). On the other hand, the water matrices used in the present study for the degradation of the selected ECs were: ultrapure water (UP) obtained from a Milipore Milli-Q system; a surface water collected from the public reservoir "Peña del Aguila" (PA), located in the Extremadura Community (southwest Spain); and two secondary effluents from municipal wastewater treatment plants, located in Badajoz (BA) and La Albuera (LA). All these effluents were collected, filtered through a 0.45 μm cellulose nitrate filter within the first 24 hours and stored at 4 ºC until used. Their main quality parameters are compiled in Table 1. It must be noted that chemical oxygen demand (COD), UV absorbance and TOC contents constitute a significant indication of the total dissolved organic matter (DOM) present in these waters.

Table 1. Quality parameters of the water matrices used.

Water matrix	pH	TOC ($mg\cdot L^{-1}$)	COD ($mg\cdot L^{-1}$)	$A_{254\,nm}$ (cm^{-1})	Alkalinity x10^3 ($mg\cdot L^{-1}$ $CaCO_3$)	Conductivity ($\mu S\cdot cm^{-1}$)
UP	7.0	< 1.0	< 5	< 0.001	< 5	4
LA	7.9	2.9	7	0.041	335	570
PA	7.4	5.2	18	0.187	30	80
BA	8.3	11.1	56	0.245	325	550

The three selected ECs were analysed by HPLC in a Waters Chromatograph equipped with a 996 Photodiode Array Detector and a Waters Nova-Pak C18 Column (5 μm 150x3.9 mm). This equipment was sensitive enough to analyze ECs in sub-micromolar concentration range. The Limit of Quantitation for selected ECs is around 0.01 μM. The detection was performed at 238 nm for AH and MS; and 220 nm for PE. The mobile phase was a mixture of methanol and 0.01 M aqueous phosphoric acid solution in different proportions, depending on the mixture analysed. The elution flow rate was 1 mL min^{-1} and the injection volume was 100 μL in all samples. Chlorine concentration was determined spectrophotometrically according to the ABTS (2,2-azino-bis (3-ethylbenzothiazoline)-6-sulfonicaciddiammoniumsalt) method (Pinkernell et al., 2000).

3. RESULTS AND DISCUSSION.

3.1. Individual degradation of selected ECs in UP water.

As previously reported, the individual degradation of the three selected ECs in UP water by the UV/Cl_2 AOP was investigated in experiments carried out at 20 ºC with the 254 nm monochromatic radiation lamp already described in the Experimental Section. The initial concentration of free chlorine was varied between 5x10^{-6} and 15x10^{-6} M, and the pH from 3 to 9. In addition, degradation of individual ECs by single UV photolysis or chlorine (10x10^{-6} M) was also investigated at pH 7 for comparative purposes. Table 2 summarizes the operating conditions for this group of experiments, as well as the percentage of EC degradation obtained after 7 min of reaction (X_7), which is time enough to reach a significant removal in all cases. This parameter X_7 indicates, in a first approach, the efficiency of this process for the removal of selected ECs in the experimental conditions applied.

3.1.1. Comparison of ECs degradation by chlorine, UV photolysis and the UV/Cl_2 AOP.

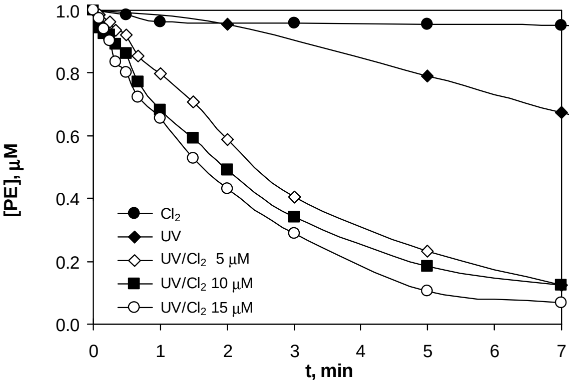
Figure 1 shows the time-dependent degradation of selected ECs by single UV photolysis, single chlorination and by the UV/Cl_2 AOP. Both, single UV photodegradation and single chlorination of the three selected ECs at similar operating conditions than those applied in the present work have been investigated previously in detail (Real et al., 2012; 2015). From the degradation curves shown in Figure 1 and the results of X_7 summarized in Table 2 for the three selected ECs, it can be deduced that the UV/Cl_2 AOP provided significant higher removals than the single degradation processes (single UV radiation or chlorine alone).

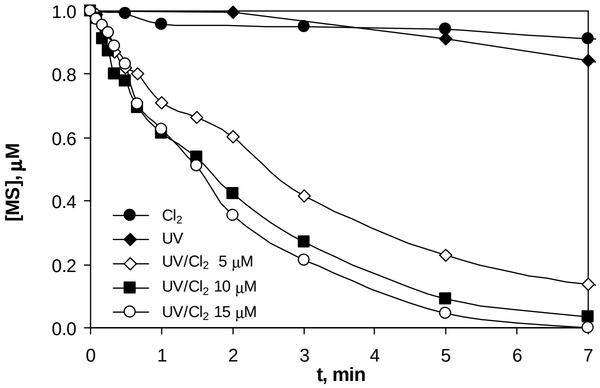
Table 2. Degradation of individual ECs in UP water by the UV/Cl_2 AOP: degradation levels after 7 min (X_7) and pseudo-first-order rate constants.

Expt.	pH	$[Cl_2]_0$ x10^{-6}, M	X_7, %	k_T, min^{-1}	k_{UV}, min^{-1}	k_R, min^{-1}
PE-1	3	10	95.1	0.42	0.069	0.36
PE-2	5	10	95.3	0.39	0.071	0.32
PE-3	7	5	87.8	0.30	0.091	0.21
PE-4	7	10	90.5	0.35	0.091	0.26
PE-5	7	15	93.2	0.41	0.091	0.32
PE-6	9	10	83.8	0.21	0.120	0.09
PE-7	7	0	32.4	0.091	0.091	-
PE-8*	7	10	5.0	0.002	-	-
MS-1	3	10	100	0.60	0.058	0.54
MS-2	5	10	100	0.59	0.054	0.53
MS-3	7	5	86.4	0.28	0.052	0.23
MS-4	7	10	96.5	0.44	0.052	0.39
MS-5	7	15	99.9	0.52	0.052	0.47
MS-6	9	10	92.6	0.42	0.055	0.37
MS-7	7	0	15.5	0.052	0.052	-
MS-8*	7	10	8.9	0.008	-	-
AH-1	3	10	100	0.82	0.11	0.72
AH-2	5	10	95.5	0.68	0.12	0.56
AH-3	7	5	82.4	0.47	0.13	0.33
AH-4	7	10	94.1	0.56	0.13	0.43
AH-5	7	15	100	1.27	0.13	1.13
AH-6	9	10	90.5	0.46	0.21	0.25
AH-7	7	0	56.0	0.13	0.13	-
AH-8*	7	10	41.5	0.076	-	-

* Experiments PE-8, MS-8 and AH-8 were carried out with chlorine alone (absence of UV radiation).

While the removal of PE and MS with chlorine alone was not appreciable, the removal of AH was lower that 50% after 10 min of chlorination. In a similar way, single UV irradiation was able to partially remove AH, while the degradation of PE and MS was not important. Moreover, slightly higher degradation of ECs was obtained with single UV photolysis than with 10x10^{-6} M of chlorine at pH 7. On the other hand, the increase in the degradation rates in the UV/Cl$_2$ AOP is due to the generation of very reactive radicals, such as HO· and Cl·. In effect, the radical pathway, which will be quantified later, promotes an important contribution to the overall degradation process in addition to the contribution of single UV photolysis and chlorine. Finally, the comparison of the X$_7$ values for the three selected ECs allows establishing that the level of degradation at the same operating conditions is: AH > MS > PE.





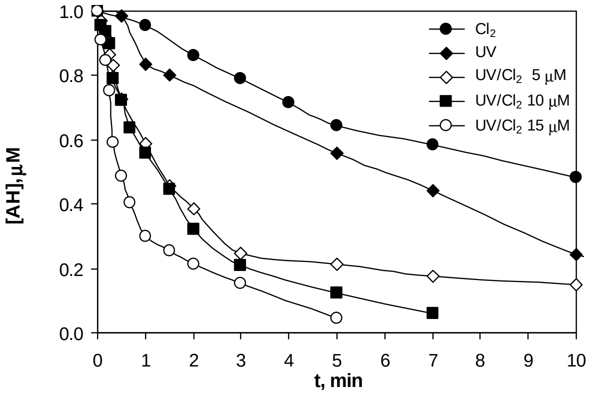


Figure 1. Evolution of PE (A), MS (B) and AH (C) concentration with reaction time in experiments performed with UV radiation alone, chlorine alone and the combination UV/Cl$_2$ at different initial concentration of chlorine. Experimental conditions: [ECs]$_0$=1 μM, T=20 ºC, pH=7.

Figure 2 shows the evolution of the residual chlorine concentration during the degradation of AH by chlorine alone and by the UV/Cl$_2$ AOP at pH 7. Similar trends were obtained for PE and MS (data not shown). The UV/Cl$_2$ AOP consumed chlorine more rapidly due to its UV photolysis to form HO· and Cl· radicals. A significant reduction in chlorine concentration after 7 min was observed for the UV/Cl$_2$ AOP, suggesting that the majority of chlorine was used for ECs degradation. Chlorine consumption is another reason for selecting 7 min to calculate the percentage of EC degradation, since this time corresponds to the main removal of ECs.

The shape of the decreasing concentration of ECs as a function of reaction time shown in Figure 1 suggests a pseudo-first order reaction with respect to the EC concentration. Then, a pseudo-first-order kinetics approach can be applied to the reaction between each selected EC and the UV/Cl$_2$ system. Similarly, the degradation of selected ECs by single UV photolysis and chlorine alone also follows pseudo-first-order kinetics (Real et al., 2012; 2015). According to this model, a plot of ln [EC]$_0$/[EC] *vs* reaction time should result in a straight line, whose slope provides the desired pseudo-first-order rate constant k$_T$. Following this procedure and after regression analysis (R^2 > 0.99), the rate constant values were deduced for every experiment conducted, being the obtained results summarized in Table 2.

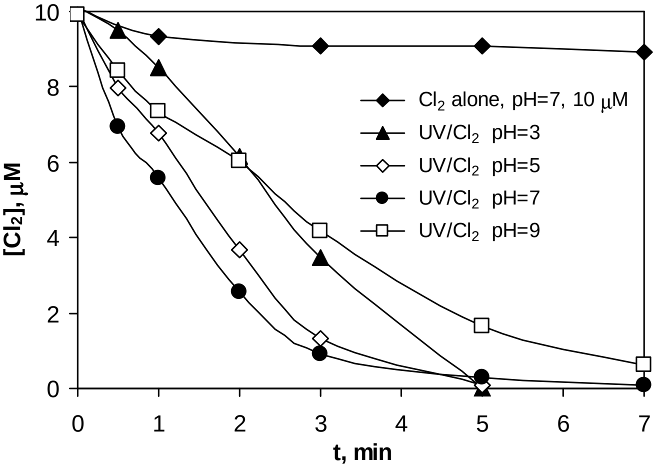


Figure 2. Evolution of chlorine concentration with reaction time in the degradation of amitriptyline hydrochloride with chlorine alone (pH=7) and the combination UV/Cl_2 at different pH. Experimental conditions: $[AH]_0$=1 µM, $[Cl_2]_0$=10 µM, T=20 ºC.

From the values of k_T, some conclusions can be deduced. Firstly, much higher values were obtained in the combined process in comparison to the single photochemical process or the single chlorination (see Expts. 4 and 7 or 8 for each compound, PE, MS or AH, respectively). For example, in the case of PE the rate constants decreased from 0.35 min^{-1} in the combination UV/Cl_2 to 0.091 min^{-1} for the single UV radiation process; and 0.002 min^{-1} for the single chlorination process. Similar trends are deduced for AH and MS.

Secondly, the rate constants in the combined UV/Cl_2 system at the same operating conditions again confirm the trend previously observed in the degradation percentage X_7: AH > MS > PE.

3.1.2. Influence of chlorine dose and pH on ECs degradation by UV/Cl_2.

As was previously stated, Figure 1 shows the evolution of the normalized concentration of ECs with reaction time in experiments performed with the combined system UV/Cl_2 at pH=7, where the initial concentration of chlorine was varied from 5 x10^{-6} to 15x10^{-6} M. It can be clearly observed a positive effect of the initial concentration of free chlorine on the degradation process. This positive effect was also deduced from X_7 values reported in Table 2 (Expts. AH-3, AH-4 and AH-5 for amitriptyline hydrochloride; Expts. PE-3, PE-4 and PE-5 for methyl salicylate; and MS-3, MS-4 and MS-5 for 2-phenoxyethanol). And consequently, it can be also appreciated from the values of k_T, with increasing pseudo-first-order rate constant values when chlorine concentration was increased (see k_T values for Expts. 3, 4 and 5 for AH, MS and PE, respectively). For example, in the case of PE, rate constants were 0.30, 0.35 and 0.41 min^{-1} for $[Cl_2]_o$=5, 10 and 15x10^{-6} M, respectively. However, the increase in the rate constant values was more significant between experiments without and with chlorine (Expts. 7 and 3 for PE, MS and AH, respectively) than when increasing the chlorine dosage. In effect, the addition of 5x10^{-6} M of chlorine produced an increase of three to five times in the rate constant values in comparison to experiments without chlorine. In contrast, the increase of k_T values in Expts. 3, 4 and 5 was rather small. These effects were similar to the observed in the oxidation of ibuprofen (Xiang et al., 2016) and benzoic acid (Fang et al., 2014) by the UV/Cl_2 system, because of the scavenging of the reactive species HO· and Cl· by excess of free chlorine (reactions 1 and 2):

$$HO\cdot + HOCl \rightarrow ClO\cdot + H_2O \qquad [1]$$

$$Cl\cdot + HOCl \rightarrow HCl + ClO\cdot \qquad [2]$$

Regarding to the pH effect, it can be deduced from the values of X_7 summarized in Table 2 for experiments performed at different pH that lower degradation of selected ECs was reached at higher pH. Therefore, there was a negative effect of pH on the removal of selected ECs by the UV/Cl_2 AOP. The rate constants summarized in Table 2 also show this trend (Expts. 1, 2, 4 and 6 for each EC). Thus, the k_T values decreased with pH from 0.42 to 0.21 min^{-1} for PE; from 0.60 to 0.42 min^{-1} for MS and from 0.82 to 0.46 min^{-1} for AH.

This negative effect of pH can be explained by several causes. Firstly, the dissociation of HOCl (with pK_a of 7.54) is affected by pH and the quantum yield of HOCl at 254 nm light is much higher than that of OCl^- (1.45 *vs* 0.97) (Carlin et al., 1990), favouring the formation of HO· and Cl· at lower pH. On the other hand, the rate constants for the reactions of HO· and Cl· with HOCl are lower than those with OCl^- (Carlin et al., 1990; Fang et al., 2014; Kong et al., 2016), indicating that the radical scavenging effect of chlorine species is higher at basic pH. Finally, this trend can also be attributed to the fact that amitriptyline hydrochloride and methyl salicylate present pK_a values of 9.4 and 9.9, respectively (Blesse et al., 1974; Serjeant et al., 1979). Therefore, as the maximum pH used in this work was 9, the un-dissociated forms, which are generally less reactive, predominated over the dissociated form. The same negative pH effect was observed in the degradation of similar organic compounds by UV/Cl_2 (Xiang et al., 2016; Kong et al., 2016).

In addition, the chlorine consumption rate by UV/Cl_2 increased with pH in the interval 3-7 as can be observed in Fig. 2 for AH. However, the consumption of chlorine was slower at pH 9. Similar trends were obtained for PE and MS. The decrease of chlorine consumption at pH above 7 can be explained by the lower quantum yield of OCl^- (the dominant chlorine species) as well as by its higher reactivity with HO· and Cl·.

3.1.3. Contribution of the radical pathway to the ECs degradation by UV/Cl_2.

As commented before, an additional contribution to the single photoreaction or single chlorination is promoted by the radical pathway that takes place in the UV/Cl_2 AOP. In effect, this supplementary contribution can be specified by considering the mechanism of the combined process. The contribution of single chlorination can be neglected according to the low degradation level of selected ECs shown in Table 1 and discussed above. Thus, in addition to the direct photoreaction, the generation of HO· and Cl· must be taken into account. Therefore, ECs can be degraded by HO· or Cl· according to the following reactions:

$$\mathrm{EC} + \mathrm{HO}\cdot \rightarrow \mathrm{EC_{oxid}} \qquad [3]$$

$$\mathrm{EC} + \mathrm{Cl}\cdot \rightarrow \mathrm{EC_{oxid}} \qquad [4]$$

This radical contribution can be evaluated for each EC. Thus, the overall reaction rate (r_T) for the combined process can be assumed to be the addition of the rate corresponding to the direct photochemical reaction (r_{UV}) plus the rate corresponding to the radical reaction (r_R):

$$-r_T = -\frac{[dEC]}{dt} = -(r_{UV} + r_R) = (k_{UV} + k_R)[EC] = k_T[EC] \quad [5]$$

In accordance to Eq (5), the rate constants for the radical reaction k_R are easily deduced by subtracting from k_T values those k_{UV} values obtained for the experiments performed with UV radiation alone (Expts. PE-7, MS-7 and AH-7 for PE, MS and AH, respectively). Table 2 summarizes the k_{UV} values, as well as the values of k_R obtained in the experiments performed with the combined system UV/Cl_2.

The comparison of k_R values obtained for the three compounds tested in the UV/Cl_2 AOP with the values of k_{UV} for single photolysis confirms that the radical reaction has a greater contribution to the overall reaction than the direct photolysis, especially at higher chlorine concentrations. More specifically, by considering AH, the contribution to the overall reaction rate of the direct photolysis was only 11.1 % compared to 88.9 % of the radical pathway in the experiment performed with the highest initial chlorine concentration (Expt. AH-5). On the contrary, in the case of the experiment carried out with the lowest chlorine concentration (Expt. AH-3), the direct photolysis contribution was more significant: 28.5 % for direct photolysis while the radical pathway contributed the remaining 71.5 %. Similarly, in the case of MS, the contribution of the radical pathway was predominant: 90.0 % for the experiment with $[Cl_2]_0$= 15x10^{-6} M (Expt. MS-5), and a 81.4 % for the reaction with $[Cl_2]_0$= 5x10^{-6} M (Expt. MS-3). The same considerations can be deduced for PE (see Expts. PE-3 and PE-5). These results indicate that, in the presence of high concentration of chlorine, the role of the direct photochemical degradation is much lower, and the radiation energy emitted by the lamp is mainly absorbed by chlorine species to generate HO· and Cl·.

At the same time, it must be noted that the values of k_R decreased with pH for the three selected ECs, which indicate that the contribution of the radical pathway to the overall degradation of EC decreases at higher pH. These results are consistent with the lower production and higher consumption of HO· and Cl· at high pH, as commented above.

Since values of rate constants for the reactions of ECs with Cl· have not been reported, the roles of HO· and Cl· in the degradation of selected ECs could not be evaluated. Kong et al. 2016, tried to determine the roles of HO· and Cl· in the degradation of atrazine by using nitrobenzene (NB) as HO· scavenger (while NB reacts fast with HO·, its degradation by Cl· is negligible). However, NB adsorbed UV light strongly, thus inhibiting the chlorine photolysis and the radical formation. Nevertheless, Fang et al. 2014, could calculate by kinetic modelling a higher contribution of Cl· than of HO· in the degradation of benzoic acid (using NB as HO· scavenger). Since we could not find another HO· scavenging compound with low reactivity towards Cl· and low UV absorption, it was difficult to distinguish the role of HO· and Cl· in the degradation of selected contaminants.

3.2. Oxidation of the ECs in natural water and treated water.

In a next stage, the simultaneous degradation of mixtures of selected ECs (initial concentration of 1µM for each compound) dissolved in different types of waters was carried out by the combined UV/Cl_2 system. As was described in the Experimental Section, these water matrices were: ultra-pure water (UP), reservoir water (PA), and two secondary effluents from municipal WWTPs (LA and BA). The oxidation process was conducted at the natural pH of each water, T=20 °C, and with an initial chlorine concentration of $10x10^{-6}$ M. For comparison purposes, results from similar experiments performed by applying single photolysis and the UV/H_2O_2 and UV/$S_2O_8^{2-}$ AOPs are used. These results concerning the degradation processes of selected ECs by the single photolysis and the UV/H_2O_2 and UV/$S_2O_8^{2-}$ AOPs were reported in previous publications (Real et al., 2012; 2016), where an oxidant (H_2O_2 or $S_2O_8^{2-}$) concentration of $10x10^{-6}$ M was applied. Table 3 summarizes all these experiments and the main results obtained.

The efficiency of the UV/Cl_2 system for the degradation of selected ECs was compared to the oxidant or combinations of oxidants mentioned. Thus, Figure 3 shows, as an example, the decrease of MS concentration with reaction time in experiments carried out with those different oxidation systems in BA water. Similar trends were obtained for the rest of compounds and water matrices. It is clearly observed that the combined UV/Cl_2 system provided the best degradation rates; intermediate rates were obtained with the UV/$S_2O_8^{2-}$ and UV/H_2O_2 AOPs, and the lowest rates corresponded to the single photodegradation process.

Table 3. Degradation of ECs in real waters by different AOPs: pseudo-first-order rate constants for EC removal.

Water matrix	Treatment	Initial concentration of oxidant (μM)	k_{PE} (min^{-1})	k_{MS} (min^{-1})	k_{AH} (min^{-1})
UP	UV-Cl_2	10	0.14	0.25	0.38
	UV	0	0.029	0.020	0.086
	UV-H_2O_2	10	0.056	0.074	0.13
	UV-$S_2O_8^{2-}$	10	0.11	0.13	0.26
PA	UV-Cl_2	10	0.075	0.13	0.30
	UV	0	0.017	0.016	0.046
	UV-H_2O_2	10	0.018	0.018	0.084
	UV-$S_2O_8^{2-}$	10	0.048	0.056	0.14
LA	UV-Cl_2	10	0.074	0.15	0.19
	UV	0	0.013	0.066	0.088
	UV-H_2O_2	10	0.014	0.078	0.12
	UV-$S_2O_8^{2-}$	10	0.045	0.093	0.15
BA	UV-Cl_2	10	0.051	0.063	0.10
	UV	0	0.0067	0.010	0.068
	UV-H_2O_2	10	0.0094	0.014	0.073
	UV-$S_2O_8^{2-}$	10	0.036	0.054	0.091

Again, this trend can be explained by the generation of higher reactive radical species, such as HO· and Cl·. This Cl· radical is a more selective oxidant than HO·, and has been reported to be more reactive with electron-rich contaminants, such as benzoic acid (Fang et al., 2014). Other photochemical AOPs, especially UV/H_2O_2 system, have shown lower treatment efficiencies (Jin et al., 2011; Carlin et al., 1990).

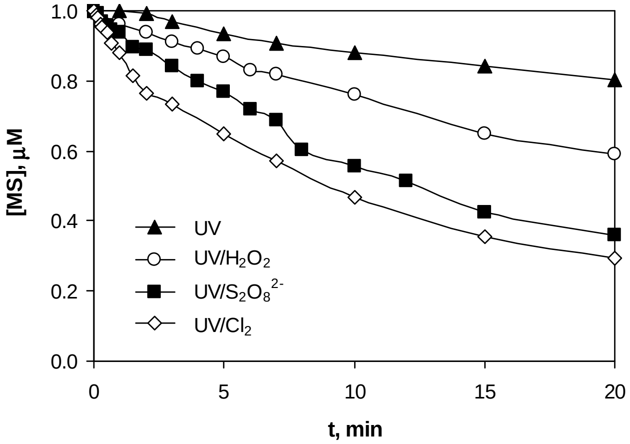


Figure 3. Degradation of methyl salicylate by different oxidation systems in BA water. Experimental conditions: $[MS]_0$=1 µM, $[oxidant]_0$=10 µM, T=20 ºC.

Similarly, it is interesting to establish the influence of the nature of the ECs on the degradation rate. Thus, Fig. 4 shows the degradation curves for the three selected compounds by UV/Cl_2 in PA water, taken as example. It can be observed that 2-phenoxyethanol presented the lowest elimination rate, intermediate for methyl salicylate, while amitriptyline hydrochloride reached the highest elimination rate. Similar results were obtained in the remaining water systems. Once again, this disappearance rate sequence completely agrees with the sequence of rate constants r_T for AH, MS and PE during the individual degradation of these ECs in UP water by the UV/Cl_2 system, as was reported in the preceding Section**.** These results are confirmed with the evaluation of the pseudo-first-order rate constants (k_{PE}, k_{MS} and k_{AH} for PE, MS and AH, respectively) for the disappearance rates of the selected ECs, whose values are also compiled in Table 3: it can be observed that the commented sequence of degradation rates was fulfilled in the four water matrices tested.

In addition, the same sequence of degradation rate (AH > MS > PE) was obtained for the UV/$S_2O_8^{2-}$ and UV/H_2O_2 AOPs. As reported in previous publications (Real et al., 2012, 2016), while HO· were the dominant oxidant species for the degradation of selected ECs by the UV/H_2O_2 AOP, both HO· and $SO_4·^-$ were important in their degradation by UV/$S_2O_8^{2-}$. This sequence of degradation can be explained by the values of rate constants of selected ECs with HO· ($1.0x10^{10}$ M^{-1} s^{-1} for AH, $7.1x10^9$ M^{-1} s^{-1} for MS and $4.3x10^9$ M^{-1} s^{-1} for PE) and with $SO_4·^-$ ($4.8x10^9$ M^{-1} s^{-1} for AH, $9.2x10^8$ M^{-1} s^{-1} for MS and $1.4x10^9$ M^{-1} s^{-1} for PE).

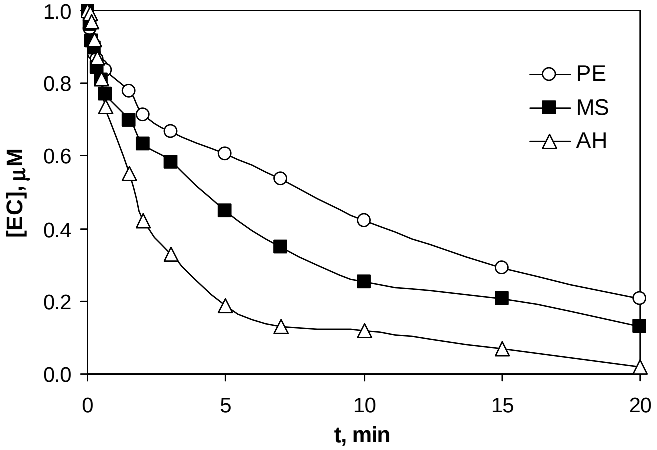


Figure 4. Degradation the three selected compounds by the UV/Cl_2 AOP in PA water. Experimental conditions: $[ECs]_0$=1 µM, $[Cl_2]_0$=10 µM, T=20 ºC.

Finally, the effect of the water matrix nature on the ECs decomposition is shown in Fig. 5, where the concentration curves of methyl salicylate, taken as example, are plotted *vs* reaction time in experiments performed with the UV/Cl_2 system. It can be observed that the fastest degradation was obtained in UP water (higher pseudo-first-order rate constants in Table 3), followed by PA and LA waters with intermediate degradation rates, and much lower eliminations in BA water. Similar results were obtained for amitriptyline hydrochloride and 2-phenoxyethanol, as can be deduced from the values of k_{AH} and k_{PE} summarized in Table 3.

The highest rates of ECs removal in UP water can be expected in advance: in effect, in this water there is an almost total absence of organic and inorganic matter that could consume direct UV radiation and radicals; and consequently, all the oxidant load is consumed in the degradation of the ECs. On the contrary, in PA, LA and BA waters, the presence of some organic compounds and bicarbonate ion promotes the absorption of UV radiation and the consumption of radicals; and consequently, the effective radical concentration available to react with the ECs decreases. In other words, there is a competition between ECs and the organic and inorganic matter present in the water for the absorption of UV radiation and the consumption of radical species.

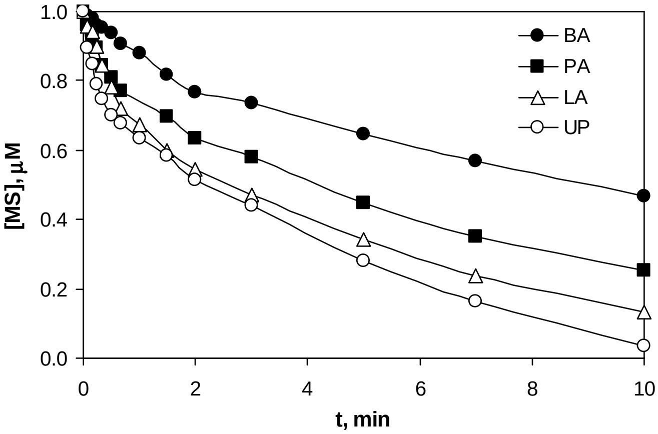


Figure 5. Effect of the water matrix on the degradation of methyl salicylate by the combination UV/Cl_2. Experimental conditions: $[MS]_0$=1 µM, $[Cl_2]_0$=10 µM, T=20 ºC.

Therefore, according to the quality parameters values shown in Table 1, the presence of DOM (measured as absorbance at 254 nm, TOC and COD) in the water matrices PA and especially in BA, and the presence of bicarbonate ions (alkalinity) in LA and BA water matrices are responsible of the increasing decay of the degradation efficiency in every water system. In that sense, several researchers (Fang et al., 2014; Xiang et al., 2016) have reported the competitive effect of DOM and bicarbonate ions with the contaminant for reactions with the radical species HO· and Cl·. In conclusion, higher doses of oxidants are required for the removal of pollutant substances in real water matrices.

4. CONCLUSIONS.

Three emerging contaminants were selected to be oxidized in different water matrices by the combined oxidation process constituted by UV radiation plus chlorine, and the following conclusions were established:

- Amitriptyline hydrochloride was the most reactive compound towards this AOP; methyl salicylate showed intermediate reactivity, while 2-phenoxyethanol was found to be the least reactive.

- While the degradation of selected ECs was improved with increasing the initial concentration of chlorine, the pH exerted a negative influence on ECs removal.

- Pseudo-first-order rate constants were determined, and the values obtained confirmed the reactivity sequence and the influences of chorine concentration and pH previously established.

- Simultaneous oxidation experiments of the selected ECs performed in four water matrices by the combined UV/Cl_2 system confirmed the trend previously stated about the reactivity of the compounds: amitriptyline hydrochloride > methyl salicylate > 2-phenoxyethanol.

- A direct effect between the ECs reactivity in every water tested and the organic and inorganic content of each water (measured as absorbance at 254 nm, TOC and bicarbonate) could be also established.

- The combined UV/Cl_2 system provided higher degradation rates than the UV/$S_2O_8^{2-}$ and UV/H_2O_2 AOPs when the same oxidant concentration was applied. Therefore, the UV/Cl_2 AOP is expected to be a promising solution for EC control in surface water and WWTP effluents.

REFERENCES

Blesse K.W.; Rudy B.C.; Senkowsky B.Z. Analytical Profiles of Drug Substances,Vol. 3, ed by Florey K. Academic Press, London.**1974**.

Carlin V.; Minero C.; Pelizzetti E. Effect of chlorine on photocatalytic degradation of organic contaminants, Environ. Technol. **1990**, 11, 919-926 .

Clesceri L.S.; Greenberg A.E. and Trussell R.R. Standard methods for the examination of water and wastewater, 17th ed., APHA, AWWA, WPCF, Washington DC. **1989**.

Deborde M. and von Gunten U. Reactions of chlorine with inorganic and organic compounds during water treatment-Kinetics and mechanism: A critical review, Water Res. **2008**, 42, 13-51.

Fang J.; Fu Y. and Shang C. The roles of reactive species in micropollutant degradation in the UV/free chlorine system, Environ. Sci. Technol. **2014**, 48, 1859-1868.

Ikehata K.; El-Din M.G. and Snyder S.A. Ozonation and advanced oxidation treatment of emerging organic pollutants in water and wastewater. Ozone: Science and Engng. **2008**, 30, 21-26.

Jin J.; El-Din M.G. and Bolton J.R. Assesment of the UV/chlorine process as an advanced oxidation process, Water Res. **2011**, 45, 1890-1896.

Jjemba P.K. Excretion and ecotoxicity of pharmaceuticals and personal care products in the environment. Ecotoxicol. Environ. Safety. **2006**, 63, 113-159.

Kong X.; Jiang J.; Ma J. et al. Degradation of atrazine by UV/chlorine: efficiency, influencing factors, and products, Water Res. **2016**, 90, 15-23.

Lapworth D.J.; Baran N.; Stuart M.E. et al. Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environ. Pollut. **2012**, 163, 287-303.

Noutsopoulos C.; Mamais D.; Mpouras T. et al. The role of activated carbón and disinfection of the removal of endocrine disrupting chemicals and non-steroidal anti-inflammatory drugs for wastewater, Environ. Technol. **2014**, 35, 698-708.

Pinkernell U.; Nowack B.; Gallard H. et al. Methods for the photometric determination of reactive bromine and chlorine species with ABTS, Water Res. **2000**, 34, 4343-4350.

Real F.J.; Benitez F.J.; Acero J.L. et al. Elimination of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in ultrapure water and secondary effluents by photolytic and radicalary pathways, Ind. Engng. Chem. Res. **2012**, 51, 16209-16215.

Real F.J.; Benitez F.J.; Acero J.L. et al. Comparison between chlorination and ozonation treatments for the elimination of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in surface waters and secondary effluents, J. Chem. Technol. Biotechnol. **2015**, 90, 1400-1407.

Real F.J.; Acero J.L.; Benitez F.J. et al. Oxidation of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol by persulfate activated by UV irradiation, J. Chem. Technol. Biotechnol. **2016**, 91, 1004-1011.

Serjeant E.P.; Dempsey B. Ionisation constants of organic acids in aqueous solution, International Union of Pure and Applied Chemistry (IUPAC). Chemical Data Series No 23, Pergamon Press, New York. **1979**.

Sharma V.K. Oxidative transformation of environmental pharmaceuticals by Cl_2, ClO_2, O_3, and Fe (VI): Kinetics assessment, Chemosphere. **2008**, 73, 1379-1386.

Sichel C.; Garcia C.; Andre K. Feasibility studies: UV/chlorine advanced oxidation treatment for the removal of emerging contaminants, Water Res. **2011**, 45, 6371-6380.

Xiang Y.; Fang J.; Shang C. Kinetics and pathways of ibuprofen degradation by the UV/chlorine advanced oxidation process, Water Res. **2016**, 90, 301-308.

Yamal-Turbay E.; Pérez-González L.; Graells M. et al. Degradation of sulphamethazine by means of an improved photo-Fenton process involving a hydrogen peroxide systematic dosage*,* Environ. Technol. **2014**, 35, 1695-1701.

3.6. The use of ultrafiltration and nanofiltration processes for the elimination of three selected emerging contaminants: amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol.

Accepted for publication in Environment Protection Engineering.

3.6. THE USE OF ULTRAFILTRATION AND NANOFILTRATION PROCESSES FOR THE ELIMINATION OF THREE SELECTED EMERGING CONTAMINANTS: AMITRIPTYLINE HYDROCHLORIDE, METHYL SALICYLATE AND 2-PHENOXYETHANOL.

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ABSTRACT

The emerging contaminants amitriptyline hydrochloride (AH), methyl salicylate (MS) and 2-phenoxyethanol (PE) were treated by means of filtration processes for their elimination from ultrapure (UP) water in a first stage, and from three water matrices (a surface water from a reservoir, and two effluents from two municipal wastewater treatment plants) in a second stage. For this purpose, ultrafiltration and nanofiltration membranes were used in a cross-flow laboratory equipment. The permeate fluxes at the steady state were determined, and the resistances to the permeate flux were established. It was found that the inherent resistance of the clean membranes provided a much larger resistance than the fouling resistance. The retention coefficients for each individual contaminant were evaluated, as well as the retention coefficients referred to three water quality parameters: absorbance at 254 nm, COD and TOC. These parameters provide the effectiveness of the filtration processes for the elimination of the organic matter present in the selected water matrices.

Keywords: Emerging contaminants, ultrafiltration and nanofiltration membranes, permeate flux, resistances, retention coefficients, UP and natural waters.

1. INTRODUCTION.

At recent times, an increasing public health concern has grown in relation to a new group of hazard pollutants that are frequently present in water systems, since little is known about their potential effects in humans and animals. The referred compounds are commonly known as emerging contaminants (ECs), because they are still unregulated or in the process of being regulated. This group is constituted by numerous chemical substances that include nanomaterials, pesticides, pharmaceuticals and personal care products, industrial compounds, fragrances water treatment by-products, flame retardants and surfactants, etc. (Bolong et al., 2009). They can be found in surface and ground waters, and even in drinking water (Jelic et al., 2011; Petrie et al., 2015; Tijani et al., 2013; Sim et al., 2011), being their main source municipal treated wastewater, due to the fact that wastewater treatment plant (WWTP) technologies are very often unable to entirely degrade such persistent pollutants. As these ECs constitute a potential risk for human health, since they can cause unexpected physiological consequences, their elimination from waters, together with other priority pollutants, is an important goal in environmental issues.

Due to this concern, and among other technologies, membrane processes employing ultrafiltration (UF) and nanofiltration (NF) membranes are increasingly used in wastewater reclamation to remove micropollutants in general, and ECs in particular, as well as natural organic matter (NOM) (Yoon et al., 2006; Kim et al., 2008; Verliefde, 2009). In effect, retention of organic micropollutants by UF membranes is attributed to several causes: adsorption on the membrane during the early stages of filtration, or to interactions with the membrane fouling layer, and/or interactions with dissolved NOM in solution (Wray et al., 2014). On the other hand, NF membranes remove organic solutes by three main mechanisms, i.e., size exclusion, electrostatic repulsion and adsorption (Verliefde et al., 2007; Anwar et al., 2014).

According to these considerations, the present research was designed for the specific elimination of three frequently found emerging contaminants in water systems by means of UF and NF membranes. These ECs selected were: amitriptyline hydrochloride (AH), methyl salicylate (MS) and 2-phenoxyethanol (PE). Specifically, amitriptyline hydrochloride is the most widely used tricyclic antidepressant. Its mechanism of action involves the inhibition of reuptake of norepinephrine and serotonin. Methyl salicylate is a salicylic acid derivative, naturally produced by many species of plants, although nowadays it is industrially produced by esterification of the acid with methanol. At high concentrations, this drug acts as a rubefacient, analgesic, and anti-inflammatory. Finally, 2-phenoxyethanol is a bactericide generally combined with quaternary ammonium compounds. It is often used in dermatological products, such as skin creams and sunscreens; and also, as a fixative for perfumes, insecticides, and topical antiseptics.

Although some information on the elimination of ECs by filtration processes can be found in the literature, no studies on the elimination of these specific emerging contaminants, which are selected in this research, have been provided.

Then, in the first stage of this work, the selected ECs were dissolved in ultrapure (UP) water and subjected to UF and NF experiments. Similarly, in the second stage, they were dissolved in different real water matrices, in order to reproduce more realistic conditions as those carried in treatments plant. With the results obtained, several objectives are pursued: the study of the evolution of the permeate flux with filtration time and volume retention factors; the establishment of the effect of several operating parameters (pH and nature and molecular weight cut-off (MWCO) of the membranes) on the steady-state permeate flux; the evaluation of the partial contribution of the different membrane resistances to the total resistance; and the determination of retention coefficients for each EC. Finally, the influence of the presence of natural organic matter in the water matrices on the filtration process is also established.

2. MATERIALS AND METHODS.

2.1. Models compounds, membranes and water systems.

The selected ECs (PE, MS and AH) were purchased from Sigma–Aldrich (Germany) with the highest purity available. Table 1 summarizes the molecular structures and molecular weights (MW) of these model compounds, as well as their pK_a values and the log K_{ow} values, which constitute a measurement of their hydrophobic/hydrophilic character.

Table 1. Physico-chemical properties of model compounds.

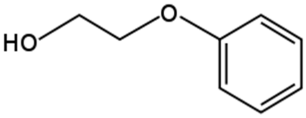
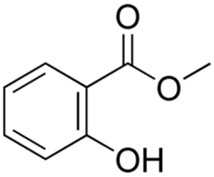
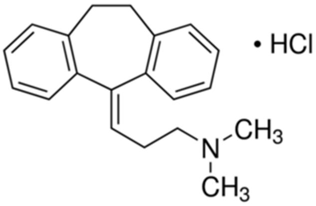
Emerging contaminant	Chemical Structure	MW, $g{\cdot}mol^{-1}$	pK_a	log K_{OW}
2-phenoxyethanol (PE)		138.17	-	1.16
Methyl salicylate (MS)		152.15	9.87	2.55
Amitriptyline hydrochloride (AH)		313.87	9.4	5

Table 2 summarizes the commercial selected membranes used. They were flat-sheet membranes provided by GE Osmonics Inc. (Florida, USA), with the same effective surface area of 28 cm^2 in all cases. In the UF process, the three membranes are commercially called PW, PT, and GK, with molecular weight cut-off (MWCO) of 20000, 5000 and 2000 Da, respectively. The NF membranes are commercially called HL, DL, and CK, all of them with similar MWCO in the range 150-340 Da, according to the data provided by the manufacturer. The nature of these membranes is as follows: the GK membrane is a thin film composite membrane, with a cross-linked aromatic polyamide top layer; on the other hand, the PT and PW membranes were made of polyethersulfone. All of them present hydrophilic character. Regarding to the NF membranes, the DL and HL were made of thin film composite (polypyperazinamide skin layer on a polyester support), and the CK was of cellulose acetate. According to previous studies (Park et al., 2007; Jin et al., 2007) which measured their contact angles, polyamide membranes are less hydrophobic than polyethersulfone membranes.

Table 2. Properties of target membranes: material, MWCO, pH range and pure water permeability (PWP) values.

Membrane	Material	MWCO, Da	pH	PWP, $dm^3\ h^{-1}\ m^{-2}\ MPa^{-1}$
PW (UF)	PES	20000	2-11	776
PT (UF)	PES	5000	2-11	213
GK (UF)	TF	2000	2-11	68
HL (NF)	PTFE	150-300	3-9	125
DL (NF)	PTFE	340	2-11	26
CK (NF)	CA	150-300	2-8	24

As mentioned previously, the filtration experiments were carried out with the ECs dissolved in UP water, and also, by using several water matrices, in order to reproduce more realistic water treatment conditions. These aquatic systems, whose main quality parameters are compiled in Table 3, were the following: a surface water collected from the public reservoir “Peña del Aguila” (PA), located in the Extremadura Community, south-west of Spain; and two secondary effluents from WWTPs corresponding to the cities of Badajoz

(BA) and La Albuera (LA), also in the Extremadura Community. These water systems were filtered through a 0.45 µm cellulose nitrate filter within the first 24 h after collection and stored at 4 ºC until use. Specifically, UV absorbance and TOC content constitute a significant index of the total dissolved organic matter (DOM) present in these effluents, which has a great influence on the performance of the different filtration processes. In all cases, the solutions were prepared by dissolving the ECs (1 µmol dm^{-3} of each) in UP water (from a Milli-Q system, Millipore Ibérica, Spain) or in the three real water matrices selected.

Table 3. Quality parameters of the selected real water matrices.

	PA	**LA**	**BA**
pH	7.4	7.9	8.3
Conductivity (µS cm^{-1})	80	570	550
A254 nm (cm^{-1})	0.187	0.041	0.245
COD (mg O_2 dm^{-3})	18	7	56
Alkalinity (mg $CaCO_3$ dm^{-3})	30	335	325
TOC (mg C dm^{-3})	5.2	2.9	11.1
Total nitrogen (mg N dm^{-3})	1.51	21.3	35.5
Total phosphorus (mg P dm^{-3})	0.041	0.156	1.76

2.2. Experimental equipment procedures.

The experiments were carried out in a laboratory membrane filtration unit model P-28^{TM} supplied by CM-CELFA Membrantechnik AG (Seewen, Switzerland), operating in cross-flow mode (feed stream flowing tangentially to the membrane surface). It was constituted by a 500 cm^3 pressurized storage vessel and a gear pump which fed the solution to the flat-sheet membrane module at the desired flow rates. Additional details of this equipment were provided in a previous publication (Benitez et al., 2008). During each experiment the permeate stream was collected separately and its cumulative volume was measured with a Mettler balance. At the same time, the retentate stream was recycled to the feed tank, and therefore, batch concentration mode was followed. The tangential velocity (1 m s^{-1}) and transmembrane pressure (TMP, 0.3 MPa in the UF experiments and 2 MPa in the NF experiments) were remained constant. This TMP was controlled by feeding nitrogen gas to the head of the storage vessel.

A new membrane was used for every experiment conducted, and the operating protocol consisted in the following stages: firstly, ultrapure water was filtered for 3 hours, and the water permeate flux (J_w) was measured, in order to determine the membrane hydraulic permeability (PWP) as will be discussed later. The second stage consisted in the filtration experiments of the ECs solutions (300 cm^3), where the model compounds were dissolved in UP or in the water matrices (1 µmol dm^{-3} for each compound). During these experiments, the permeate volume (V_p) was regularly collected for the determination of the pollutants permeate flux (J_v). At the same time, samples of the feed, retentate and permeate streams were collected for analysis and measurement of the ECs concentration. Additionally, in the case of the real water matrices, the following global quality parameters were also evaluated: absorbance at 254 nm, COD and TOC. The experiments ended when a volume reduction factor (VRF) around 3 was reached. Once the filtration of ECs was ended, the feed tank was emptied and filled with UP water in a third stage, and then the membrane was rinsed by filtrating UP water again. In this way, the cake layer formed on the membrane surface was removed, and the final pure water flux was again measured, as will be explained in the Discussion Section.

2.3. Analytical methods.

The three selected ECs were analysed by HPLC in a Waters Chromatograph (Alliance 2695) equipped with a 996 Photodiode Array Detector and a Waters Nova-Pak C18 Column (5 µm, 150 × 3.9 mm). The detection was performed at 238 nm for AH and MS; and 220 nm for PE. The mobile phase was a mixture of methanol and 0.01 mol dm^{-3} aqueous phosphoric acid solution, operating in gradient mode. The elution flow rate was 1 cm^3 min^{-1} and the injection volume was 100 µl in all samples.

The analytical methods for the characterization of the selected water matrices were followed according to the Standard Methods (Clesceri et al., 1999). TOC was determined by using a total organic carbon analyzer TOC-multi N/C 3100 (Analytik Jena). Absorbance at 254 nm was measured in a spectrophotometer Unicam Helios Beta; and COD was determined by using Dr. Lange kits.

2.4. Theorical calculations

In a filtration process, the permeate flux (J_w in the case of UP water, or J_v in the aqueous solutions of ECs dissolved in UP water, synthetic water or real water matrices) (dm^3 h^{-1} m^{-2}) was determined by using the expression:

$$J_W \text{ or } J_V = \frac{\Delta V_P}{\Delta t\, A} \qquad [1]$$

where ΔV_p represents the cumulative permeate volume difference (dm^3), Δt is the time difference (h) and A is the membrane area (m^2). The water permeate fluxes J_w are used for the later determination of hydraulic permeability PWP (dm^3 h^{-1} m^{-2} MPa^{-1}) of the membranes by means of the following equation:

$$PWP = \frac{J_W}{TMP} \qquad [2]$$

The volume reduction factor (VRF) is defined as the ratio between the feed volume V_f (dm^3) and the retentate volume $V_r = V_f - V_p$ (dm^3), and can be calculated by using the equation:

$$VRF = \frac{V_f}{V_r} \qquad [3]$$

Regarding to the resistances to the permate flux, the total hydraulic resistance R_t (m^{-1}) was evaluated from the permeate flux J_v, according to the general Darcy's law (Yoon et al., 2006):

$$R_t = \frac{TMP}{\mu J_V} \quad [4]$$

where TMP is the transmembrane pressure (MPa), and μ is the solution viscosity (μ_w in the case of UP water, or μ in the aqueous solutions of ECs dissolved in UP water, synthetic water or real water matrices, which were experimentally measured) (m^2 h^{-1}). This R_t is the result of several resistances in series:

$$R_t = R_m + R_f = R_m + R_{if} + R_{ef} \quad [5]$$

where R_m is the intrinsic resistance of clean membrane, and R_f is the fouling resistance with two components, the internal (R_{if}) and external (R_{ef}) fouling (all resistances in m^{-1}).

One of the best parameters which provide the efficiency of a membrane in a filtration process is the retention coefficient, which was determined for the selected ECs by the equation:

$$R = \frac{C_f - C_p}{C_f} \cdot 100 \quad [6]$$

where C_f and C_p are the concentrations of each EC (mol dm^{-3}) in the feed and permeate streams, respectively. Similarly, retention coefficients were evaluated for the water quality parameters selected in the present work. For the specific case of COD (mg O_2 dm^{-3}), this coefficient was defined by the expression:

$$R_{COD} = \frac{COD_f - COD_p}{COD_p} \cdot 100 \quad [7]$$

where COD_f and COD_p represent the COD (mg O_2 dm^{-3})in the feed and permeate streams, respectively. Similar equations were used for TOC (R_{TOC}), and UV absorbance at 254 nm (R_{254}).

3. RESULTS AND DISCUSSION.

3.1. Water permeability of the membranes.

Firstly, the filtration of pure water through the selected membranes was conducted, in order to evaluate the hydraulic permeability (PWP) of the membranes. For this purpose, the water permeate volume (V_p) was continuously collected through each experiment, and the water permeate flux (J_w) was determined by means of Eq. (1). Once the water permeate fluxes J_w were determined for each membrane, the values for PWP were deduced by using Eq. (2). These PWP values obtained for the selected membranes are also summarized in Table 2. As it is observed, an increase in the hydraulic permeability is clearly obtained with the increase in the MWCO in the UF membranes, as could be expected, because larger pore sizes lead to higher pure water fluxes. However, in the NF membranes, as the membranes have similar MWCO, different properties are responsible of the PWP values: in addition to MWCO, the internal structure and composition of the membrane, and the morphology and hydrophobicity/hydrophilicity of the membranes also contribute to PWP. They can explain the lower PWP values obtained for the CK and DL membrane in comparison to the HL membrane, whose higher PWP value is also reported in previous works (Zahng et al., 2004; Al-Amoudi et al., 2007).

3.2. Filtration of the ECs in ultrapure water.

The selected ECs dissolved together in UP water were subjected to filtration experiments by using the UF and NF membranes already described. The operating conditions (TMP and pH) applied to the different experiments were varied according to the values that are summarized in Table 4. These pH values were adjusted by means of phosphoric acid/phosphate buffer (0.01 mol dm^{-3}) and also remained constant during the whole experiment.

At this point, it must be taken into account the VRF factor, already defined by Eq. (3). As was previously noted, the experiments ended when VRF is around 3; that is, when volumes around 200 and 100 (cm^3) were collected for permeate and retentate streams, respectively.

In the filtration experiments of ECs, the permeate flux of the solutions (now represented by J_v) was measured at time intervals by means of Eq. (1), where J_w is substituted by J_v. The J_v evolution with VRF is represented in Fig. 1 for several experiments taken as examples, being the same performance in the remaining experiments. It revealed that there was an initial decrease in J_v with the increase of VRF; and later, this permeate flux remained almost constant. This permeate flux decay is a consequence of the increasing membrane fouling, which can be due to different causes, such as pore blocking or adsorption of solutes onto the membranes (Comerton et al., 2008; Maximous et al., 2009; Nghiem et al., 2010). In this case, where model compounds dissolved in UP water with low concentrations are processed, the fouling effect is generally low, and therefore, the decay is probably due to adsorption of the ECs on the membrane. The mentioned constant permeate flux is obtained around VRF=3 in most of the experiments carried out, and consequently, it is considered as the steady-state permeate flux (J_{vss}), whose values for all the experiments conducted, are also compiled in Table 4.

Focusing in these values of J_{vss}, it can be observed that they are affected by the operating parameters. Thus, a direct influence of the MWCO on J_{vss} is clearly deduced in the UF process: in effect, at pH=7 and TMP= 0.3 MPa, there was an increase of the permeate flux when increasing the MWCO of the selected membranes (Expts. UPUF-1, UPUF-4 and UPUF-6), with values of 16.5, 56.7 and 185.8 dm^3 h^{-1} m^{-2} for GK, PT and PW membranes, respectively. These results are due to the fact that a membrane with lower MWCO presents a greater resistance for the solution to cross the membrane; and consequently, lower permeate fluxes are obtained. In the NF process no conclusion could be drawn based on the MWCO, because these membranes had the same nominal pore size (in the range 150–340 Da). However, the results indicate that at similar operating conditions, the HL membrane presented a higher permeate flux than the CK or DL membranes: 138.1 vs. 41.6 and 54.9 dm^3 h^{-1} m^{-2} (Expts. UPNF-3, UPNF-5 and UPNF-6). These differences are a consequence of the different nature of the membranes, and agree with the results previously reported and discussed for PWP, where the hydraulic permeability was much higher for the HL membrane than for the CK and DL membranes. On the other hand, and regarding to the pH influence, the UF PT membrane presents a very slight decrease in J_{vss} with the increase in the pH (Expts. UPUF-2, UPUF-3, UPUF-4, and UPUF-5); however, this effect is almost negligible in the NF HL membrane (Expts. UPNF-1, UPNF-2, UPNF-4, and UPNF-4).

Table 4. Filtration experiments performed with ECs dissolved in different water matrices: UP water and real water matrices (PA, LA and BA).

Expt.	Membrane	TPM, MPa	pH	J_{vss}, $dm^3\ h^{-1}\ m^{-2}$
UPUF-1	GK	0.3	7	16.5
UPUF-2	PT	0.3	3	57.8
UPUF-3	PT	0.3	5	57.2
UPUF-4	PT	0.3	7	56.7
UPUF-5	PT	0.3	9	54.5
UPUF-6	PW	0.3	7	185.8
UPNF-1	HL	2	3	138.4
UPNF-2	HL	2	5	137.1
UPNF-3	HL	2	7	138.1
UPNF-4	HL	2	9	138.4
UPNF-5	CK	2	7	41.6
UPNF-6	DL	2	7	54.9
PAUF	PT	0.3	7.2	54.9
LAUF	PT	0.3	8.1	61.3
BAUF	PT	0.3	8.5	49.8
PANF	HL	2	7.2	119.1
LANF	HL	2	8.1	123.2
BANF	HL	2	8.5	117.6

The permeate flux decline already commented is a consequence of the resistances found by the solutions to pass through the membranes. This decline can be analysed by means of the resistances in series model. This model and their different resistances being described in a preceding section (Eqs. (4) and (5)).

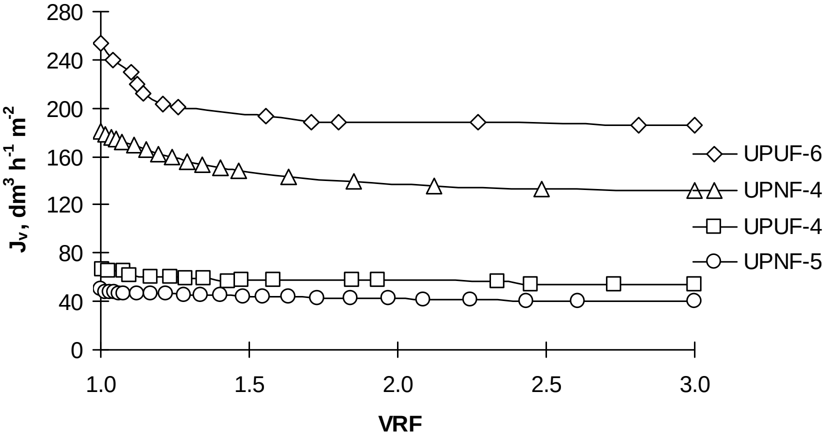


Figure 1. Evolution of the permeate flux with VRF during the filtration of emerging contaminants dissolved in UP water (Expts. UPUF-4, UPUF-6, UPNF-4 and UPNF-5).

The values of the mentioned resistances were determined according to the experimental protocol described in the experimental section: thus, R_m was evaluated by using Eq. (4) when applied to the filtration experiments of UP water with each new membrane. Obviously, the viscosity and permeate flux in that Eq. (4) corresponded to those of the UP water (μ_w and J_w). Similarly, R_t was also determined by means of Eq. (4) applied to the filtration experiments of the ECs aqueous solutions. In that case, the viscosity and the permeate flux of the solutions (μ and J_v) were used And R_f was calculated from Eq. (5), as the difference between R_t and R_m. Finally, the internal fouling resistance R_{if} was evaluated from the final filtration stage of UP water that removed the cake layer formed, but not the pore blocking. For this purpose, Eq. (4) was again applied to the water permeate flux J_w obtained in this last stage. The difference between R_f and R_{if} provided the values of the external fouling resistance R_{ef}. Following this procedure, the values obtained for these resistances in all the experiments conducted are summarized in Table 5, which also shows the ratio R_f/R_t, which indicates the partial contribution of the fouling resistance to the total resistance.

The analysis of the total resistance R_t, with values given in Table 5, shows that the higher values in the UF process corresponded to the GK membrane (R_t=6.56×10^{13} m^{-1} in Expt. UPUF-1); and the lower value corresponded to the PW membrane (R_t=0.58×10^{13} m^{-1} in Expt. UPUF-6), as a direct consequence of the increasing MWCO (2000 and 20000 Da for GK and PW membranes, respectively). Similarly, this effect was also observed for the fouling resistance R_f in these UF membranes with greater values with lower MWCO. Thus, the GK membrane presented the highest value of R_f (Expt. UPUF-1), while the PW membrane presented the lowest one (Expt. UPUF-6). In the case of the NF membranes, it is easily observed that the values of the total resistance R_t, membrane resistance R_m, and fouling resistance R_f were globally much higher than in the UF process as could be expected. As the MWCO is almost the same in these three membranes, the differences in the values can be again attributed to their different natures. Once again, the R_t, R_m and R_f resistances are in the same range for CK and DL membranes (Expts. UPNF-5 and UPNF-6), while the HL membrane provided lower values (Expt. UPNF-3): as discussed previously, higher permeate fluxes were generated in this membrane, as a consequence of its lower resistances. On the contrary, CK and DL presented lower permeate fluxes due to their higher resistances.

The comparison between R_f and R_m showed in all cases that R_f is smaller than R_m; that is, the partial contribution of the fouling resistance to the total resistance, given by the ratio R_f/R_t in Table 5, is lower than 20% in the UF experiments; and in the range 20-50% in the NF experiments. Consequently, the contribution of the inherent membrane resistance R_m is higher in comparison to the fouling resistance $R_{f,}$ which confirms that the membrane fouling is generally low in such as kind of experiments where model ECs are dissolved in UP water. A contrary effect was observed in filtration experiments of industrial wastewaters (Cassano et al., 2007), where the partial contribution of R_f to the total resistance R_t was much higher than the contribution of R_m, due to greater pollutant load in these waters, which fouled the membranes in a higher extent. Finally, with respect to the contribution of internal and external fouling to the total fouling, R_{ef} was higher than R_{if} for all the selected membranes, which indicates that polarization concentration and cake layer formation contribute to a higher extent to fouling than pore blocking and contaminants adsorption onto the membrane.

Table 5. Resistances obtained in the filtration of ECs dissolved in different water matrices at VRF=3.

Expt.	Membrane	R_t x 10^{-13}, m^{-1}	R_m x 10^{-13}, m^{-1}	R_f x 10^{-13}, m^{-1}	R_{ef} x 10^{-13}, m^{-1}	R_{if} x 10^{-13}, m^{-1}	R_f/R_t, %
UPUF-1	GK	6.56	5.31	1.25	0.96	0.29	19.1
UPUF-2	PT	1.87	1.62	0.25	0.22	0.04	13.5
UPUF-3	PT	1.93	1.68	0.25	0.19	0.06	12.9
UPUF-4	PT	1.91	1.70	0.21	0.12	0.09	11.0
UPUF-5	PT	1.98	1.79	0.19	0.17	0.02	9.6
UPUF-6	PW	0.58	0.46	0.12	0.11	0.01	20.2
UPNF-1	HL	6.60	3.41	3.20	2.89	0.31	48.4
UPNF-2	HL	5.31	3.64	1.67	1.54	0.13	31.5
UPNF-3	HL	4.24	2.96	1.28	1.09	0.19	30.2
UPNF-4	HL	3.85	2.20	1.65	1.44	0.21	42.9
UPNF-5	CK	18.2	14.6	3.59	3.22	0.37	19.7
UPNF-6	DL	13.41	11.1	2.34	1.83	0.51	17.4
PAUF	PT	1.97	1.68	0.29	0.10	0.19	14.8
LAUF	PT	1.94	1.78	0.16	0.10	0.06	8.2
BAUF	PT	2.71	2.02	0.70	0.31	0.38	25.7
PANF	HL	3.89	3.66	0.23	0.20	0.03	5.9
LANF	HL	4.26	3.66	0.60	0.33	0.27	14.0
BANF	HL	5.31	4.06	1.25	0.93	0.33	23.6

The retention coefficient constitutes an interesting parameter that provides information about the efficiency of a membrane in the filtration process of a specific solute. It relates the concentration of a substance in the permeate stream with its concentration in the feed stream, and can be determined for the selected ECs of the present work by Eq. (6). The R coefficients obtained decreased slightly with the increase in the VRF parameter during an experiment, and consequently, with processing time. This decay ended at VRF values around 3, and then, they are considered the R coefficients at steady-state conditions.

A wide range of results for these R coefficients was obtained in the experiments of the present study, results that are summarized in Fig. 2 for the different membranes tested and the selected ECs. By considering each specific compound, the NF process of AH provided R coefficients with values around 100%; that is, this contaminant was almost totally retained by these membranes. In its UF process, AH also presented elevated R coefficients, although decreasing values with the increase in the MWCO. Intermediates values were deduced for MS (in the range 80-100% for NF membranes, and 65-78% for UF membranes); and low R coefficients were obtained for PE, (30-60% for NF membranes, and 25-38% for UF membranes).

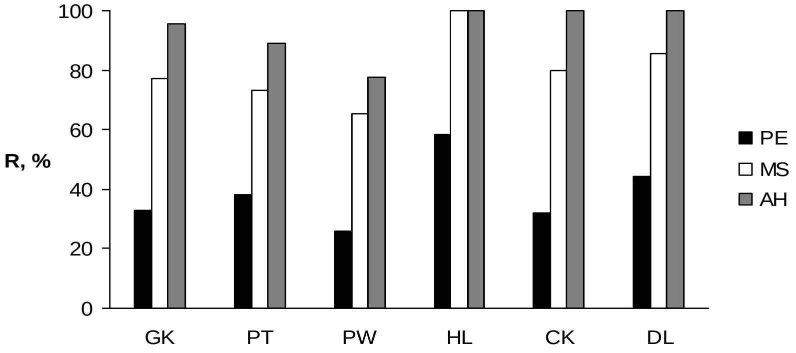


Figure 2. Values for the retention coefficients of emerging contaminants obtained with the different UF (PW, GK and PT) and NF (DL, CK and HL) membranes tested in UP water at VRF=3 and pH=7 (Expts. UPUF-1, UPUF-4, UPUF-6, UPNF-3, UPNF-5, and UPNF-6).

The high retention coefficients for the NF membranes could be expected as a consequence of their low MWCO (Chen et al., 2004). In addition, among the UF experiments, the effect of the membrane MWCO can be also observed: thus, the GK membrane provided higher retentions than the PT membrane in the UF process (excepting for PE), while the PW membrane presented the lower R coefficients. However, since the MWCO of these UF membranes is much higher than the molecular weight of the selected pollutants, other mechanisms than size exclusion must also contribute efficiently to the retention of ECs. Specially, adsorption mechanism should be also responsible for this retention in addition to size exclusion: in effect, the highest values of retention coefficients obtained for AH with the use of UF membranes is also a consequence of its hydrophobic nature, according to its high value of log K_{ow} summarized in Table 1 (log K_{ow}=5.0). Intermediate retentions were obtained for MS which also presents hydrophobic nature, although at a moderate level (log K_{ow}=2.55). On the contrary, PE is the most hydrophilic compound (log K_{ow}=1.16), and therefore it is only partially adsorbed onto the membranes, so that its retention is rather low.

In the case of the NF membranes, the differences between the R coefficients obtained for a specific compound are not attributed to the different values of membranes MWCO, since they are very similar. Then, additional considerations must be taken into account in order to explain the different retentions. Thus, on one hand, AH has a MW in the same range than the MWCO of the DL membrane, and slightly higher than those of the HL and CK membranes. Consequently, the size exclusion is the main mechanism responsible of the AH rejection, and the R values obtained are the highest (almost totally rejected). On the contrary, the MW of MS and PE are in the same range than the MWCO of these NF membranes, or even lower; and therefore, size exclusion mechanism contributes in a less extent, providing for both contaminants lower R values than for AH. In those cases, adsorption mechanism must be also responsible of retention for MS and PE, as it occurred in UF process, with lower R values for PE due to its hydrophilic nature (log K_{ow}=1.16), and higher R values for MS due to its moderate hydrophobic character (log K_{ow}=2.55) .

3.3. Filtration of ECs in real water matrices.

In a following stage of this work, the ECs were dissolved in the three selected water matrices already described in the experimental section, whose quality parameters are compiled in Table 3. UF experiments with the PT membrane and NF experiments with the

HL membrane were performed at TMP and pH values (those of the natural water matrices) that are also summarized in Table 4. The results obtained for the steady-state permeate fluxes J_{vss}, measured at VRF=3, are also shown in Table 4.

Firstly, it is again observed for these real waters that the NF process yielded higher J_{vss} values than the UF process. In addition, while values of J_{vss} in the same range are obtained in the UF process with the PT membrane for both, the UP water and the natural waters (see Expts. UPUF-3, PAUF, LAUF and BAUF), the NF process with the HL membrane yielded lower J_{vss} values in the real waters (see Expts. UPNF-3, PANF, LANF and BANF) with a flux decrease that was more pronounced in the real waters filtration process.

The influence of the water matrix on these J_{vss} can also be pointed out from the results shown in Table 4: thus, the trend obtained for the permeate J_{vss} is: LA > PA > BA. The decrease in the permeate flux trend agrees with the increase in the NOM present in the selected waters, which is measured by the values compiled in Table 3 for absorbance, and TOC and DOC contents. In effect, this increase in NOM induces several effects, such as larger adsorption of species onto the membrane, pore blocking and formation of a cake layer on the membrane surface, all these effects leading to lower J_{vss} values. Consequently, LA water, with lower NOM presence, provided higher J_{vss} values; on the contrary, the higher values of absorbance, TOC and DOC contents in BA wastewater provided the lowest J_{vss} values. Obviously, the intermediate NOM content in the PA water led to intermediate J_{vss} values.

Similarly to the UF and NF experiments of ECs dissolved in UP water, the values of the resistances R_t, R_m and R_f were evaluated for both, UF and NF filtration processes of the ECs dissolved in real water matrices. The values obtained are also shown in Table 5, which also compiles the partial contribution of the fouling resistance to the total resistance, represented by the term R_f/R_t. Once again, much lower contributions of R_f resistance to the total resistance R_t were observed (below 25% in all cases), as a consequence of the low fouling effect that occur in these systems, while the contribution of the membrane resistance R_m is higher (above 75% in all cases).

Similarly, the efficiency of the membranes for the retention of the selected pharmaceuticals when they are present in the waters tested was also determined by the evaluation of the retention coefficients. Figures 3a and 3b show the R values at VRF=3, by representing the retention coefficients for the three compounds in both, the UF and NF processes with the PT and HL membranes, respectively. On one hand, the retentions were considerably higher in the NF process than in the UF process, as a consequence of the lower MWCO of the CK membrane, as was already discussed for UP water. Additionally, the sequence of retentions already obtained for UP water was again confirmed: AH>MS>PE. On the other hand, by considering the nature of the water matrices, the retention coefficients for a specific compound reveal that slightly higher retentions were obtained in the municipal wastewater treatment plant BA that was followed by the reservoir PA water, while lower values were obtained in the LA water. This effect could be expected according to the NOM contents shown in Table 3: the BA water, with higher NOM contents, induces higher fouling on the membranes due to adsorption and pore blocking; and this membrane fouling decreases the pore size and increases the ECs retention. Additionally, the formation of an organic layer (cake) on the membrane leads to the possibility that the adsorption of the pollutants on this layer increases their retention.

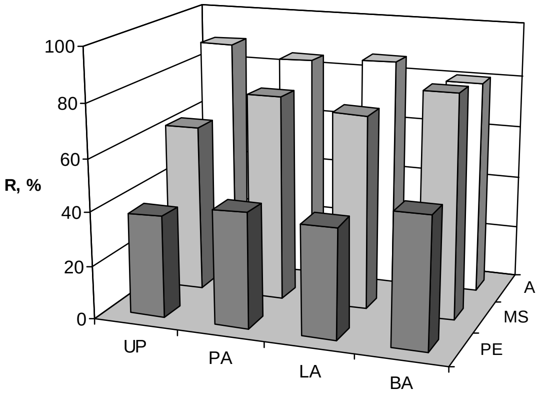


Figure 3a. Retention coefficients at VRF=3 for the three ECs in different water systems in UF experiments using the PT membrane.

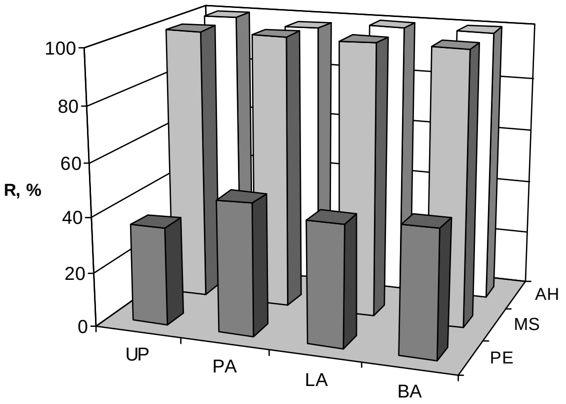


Figure 3b. Retention coefficients at VRF=3 for the three ECs in different water systems in NF experiments using the HL membrane.

Finally, the effectiveness of the filtration processes for the elimination of the organic matter present in these water matrices can be also evaluated by the retention coefficients referred to the selected water quality parameters: COD, and TOC, and absorbance at 254 nm (R_{COD}, R_{TOC} and R_{254}, respectively). These coefficients were evaluated at different filtration times by means of Eq. (7), and a slight decrease with filtration time was observed, due to the increase of the concentration gradient; and consequently, to the decrease in the retention rate during the experiments because of the saturation of the membrane. At advanced processing times, around VRF=3, the steady-state conditions were reached, and the values for the retention coefficients of these quality parameters are summarized in Table 6.

Several facts can be deduced from these values in Table 6: on one hand, the retentions were higher in the NF process than in the UF process, as a consequence of the lower MWCO of the HL membrane, as previously discussed for UP water. Thus, values in the ranges 40-71% for TOC, 28-53% for COD and 52-67% for absorbance, were obtained in the UF process. At the same time, values in the range 74-92 % for TOC, 52-59% for COD and 74-100% for absorbance were obtained in the NF process. In conclusion, these filtration processes led to moderate (UF) and high (NF) elimination of the organic matter content present in the water matrices tested. Finally, the UF PT membrane provided lower retentions of the ECs in natural waters than in the filtration in UP water, because the NOM present in these waters competes with the ECs for the retention into the pores.

From these results, it can be qualitatively deduced that the HL membrane is adequate for the elimination of ECs from natural waters to produce drinking water, and for the purification of not very contaminated secondary effluents for reuse. However, the retentate stream that is generated constitutes a concentrated fraction with high content in hazardous materials, and needs additional treatments for its purification before its disposal, such as some chemical oxidation or physical treatments.

Table 6. Retention coefficients obtained for several quality parameters in filtration experiments with real waters at VRF=3.

Expt.	Membrane	R_{254}, %	R_{COD}, %	R_{TOC}, %
PAUF	PT	52.4	28.2	40.9
LAUF	PT	67.7	53.6	71.4
BAUF	PT	52.4	28.2	40.9
PANF	HL	87.8	53.8	76.8
LANF	HL	74.3	59.3	74.5
BANF	HL	100	51.2	92.3

4. CONCLUSIONS.

The results of the UF and NF experiments of three emerging contaminants dissolved in ultrapure water, or present in three real waters, allowed the following conclusions to be drawn:

- A continuous decrease of the flux decline with processing time is observed, until an almost constant value was reached at volume reduction factor around 3.
- A direct influence of the MWCO on the values of the permeate flux at the steady state is deduced in the UF process, while these permeate fluxes are mainly affected by the nature of the membranes in the NF process.
- The calculated different types of resistances to the permeate flux reveal that the inherent resistance of the clean membranes is much larger than the fouling resistance.
- According to the values of the retention coefficients, the nanofiltration thin film composite membrane with MWCO=150-300 Da was the most appropriate for the removal of the selected emerging contaminants from the waters tested.
- The above referred membrane also provided the high retention for absorbance at 254 (in the range 75-100%), and TOC (in the range 76-92%); and moderate for COD in the range (51-59%).

REFERENCES

Al-Amoudi A.; Willians P.; Mandele S. and Lovitt R.W. Cleaning results of new and fouled nanofiltration membrane characterized by zeta potential and permeability. Sep. Purif. Technol. **2007**, 54, 234-240.

Anwar Sadmani A.H.M.; Andrews R.C. and Bagley D.M. Nanofiltration of pharmaceutically active compounds as a function of compound interactions with DOM fractions and cations in natural water. Sep. Purif. Technol. **2014**, 122, 462-471.

Benitez F.J.; Leal A.I.; Real F.J.; Acero J.L. and Gloria R. Elimination of organic matter present in wastewaters from the cork industry by membrane filtration. J. Chem. Tech. Biotech. **2008**, 83, 309-316.

Bolong N.; Ismail A.F.; Salim M.R. and Matsuura T. A review of the effects of emerging contaminants in wastewater and options for their removal. Desalination **2009**, 239, 229-246.

Cassano A.; Donato L. and Drioli E. Ultrafiltration of kiwifruit juice: Operating parameters, juice quality and membrane fouling. J. Food Engng. **2007**, 79, 613-621.

Clesceri L.S.; Greenberg A.E. and Eaton A.D. Standard Methods for the Examination of Water and Wastewater (20th ed.). APHA-AWWA-WPCF, Washington, DC, **1999**.

Comerton A.M.; Andrews R.C.; Bagley D.M. and Hao C. The rejection of endocrine disrupting and pharmaceutically active compounds by NF and RO membranes as a function of compound and water matrix properties. J. Membr. Sci. **2008**, 313, 323-335.

Chen S-S.; Taylor J.S.; Mulford L.A. and Norris C.D. Influences of molecular weight, molecular size, flux, and recovery for aromatic pesticide removal by nanofiltration membranes. Desalination **2004**, 160, 103-111.

Jelic A.; Gros M.; Ginebreda A.; Cespedes-Sánchez R.; Ventura F.; Petrovic M. and Barcelo D. Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. Water Res. **2011**, 45**,** 1165-1176.

JIn X.; Hu J. and Ong S.L. Influence of dissolved organic matter on estrone removal by NF membranes and the role of their structure. Water Res. **2007**, 41, 3077-3088.

Kim J.H.; Park P.K.; Lee C.H. and Kwoh H.H. Surface modification of nanofiltration membranes to improve the removal of organic micro-pollutants (EDCs and PhACs) in drinking water treatment: graft polymerization and cross-linking followed by functional group substitution. J. Membr. Sci. **2008,** 321, 190-198.

Maximous N.; Nakhla G. and Wan W. Comparative assessment of hydrophilic membrane fouling in wastewater applications. J. Membr. Sci. **2009**, 339, 93-99.

Nghiem L.D.; Coleman P.J. and Espendiller C. Mechanisms underlying the effects of membrane fouling on the nanofiltration of trace organic contaminants. Desalination **2010**, 250, 682-687.

Park N.; Lee Y.; Lee S. and Cho J. Removal of taste and odor model compound (2,4,6-trichloroanisole) by tight ultrafiltration membranes. Desalination **2007**, 212, 28-36.

Petrie B.; Barden R. and Kasprzyk-Hordern B. A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring. Water Res. **2015**, 72, 3-27.

Sim W-J.; Lee J-W.; Lee E-S; Shin S-K.; Hwang S-R. and Oh J-E. Occurrence and distribution of pharmaceuticals in wastewater from households, livestock farms, hospitals and pharmaceutical manufactures. Chemosphere **2011**, 82, 179-186.

Tijani O.J.; Fatoba O.O. and Petrik L.F. A review of pharmaceuticals and endocrine-disrupting compounds: sources, effects, removal and detections. Water Air Soil Poll. **2013**, 224, 1770-1799.

Verliefde A.R.D.; Heijman S.G.J.; Cornelissen E.R.; Amy G.; Van der Bruggen B. and Van Dijk J.C. Nanofiltration as a treatment method for the removal of pesticides from groundwater. Water Res. **2007**, 41, 139-147.

Verliefde A.R.D.; Cornelissen E.R.; Heijman S.G.J.; Petrinic I.; Luxbacher T.; Amy G.L.; Van der Bruggen B. and Van Dijk J.C. Influence of membrane fouling by (pretreated) surface water on rejection of pharmaceutically active compounds (PhACs) by nanofiltration membranes. J. Membr. Sci. **2009**, 330, 90-103.

Wray H.E.; Andrews R.C. and Berube P.R. Surface shear stress and retention of emerging contaminants during ultrafiltration for drinking water treatment. Sep. Purif. Technol. **2014**, 122, 183-191.

Yoon Y.; Westerhoff W.; Snyder S.A. and Wert E.C. Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products. J. Membr. Sci**. 2006**, 270, 88-100.

Zhang Y.; Van der Bruggen B.; Chen G.X.; Braeken L. and Vandecasteele C. Removal of pesticides by nanofiltration: effect of the water matrix. Sep. Purif. Technol. **2004**, 38, 163-172.

3.7. Adsorption of selected emerging contaminants onto PAC and GAC: equilibrium isotherms, kinetics, and effect of the water matrix.

Submitted for publication in Journal Environmental Science and Health Part A.

3.7. ADSORPTION OF SELECTED EMERGING CONTAMINANTS ONTO PAC AND GAC: EQUILIBRIUM ISOTHERMS, KINETICS, AND EFFECT OF THE WATER MATRIX.

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Submitted for publication in Journal Environmental Science and Health Part A.

ABSTRACT

The removal of three emerging contaminants (ECs) (amitriptyline hydrochloride (AH), methyl salicylate (MS) and 2-phenoxyethanol (PE)) dissolved in several water matrices by means of their adsorption onto powdered activated carbon (PAC) and granular activated carbon (GAC) has been investigated. When dissolved in ultrapure water, adsorption of the ECs followed the trend AH > MS > PE, with a positive effect of the adsorbent dose. According to the analysis of the adsorption isotherms and adsorption kinetics, PAC showed strongly higher adsorption efficiency in both, capacity and velocity of adsorption, in agreement with its higher mesoporosity. Equilibrium isotherm data were fitted by Langmuir and Freundlich models. Pseudo-second order kinetics models reproduced very successfully the adsorption process.

Finally, the effect of the dissolved organic matter (DOM) of the water matrix (ultrapure water, a surface water and two effluents from wastewater treatment plants) on the adsorption of the selected ECs onto PAC was established, as well as its performance on the removal of water quality parameters. Results show a negative effect of the DOM content on the adsorption efficiency. Organic matter removal over 50% was obtained with high PAC doses, revealing that adsorption onto PAC is an effective technology to remove both, micro-pollutants and DOM, from water matrices.

Keywords: Emerging contaminants; amitriptyline hydrochloride; methyl salicylate; 2-phenoxyethanol; Municipal secondary effluent; Adsorption; PAC; GAC

1. INTRODUCTION.

A large number of chemical compounds present in natural waters and wastewaters are refractory towards conventional water treatments, and remain dissolved at very low concentrations even in treated effluents (Lapworth et al., 2012). Many of these micro-pollutants may present ecological threat for the aquatic environment (Thomaidi et al., 2015) and may cause a risk to human health, since they can cause unexpected physiological consequences. Among these substances, a group usually called “emerging contaminants” (ECs) plays an important role in the pollution of waters. This group of contaminants is constituted, among others, by pesticides, pharmaceuticals, personal care products, fuel additives, flame-retardants, plasticizers and numerous other industrial pollutants.

Among the treatment processes more successfully used in the removal of ECs from wastewaters, adsorption by using commercial activated carbons, such as powdered activated carbon (PAC) and granular activated carbon (GAC), is an efficient technology able to separate resistant micro-pollutants such as most of ECs present in wastewaters (Sotelo et al., 2013; Rakic et al., 2015). Generally, the success of the adsorption process in the elimination of micro-pollutants in waters is due to its high specific surface (more than 400 m^2 g^{-1}), and the combination of a well-developed porous structure and the surface chemistry properties (Alvarez-Torrellas et al., 2016).

With these considerations in mind, a study was designed for the elimination of ECs that could be present in surface water and municipal wastewater by adsorption treatment. For this purpose, the following three ECs were selected as model compounds of this important group of contaminants: amitriptyline hydrochloride (AH), methyl salicylate (MS) and 2-phenoxyethanol (PE). AH is the most widely used tricyclic antidepressant; MS is a salicylic acid derivative produced by esterification with methanol and used as rubefacient, analgesic and anti-inflammatory; and PE is a bactericide often used in dermatological products, fixative for perfumes, insecticide and topical antiseptic.

The present work focuses on the elimination of these selected ECs from aqueous phases by applying adsorption treatment onto PAC and GAC. First of all, the main parameters related to the performance of the process (equilibrium isotherms and adsorption kinetics) were determined. Then, the adsorption of the ECs dissolved in several water matrices, such as ultrapure water, surface water and secondary effluent from a municipal wastewater treatment plant (WWTP), was investigated. The main objective was to evaluate the effect of the dissolved organic matter (DOM) on the adsorption process, as well as the specific removal of this DOM from the water matrices assayed.

2. MATERIALS AND METHODS.

2.1. Emerging contaminants, water matrices and adsorbents.

Amitriptyline hydrochloride (AH, $C_{20}H_{23}N\cdot HCl$, ≥99%), methyl salicylate (MS, $C_8H_8O_3$, ≥98%) and 2-phenoxyethanol (PE, $C_8H_{10}O_2$, ≥99%) were purchased from Sigma-Aldrich (Spain). Table 1 summarizes the molecular structures and molecular weights (MW) of these model compounds, as well as their pK_a values.

The adsorption experiments were carried out by dissolving the ECs in ultrapure (UP) water (from a Milli-Q system, Millipore Iberica, Spain), and also, in several water matrices, in order to reproduce more realistic water treatment conditions. These aquatic systems, whose main quality parameters are compiled in Table 2, were the following: a surface water collected from the public reservoir “Peña del Aguila” (PA), located in the Extremadura Community, south-west of Spain; and two secondary effluents from wastewater treatment plants from the cities of Badajoz (BA) and La Albuera (LA), also in the Extremadura Community. These water systems were filtered through a 0.45 μm cellulose nitrate filter within the first 24 h after collection and stored at 4ºC until use. Specifically, UV absorbance at 254 nm (A_{254nm}), chemical oxygen demand (COD) and total organic carbon (TOC) content constitute a significant index of the total DOM content present in these effluents, which is expected to affect the performance of the adsorption process. In all cases, the solutions were prepared by dissolving the ECs in the four selected water matrices.

Table 1. Selected ECs and their physico-chemical properties.

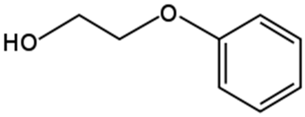
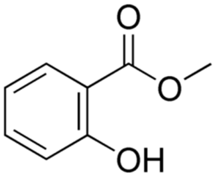
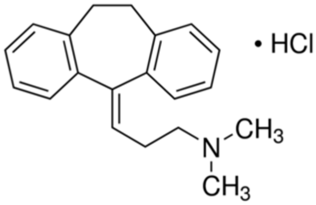
EC	Chemical Structure	MW, g·mol^{-1}	pK$_a$
2-phenoxyethanol (PE)		138.17	-
Methyl Salicylate (MS)		152.15	9.87
Amitriptyline hydrochloride (AH)		313.87	9.4

Table 2. Quality parameters of the selected real water matrices.

	PA	LA	BA
pH	7.4	7.9	8.3
Conductivity (µS cm^{-1})	80	570	550
A_{254nm} (cm^{-1})	0.187	0.041	0.245
COD (mg O_2 L^{-1})	18	7	56
TOC (mg L^{-1})	5.2	2.9	11.1
Alkalinity (mg $CaCO_3$ L^{-1})	30	335	325
Total nitrogen (mg N L^{-1})	1.51	21.3	35.5
Total phosphorus (mg P L^{-1})	0.041	0.156	1.76

The PAC and GAC used in the adsorption process were supplied by Panreac. The particles were soaked overnight in UP water, later oven-dried at 105ºC for 2 h and stored in a desiccator until use. The analysis of these adsorbents is provided in Section 2.3.

2.2. Experimental procedures and analytical methods.

In order to determine adsorption isotherms for the adsorbents assayed, PAC and GAC, individual ECs solutions were prepared in UP water at pH 7, and with initial concentrations in the range 5-20 mg L^{-1}. The selected compounds were added into a series of Erlenmeyer flasks, and afterwards, the adsorbent (10-400 mg L^{-1}) was added. Then, the flasks were transferred to a temperature controlled shaking water bath. After the equilibrium was reached (24 h for PAC, 6-8 days for GAC), the solutions were filtered through 0.45 µm cellulose nitrate filters to separate the adsorbent, and the remaining concentrations of emerging contaminants in the liquid phase was analysed by HPLC.

Additional experiments were carried out in order to study the adsorption kinetics. They were performed in a similar way to those for the determination of the adsorption isotherms, but by using a fixed initial PAC or GAC concentration in each experiment, in the range 10-20 mg L^{-1}, and by varying the pH in the range 3-9. The initial concentration of ECs was 1 mg L^{-1}, except for AH in PAC experiments which was 5 mg L^{-1}. At regular times, samples were taken and filtered in order to determine the remaining aqueous EC concentration by HPLC analysis. Several kinetic models were applied to the experimental data obtained as will be discussed later.

In a final stage, adsorption experiments were carried out by dissolving a mixture of the three ECs in different water matrices, in order to establish the influence of the DOM of each water matrix on the adsorption of these compounds. An initial concentration of each EC of 1 mg L^{-1} was used, while the PAC dose was modified in the range 20-100 mg L^{-1}. Evolution of main water quality parameters, such as COD, TOC and absorbance at 254 nm was examined.

The selected ECs were analysed by HPLC in a Waters Chromatograph (Waters, Milford, MA, USA) equipped with a 996 Photodiode Array Detector and a Waters Nova-Pak C18 Column (5 µm 150x3.9 mm). The detection was performed at 238 nm for AH and MS, and 220 nm for PE. The mobile phase was a mixture of methanol and 0.01 M aqueous phosphoric acid solution in different proportions, depending on the compounds analysed. The elution flow rate was 1 mL min^{-1} and the injection volume was 100 µL in all samples.

The analytical methods for the characterization of the secondary effluent and determination of water quality parameters were followed according to the Standard Methods (Clesceri et al., 1989).

2.3. PAC and GAC characterization.

The main physical and chemical characteristics of the activated carbons used in this work were determined after a complete analysis. Scanning electron microscopy (SEM) images of PAC and GAC shown in Figure 1a and 1b, respectively, reveal a porous surface and a particle size of 20-70 μm for PAC and around 2 mm for GAC. The Brunauer-Emmett-Teller (BET) surface area and micro, meso and macropore volumes were determined from the adsorption isotherm of N_2 at 77 K. The determined S_{BET} values were 990.4 $m^2\ g^{-1}$ for PAC and 995.8 $m^2\ g^{-1}$ for GAC, indicating that both carbons have the same nature, but different particle grading. Figure 1c shows the adsorption isotherm of N_2 at 77 K onto PAC and GAC. The isotherms presented a rounded knee at a low relative pressure that is indicative of a micropore volume in the carbon nanomaterial. Moreover, the steep slope observed for PAC suggests a considerable mesopore volume and the adsorption tail at high pressure, macropore volume. On the other hand, the almost horizontal curve observed for GAC at medium and high relative pressures indicates negligible meso and macropore volume. Also, a desorption hysteresis loop due to nitrogen condensation in mesopores (a typical type-II isotherm) is observed for both adsorbents (Lin and Teng, 2002). Based on these data, the determined micro, meso and macropore volumes were 0.414, 0.360 and 1.66 $cm^3\ g^{-1}$ for PAC and 0.388, 0.023 and 0.07 $cm^3\ g^{-1}$ for GAC. It is remarkable the great difference observed for meso- and macropore volumes.

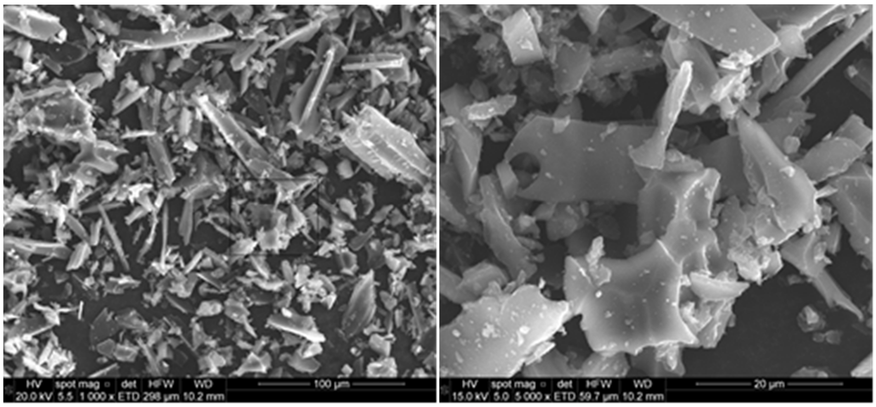


Figure 1a. Characterization of the adsorbents. SEM micrographs of PAC at 1000X and 5000X.

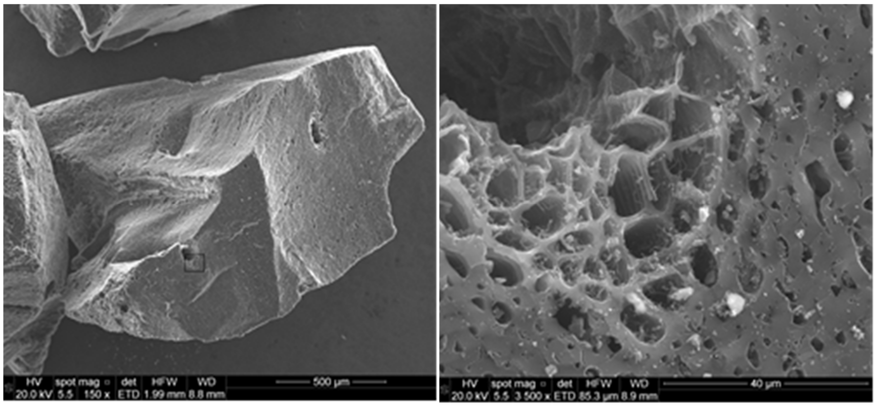


Figure 1b. Characterization of the adsorbents. SEM micrographs of GAC at 150X and 3500X.

The X-ray spectroscopic analysis of the adsorbents provided the main functional groups present in the external layers of the activated carbons (Moulder et al., 1995). Similar distribution of functional groups was found for both adsorbents, being graphitic or aromatic carbon the most abundant with 70%, followed by single carbon-oxygen bonds, with 13% in both PAC and GAC. The main differences between carbons were observed for carbonyl and carboxyl groups, with greater presence in PAC, and $\pi \rightarrow \pi^*$ transitions, more abundant in GAC. The deconvolution of O1s region revealed greater oxygen content tied to inorganic matter (O-II) in PAC, as well as more C=O bonds associated to carbonyl or quinone groups, and C-O bonds related with phenolic, ether, lactone and anhydride groups; whereas GAC showed more carboxylic groups.

The superficial acid character of the adsorbents was determined by using the slurry pH method (Wang and Lu, 1998), measuring the final pH after keeping stirred suspensions of the adsorbent for 24 hours, being the calculated slurry values of 8.1 and 8.8 for PAC and GAC, respectively.

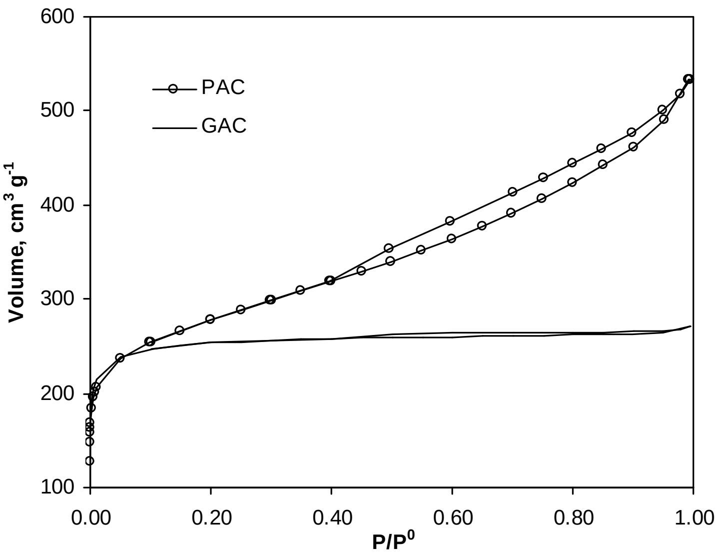


Figure 1c. Adsorption isotherm of N_2 at 77 K onto PAC and GAC.

3. RESULTS AND DISCUSSION.

3.1. Equilibrium isotherms.

The equilibrium isotherm data for adsorption at 20ºC and pH 7 of the selected ECs onto PAC and GAC were fitted by Langmuir (Langmuir, 1918) and Freundlich (Freundlich and Heller, 1939) models. Langmuir model assumes monolayer adsorption and its isotherm equation (Putra et al., 2009) can be expressed by:

$$q_e = \frac{q_s\ K_L\ C_e}{1 + K_L\ C_e} \tag{1}$$

where q_e (mg g^{-1}) is the amount of EC adsorbed at equilibrium; q_s (mg g^{-1}) is the maximum monolayer adsorption capacity; K_L (L mg^{-1}) is the Langmuir constant that is related to the apparent energy of adsorption, and C_e is the equilibrium aqueous concentration of EC.

On the other hand, Freundlich model provides an empirical isotherm equation which is used to describe heterogeneous surface systems (Sotelo et al., 2013; Lu et al., 2011). This equation is defined as:

$$q_e = K_f\ C_e^{1/n} \tag{2}$$

where K_f is the Freundlich constant, which indicates the relative adsorption capacity; and n is a constant depicting the sorption intensity.

The fitted Langmuir and Freundlich parameters for adsorption of the selected ECs dissolved in UP water onto PAC and GAC are given in Table 3. The data obtained show a better efficiency of the adsorption onto PAC. On the contrary, GAC showed lower adsorption capacity, as can be deduced from the values of the parameters q_s for Langmuir and K_f for Freundlich model. This performance can be explained from the lower mesopore and macropore volume of GAC reported in Section 2.3, that hinders the diffusion of each ECs towards the active sites located in the microporous surface. Regarding the values of R^2 listed in Table 3, it can be observed that Langmuir model correlated the adsorption isotherms slightly better than Freundlich in most experiments. Therefore, monolayer adsorption of the selected emerging contaminants probably occurred, although Freundlich model can also represent the equilibrium data reasonably well for most of the experiments. Based on these findings, Figure 2 depicts the adsorption isotherms at 20ºC of the selected ECs onto PAC, representing the experimental values by symbols, and the calculated values with the most appropriate model by lines; that is, Langmuir equation for MS and PE and Freundlich for AH. As can be noted, an excellent correlation is appreciated between experimental and calculated values, indicating the goodness of the models selected. According to the values of q_s and also K_f listed in Table 3 and the results depicted in Figure

1, it is also deduced that the PAC adsorption capacity order is AH ≈ MS > PE, while for GAC the capacity trend is: AH > MS ≥ PE.

Table 3. Langmuir and Freundlich isotherm parameters for the adsorption at 20ºC of ECs onto PAC and GAC.

Compound	Langmuir			Freundlich		
	q_s, ($mg\ g^{-1}$)	K_L, ($L\ mg^{-1}$)	R^2	K_f, ($mg/g(L/mg)^{1/n}$)	n	R^2
AH-PAC	230.5	0.144	0.962	193.4	3.98	0.988
MS-PAC	222.6	0.103	0.991	191.4	5.01	0.977
PE-PAC	126.3	0.536	0.978	75.29	3.67	0.971
AH-GAC	178.2	3.29	0.964	40.8	1.30	0.927
MS-GAC	45.4	0.829	0.961	26.6	1.52	0.977
PE-GAC	39.4	0.667	0.980	25.3	1.63	0.971

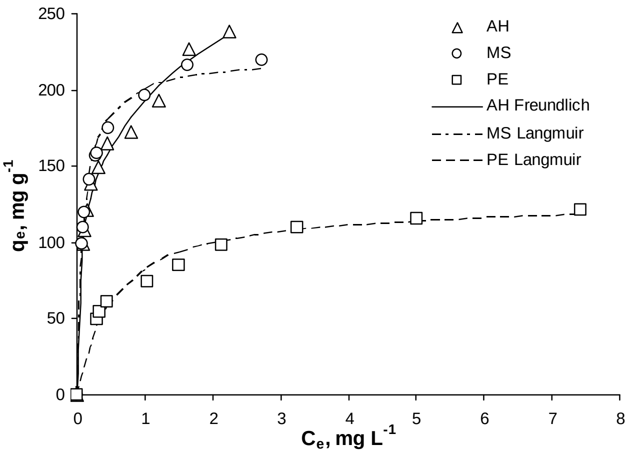


Figure 2. Adsorption isotherms of the selected ECs onto PAC at 20ºC. Symbols: experimental data; lines: proper adsorption model.

3.2. Adsorption kinetics of ECs in UP water and elimination efficiency.

Several PAC and GAC adsorption experiments with each EC dissolved individually in UP water were performed in order to investigate the kinetics of the process. Tables 4 and 5 show the experimental conditions of each experiment, as well as the kinetic parameters determined for the adsorption process by PAC and GAC, respectively. Based on the results obtained in the previous section, the number of experiments and operative variables analysed were considerably greater for adsorption onto PAC, since it seemed a more promising procedure for the elimination of the ECs. Thus, different pH (3-9) and adsorbent concentration (10-20 mg L^{-1}) were applied in the experiments carried out with PAC. As expressed in Table 4, the initial concentration of each individual EC in every experiment was set at 1 mg L^{-1}, except for AH in the adsorption experiments onto PAC, whose initial concentration was increased up to 5 mg L^{-1}, since its fast kinetics and high capacity of adsorption promoted the total elimination of this micro-pollutant. In the case of GAC experiments (Table 5), the lower capacity of this adsorbent allowed to carry out all the experiments at 1 mg L^{-1}. Additionally for AH, another experiment with initial concentration of 5 mg L^{-1} was conducted for comparison purposes.

Three different kinetic models were fitted to experimental adsorption data in order to study the kinetics of the adsorption process: pseudo-first order, pseudo-second order and Elovich models. Among them, the pseudo-second order model provided by far the best agreements, leading to completely fitted curves and $R^2 > 0.999$ in all the experiments. This indicates that chemisorption is a rate-limiting step of the process (Ho and Mckay, 2000; Sotelo et al., 2013). According to Ho and McCay (Ho and Mckay, 1998), this model can be expressed by the following equation:

$$q = \frac{k_2\, q_e\, t}{1 + k_2\, q_e\, t} \tag{3}$$

where k_2 is the rate constant of the pseudo-second order adsorption, and q_e is again the amount of EC adsorbed at equilibrium. This equation can be linearized, leading to equation (4):

$$\frac{t}{q} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e} \tag{4}$$

After linear regression of the experimental data according to equation (4), the parameters q_e and k_2 can be deduced for the adsorption of each EC onto PAC and GAC (data shown in Tables 4 and 5, respectively). From these parameters, the half-adsorption time $t_{1/2}$ (time required to reach half of the maximum adsorption capacity) and the initial adsorption rate v_0, can be determined according to equations (5) and (6), respectively, being both parameters also included in Tables 4 and 5.

$$t_{1/2} = \frac{1}{k_2\, q_e} \tag{5}$$

$$v_0 = k_2\, q_e^2 \tag{6}$$

The analysis of the results obtained allows us to establish several conclusions. First of all, with respect to the kinetics of the process, the results obtained with PAC confirmed the greater efficiency of PAC compared to GAC, with half-adsorption times around 10-20 times lower and initial adsorption rates 10-20 times higher. These results are in agreement with the higher mesoporosity showed by PAC (Alvarez-Torrellas, 2015). Indeed, pseudo-second order kinetic model is concordant with faster adsorption onto carbon with high mesopore volumes, indicating that they can be considered as transport pores, which favor the adsorbate diffusion into the porous structure (Delgado et al., 2012; Mestre et al., 2009). The amount of EC adsorbed at the equilibrium q_e is to some extent better by using PAC as adsorbent, although the initial EC concentration induces a greater positive effect on this parameter than the nature of the adsorbent. The close similarity between the experimental and calculated EC amount adsorbed at the equilibrium (q_e exp and q_e cal, respectively) is a consequence of the excellent performance of the pseudo-second order model. In general terms, the values of q_e were lower for GAC if experiments carried out with equal C_0/W ratio and pH are compared. Thus, the amount of AH adsorbed at equilibrium was 211.5 mg g^{-1} and 321.4 mg g^{-1} for Expts. GAH-2 and P-1, respectively (C_0/W ratio: 0.5). Moreover, the time required to reach the equilibrium in GAC experiments was much larger (6-8 days versus 24 hours for PAC).

Table 4. Kinetic data obtained according to the pseudo-second order model for adsorption at 20ºC of the selected ECs onto PAC. (Initial concentration (C_0) of ECs: 5 mg L^{-1} of AH and 1 mg L^{-1} of MS and PE).

EC	Parameter	P-1	P-2	P-3	P-4	P-5	P-6
	W (mg L^{-1})	10	15	20	10	10	10
	pH	7	7	7	3	5	9
AH	q_e exp (mg g^{-1})	321.4	227.6	205.2	190.6	283.0	296.7
	q_e cal (mg g^{-1})	322.6	228.3	205.8	190.8	284.1	299.4
	k_2x10^2 (g mg^{-1} h^{-1})	1.16	1.84	2.17	4.99	2.25	1.10
	$t_{1/2}$ (h)	0.27	0.24	0.22	0.11	0.16	0.31
	v_0 (mg g^{-1} h^{-1})	1196	955	913	1813	1805	972
	R (%)	69.4	74.6	83.7	38.1	56.6	64.1
MS	q_e exp (mg g^{-1})	91.9	57.4	45.3	90.0	82.4	82.1
	q_e cal (mg g^{-1})	92.8	57.6	45.3	90.4	82.9	82.5
	k_2x10^2 (g mg^{-1} h^{-1})	5.21	21.1	57.9	6.51	7.31	11.0
	$t_{1/2}$ (h)	0.21	0.08	0.04	0.17	0.17	0.11
	v_0 (mg g^{-1} h^{-1})	440	694	1187	527	496	745
	R (%)	91.9	94.1	96.0	90.0	92.3	92.0
PE	q_e exp (mg g^{-1})	80.9	55.5	45.5	63.5	70.0	66.2
	q_e cal (mg g^{-1})	81.2	55.7	45.6	63.8	70.3	66.5
	k_2x10^2 (g mg^{-1} h^{-1})	8.87	21.5	26.9	12.7	11.8	13.9
	$t_{1/2}$ (h)	0.14	0.08	0.08	0.12	0.12	0.11
	v_0 (mg g^{-1} h^{-1})	580	662	556	510	579	610
	R (%)	80.9	84.4	90.9	66.0	72.7	68.9

Table 5. Kinetic data obtained according to the pseudo-second order model for adsorption at 20ºC of the selected ECs onto GAC.

Parameter	GAH-1	GAH-2	GMS-1	GPE-1
W (mg L^{-1})	10	10	10	10
pH	7	7	7	7
C_0 (mg L^{-1})	1	5	1	1
q_e exp (mg g^{-1})	60.5	211.5	62.4	58.4
q_e cal (mg g^{-1})	60.2	209.6	61.6	58.9
k_2x10^2 (g mg^{-1} h^{-1})	4.58	2.22	6.09	5.25
$t_{1/2}$ (h)	3.61	2.13	3.63	3.26
v_0 (mg g^{-1} h^{-1})	16.8	99.4	23.7	17.9
R (%)	60.5	42.3	72.4	67.7

The effect of the adsorbent concentration (W) was only studied for adsorption onto PAC. This variable showed a positive influence on the kinetic rate constant k_2 for the three selected ECs, although $t_{1/2}$ and v_0 were not significantly affected in the case of AH and PE when increasing the PAC dose from 10 to 20 mg L^{-1}. Finally, the pH had not a significant effect on the equilibrium or the kinetics of the process in the studied range (pH 3-9). This is probably due to the low acid dissociation capacity of these ECs, with pK_a higher than 9 for MS and AH, and no dissociation for PE (see Table 1). The possible dissociation of some functional groups present on the surface of PAC seems not to affect the adsorption process.

A simple way to establish the level of micro-pollutants elimination by using adsorption treatment is to determine the percentage of removal of each EC in the aqueous phase, which can be evaluated by the following equation:

$$R=\frac{C_0-C_e}{C_0}\cdot 100 \tag{7}$$

where C_0 and C_e represent the initial and equilibrium aqueous concentrations of each EC, respectively. The values of R for each experiment and EC are also collected in Tables 4 and 5. As can be expected, the results show higher values of elimination of ECs by using PAC than by GAC. Thus, EC removal percentages were 91.9% for MS and 80.9% for PE in Expt. P-1, while values of 72.4% and 67.7% were obtained for MS and PE, respectively, when using GAC (Expts. GMS-1 and GPE-1). Meanwhile, for AH, a removal percentage of 69.4% was obtained in Expt. P-1 and only 42.3% of removal in Expt. GAH-2 (both with an initial AH concentration of 5 mg L^{-1} in order not to miss the aqueous EC at equilibrium in the adsorption process onto PAC). This higher initial concentration justifies the lower AH removal percentage obtained in P-1, when compared to those of MS and PE. In fact, R values around 100% would be obtained using 1 mg L^{-1} initial AH concentration in PAC process, which are significantly greater than those obtained with GAC. Consequently, the trend AH > MS > PE can be globally proposed when comparing the relative efficiency towards adsorption of the ECs involved in this research.

The effect of the AH initial concentration on the R values obtained can be deduced from the GAC experiments, according to the results of Table 5. Indeed, a decrease of this R value from 60.5% to 42.3% is observed in experiments GAH-1 and GAH-2 when AH initial dose increased from 1 to 5 mg L^{-1}, indicating a negative effect of this variable.

Moreover, a positive effect of the adsorbent dose used on the EC removal percentages can be determined for the PAC experiments according to the results exposed in Table 4 (Expts. P-1, P-2 and P-3, using PAC doses of 10, 15 and 20 mg L^{-1}, respectively). Concretely, R values continuously increased from 69.4% to 83.7% for AH; from 91.9% to 96.0% for MS and from 80.9% to 90.9% for PE, when the PAC dose increased from 10 to 20 mg L^{-1}. Finally, the pH did not show any significant effect on the R values listed in Table 4, being only observed a slight positive effect of the pH on the removal of AH in the range studied. Results at pH 7 were optimal or near the maximum for the three ECs. Therefore, no modification of the natural pH of the contaminated aqueous effluents is recommended before adsorption treatment.

3.3. Adsorption in natural waters and secondary effluents

In order to investigate the influence of the water matrix constituents on the simultaneous adsorption of the selected ECs, several experiments were performed with the water matrices listed in Section 2.1 and Table 2. Based on the results obtained, only PAC was used as adsorbent, due to its better performance, with doses ranging from 20 to 100 mg L^{-1}. An initial concentration of 1 mg L^{-1} of each EC was used in the experiments, which were performed at 20ºC and the natural pH of the water matrices. Table 6 lists the experiments carried out as well as the amounts adsorbed and removals obtained at equilibrium for each EC.

Table 6. Adsorption experiments onto PAC of the ECs simultaneously dissolved in several water matrices: amount of EC adsorbed and removal percentages at equilibrium.

Expt.	W (mg L^{-1})	$q_{e\ AH}$ (mg g^{-1})	$q_{e\ MS}$ (mg g^{-1})	$q_{e\ PE}$ (mg g^{-1})	R_{AH} (%)	R_{MS} (%)	R_{PE} (%)
UP-1	20	46.8	47.6	23.4	93.5	95.3	46.7
PA-1	20	44.1	45.0	22.0	91.8	93.6	45.8
PA-2	50	20.0	20.0	18.3	100	100	92.3
PA-3	100	10.0	10.0	9.6	100	100	96.9
LA-1	20	44.5	43.6	22.6	92.7	90.8	47.0
LA-2	50	20.0	20.0	18.7	100	100	95.8
LA-3	100	10.0	10.0	9.7	100	100	97.5
BA-1	20	45.2	45.1	16.2	90.4	90.2	32.4
BA-2	50	48.0	48.3	14.2	96.0	96.6	71.4
BA-3	100	10.0	10.0	9.5	100	100	94.6

From the results depicted in the table, it can be deduced the following trend of water matrices according to its performance: UP > LA > PA > BA. This sequence is inversely coincident with the DOM content of these water matrices (values of A_{254nm}, COD and TOC summarized in Table 2). This effect suggests that DOM competes with ECs for the active sites of the adsorbent, resulting in a fall of PAC capacity for micro-pollutants adsorption. As an example, Fig. 3 depicts the evolution of the amount of PE adsorbed in experiments carried out with the four water matrices assayed (experiments UP-1, PA-1, LA-1 and BA-1). Results shown in Fig. 3 confirm the trend previously commented.

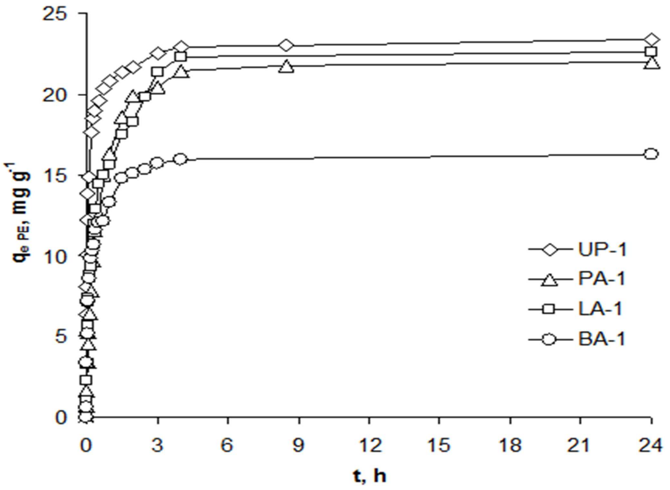


Figure 3. Evolution of the amount of PE adsorbed onto PAC in different water matrices. PAC dose: 20 mg L^{-1}.

The influence of the PAC dose was also investigated in the three real water matrices. It can be observed from the results exposed in Table 6 a decrease in the amount of EC adsorbed at equilibrium (q_e) in all waters when increasing the PAC concentration from 20 to 100 mg L^{-1}, due to the lower C_0/W ratio. Meanwhile, the removal of ECs increased with higher doses of PAC in all water matrices, even reaching total removal for AH and MS. PE adsorption was always lower, requiring higher PAC doses for outstanding adsorption performance, especially in BA water matrix, which is probably due to its higher DOM content.

Finally, several main water quality parameters have been determined during the adsorption experiments of ECs dissolved in the selected water matrices. Concretely, COD, TOC and absorbance at 254 nm were chosen as indexes of the organic matter content. By measuring these parameters at the beginning and final equilibrium (at 24 h) of each experiment, the percentage removals R of each one were determined, according to equations similar to expression (7). Table 7 shows these water quality parameters removals R for every experiment. It must be noted that Expt. UP-1 was ignored since it was performed with UP water.

Table 7. Adsorption experiments onto PAC of the mixture of ECs dissolved in several water matrices: removals for the main water quality parameters.

Expt.	W (mg L^{-1})	R_{COD}, %	R_{TOC}, %	R_{A254}, %
PA-1	20	38.1	30.3	49.1
PA-2	50	52.4	46.7	57.5
PA-3	100	66.7	56.9	79.1
LA-1	20	61.4	56.9	69.9
LA-2	50	75.7	71.9	78.5
LA-3	100	82.1	82.9	84.9
BA-1	20	20.0	22.0	36.3
BA-2	50	37.5	37.3	55.0
BA-3	100	67.5	51.0	70.1

Results in Table 7 confirm the trends observed above: that is, higher removals for experiments conducted in LA and lower in BA experiments, in agreement with the DOM content of each water matrix. Also, increasing removals of the water quality parameters when increasing the PAC dose were observed, reaching over 80% removal of COD, TOC and

A_{254} in LA water. For PA and BA waters, over 65% of COD, 50% of TOC and 70% of A254 were reached. As a conclusion, adsorption onto PAC of micro-pollutants present in natural water matrices or secondary effluents with moderate DOM content is not only feasible, but also contributes to an effective elimination of the organic matter from the aqueous phase.

4. CONCLUSIONS.

The removal of three selected ECs (AH, MS and PE) from aqueous phase by adsorption onto PAC and GAC reveals several findings:

- Results suggest a good fit of adsorption isotherms with Langmuir and Freundich models, being the first one the best in most experiments.
- PAC showed higher adsorption capacity at equilibrium than GAC. Besides that, the kinetics of the process was much faster for PAC, based on its higher mesoporosity with shorter times required to reach the equilibrium (24 hours versus 6-8 days for GAC).
- Among several kinetic models tested to simulate the adsorption process, pseudo-second order kinetics provided excellent agreements, with $R^2 > 0.999$ in all the experiments.
- Adsorption onto PAC showed much higher initial adsorption rates and lower half-adsorption times than onto GAC.
- The increase of PAC dose led to an improvement on the kinetics of the adsorption, with increasing ECs removal levels at equilibrium. On the contrary, pH did not cause significant effects.
- Adsorption of the ECs followed the following trend: AH > MS > PE.
- Results obtained on the adsorption of the ECs dissolved in real water matrices show a negative effect of the DOM content, suggesting that DOM can compete

with ECs for the active sites of the adsorbent, and causing a decay of the PAC capacity.

- Simultaneously, the DOM content of the water matrices were considerably reduced, with TOC removals over 50% and COD removals over 65% with PAC doses around 100 mg L^{-1} in all the water matrices tested.
- In conclusion, adsorption onto PAC has been shown an effective technology to remove both, micro-pollutants and DOM, from water matrices.

REFERENCES

Alvarez-Torrellas, S.; Garcia-Lovera, R.; Escalona, N.; Sepulveda, C.; Sotelo, J.L.; Garcia, J. Chemical-activated carbons from peach stones for the adsorption of emerging contaminants in aqueous solutions. Chem. Eng. J. **2015**, 279, 788-798.

Alvarez-Torrellas, S.; Rodriguez, A.; Ovejero, G.; Garcia, J. Comparative adsorption performance of ibuprofen and tetracycline from aqueous solution by carbonaceous materials. Chem. Eng. J. **2016**, 283, 936-947.

Clesceri, L.S.; Greenberg, A.E.; Trussell, R.R. Standard Methods for the Examination of Water and Wastewater, 17th ed., APHA, AWWA, WPCF, Washington, DC, **1989**.

Delgado, L.F.; Charles, P.; Glucina, K.; Morlay, C. The removal of endocrine disrupting compounds, pharmaceutically activated compounds and cyanobacterial toxins during drinking water preparation using activated carbon-A review. Sci. Total Environ. **2012**, 435-436, 509-525.

Freundlich, H.; Heller, W. The adsorption of cis- and trans-Azobenzene, J. Am. Chem. Soc. **1939**, 61, 2228-2230.

Ho, Y.S.; McKay, G. Sorption of dye from aqueous solution by peat. Chem. Eng. J. **1998**, 70, 115-124.

Ho, Y.S.; McKay, G. The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. **2000**, 34, 735-742.

Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. **1918**, 40, 1361-1403.

Lapworth, D.J.; Baran, N.; Stuart, M.E.; Ward, R.S. Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. Environ. Pollut. **2012**, 163, 287-303.

Lin, Y.R.; Teng, H. Mesoporous carbons from waste tyre char and their application in wastewater discoloration. Micropor. Mesopor. Mater. **2002**, 54, 167-174.

Liu, W.; Zhang, J.; Zhang, C.; Ren, L. Sorption of norfloxacin by lotus stalk-based activated carbon and iron-doped activated alumina: Mechanisms, isotherms and kinetics, Chem. Eng. J. **2011**, 171, 431-438.

Mestre, A.S.; Pires, J.; Nogueira, J.M.F.; Parra, J.B.; Carvalho, A.P.; Ania, C.O. Waste-derived activated carbons for removal of ibuprofen from solution: role of surface chemistry and pore structure. Bioresource Technol. **2009**, 100, 1720-1726.

Moulder, J.F.; Stickle, W.F.; Sobol, P.E.; Bomden, K.D. Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for identification and Interpretation of XPS Data (Hardcover), Physical Electronics, Eden Prairie, Minnesota, **1995**.

Putra, E.K.; Pranowo, R.; Sunarso, J.; Indrawati, N.; Ismadji, S. Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: Mechanisms, isotherms and kinetics, Water Res. **2009**, 43, 2419-2430.

Rakic, V.; Rac, V.; Krmar, M.; Otman, O.; Auroux, A. The adsorption of pharmaceutically active compounds from aqueous solutions onto activated carbons. J. Hazard. Mater. **2015**, 282, 141-149.

Sotelo, J.L.; Ovejero, G.; Rodriguez, A.; Alvarez, S.; Garcia, J. Analysis and modeling of fixed bed column operations on flumequine removal onto activated carbon: pH influence and desorption studies. Chem. Eng. J. **2013**, 228, 102-113.

Thomaidi, V.S.; Stasinakis A.S.; Borova V.L.; Thomaidis N.S. Is there a risk for the aquatic environment due to the existence of emerging organic contaminants in treated domestic wastewater? Greece as a case-study. J. Hazard. Mater. **2015**, 283, 740-747.

Wang, S.; Lu, G.Q. Effects of acidic treatments on the pore and surface properties of Ni catalyst supported on activated carbon. Carbon **1998**, 36, 283-292.

4. CONCLUSIONES

4. CONCLUSIONES.

El estudio realizado en la presente Tesis Doctoral sobre la eliminación de diversos contaminantes emergentes modelo disueltos en diferentes matrices acuosas, mediante procesos físico-químicos, ha permitido extraer las siguientes conclusiones generales:

- La oxidación química de los contaminantes emergentes (ECs) seleccionados (clorhidrato de amitriptilina, salicilato de metilo y 2-fenoxietanol), empleando diversos agentes individuales (radiación UV, ozono, cloro, reactivo de Fenton, reactivo de Fenton-Like), así como distintas combinaciones de tales agentes (UV/H_2O_2, $UV/Fe^{2+}/H_2O_2$ o sistema foto-Fenton, $UV/Fe^{3+}/H_2O_2$ o sistema foto-Fenton like, UV/Cl_2, $UV/S_2O_8^{2-}$) han dado lugar a una gran variedad de niveles de eliminación de tales contaminantes, como consecuencia de la distinta naturaleza de los mismos y de los oxidantes empleados, así como de los diversos rangos de variables operativas aplicadas. El compuesto más reactivo en todos los casos resultó ser clorhidrato de amitriptilina.
- La eficacia de los procesos de oxidación se vio también influida por las matrices acuosas empleadas, observándose un descenso en la degradación de contaminantes cuanto mayor era el contenido de materia orgánica disuelta en las mismas. Dicha materia orgánica compite con los propios contaminantes en el consumo de los oxidantes en las reacciones de oxidación. Por lo tanto, mayores dosis de agentes oxidantes son requeridas en aquellas matrices acuosas con elevado contenido en materia orgánica.
- El tratamiento con radiación UV monocromática a 254 nm, aplicado de forma individual a cada contaminante, permitió establecer el siguiente orden de fotodegradación: clorhidrato de amitriptilina > 2-fenoxietanol > salicilato de metilo. A excepción del salicilato de metilo, los demás compuestos presentaron un aumento en la degradación al incrementarse el pH en un intervalo entre 3 y 11. La temperatura por su parte ejerció un efecto positivo en la eliminación del clorhidrato de amitriptilina. Los rendimientos cuánticos obtenidos confirmaron asimismo el

efecto positivo del pH y de la temperatura en la eliminación de los contaminantes mediante radiación UV.

- El estudio por separado de las vías directa y radicalaria de este proceso de fotodegradación por radiación UV simple permitió deducir que la principal vía de reacción es la radicalaria.
- Desde el punto de vista cinético, la capacidad de eliminación de la radiación UV fue mejorada mediante la adición de otros agentes oxidantes como: peróxido de hidrógeno, ión persulfato o cloro. Esto es debido a la generación adicional de radicales (HO·, SO_4^-·, Cl·) que contribuyen a la oxidación global.
- La oxidación química mediante reactivo de Fenton permitió determinar las constantes de velocidad para la reacción radicalaria de segundo orden entre cada compuesto individual y los radicales hidroxilo. Los valores que se obtuvieron fueron: $(10.3\pm0.1)x10^9$ $M^{-1}S^{-1}$ para clorhidrato de amitriptilina, $(7.1\pm0.1)x10^9$ M^{-1} s^{-1} para salicilato de metilo y $(4.3\pm0.1)x10^9$ M^{-1} s^{-1} para 2-fenoxietanol. La presencia adicional de radiación UV (sistema foto-Fenton) produce un aumento en la velocidad de degradación de los contaminantes, mientras que el uso de Fe^{3+} como catalizador (sistema Fenton-Like) conduce a un nivel de eliminación que es sensiblemente inferior.
- Los agentes oxidantes individuales ozono y cloro fueron bastante eficaces para la eliminación de clorhidrato de amitriptilina, mientras que 2-fenoxietanol resultó ser el menos reactivo con ambos agentes. La determinación de las constantes aparentes de velocidad para la reacción de cloración y la reacción de ozonización pone de manifiesto que estas últimas son de alrededor de tres órdenes de magnitud superiores a las de cloración, lo que sugiere una mayor eficacia del proceso de ozonización.
- El estudio cinético del sistema combinado UV/persulfato permitió establecer la influencia positiva que ejerce la concentración inicial de $S_2O_8^{2-}$ y la temperatura de operación, mientras que el efecto del pH fue diferente para cada EC estudiado.

- Por su parte, el uso de agentes secuestrantes de radicales HO· y $SO_4^{-}\cdot$ reveló que la contribución de radicales hidroxilo es más importante en la oxidación de amitriptilina y menos significativa para salicilato de metilo y 2-fenoxietanol.
- La aplicación de persulfato activado térmicamente conduce a eliminaciones de los ECs entre 15 y 50 veces menor que el proceso activado por radiación UV.
- Los valores de las constantes de segundo orden deducidas para la reacción directa entre los radicales sulfato y cada EC son: $(4.8 \pm 0.6)x10^{9}$ $M^{-1}\cdot s^{-1}$ para clorhidrato de amitriptilina, $(9.2 \pm 0.9)x10^{8}$ $M^{-1}\cdot s^{-1}$ para salicilato de metilo y $(1.38 \pm 0.02)x10^{9}$ $M^{-1}\cdot s^{-1}$ para 2-fenoxietanol.
- La combinación de radiación UV con cloro conduce a una mejora sensible en los niveles de eliminación de estos ECs con respecto al uso de radiación UV y Cl_2 como agentes oxidantes individuales. Esta combinación resultó ser más eficaz que la combinación UV/persulfato para la eliminación de los ECs cuando se empleó la misma dosis de oxidante (cloro o persulfato).
- Las tecnologías de membranas ensayadas fueron efectivas en la eliminación del clorhidrato de amitriptilina y salicilato de metilo, siendo por tanto aptas para ser usadas con este fin en plantas de tratamiento de agua. Sin embargo, el nivel de retención de 2-fenoxietanol resultó ser bajo, lo que dificulta la aplicación de la filtración mediante membranas para su eliminación.
- El principal mecanismo de retención de los contaminantes en el proceso de ultrafiltración fue la adsorción, siendo la membrana GK (2 kDa) la más eficaz entre las estudiadas. Por su parte, en el proceso de nanofiltración, la exclusión por tamaño molecular y la adsorción fueron los mecanismos de retención dominantes, siendo la membrana HL la más eficaz para la retención de los contaminantes seleccionados así como de la materia orgánica.
- La presencia de materia orgánica en las aguas reales ensayadas produce una disminución en el flujo de permeado debido a diversas causas: adsorción de especies en la membrana, bloqueo de poros y formación de una torta en la superficie de la membrana. Al igual que en la eliminación de los ECs en agua UP, se consiguen

mejores resultados en la eliminación de materia orgánica en las aguas reales mediante el proceso de nanofiltración.

- El estudio del proceso de adsorción de los contaminantes seleccionados con carbón activo permitió establecer que los resultados se ajustan de forma más satisfactoria al equilibrio representado por la isoterma de Langmuir.
- De los dos soportes de carbón activo ensayados, el carbón activo en polvo (PAC) presenta una mayor capacidad de adsorción que el carbón activo granular (GAC) y unos tiempos de equilibrio mucho más cortos, en consonancia con su mayor volumen de mesoporos. Los datos experimentales se ajustan satisfactoriamente al modelo cinético de pseudo-segundo orden.
- La presencia de materia orgánica compite con los ECs por los centros activos del adsorbente, causando una disminución en la capacidad de adsorción del PAC. Entre otros parámetros, los valores de eliminación de TOC en todas las aguas son superiores al 50% con dosis de PAC de alrededor de 100 mg L^{-1}. Asimismo, la eliminación de DQO es superior al 65%. Estos niveles de eliminación demuestran que el uso de PAC resulta ser una tecnología eficaz, tanto para eliminación de microcontaminantes como para la reducción de materia orgánica presente en aguas reales.

5. PUBLICACIONES

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Real F.J.; Benitez J.; Acero J.L.; Roldan G. and Casas F. Elimination of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in ultrapure water and secondary effluents by photolytic and radicalary pathways. Ind. Eng. Chem. Res. **2012**, 51 (50), 16209-16215.

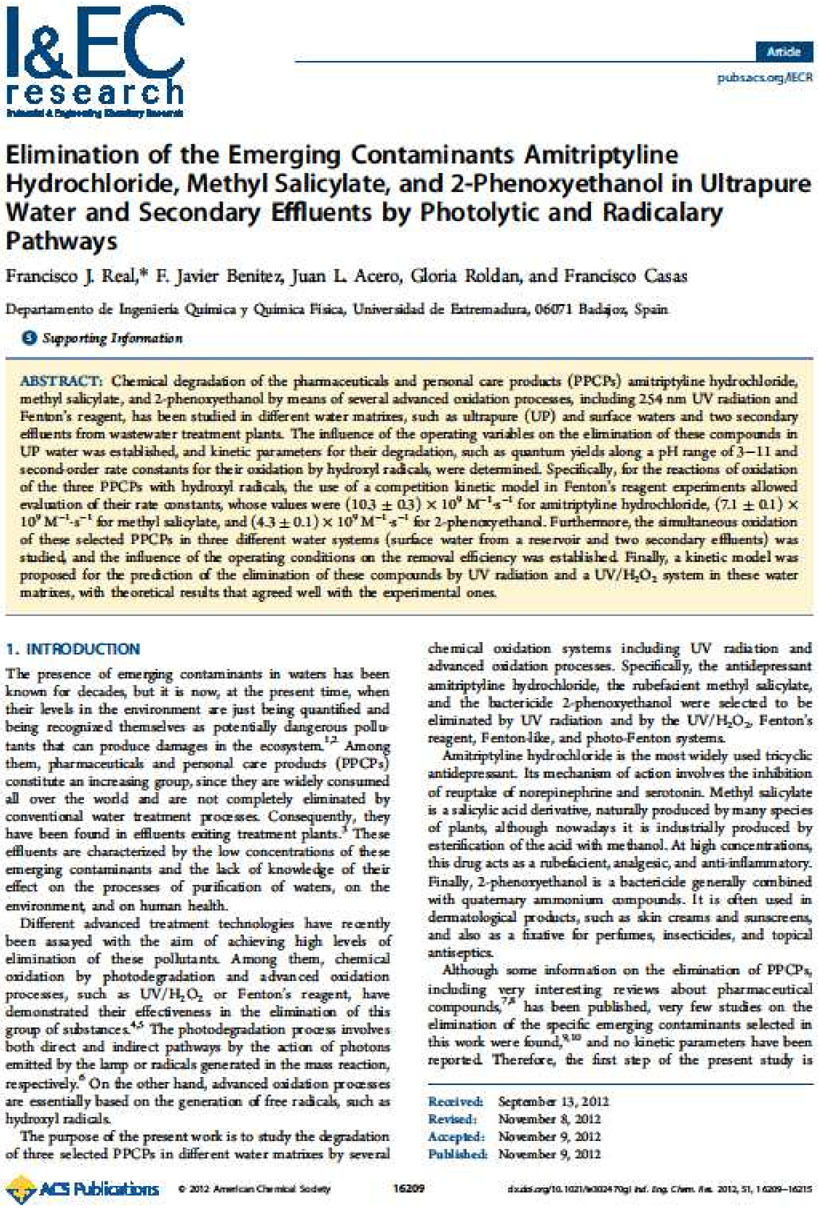
Real F.J.; Benitez J.; Acero J.L. and Casas F. Comparison between chlorination and ozonation treatments for the elimination of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in surface waters and secondary effluents. Journal of Chemical Technology and Biotechnology 2015, 90 (8), 1357-1544.

Real F.J.; Benitez J.; Acero J.L.; Roldan G. and Casas F. Oxidation of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol by persulfate activated by UV irradiation. Journal of Chemical Technology and Biotechnology **2016**, 91 (4), 1004-1011.

Real F.J.; Benitez J.; Acero J.L. and Casas F. Assessment of the UV/Cl_2 advanced oxidation process for the degradation of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in water systems. **Accepted for publication in Environmental Technology.**

Real F.J.; Benitez J.; Acero J.L. and Casas F. The use of ultrafiltration and nanofiltration processes for the elimination of three selected emerging contaminants: amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol. **Accepted for publication in Environment Protection Engineering.**

Real F.J.; Benitez J.; Acero J.L. and Casas F. Adsorption of selected emerging contaminants onto PAC and GAC: equilibrium isotherms, kinetics, and effect of the water matrix. **Submitted for publication in Journal Environmental Science and Health Part A.**



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Elimination of the Emerging Contaminants Amitriptyline Hydrochloride, Methyl Salicylate, and 2-Phenoxyethanol in Ultrapure Water and Secondary Effluents by Photolytic and Radicalary Pathways

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Supporting Information

ABSTRACT: Chemical degradation of the pharmaceuticals and personal care products (PPCPs) amitriptyline hydrochloride, methyl salicylate, and 2-phenoxyethanol by means of several advanced oxidation processes, including 254 nm UV radiation and Fenton's reagent, has been studied in different water matrixes, such as ultrapure (UP) and surface waters and two secondary effluents from wastewater treatment plants. The influence of the operating variables on the elimination of these compounds in UP water was established, and kinetic parameters for their degradation, such as quantum yields along a pH range of 3−11 and second-order rate constants for their oxidation by hydroxyl radicals, were determined. Specifically, for the reactions of oxidation of the three PPCPs with hydroxyl radicals, the use of a competition kinetic model in Fenton's reagent experiments allowed evaluation of their rate constants, whose values were $(10.3 \pm 0.3) \times 10^9\ M^{-1} \cdot s^{-1}$ for amitriptyline hydrochloride, $(7.1 \pm 0.1) \times 10^9\ M^{-1} \cdot s^{-1}$ for methyl salicylate, and $(4.3 \pm 0.1) \times 10^9\ M^{-1} \cdot s^{-1}$ for 2-phenoxyethanol. Furthermore, the simultaneous oxidation of these selected PPCPs in three different water systems (surface water from a reservoir and two secondary effluents) was studied, and the influence of the operating conditions on the removal efficiency was established. Finally, a kinetic model was proposed for the prediction of the elimination of these compounds by UV radiation and a UV/H_2O_2 system in these water matrixes, with theoretical results that agreed well with the experimental ones.

1. INTRODUCTION

The presence of emerging contaminants in waters has been known for decades, but it is now, at the present time, when their levels in the environment are just being quantified and being recognized themselves as potentially dangerous pollutants that can produce damages in the ecosystem.[1,2] Among them, pharmaceuticals and personal care products (PPCPs) constitute an increasing group, since they are widely consumed all over the world and are not completely eliminated by conventional water treatment processes. Consequently, they have been found in effluents exiting treatment plants.[3] These effluents are characterized by the low concentrations of these emerging contaminants and the lack of knowledge of their effect on the processes of purification of waters, on the environment, and on human health.

Different advanced treatment technologies have recently been assayed with the aim of achieving high levels of elimination of these pollutants. Among them, chemical oxidation by photodegradation and advanced oxidation processes, such as UV/H_2O_2 or Fenton's reagent, have demonstrated their effectiveness in the elimination of this group of substances.[4,5] The photodegradation process involves both direct and indirect pathways by the action of photons emitted by the lamp or radicals generated in the mass reaction, respectively.[6] On the other hand, advanced oxidation processes are essentially based on the generation of free radicals, such as hydroxyl radicals.

The purpose of the present work is to study the degradation of three selected PPCPs in different water matrixes by several chemical oxidation systems including UV radiation and advanced oxidation processes. Specifically, the antidepressant amitriptyline hydrochloride, the rubefacient methyl salicylate, and the bactericide 2-phenoxyethanol were selected to be eliminated by UV radiation and by the UV/H_2O_2, Fenton's reagent, Fenton-like, and photo-Fenton systems.

Amitriptyline hydrochloride is the most widely used tricyclic antidepressant. Its mechanism of action involves the inhibition of reuptake of norepinephrine and serotonin. Methyl salicylate is a salicylic acid derivative, naturally produced by many species of plants, although nowadays it is industrially produced by esterification of the acid with methanol. At high concentrations, this drug acts as a rubefacient, analgesic, and anti-inflammatory. Finally, 2-phenoxyethanol is a bactericide generally combined with quaternary ammonium compounds. It is often used in dermatological products, such as skin creams and sunscreens, and also as a fixative for perfumes, insecticides, and topical antiseptics.

Although some information on the elimination of PPCPs, including very interesting reviews about pharmaceutical compounds,[7,8] has been published, very few studies on the elimination of the specific emerging contaminants selected in this work were found,[9,10] and no kinetic parameters have been reported. Therefore, the first step of the present study is

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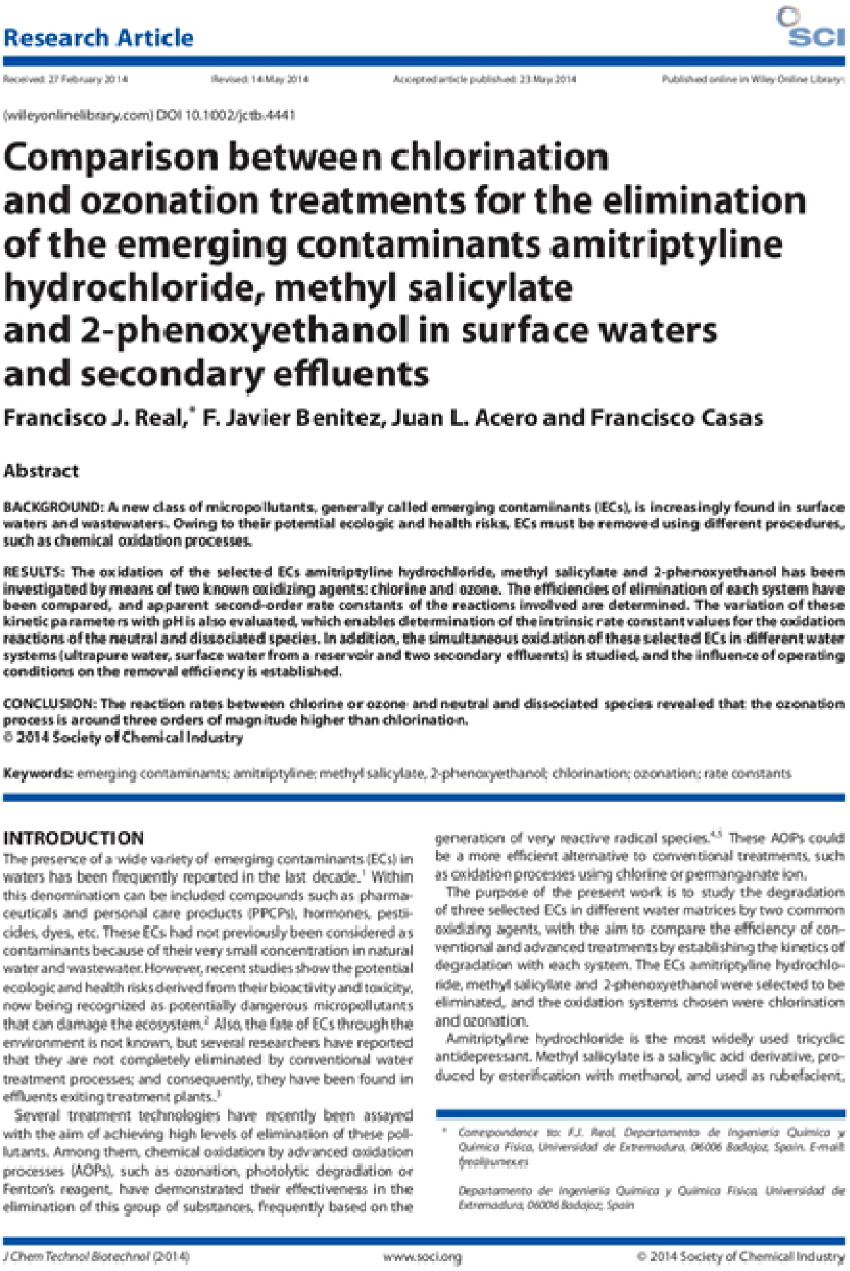

Research Article

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Comparison between chlorination and ozonation treatments for the elimination of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in surface waters and secondary effluents

Francisco J. Real,* F. Javier Benitez, Juan L. Acero and Francisco Casas

Abstract

BACKGROUND: A new class of micropollutants, generally called emerging contaminants (ECs), is increasingly found in surface waters and wastewaters. Owing to their potential ecologic and health risks, ECs must be removed using different procedures, such as chemical oxidation processes.

RESULTS: The oxidation of the selected ECs amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol has been investigated by means of two known oxidizing agents: chlorine and ozone. The efficiencies of elimination of each system have been compared, and apparent second-order rate constants of the reactions involved are determined. The variation of these kinetic parameters with pH is also evaluated, which enables determination of the intrinsic rate constant values for the oxidation reactions of the neutral and dissociated species. In addition, the simultaneous oxidation of these selected ECs in different water systems (ultrapure water, surface water from a reservoir and two secondary effluents) is studied, and the influence of operating conditions on the removal efficiency is established.

CONCLUSION: The reaction rates between chlorine or ozone and neutral and dissociated species revealed that the ozonation process is around three orders of magnitude higher than chlorination.

Keywords: emerging contaminants; amitriptyline; methyl salicylate, 2-phenoxyethanol; chlorination; ozonation; rate constants

INTRODUCTION

The presence of a wide variety of emerging contaminants (ECs) in waters has been frequently reported in the last decade.[1] Within this denomination can be included compounds such as pharmaceuticals and personal care products (PPCPs), hormones, pesticides, dyes, etc. These ECs had not previously been considered as contaminants because of their very small concentration in natural water and wastewater. However, recent studies show the potential ecologic and health risks derived from their bioactivity and toxicity, now being recognized as potentially dangerous micropollutants that can damage the ecosystem.[2] Also, the fate of ECs through the environment is not known, but several researchers have reported that they are not completely eliminated by conventional water treatment processes; and consequently, they have been found in effluents exiting treatment plants.[3]

Several treatment technologies have recently been assayed with the aim of achieving high levels of elimination of these pollutants. Among them, chemical oxidation by advanced oxidation processes (AOPs), such as ozonation, photolytic degradation or Fenton's reagent, have demonstrated their effectiveness in the elimination of this group of substances, frequently based on the generation of very reactive radical species.[4,5] These AOPs could be a more efficient alternative to conventional treatments, such as oxidation processes using chlorine or permanganate ion.

The purpose of the present work is to study the degradation of three selected ECs in different water matrices by two common oxidizing agents, with the aim to compare the efficiency of conventional and advanced treatments by establishing the kinetics of degradation with each system. The ECs amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol were selected to be eliminated, and the oxidation systems chosen were chlorination and ozonation.

Amitriptyline hydrochloride is the most widely used tricyclic antidepressant. Methyl salicylate is a salicylic acid derivative, produced by esterification with methanol, and used as rubefacient,

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Research Article

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Oxidation of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol by persulfate activated by UV irradiation

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Abstract

BACKGROUND: Despite the small concentration of emerging contaminants (ECs) in water systems, in recent years numerous works have reported potential toxicological risks associated with their presence in the environment, and recommending their elimination by different procedures, such as chemical oxidation processes.

RESULTS: The elimination of three selected ECs, amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in aqueous solutions by photochemically activated persulfate has been investigated. The main operating conditions, such as persulfate dose, temperature, pH and buffer used, were varied and efficiencies of elimination and apparent pseudo-first-order rate constants of the oxidation reactions were determined for comparison purposes. The role of reactive oxygen species generated in the system, such as $SO_4{\cdot}^-$ and HO·, in the overall oxidation of the ECs was determined by using suitable scavenger compounds. Moreover, thermally activated persulfate was around 15–50 times less reactive than the UV/persulfate system. Finally, second-order rate constants for the reaction between sulfate radical and each EC were determined by competition kinetics, and the values obtained were $(4.8 \pm 0.6) \times 10^9\ M^{-1}\ s^{-1}$ for amitriptyline hydrochloride, $(9.2 \pm 0.9) \times 10^8\ M^{-1}\ s^{-1}$ for methyl salicylate, and $(1.38 \pm 0.02) \times 10^9\ M^{-1}\ s^{-1}$ for 2-phenoxyethanol.

CONCLUSION: Both radical species $SO_4{\cdot}^-$ and HO· play important roles in the oxidation of the ECs investigated when using the UV/persulfate system, with the contribution of sulfate radicals predominating for those compounds with low reactivity towards HO radicals.

Keywords: emerging contaminants; amitriptyline; methyl salicylate; 2-phenoxyethanol; persulfate; rate constants

INTRODUCTION

During recent years, the contamination of water resources by micropollutants has become a growing concern. Among them, emerging contaminants (ECs) are particularly relevant, being frequently identified during the last decade in wastewaters and aquatic environments.[1] The term ECs is generally used to cover not only newly developed compounds but also compounds newly discovered in the environment, often due to analytical developments.[2] Nevertheless, published results concerning occurrence, and especially potential toxicological effects and treatment of ECs, are limited. Due to their large number (in the order of thousands),[3–5] only few of these compounds have been evaluated.

Several technologies have been assayed successfully with the aim of reaching high levels of elimination of these ECs.[4–6] Among them, advanced oxidation processes (AOPs) have shown to be very effective towards these compounds, even in the cases of ECs that were very refractory to conventional treatments, such as oxidation processes using chlorine or permanganate ion.[7]

In this work, elimination of three selected ECs (amitriptyline hydrochloride, methyl alicylate and 2-phenoxyethanol) by means of an AOP based on sulfate radicals has been studied in experiments carried out in aqueous solutions. Amitriptyline hydrochloride is the most widely used tricyclic antidepressant; methyl salicylate is a salicylic acid derivative produced by esterification with methanol and used as rubefacient, analgesic and anti-inflammatory; and 2-phenoxyethanol is a bactericide often used in dermatological products, fixatives for perfumes, insecticides and topical antiseptics.

Sulfate radical ($SO_4 \cdot^-$) is a very strong oxidant ($E° = 2.43$ V) which can react quickly with aromatic compounds with a selectivity slightly higher than hydroxyl radical.[8] An advantage of AOPs

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Assessment of the UV/Cl_2 advanced oxidation process for the degradation of the emerging contaminants amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol in water systems

By

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Environment Protection
Engineering

The use of ultrafiltration and nanofiltration processes for the elimination of three selected emerging contaminants: amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol

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ABSTRACT

The emerging contaminants amitriptyline hydrochloride (AH), methyl salicylate (MS) and 2-phenoxyethanol (PE) were treated by means of filtration processes for their elimination from ultrapure (UP) water in a first stage, and from three water matrices (a surface water from a reservoir, and two effluents from two municipal wastewater treatment plants) in a second stage. For this purpose, ultrafiltration and nanofiltration membranes were used in a cross-flow laboratory equipment. The permeate fluxes at the steady state were determined, and the resistances to the permeate flux were established. It was found that the inherent resistance of the clean membranes provided a much larger resistance than the fouling resistance. The retention coefficients for each individual contaminant were evaluated, as well as the retention coefficients referred to three water quality parameters: absorbance at 254 nm, COD and TOC. These parameters provide the effectiveness of the filtration processes for the elimination of the organic matter present in the selected water matrices.

Keywords.- Emerging contaminants, ultrafiltration and nanofiltration membranes, permeate flux, resistances, retention coefficients, UP and natural waters.

Adsorption of selected emerging contaminants onto PAC and GAC: equilibrium isotherms, kinetics, and effect of the water matrix

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ABSTRACT

The removal of three emerging contaminants (ECs) (amitriptyline hydrochloride (AH), methyl salicylate (MS) and 2-phenoxyethanol (PE)) dissolved in several water matrices by means of their adsorption onto powdered activated carbon (PAC) and granular activated carbon (GAC) has been investigated. When dissolved in ultrapure water, adsorption of the ECs followed the trend AH > MS > PE, with a positive effect of the adsorbent dose. According to the analysis of the adsorption isotherms and adsorption kinetics, PAC showed strongly higher adsorption efficiency in both, capacity and velocity of adsorption, in agreement with its higher mesoporosity. Equilibrium isotherm data were fitted by Langmuir and Freundlich models. Pseudo-second order kinetics models reproduced very successfully the adsorption process.

Finally, the effect of the dissolved organic matter (DOM) of the water matrix (ultrapure water, a surface water and two effluents from wastewater treatment plants) on the adsorption of the selected ECs onto PAC was established, as well as its performance on the removal of water quality parameters. Results show a negative effect of the DOM content on the adsorption efficiency. Organic matter removal over 50% was obtained with high PAC doses, revealing that adsorption onto PAC is an effective technology to remove both, micro-pollutants and DOM, from water matrices.

***Keywords**: Emerging contaminants; amitriptyline hydrochloride; methyl salicylate; 2-phenoxyethanol; Municipal secondary effluent; Adsorption; PAC; GAC*