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Diana Martínez Pachón

Sistemas Electro-Fenton y Foto Electro-Fenton como métodos de eliminación de contaminantes emergentes presentes en aguas residuales.

Palabras Clave:

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Sistemas Electro-Fenton y Foto Electro-Fenton como métodos de eliminación de contaminantes emergentes presentes en aguas residuales.

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Director Temático: Alejandro Moncayo Lasso., Ph. D.

Director Metodológico: Rafael María Gutiérrez., Ph. D.

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Con todo mi amor a mis Padres
Jael y Ricardo

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Resumen

En la actualidad, la reutilización de aguas residuales es una opción para la conservación del recurso hídrico, sin embargo, la presencia de una gran variedad de contaminantes como los productos de cuidado e higiene personal, compuestos farmacéuticos, drogas de abuso, pesticidas, entre otras, que no se eliminan por completo en la mayoría de los sistemas de tratamiento convencionales, haciendo poco viable esta opción.

Por lo cual, se evalúa la potencial aplicación de nuevas tecnologías, con el fin de eliminar este tipo de contaminantes conocidos como Contaminantes Emergentes (CEs), pues dicha eliminación no es completa, en la mayoría de los sistemas de tratamientos convencionales. Una interesante alternativa son los Procesos Avanzadas de Oxidación (AOPs), dentro de los que se encuentran los procesos Electro Fenton (EF) y Foto-Electro-Fenton (PEF), los cuales han sido estudiados ampliamente en los últimos años por su eficiencia en la remoción de una gran variedad de contaminantes orgánicos. El sistema EF produce reactivos *in-situ* como el H_2O_2 y el Fe^{2+}, necesarios para llevar a cabo la reacción de Fenton y obtener radicales hidroxilo $^{\bullet}OH$, especies altamente oxidantes y fundamentales para la degradación de estos contaminantes. Adicionalmente, si este proceso es estimulado con radiación de longitud de onda entre los 250 y 500 nm, el proceso puede verse beneficiado gracias a la regeneración de los iones Fe^{2+} mediante la reducción de complejos de Fe^{3+} fotoactivos.

Este trabajo tiene como objetivo la optimización de los parámetros del sistema para el tratamiento de muestras del efluente de la planta de tratamiento de aguas residuales (PTAR) el "Salitre" de Bogotá con el fin de proponer un producto de propiedad intelectual (patente) de un sistema de tratamiento de aguas, basado en los sistemas EF y PEF.

El documento está organizado en 5 capítulos: El capítulo 1, inicia con una breve introducción al problema de investigación, los objetivos y la metodología a utilizar. En el Capítulo 2, el Estado del Arte en el que se abordan los tratamientos convencionales y la descripción de los procesos EF y PEF como una alternativa de solución dentro de los AOPs. En el capítulo 3, una breve justificación de la presencia de fármacos como problemática del agua en Colombia. En el capítulo 4, los resultados de investigación recopilados en 3 publicaciones (2 aceptadas con correcciones y 1 sometida), 1 escrito pendiente de publicación, 2 póster y 1 propuesta de patente de invención en proceso. Finalmente, en el capítulo 5 las conclusiones generales del trabajo.

Adicionalmente, los resultados de la investigación se recopilan de la siguiente forma:

- En la publicación número 1 se realizó el seguimiento de un grupo de fármacos en el afluente y efluente de la PTAR "Salitre" para determinar su persistencia, a pesar, de haber sido sometidos al tratamiento convencional.
- En la publicación número 2 se evaluó la eficiencia de los procesos EF y PEF con relación a la capacidad de degradación utilizando un cátodo de difusión de gas (GDE) y un ánodo dimensionalmente estable (DSA) de soluciones preparadas en Agua Milli-Q de concentración conocida del antihipertensivo Valsartán (VAL), el cual fue identificado en el efluente de la PTAR "Salitre" de Bogotá. En el sistema se evaluaron parámetros tales como el pH de la solución a tratar, tiempo de exposición al tratamiento, intensidad de corriente y tipo de electrólito, con el fin de establecer las condiciones para su remoción, degradación y/o mineralización.
- En la publicación número 3 la evaluación de eficiencia con relación a la capacidad de degradación del proceso PEF utilizando un electrodo de difusión de gas (GDE) y un ánodo dimensionalmente estable (DSA) de soluciones preparadas en Agua Milli-Q de concentración conocida de los antihipertensivos Valsartán (VAL) y Losartán (LOS). En este sistema se propuso el uso de ácidos orgánicos de cadena corta con el fin de mejorar la eficiencia del proceso a pH cercano al neutro, mediante la formación de Complejos Fe (III)-carboxilatos, los cuales, al ser fotoactivos en presencia de luz permiten tener el Fe^{2+} disponible en la solución para la reacción Fenton.
- En el documento pendiente por someter se implementaron los procesos EF y PEF bajo los parámetros que presentaron los mejores resultados en la remoción, degradación y/o mineralización de los compuestos farmacéuticos propuestos, en el tratamiento de muestras de agua del efluente de la PTAR "Salitre" de Bogotá, demostrando no solo una mejora significativa en las propiedades organolépticas del agua, sino en una baja significativa en la concentración de los fármacos identificados.
- Una propuesta de patente de invención en proceso de financiación por COLCIENCIAS.

Además, 2 póster presentados en la 3ª Conferencia Iberoamericana de Tecnologías Avanzadas de Oxidación (III CIPOA) y la 2ª Conferencia Colombiana sobre Procesos de Oxidación Avanzada (II CCPAOX), con información complementaria que demuestra las ventajas de estos sistemas utilizando otros materiales anódicos y su posible aplicación en la eliminación de microorganismos.

Abstract

Currently, the reuse of wastewater is one option to conserve water resources. However, the presence of a variety of emerging contaminants (CE) such as personal care and hygiene products, pharmaceutical compounds, drugs of abuse, pesticides, which are not completely eliminated in most conventional treatment systems, means that this option is not viable at the moment.

In this paper, the potential application of new methodologies to eliminate emerging contaminants is evaluated. An interesting alternative to conventional treatment is Advanced Oxidation Processes (AOPs), which include Electro-Fenton processes (EF) and Photo-Electro-Fenton (PEF). They have been studied extensively in recent years for their efficiency in the removal of a wide variety of organic pollutants. The EF system produces *in-situ* reagents such as H_2O_2 and Fe^{+2}, which are necessary to carry out the Fenton reaction and obtain hydroxyl radicals $^{\bullet}OH$ a highly oxidizing species that are fundamental to the degradation of emerging contaminants. When this PEF process is stimulated with wavelength radiation between 250 and 500 nm, it improves due to the regeneration of Fe^{2+} ions through the reduction of photoactive Fe^{3+} complexes.

This work involves the optimization of system parameters in the treatment of effluent samples from the wastewater treatment plant (WWTP) "Salitre" in Bogotá. The eventual aim is to propose an intellectual property product (patent) for a treatment system of water, based on the EF and PEF systems.

This document is organized as follows: Chapter 1 is a brief introduction to the research problem, the objectives and the methodology to be used. In chapter 2, the state-of-the-art in conventional treatments is presented and the description of the EF and PEF processes, as an alternative solution within AOPs, is described. Chapter 3 provides a brief explanation for the presence of drugs as a water problem in Colombia. Chapter 4 presents the research results from the various publications flowing from this research: one research article pending publication, two research articles accepted with corrections and one submitted, two posters at conferences and one patent proposal that is in the process of approval. Finally, chapter 5 contains the general conclusions of the work.

The results of the research are compiled as follows:

- In publication number 1, a group of drugs was monitored in the effluent of the "Salitre"

WWTP to determine the persistence of emerging contaminants, despite being submitted to conventional treatment.

- In publication number 2, the efficiency of the EF and PEF processes was evaluated in relation to their capacity to degrade contaminants, using a gas diffusion cathode (GDE) and a dimensionally stable anode (DSA) in solutions prepared in Milli-Q Water concentration known anti-hypertensive Valsartan (VAL), which was identified in the effluent of the WWTP "Salitre" in Bogotá. Parameters, such as the pH of the solution to be treated, time of exposure to the treatment, current intensity and type of electrolyte, were evaluated in order to establish the conditions for their removal, degradation and/or mineralization.

- Publication number 3 evaluated the efficiency of the degradation capacity of the PEF process, using a gas diffusion electrode (GDE) and a dimensionally stable anode (DSA) of solutions prepared in Water Milli-Q of known concentration of the anti-hypertensive drugs Valsartan (VAL) and Losartan (LOS). The use of short-chain organic acids was proposed in order to improve the efficiency of the process at a pH close to neutral, through the formation of Fe (III)-carboxylates complexes, which, being photoactive in the presence of light, enable the availability of Fe^{2+} in the solution for the Fenton reaction.

- In the article to be submitted, the EF and PEF processes were implemented under the parameters that presented the best results during the removal, degradation and/or mineralization of the proposed pharmaceutical compounds in the treatment of water samples from the "Salitre" WWTP effluent in Bogotá. It showed not only a significant improvement in the organoleptic properties of water, but also a significant decrease in the concentration of the identified drugs.

- A proposal for an invention patent in the process of financing by COLCIENCIAS.

The two posters presented at the 3rd Iberoamerican Conference on Advanced Oxidation Technologies (III CIPOA) and the 2nd Colombian Conference on Advanced Oxidation Processes (II CCPAOX), contained complementary information that demonstrated the advantages of these EF systems using other anodic materials, as well as their possible application in the elimination of microorganisms.

Lista de Abreviaturas y Acrónimos

(CEs)	Contaminantes Emergentes
(EF)	Electro-Fenton
(PEF)	(Photo-Electro-Fenton) Foto-Electro-Fenton
(SPEF)	(Solar Photo-Electro-Fenton) Foto-Electro-Fenton Solar
(PTAR)	Planta de Tratamiento de Aguas Residuales
(MAVDT)	Ministerio de Ambiente, Vivienda y Desarrollo Territorial
(IDEAM)	Instituto de Hidrología, Meteorología y Estudios Ambientales
(UNODC)	(United Nations Office on Drugs and Crime) Oficina de Naciones Unidas contra la Droga y el Delito
(SPA)	Sustancias Psicoactivas
(I+D+i)	Investigación Desarrollo e Innovación
(TRL)	Tecnology Readiness Levels
(SST)	sólidos suspendidos totales
(AOPs)	(Advanced Oxidation Processes) Procesos Avanzados de Oxidación
(EAOPs)	(Electrochemical Advanced Oxidation Processes) Procesos Avanzados de Oxidación Electroquímicos
(AO)	(Anodic Oxidation) Oxidación Anódica
(DSA)	(Dimensionally Stable Anode) Ánodo Dimensionalmente Estable
(BDD)	(Boron-Doped Diamond) Ánodo de Diamante Dopado con Boro
(GDE)	(Gas Diffusion Electrode) Electrodo de Difusión de Gas
(VAL)	Valsartán
(LOS)	Losartán
(TOC)	(Total Organic Carbon) Carbono Orgánico Total
(LED)	(Light-Emitting Diode) Diodo de Emisión de Luz.
(UV)	Luz Ultravioleta
(HPLC)	(High Performance Liquid Chromatography) Cromatografía liquida de alta resolución

(UPLC)	(Ultra-Performance Liquid Chromatography) Cromatografía liquida de ultra alta resolución
(HRMS)	(High Resolution Mass Spectrometry) Espectrometría de masas de alta resolución
(UPLC-MS/MS)	(Ultra Performance Liquid Chromatography and high resolution Mass Spectrometry) Cromatografía líquida de ultra alta Resolución acoplada a espectrometría de masas
(QqQ)	(Triple Quadrupole Analyzer) Analizador de triple cuadrupolo
(QTOF)	(Quadrupole Time of Flight Analyzer) Analizador híbrido de cuadrupolo-tiempo de vuelo

Índice general

Capítulo 1

Introducción

El agua es un componente fundamental para el sostenimiento y la reproducción de la vida en el planeta, pues constituye un factor indispensable para el desarrollo de los procesos biológicos y es el eje básico para mantener el equilibro ambiental, social y económico. De ahí la preocupación por la calidad del agua debido a su carácter transversal destacando el impacto de su contaminación sobre la estabilidad y sostenibilidad en nuestro planeta. Esto ha llevado a la comunidad científica, a través del avance en técnicas instrumentales, a identificar una gran cantidad de "nuevos" contaminantes orgánicos, los cuales pueden llegar a generar problemas en la salud humana, [1] en consecuencia proponer nuevos y mejores métodos para su tratamiento.

La mejora de la sensibilidad en las técnicas analíticas de detección utilizadas permitió identificar un amplio grupo de nuevas sustancias, denominadas como contaminantes emergentes (CEs), ya que ha permitido identificarlos por lo que su presencia en el ambiente había pasado desapercibida hasta hace pocos años. Su uso indiscriminado implica riesgos para la salud humana los animales y el ambiente y en algunos países pueden llegar a ser consumidos en toneladas por año. Debido a su elevada producción y consumo, y a la continua introducción de estos compuestos a los cuerpos de agua, no necesitan ser persistentes para ocasionar efectos negativos aunque no se conoce a profundidad sus efectos ecotoxicológicos [2].

Estos compuestos pueden llegar a los cuerpos de agua a través de diversas vías de contaminación, siendo la principal, su ingestión y posterior excreción. El compuesto consumido puede sufrir una transformación en el cuerpo humano dando lugar a sustancias más solubles y polares (metabolitos), o unirse a otras moléculas para formar un compuesto conjugado [3]. Posteriormente, los compuestos ingeridos inalterados y/o sus metabolitos se excretan en la orina y heces fecales llegando a las PTARs, en el mejor de los casos a través de las aguas residuales domésticas u hospitalarias, de lo contrario llegan directamente a las fuentes de agua. Por otro lado, la eliminación de los fármacos caducos o no utilizados, son desechados a través del inodoro o en la basura que contribuyen a la contaminación hídrica, aunque en menor proporción que por su excreción [4, 5].

Algunos investigadores han establecido la presencia de antibióticos, analgésicos, anticonvulsivos, β-bloqueadores, anticonceptivos, antihipertensivos, esteroides y antidepresivos [6, 7, 8] en mayor proporción en cuerpos de agua, por lo que requiere una atención especial por parte de la comunidad científica [9] con el fin de buscar alternativas para eliminarlos.

En el caso particular de las sustancias farmacológicas los datos de consumo y eliminación no son fáciles de establecer. En Colombia, especificamente, la situación es complicada si se tiene en cuenta que existen diferentes condiciones de acceso a las fuentes hidricas en las diferentes regiones del país. Sin embargo, su destino ambiental y su potencial de contaminación pueden predecirse o evaluarse sobre la base de sus características fisicoquímicas y biológicas [10]. Estas características incluyen el polimorfismo, su introducción en el ambiente después del metabolismo humano, su estructura química compleja y el hecho de tener múltiples sitios de ionización repartidos por toda la molécula [11].

Actualmente, los tratamientos de depuración empleados en las PTAR no son capaces de eliminar por completo la mayoría de estos compuestos [12]. Según las propiedades fisicoquímicas de los fármacos, sus metabolitos y sus productos de degradación [2] pueden alcanzar otros acuíferos, ser adsorbidos por los suelos y los sedimentos, generar complejos con metales y compuestos orgánicos, oxidarse químicamente, sufrir procesos de fotólisis y volatilizarse, llegando a afectar los ecosistemas y las diferentes cadenas tróficas. Este hecho motiva el desarrollo de diversos métodos más eficaces para eliminar este tipo de contaminantes.

Los procesos avanzados de oxidación (AOPs) han demostrado una alta eficiencia en la degradación de un amplio espectro de este tipo de contaminantes, los cuales son degradados a través de una serie de reacciones particulares donde se generan los radicales $^\bullet$OH, favoreciendo la transformación y/o eliminación generando un menor impacto en la salud humana y el ambiente en general [13, 14].

Dentro de los AOPs, los procesos electroquímicos (EAOPs) permiten la degradación del contaminante por diferentes vías; por un lado, esta la oxidación directa del contaminante mediante transferencia electrónica como la oxidación anodina (AO); y por otro, la degradación indirecta por reacción de los contaminantes con especies oxidantes formadas en la superficie de los electrodos [15]. En el último caso, los procesos Electro-Fenton (EF) y Foto-Ellectro-Fenton (PEF) son ejemplos típicos y se basan en la producción de radicales hidroxilo ($^\bullet$OH) *in-situ.* Para esto, se pueden electro-generar los reactivos, como el peróxido de hidrógeno (H_2O_2) y/o el ion ferroso (Fe^{+2}), los cuales al reaccionar producen $^\bullet$OH, además se pueden producir en el proceso por descomposición de las moléculas de H_2O_2, atacando los contaminantes y sus productos intermediarios.

Objetivos

Objetivo General:

Proponer un producto de innovación tecnológica basada en los proceso Electro-Fenton y Foto-Electro-Fenton con alta capacidad para la remoción, degradación y/o mineralización de contaminantes emergentes presentes en muestras de agua residuales urbanas.

Objetivos Específicos:

- Realizar la determinación cuantitativa de un grupo de fármacos presentes en el afluente y el efluente de la planta de tratamiento "El Salitre" de Bogotá, mediante UHPLC-MS/MS con analizador de triple cuadrupolo, con el fin de determinar la capacidad de remoción de este tipo de compuestos en la PTAR.
- Establecer el efecto de parámetros como el pH, tipo de electrólito soporte, densidad de corriente, tiempo de exposición al tratamiento y el tipo de material anódico en la degradación de VAL y LOS como analitos modelo, utilizando los procesos EF y PEF.
- Determinar las mejores condiciones de trabajo para la degradación de VAL y LOS en los procesos EF y PEF, para el tratamiento de muestras de agua del efluente de la planta de tratamiento "El Salitre" de Bogotá, con el fin de establecer su eficiencia en la eliminación de los fármacos identificados.
- Proponer un producto de innovación tecnológica basado en los sistemas EF y PEF.

Metodología:

Determinación cuantitativa de fármacos presentes en el efluente de la planta de tratamiento "Salitre" de Bogotá:

Se realizó el seguimiento de 32 fármacos en aguas residuales del afluente y el efluente de la PTAR "Salitre" de Bogotá. Estos fueron seleccionados por su consumo y amplia distribución en el mercado nacional, entre los que se incluyeron varios antibióticos de diferentes familias, analgésicos y antiinflamatorios, antiepilecticos, antihipertensivos y antidepresivos. Las muestras investigadas fueron aguas residuales urbanas recolectadas durante una semana antes (afluente) y después del tratamiento en la PTAR " el Salitre" de Bogotá (efluente).

La técnica de análisis implementada fue (LC-MS/MS QqQ) demostrando una alta prevalencia de productos farmacéuticos en todas las muestras analizadas.

Evaluación de parámetros en la implementación de los procesos Electro-Fenton y Foto-Electro-Fenton en la degradación de contaminantes emergentes:

Para establecer las mejores condiciones de trabajo en los procesos EF y PEF se evaluaron las siguientes condiciones: Un reactor de boro silicato de 250 mL, con una tapa de teflón en la que se ubicaron (Ánodo y Cátodo). Ánodo de difusión de gas con una malla de grafito (GDE) y cátodos de: grafito en forma de laminas y barras, acero en forma de laminas, diamante dopado con boro (BDD) sobre borosilicato en lamina y un ánodo dimensionalmente estable, (DSA) de Ti con recubrimiento en SnO_2 y Sb_2O_3. Todos estos materiales fueron sometidos a 4 intensidades de corriente 5, 10 15 y 20 mA. Cada una de las parejas de electrodos fue evaluada en presencia de diferentes electrólitos (cloruro de sodio (NaCl); sulfato de sodio (Na_2SO_4) y nitrato de sodio ($NaNO_3$)). De igual forma, las soluciones fueron sometidas a diferentes valores de pH (3.0, 5.0, sin modificación de pH y en presencia de ácido oxálico).

También, se emplearon 2 tipo de lámparas (en el sistema PEF) con diferentes tipos de radiación incidente: ultra violeta (368 nm) y LED (entre 400 y 700 nm), evaluando su eficiencia en la degradación de los compuestos modelo. Los compuestos farmacéuticos modelo seleccionados fueron los antihipertensivos Valsartan (VAL) y Losartan (LOS), presentes en las aguas residuales en niveles superiores a 1 µg/L. Además, la realización de ensayos "adicionales" con materiales como chatarra férrica y acero inoxidable como electrodos de sacrificio para la electrogeneración de hierro ferroso.

Seguimiento de parámetros y condiciones de los sistemas propuestos:

- La producción de H_2O_2 evaluada por espectrometría (método Yodométrico).
- La concentración de los analitos en los procesos de degradación usando cromatografía liquida de alta resolución en fase reversa (HPLC - RP).
- El grado de mineralización determinada midiendo el TOC.
- Los intermediarios fueron identificados por (UPLC/Q - QTOF MS/MS).
- El seguimiento de los ácidos carboxílicos de cadena corta por Cromatografía de Exclusión Iónica.
- La evaluación de la biodegradabilidad de estos compuestos con lodos activados.

Implementación de los procesos Electro-Fenton y Foto-Electro-Fenton en el tratamiento de muestras de agua del efluente de la PTAR “El Salitre” de Bogotá:

Una vez identificados los parámetros con mejores resultados en el tratamiento de la remoción, degradación y/o mineralización de VAL y LOS hallados en el item anterior, se implementaron dichos parámetros en los procesos EF y PEF con muestras del efluente de la PTAR-”Salitre” de Bogotá (en ensayos de 3 horas con alícuotas a los 0, 60, 120 y 180 minutos de tratamiento). Se analizaron las muestras por (LC - MS/MS QqQ) mediante un método analítico multiresiduo que permitió la detección e identificación de 16 de los 32 compuestos propuestos, con el fin de realizar el seguimiento de su concentración y evaluar su eficiencia.

Propuesta de un Sistema de eliminación de contaminantes emergentes:

La generación de una propuesta de propiedad intelectual de un producto y un proceso a escala de laboratorio, que será sometida a la Superintendencia de Industria y Comercio de Bogotá-Colombia. Este desarrollo fue llevada a cabo mediante la metodología Tecnology Readiness Levels (TRL) que permitió establecer el nivel de avance y desarrollo de la tecnología basada en los procesos EF y PEF.

Capítulo 2

Estado del Arte

Disponibilidad del Agua en el mundo:

Del agua disponible en el mundo, el 97 % está en forma de agua salada, y solo un 3 % corresponde al agua dulce, de la cual, la mayor parte se encuentra atrapada en los glaciares y casquetes polares, por lo que se tiene acceso solo al 0.3 % y ésta se encuentra distribuida en lagos, ríos y mantos acuíferos. Durante el último siglo, el consumo de agua ha aumentado a un ritmo dos veces mayor que la población mundial. La escasez afecta al 40 % de los habitantes del planeta, los pronósticos indican que para el año 2025, 1800 millones de personas vivirán en países o regiones con una drástica falta de agua y dos tercios de la población se podrían ver enfrentados por la escasez del vital líquido [16].

En muchos lugares el agua limpia y fresca se da por hecho, en otros es un recurso limitado debido a la falta de agua o a la contaminación de sus fuentes. Aproximadamente 1.100 millones de personas, es decir, el 18 por ciento de la población mundial, no tienen acceso a fuentes seguras de agua potable, y más de 2.400 millones de personas carecen de saneamiento adecuado [17]. En los países en desarrollo, más de 2.200 millones de personas, la mayoría de ellos niños, mueren cada año a causa de enfermedades asociadas con la falta de acceso al agua potable, saneamiento inadecuado e insalubridad.

Condiciones del agua en Colombia:

Colombia se ubica entre los países con mayor riqueza en recursos hídricos en el mundo, debido a sus características geográficas y gran variedad de climas. Según estimaciones del IDEAM [18], la riqueza hídrica colombiana manifiesta por los grandes índices de precipitación y escorrentía y por la favorable condición de almacenamiento superficial, representada por la existencia de cuerpos de agua lénticos, distribuidos en buena parte de la superficie total y por la presencia de enormes extensiones de ecosistemas de humedales. El volumen total de agua superficial es almacenada principalmente en pantanos, lagos naturales y en los páramos, constituyéndose en la oferta de almacenamiento ambiental, que bajo ciertas condiciones, puede ser utilizada bien sea para usos productivos o para el funcionamiento de los sistemas naturales [19].

Se calcula que el rendimiento hídrico para el año 2014 fue de (56 L/s.km^2). Este rendimiento está por encima del promedio mundial (10 L/s.km^2) y del latinoamericano (21 L/s.km^2) [20]. Bajo estas condiciones se alcanza una escorrentía superficial de 1.764 mm, equivalente a un volumen anual de 2.012 km^3. De acuerdo con lo anterior, el 62 % de la precipitación se convierte en escorrentía, equivalente a un caudal medio de 63.789 m^3/s.

Sin embargo, cuando se considera en detalle a la población y las actividades socio económicas ubicadas en regiones con baja oferta hídrica, se observan necesidades hídricas insatisfechas y un impacto mayor de origen antrópico sobre el agua; se concluye que la disponibilidad del recurso es cada vez menor como lo indica el Viceministerio del Medio Ambiente en la política nacional para la gestión integral del recurso hídrico [21]. Además, uno de los más grandes riesgos en la gestión del recurso hídrico está relacionado con su manejo asociado al cuidado de las cuencas hidrográficas deterioradas, al crecimiento no planificado de la demanda sobre una oferta neta limitada y a conflictos por el uso del agua según el informe sobre el estado de los recursos naturales y del ambiente 2010-2011 de la Contraloría General de la Nación.

Usos del Agua	**Uso total del agua 2012**	**Participación Porcentual**	**Flujos de retorno Mm^3**	**Pérdidas Mm^3**
Doméstico	2963	8,2 %	1670,5	4921,6
Agrícola	16760,3	46,6 %	s.I	s.I
Acuícola	3049,4	8,5 %	s.I	563,4
Pecuario	1654,1	4,6 %	1654,1	s.I
Industria	2106,0	5,9 %	2000,7	493,5
Hidrocarburos	7738,6	21,5 %	1273,6	364,4
Energía	592,8	1,6 %	s.I	s.I
Minería	640,6	1,8 %	s.I	s.I
Servicios	481,8	1,3 %	433,6	137,7
Total Nacional	35987,1	100 %	7032,6	2480,5

s.I: Sin Información / Mm^3 = Millones de metros cúbicos / Los factores de retorno de agua fueron tomados de (BID, IMTA, MAVDT, 2008).

Tabla 2.0.1: Uso del Agua en Colombia Tomado de: (IDEAM 2014)

Así mismo, según el IDEAM en el 2014 [20] como se muestra en la tabla 2.0.1 la demanda de agua para diferentes actividades se distribuyó de la siguiente manera: El sector agrícola usó 16.760,33 millones de m^3 equivalentes al 46,6 %, el uso para la generación de energía fue 21,5 %, el sector pecuario 8,5 %, el uso doméstico 8,3 % y el uso en diferentes servicios de 1,3 % del total del volumen de agua utilizado en el país. Por otro lado, el aumento en la concentración de sustancias nocivas deteriora la calidad del agua, como la escasa disponibilidad de oxígeno disuelto y los elevados niveles de sólidos suspendidos totales (SST) que tienen su origen principalmente en causas naturales como la erosión del suelo causada por las labores agrícolas y de urbanización, como factores que afectan la mayor parte de los departamentos del país (ver tabla 2.0.2). Además, los vertimientos de mercurio procedentes de la minería se consideran sustancias peligrosas representativas, lo mismo que el uso de agroquímicos en las etapas de cultivo [19]., presentado por el Plan Nacional de Manejo de Aguas Residuales Municipales [22].

Lo anterior permite establecer que los sectores industrial, minero y agrícola son un importante factor de deterioro de la calidad del recurso hídrico. A nivel del sector doméstico, el uso del agua está destinado en un 100 % para consumo humano según la reglamentación técnica del sector de agua potable y saneamiento básico-RAS 2000 (Resolución 2320 de 2009 MAVDT). La superintendencia de servicios públicos domiciliarios calcula que por cada habitante/día se puede utilizar entre 90 y 150 litros de agua potable según las características climatológicas. En el caso del sector industrial es mucho más complicado calcular un porcentaje de consumo diario porque está asociado al tipo de actividad, el volumen de materia prima utilizado o producido y el nivel de la empresa (grande, mediana o pequeña) por lo que solo las autoridades ambientales tienen estos datos de consumo para determinar el cobro de la tasa por consumo de agua.

Parámetro	**Carga generada doméstico e industria (Kg)**	**Carga vertida doméstico e industria (Kg)**	**Cantidad removida (Kg)**	**Porcentaje de remoción**
DBO	1.085.127.286	736.296.107	348.831.179	32,1
DQO	2.411.886.881	1.648.621.034	763.265.847	31,6
SST	1.517.405.973	1.119.062.421	398.343.552	26,3
NT	128.890.983	126.345.302	2.545.681	2,0
PT	32.465.812	31.915.345	550.467	1,7

Contaminante	**Remoción carga**	
	Industria %	**Doméstico %**
DBO	54	15
DQO	49	14
SST	59	21
NT	3	2
PT	2	2

Tabla 2.0.2: Carga de contaminación removida en sistemas de tratamiento de aguas residuales. Tomado de: (IDEAM 2014)

Esta situación obliga al gobierno nacional a establecer mecanismos de regulación y control en el cobro del servicio de acueducto y alcantarillado a los usuarios según el tipo de desechos a depositar en los cuerpos de agua, se distinguen dos grandes categorías: el sector productivo, el cual vierte directamente sus desechos; y las empresas de acueducto y alcantarillado, las cuales captan y vierten finalmente desechos generados por terceros [23]. En ambos casos, la regulación de las tasas retributivas vigentes en Colombia establece que la facturación por parte de la autoridad ambiental debe hacerse al usuario directo del cuerpo de agua, en proporción a las cargas vertidas (las cuales pueden ser estimadas o medidas).

Normativa de vertimientos en fuentes de agua en Colombia asociado al uso y elaboración de fármacos:

Según las normas actuales que rigen en Colombia para los vertimientos de aguas residuales domésticas y no domésticas, establecidos en el Decreto 1594 de 1984 y en el Decreto 3930 del 2010 que modifica, actualiza y declara nulos algunos de sus artículos y por la resolución 0631 de 2015 se determina que en términos fisicoquímicos, los parámetros a monitorear y sus valores límites máximos permisibles varían de acuerdo a la actividad, asociada al uso, manipulación y producción, para sustancias farmacológicas se establece como se muestra en la tabla 2.0.3.

Sin embargo, la regulación en Colombia sobre los vertimientos de fármacos y sus metabolitos en los afluentes de agua es nula por las limitaciones analíticas que se tienen para su identificación y caracterización, pero son candidatos a una regulación futura y sólo se presentan algunas propiedades fisicoquímicas a mantener, sin establecer valores mínimos permitidos estandarizados. En consecuencia, la presencia y el destino de los contaminantes emergentes, no necesitan persistir en el ambiente ni estar en altas concentraciones para causar efectos tóxicos crónicos tales como: estrogénicos, genotóxicos, cancerígenos, teratogénicos y de resistencia, entre otros, puesto que sus altas tasas de transformación o remoción se ven compensadas por su introducción continua y permanente en el ambiente [60], lo que dificulta su eliminación.

Parámetros	**Unidades**	**Fabricación de productos farmacéuticos, sustancias químicas medicinales y productos botánicos de uso farmacéutico**	**Actividades domesticas industriales, de vivienda unifamiliar y multifamiliar**	**Actividades domesticas de las aguas residuales de los prestadores de servicio publico y alcantarillado**	**Actividades de atención a la salud humana. Atención medica con y sin intervención**
Generales					
pH		6,00 a 9,00	6,00 a 9,00	6,00 a 9,00	6,00 a 9,00
Demanda Química de oxígeno (DQO)	mg/L O_2	400	200	180	200
Demanda Bioquímica de oxígeno (DBO)	mg/L O_2	150		90	150
Sólidos Suspendidos Totales (SST)	mg/L	50	800	90	50
Sólidos Sedimentables (SSED)	mg/L	1	10	5,,00	5
Grasas y Aceites	mg/L	15	30	20	10
Fenoles	mg/L	Análisis y Reporte			0,2
Sustancias Activas al Azul de metileno (SAAM)	mg/L	Análisis y Reporte			Análisis y Reporte
Iones	mg/L	Todos los posibles 500,00 c/u			(Cianuros Totales) 0,50
Hidrocarburos					
Hidrocarburos totales (HTP)	mg/L			Análisis y Reporte	
Compuestos de Fósforo					
Fósforo Total (PT)	mg/L			Análisis y Reporte	Análisis y Reporte
Ortofosfato	mg/L			Análisis y Reporte	Análisis y Reporte
Compuestos de Nitrógeno (NT)					
Nitratos	mg/L			Análisis y Reporte	Análisis y Reporte
Nitritos	mg/L			Análisis y Reporte	Análisis y Reporte
Nitrógeno Amoniacal	mg/L			Análisis y Reporte	Análisis y Reporte
Nitrógeno Total (NT)	mg/L			Análisis y Reporte	Análisis y Reporte
Metales y Metaloides					
Arsénico	mg/L	0,1			
Cadmio	mg/L	0,1			0,05
Mercurio	mg/L	0,01			0,01
Cromo	mg/L				0,5
Plomo	mg/L				0,1

Tabla 2.0.3: Parámetros Fotoquímicos y sus valores limites máximos permisibles en los vertimientos puntuales de aguas residuales domesticas y no domesticas de los prestadores del servicio publico de alcantarillado a cuerpos de aguas superficiales Tomado de: (Resolución MADS 0631 de 2015)

Derivados farmacológicos como Contaminantes Emergentes:

El empleo de productos farmacéuticos, y su eliminación continua en las fuentes hídricas implica riesgos tanto para el hombre, los animales y al ambiente[24]. Así mismo, su uso indiscriminado genera resistencia y resurgencia de diferentes microorganismos y efectos indeseables en otras especies. En consecuencia, el rango de productos químicos descartados en la basura o inodoro como medicamentos para humanos o para animales y las sustancias no asimiladas en su totalidad por el cuerpo humano y excretadas en heces fecales u orina (metabolitos), terminan en las aguas residuales y se mantienen presentes en estos afluentes, incluso después de diversos tratamientos de depuración y desinfección ya que presentan un alto grado de transformación y son eliminados permanentemente[25].

Este hecho motiva el desarrollo de métodos más eficaces para tratar este tipo de contaminantes, ya que según las propiedades fisicoquímicas de los fármacos y sus metabolitos, pueden ser en su mayoría recalcitrantes para su degradación [26] y alcanzan otros acuíferos o acumularse en los suelos, afectando los ecosistemas y las diferentes cadenas tróficas.

Para la mayoría de estos contaminantes no se cuenta con datos toxicológicos, su contribución de riesgo en los ecosistemas, ni su incidencia en fenómenos ambientales de contaminación. Así es difícil establecer los posibles efectos de estas sustancias sobre la salud de los seres humanos y el ambiente. En consecuencia, se están desarrollando investigaciones que permiten evaluar más a profundidad fenómenos como la resistencia de microorganismos a los antibióticos o alteraciones de los ciclos de reproducción de peces por los elevados niveles de hormonas en el agua [60]. Por otra parte, algunas investigaciones han permitido determinar la presencia de sustancias de origen farmacológico en cuerpos de agua como antibióticos, analgésicos, antiepilépticos, β-bloqueadores, medios de contraste, anticonceptivos, esteroides y antidepresivos entre otros [28, 27]

En Colombia, estudios recientes muestran la presencia de sustancias psicoactivas ilícitas como la cocaína y metabolitos como la benzoylecgonina en concentraciones en el orden de los µg-ng/L en fuentes de agua [29]. Tanto los fármacos como las drogas ilícitas pueden ser agentes contaminantes en su forma base o como un metabolito, según estudios realizados en el 2013 en Latinoamérica se encontró que un 64 % de los fármacos son excretados en orina y un 35 % en heces fecales. A su vez, se determinó que un 42 % de estas sustancias se excretan en forma de metabolitos secundarios [30].

Técnicas de purificación convencional de aguas residuales

Las procesos empleados en la purificación del agua se establecen con el objetivo de alcanzar los estándares de calidad requeridos por ley para el consumo humano. Los métodos de purificación empleados son muy diversos y dependen de la composición de materia suspendida o disuelta en la fuente de abastecimiento, lo que determinará el tratamiento físicoquímico y biológico específico[31]. Dentro de los métodos convencionales se encuentran:

Coagulación y Floculación

Uno de los problemas más comunes a la hora de tratar una fuente de agua contaminada es la eliminación de la turbidez y la materia orgánica suspendida. Por esa razón, se implementan dos mecanismos complementarios: Por un lado, la coagulación como un proceso mediante el cual se desestabilizan químicamente las partículas coloidales suspendidas, mediante la superación de las fuerzas que las mantienen separadas, por medio de la adición de los coagulantes químicos y la aplicación de energía de mezclado [32]. Dentro de los coagulantes más usados están el sulfato de aluminio, aluminato de sodio, cloruro de aluminio, cloruro férrico, sulfato férrico y el sulfato ferroso [33]. Y por otro, la floculación como un proceso posterior a la coagulación y consiste en la agitación de la masa coagulada para permitir el crecimiento y aglomeración de los flóculos recién formados con la finalidad de aumentar el tamaño y peso necesarios para sedimentar con facilidad [34].

Filtración

Este procedimiento tiene como objetivo remover partículas suspendidas en las aguas superficiales por medio de filtros de diferentes naturalezas y tamaños. Generalmente, está precedido de los procesos de coagulación y floculación, los cuales facilitan la sedimentación de la materia orgánica. Los métodos convencionales de filtración pueden realizarse a través de filtros de arenas rápidos o lentos, filtros de tierras diatomaceas, filtración directa o empacada y filtros de carbón activado [31]. Este procedimiento puede ser el primer tratamiento efectuado para la recuperación de un cuerpo de agua o implementarse después de una serie de procesos físico químicos y/o biológicos dependiendo de la naturaleza y composición de la muestra a filtrar. Cabe resaltar que este es un proceso económico y amigable con el medio ambiente.

Desinfección

Esta es una técnica que tienen como objetivo eliminar y/o inactivar microorganismos por medios químicos. Las sustancias más utilizadas son:

- El cloro en sus diferentes presentaciones (Gas cloro o sales de cloro tales como hipoclorito de sodio o calcio) es el desinfectante más utilizado, por sus cualidades bactericidas pero si no es manipulado adecuadamente puede producir subproductos halogenados tóxicos como los trihalometanos [31]. Su potencial bactericida está definido por la capacidad que tiene para penetrar las paredes celulares debido a su bajo peso molecular y bloquear procesos metabólicos, ya que reacciona específicamente con la fosfato deshidrogenasa [35], enzima altamente sensible a los agentes oxidantes y fundamental para el metabolismo de los azúcares y la producción de energía de la célula.

- El ozono, es un agente oxidante muy fuerte con propiedades desinfectante similares al cloro [35] y en condiciones de laboratorio muestra entre 600 y 3000 veces más rápida la destrucción de bacterias que el cloro y ha demostrado ser muy eficaz en la destrucción de una variedad de compuestos orgánicos refractarios debido a su alto poder oxidante.

Procesos avanzados de oxidación (AOPs)

Las aguas contaminadas por la actividad humana pueden, en general, ser procesadas eficientemente por plantas de tratamiento o por tratamientos químicos convencionales tales como desinfección química, coagulación, floculación, sedimentación, filtración o tratamientos biológicos entre otros. Sin embargo, en algunos casos estos procedimientos resultan inadecuados para alcanzar el grado de pureza requerido por ley o por el uso posterior del efluente tratado [36, 37]. En consecuencia, la demanda actual de la sociedad para la descontaminación de aguas ha impulsado el desarrollo de nuevas tecnologías de purificación. En esa medida, la mayoría de los AOPs pueden aplicarse a la remediación y detoxificación de aguas especiales, generalmente en pequeña o mediana escala [38]. Estos métodos pueden usarse solos o combinados entre ellos o con métodos convencionales.

La eficiencia de las técnicas involucradas en estos procesos tienen una mayor factibilidad termodinámica y una velocidad de oxidación incrementada por la participación de radicales, principalmente el radical hidroxilo $^{\bullet}$OH (E° = 2.80 V) [39]. Este radical es extraordinariamente reactivo para atacar moléculas orgánicas y reaccionar más rápido y eficientemente que oxidantes alternativos como el O_3 o que el Cl_2 pues presenta mayor potencial de oxidación (Ver Tabla 2.0.4).

Dependiendo de la naturaleza del compuesto orgánico, por ejemplo algunos ácidos carboxílicos pueden degradarse en presencia del radical hidroxilo entre un 20 a un 25 % o algunos aromáticos entre un 75 y 85 % mas eficiencintemente que con procesos convencionales, sin contar que al ser fotocatalizados su eficiencia puede aumentar hasta en un 100 % [40]. El radical libre $HO_2^{\bullet}$ y su conjugado $O_2^{\bullet -}$ con frecuencia están también involucrados en los procesos de degradación, pero estos radicales son mucho menos reactivos que los radicales $^{\bullet}$OH [41]. Estos radicales, son capaces de oxidar compuestos orgánicos principalmente por abstracción de hidrógeno o por adición electrofílica a dobles enlaces, generando radicales orgánicos libres ($R^{\bullet}$) [37].

Oxidante	**Reacción de Reducción**	**E°/V vs SHE**
Flúor	$F_{2(g)} + 2H^{+} + 2e^{-} \rightarrow 2HF$	3.05
	$F_{2(g)} + 2e^{-} \rightarrow 2F$	2.87
Radical Hidroxilo	$^{\bullet}OH + H^{+} + e^{-} \rightarrow H_2O$	2.80
Anión radical sulfato	$SO_4{}^{\bullet -} + e^{-} \rightarrow SO_4{}^{2-}$	2.60
Ión Ferrato	$FeO_4{}^{2-} + 8H^{+} + 3e^{-} \rightarrow Fe^{3+} + 4H_2O$	2.20
Ozono	$O_{3(g)} + 2H^{+} + 2e^{-} \rightarrow O_{2(g)} + H_2O$	2.075
Ión Peroxodisulfato	$S_2O_8{}^{2-} + 2e^{-} \rightarrow 2SO_4{}^{2-}$	2.01
Peróxido de Hidrógeno	$H_2O_2 + 2H^{+} + 2e^{-} \rightarrow 2H_2O$	1.763
Ión Permanganato (I)	$MnO^{4-} + 2H^{+} + 2e^{-} \rightarrow MnO_{2(s)} + 2H_2O$	1.67
Ión Hidroxiperoxil (I)	$HO_2{}^{\bullet} + 3H^{+} + 3e^{-} \rightarrow 2H_2O$	1.65
Ión Permanganato (II)	$MnO^{4-} + 8H^{+} + 5e^{-} \rightarrow Mn_2 + 4H_2O$	1.51
Ión Hidroxiperoxil (II)	$HO_2{}^{\bullet} + H^{+} + e^{-} \rightarrow 2H_2O_2$	1.44
Ión Dicromato	$Cr_2O_7{}^{2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O$	1.36
Cloro	$Cl_{2(g)} + 2e^{-} \rightarrow 2\ Cl^{-}$	1.358
Dióxido de manganeso	$MnO_2 + 4H^{+} + 2e^{-} \rightarrow Mn^{2+} + 2H_2O$	1.23
Oxigeno	$O_{2(g)} + 4H^{+} + 2e^{-} \rightarrow 2H_2O$	1.229

Tabla 2.0.4: Potenciales estándar de reducción en medio acuoso de los agentes oxidantes más comúnmente reportados para la destrucción de contaminantes orgánicos (Tomado de Brillas, 2009)

Entre los AOPs, los procesos fotocatálizados son de especial interés pues generan efectos sinérgicos entre ellos, produciendo mayor destrucción de la carga orgánica, de acuerdo al tipo de reactivo que sea fotocatalizado[42].

Proceso Electro-Fenton (EF)

A fines del siglo XIX, los conocidos ensayos de Fenton demostraron que las soluciones de H_2O_2 junto con sales ferrosas eran capaces de oxidar los ácidos tartárico y málico y otros compuestos orgánicos. Más tarde, Haber y Weiss sugirieron la formación de $^{\bullet}OH$ [43, 44, 45, 46] por medio de la siguiente reacción:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + {}^{\bullet}OH \qquad (1)$$

Al ser desarrollada en medio ácido la reacción puede tener la siguiente variación:

$$Fe^{2+} + H_2O_2 + H^{+} \rightarrow Fe^{3+} + H_2O + {}^{\bullet}OH \qquad (2)$$

Dichos radicales podían reaccionar luego por dos vías, la reducción de Fe^{+3} (una reacción improductiva) y el ataque a la materia orgánica como lo muestran las reacciones 3 y 4:

$$Fe^{3+}{}_{(ac)} + {}^{\bullet}OH_{\ (ac)} \rightarrow Fe^{2+}{}_{(ac)} + HO^{-}{}_{(ac)} \tag{3}$$

$$RH_{(ac)} + {}^{\bullet}OH_{\ (ac)} + H_2O \rightarrow ROH_{(ac)} + H_3O^{+}{}_{(ac)} \tag{4}$$

La constante de velocidad para la reacción de Fe^{2+} con H_2O_2 es alta, y este se oxida a Fe^{3+} en segundos o minutos en exceso de H_2O_2. Por tanto, la destrucción de residuos orgánicos por el reactivo de Fenton es, simplemente, un proceso catalizado por Fe^{2+}/H_2O_2. Por ello, estas reacciones ocurren también con iones metálicos de transición como el Cu^{2+}[47], y se les conoce como reacciones tipo Fenton.

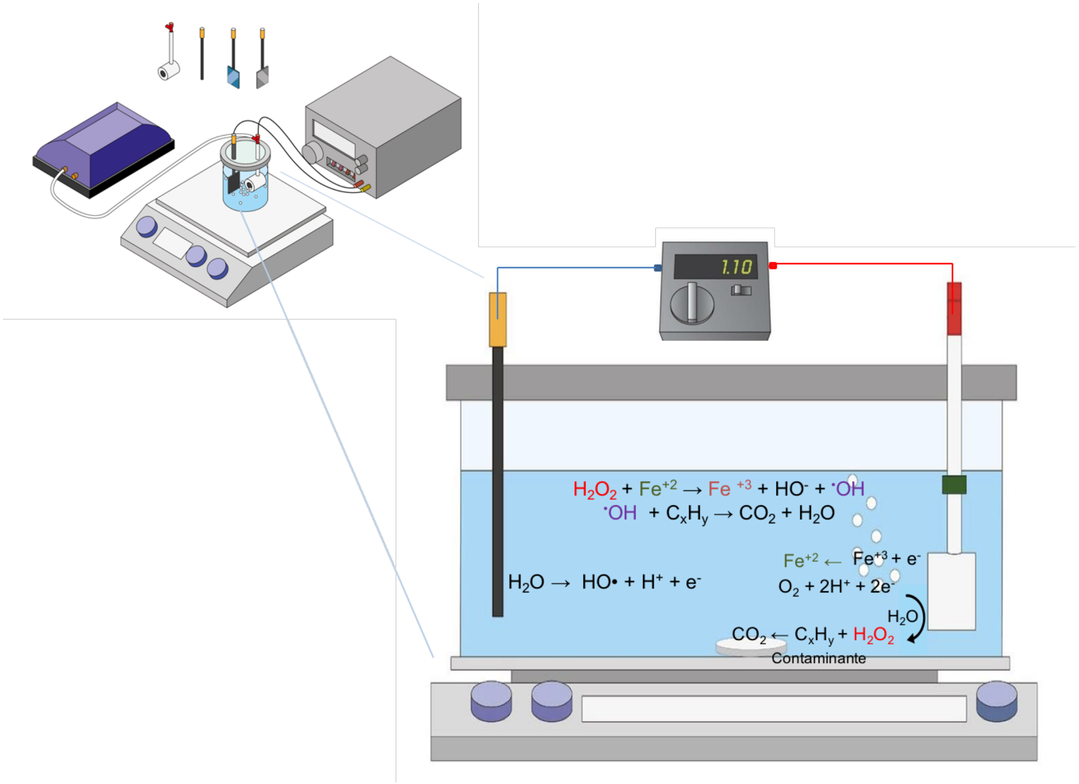

Figura 2.1: Esquema de las reacciones involucradas en el proceso Electro Fenton

De igual manera, es importante tener en cuenta que a mayor concentración del ion ferroso, mayor capacidad de mineralización del compuesto orgánico. Sin embargo, no se debe exceder este incremento porque no entrará en reacción, contribuyendo al aumento de sólidos totales, pues favorecerá la formación de $Fe(OH)_3$ evidente por la generación de un precipitado de color naranja, lo cual hace necesario calcular la cantidad de hierro a utilizar según el efluente. Esto también aplica para el peróxido ya que la cantidad no utilizada de peróxido de hidrógeno durante el proceso de Fenton contribuye a la generación de reacciones parasitarias afectando la eficiencia del proceso y pueden eliminar los radicales hidroxilo, por tal razón es mas importante ajustar el peróxido que el ion ferroso [45].

A pesar de su eficiencia el método Fenton tiene la desventaja requerir H_2O_2 continuamente durante el proceso. Por tanto, un enfoque dado para resolver este problema, es la producción de H_2O_2 in situ [41] (Ver Figura 2.1), situación que puede ser aplicada también para el hierro si se usa un ánodo de sacrificio, el cual puede aportar la cantidad de hierro necesaria. Este proceso así es llamado Electro-Fenton (EF) el cual combina las ventajas tanto del proceso clásico Fenton y los procesos electroquímicos con la reducción catódica del Fe^{3+} para generar la continua formación de Fe^{2+} en el cátodo y de ese modo minimizar la producción de hidróxido de hierro. De igual manera estimula la producción *in-situ* de H_2O_2 y la producción anódica de iones de Fe^{2+}, aunque el ion Fe^{2+} puede ser añadido de forma independiente si no se utiliza un ánodo de sacrificio [49, 50, 51, 52].

Cátodo : $O_{2(g)}$ + $2H^{+}{}_{(ac)}$+ 2e- → $H_2O_{2(ac)}$ (5)
Cátodo: $Fe^{3+}{}_{(ac)}$+ e- → $Fe^{2+}{}_{(ac)}$ (6)
Ánodo: H_2O → $^{\bullet}OH_{(ac)}$ + $H^{+}{}_{(ac)}$+ e- (7)
Ánodo de Sacrifico: Fe^{0} → $Fe^{2+}{}_{(ac)}$+ 2e- (8)

El proceso EF se puede dividir en 2 tipos de reacciones que involucran la producción in-situ de reactivos electroquímicamente (ánodicas y catódicas), estos se diferencian principalmente en la forma como el hierro entra en el sistema [40]. En el proceso catódico el hierro es adicionado como sales de hierro, mientras que en el proceso anódico, el hierro es obtenido por un electrodo de sacrificio, liberando continuamente hierro al sistema.

a. Proceso Catódico

En este proceso hay varias posibilidades, en las cuales 1 o 2 de los reactivos como el Fe^{2+} y el H_2O_2 pueden ser producidos in-situ, por lo que el H_2O_2 puede obtenerse por reducción del oxígeno molecular en el cátodo (Ver Eq. 5) y el Fe^{+2} puede ser reducido en el cátodo (Ver Eq. 6). Simultáneamente a la reducción del Fe^{3+}, la reducción del O_2 puede tomar lugar también en el cátodo en medidas comparables, conducente a una más eficiente y completa degradación del contaminante que la reacción clásica de Fenton porque se dan reacciones menos competitivas [46, 53, 54] al consumir los reactivos sin producir el radical hidroxilo.

b. Proceso Anódico

En este proceso el ánodo puede estar compuesto por materiales inertes como el Pt o el Ti. Sin embargo, si es usado un material compuesto de hierro, este se convierte en la fuente directa de Fe^{2+} (Ver Eq. 8) [55]. Este proceso tiene varias ventajas: la primera es su posible implementación en condiciones de pH neutro, mientras sí se adiciona el Fe^{2+} el pH necesariamente tendrá que ser ácido entre 2.8 y 3.0, la producción de Fe^{2+} es controlada usando el electrodo de sacrificio y no se necesita usar sales ferrosas, las cuales pueden ser agresivas con el ambiente. Los usos más frecuentes de esta tecnología han sido en el tratamiento de aguas industriales, suelos y lixiviados para degradar con éxito compuestos aromáticos, ácidos carboxílicos, policlorados, herbicidas y plaguicidas [44]. En el caso de ánodos activos, los radicales hidroxilo pueden ser obtenidos por oxidación directa del agua (Ver Eq. 7).

Proceso Foto Electro Fenton (PEF)

Usualmente, la luz es utilizada en los procesos químicos para aumentar considerablemente las velocidades de reacción, por este motivo en los AOPs cuando se implementa el uso de iluminación su eficiencia se ve mejorada [38]. Como fuente de luz se pueden utilizar diferentes tipos de lámparas (Mercurio, Xenón o en algunos casos lámparas germicidas). Sin embargo, el uso de luz solar asegura un considerable ahorro de energía y puede ser un adecuado catalizador [43, 56].

En el proceso PEF la degradación de los contaminantes se ve reforzada por la acción de la radiación con longitud de onda comprendida entre 250 nm a 500 nm. Esta puede ser producida ya sea por lamparas UV o por radiación solar, proceso conocido como Solar-Foto-Electro-Fenton (SPEF) permitiendo aprovechar directamente la energía solar que llega a la superficie terrestre [57], para provocar una serie de reacciones químicas (Redox) dando lugar a la eliminación o transformación de la materia orgánica disuelta en el agua, para tratamiento de vertimientos urbanos, industriales y agrícolas [58, 59]. En ambos casos, la radiación posibilita la reducción del Fe^{+3} a Fe^{+2} y la mineralización de complejos bastante estables formados entre el Fe^{+3} y los ácidos carboxílicos de cadena corta generados en la mineralización del contaminante. (Ver Eq. 9-11)

$$\mathrm{Fe(OH)^{2+}}_{(ac)} + hv \rightarrow \mathrm{Fe^{2+}}_{(ac)} + {}^{\bullet}\mathrm{OH}_{(ac)} \tag{9}$$

$$\mathrm{Fe^{3+}}_{(ac)} + \mathrm{AOCC}_{(ac)} \rightarrow [\mathrm{Fe^{3+}\text{-}\ AOCC}]_{(ac)} \tag{10}$$

$$[\mathrm{Fe^{3+}\text{-}\ AOCC}]_{(ac)} \rightarrow \mathrm{Fe^{2+}}_{(ac)} + \mathrm{CO}_{2(g)} \tag{11}$$

Ventajas y desventajas del Electro-Fenton frente a otros procesos avanzados de oxidación:

Los AOPs son tratamientos terciarios que permiten alcanzar un alto nivel de pureza en las aguas residuales tratadas, con el fin de degradar la de materia orgánica, mejorando la calidad del efluente y eliminando los contaminantes emergentes [39]. Durante los últimos años se han venido estudiando, desarrollando y mejorando una amplia gama de procesos homogéneos o heterogéneos, fotoquímicos o no fotoquímicos dentro de los que encontramos la ozonización en medio alcalino o con peróxido de hidrógeno, las diferentes formas de implementar el reactivo de Fenton, la fotólisis, el plasma no térmico, fotocatálisis con óxido de titanio y el ultrasonido entre muchos otros [38, 49, 60, 61].

El análisis del ciclo de vida permitió identificar una serie de criterios para determinar la actuación del proceso EF y sus variaciones como los más eficiente de los AOPs frente a diferentes contaminantes [62, 63], dentro de los que se resaltan: la eficiencia en la degradación del contaminante, los costos relacionados con la construcción de la infraestructura necesaria para desarrollarlo y el consumo de reactivos y de energía. A continuación se presentan las ventajas y desventajas en la implementación del proceso EF generadas a partir de dicho análisis. (Ver Tabla 2.0.5)

Ventajas	**Desventajas**
1. Es un proceso generador de un potente oxidante (los radicales $^{\bullet}$OH) a presión y temperatura ambientales 2. Utiliza recursos renovables: oxígeno como materia prima y luz solar puede ser parte del proceso. 3. Consume reactivos inocuos y se producen in situ: ▪ El Fe^{+2} es catalítico, abundante en la naturaleza y no tóxico. ▪ El H_2O_2 es fácil de manejar y ambientalmente benigno en bajas concentraciones 4. No existen limitaciones de transferencia de masa por ser un sistema homogéneo. 5. Cambian de fase al contaminante, transformándose químicamente. 6. Usualmente no generan lodos. 7. Son muy útiles para contaminantes refractarios que resisten otros métodos de tratamiento. 8. Sirven para tratar contaminantes a muy baja concentración. 9. No se forman subproductos de reacción, o se forman en baja concentración. 10. Son ideales para disminuir la concentración de compuestos formados por pre-tratamientos alternativos. 11. El sistema EF puede ser mejorado cuando se implementa luz en el espectro visible como catalizador lo que mejora el rendimiento y la velocidad de reacción.	1. Presenta un mayor costo que otros procesos por el uso de energía eléctrica para el proceso electrolítico. 2. Requiere de la adición continua de Fe^{+2} a menos que se presente de forma heterogénea o esté adherido sobre alguna superficie. 3. El Hierro utilizado como catalizador puede precipitarse como $Fe(OH)_3$, para evitarlo el sistema requiere mantener bajos los niveles de pH entre 2.8 y 3.0. 4. El escalamiento depende de las condiciones y ubicación del sistema a tratar. 5. Este tipo de procesos se debe implementar en aguas libres de sustancias con alto nivel de adsorción o con altos sólidos en suspensión, porque impiden el paso de la luz disminuyendo la eficiencia. 6. Los AOPs se recomiendan para tratar caudales o volúmenes pequeños y medianos de concentraciones no muy elevadas.

Tabla 2.0.5: (Ventajas y Desventajas del sistema Electro-Fenton)

Patentes asociadas al proceso Electro-Fenton en el mundo:

La innovación es un proceso complejo para definir la capacidad de generar nuevos productos y es clave para en la comprensión del nivel de desarrollo tecnológico de una región, un país o una institución. Si bien no resulta fácilmente medible, las patentes constituyen indicadores en la información no solo de los resultados del proceso de investigación, sino también los de invención desarrollados y de sus capacidades tecnológicas. A partir de las diferentes investigaciones, desarrolladas en los últimos años sobre los AOPs y en especial el proceso EF a nivel de laboratorio, se han generado nuevos productos e invenciones con el fin de implementar este proceso como un mecanismo complementario y altamente efectivo en la degradación de sustancias tóxicas orgánicas presentes en las aguas residuales y explotarlo comercialmente.

Para llevar a cabo este análisis se realizó una búsqueda de las solicitudes de patentes presentadas y aprobadas en diferentes buscadores tales como: Espacenet, SIPO, Google Patents, The Lens y Patentscope. Durante este proceso de revisión y seguimiento se ha podido identificar a China, USA, España y Alemania como pioneros en la generación e implementación de este tipo de desarrollos, asimismo, se pudo identificar patentes asociadas a:

- **Electrodos:** Composición química y concentración, ubicación, y estructura.
- **Reactor:** Entradas y salidas de agua, manejo de residuos, estructura y forma.
- **Electrólitos:** Composición química, ubicación y concentración.
- **Energía Requerida:** (Voltaje y/o Amperaje) de acuerdo al sistema propuesto.
- **Productos obtenidos:** Cantidades de peróxido de hidrógeno producidos.
- **Tiempos de procesamiento y metodologías de uso**.

Por otro lado, una gran variedad de patentes tecnológicas en el mundo involucran la reacción de Fenton las cuales son utilizadas por varias compañías para la remediación y descontaminación de suelo y agua [54], entre las industrias que más extensamente lo usan están:

- The Geo-Cleanse Process®, por Geo-cleanse International, Inc.

(http://www.geocleanse.com/gci/geocleanse-process/)

- The CleanOX Process, por ManTec, Inc. (MECx).

(http://www.mecx.net/links/*in-situ*_chemical_oxidation.html)

- ISOTECHSM por *In-situ* Oxidative Technologies, Inc.

(http://www.insituoxidation.com/reagent)

- The BIOX® Process, es utilizado por varias compañías tales como BioManagement Services, Inc. (BMS). e Innovative Remediation Technologies. Inc,

(http://www.biomin.co.za/biox/technology.html) y (http://www.bioxservices-bioremediation.com/irt-enhanced-situ-treatment-options/)

- The On-contact Remediation Process® por Environmental Remediation and Financial Services, Inc. (http://www.erfs.com/services/remediation).

Estos procesos presentan condiciones particulares para su funcionamiento, en el caso de Geo-Cleanse opera en condiciones ligeramente ácidas (alrededor de 4-6) y no es recomendado para aguas subterráneas con pH por encima de 8, tampoco es recomendable su uso en suelos ricos en turba. En el caso de ISOTECH, es un proceso que modifica la reacción Fenton permitiendo la adecuada dispersión del radical hidroxilo, el catalizador contiene un complejo de hierro manteniéndolo precipitado y posibilitando su operaración a pH alrededor del neutro. Kakarla (2002), [64] reporta resultados de su aplicación a gran escala de esta tecnología en una lavandería del sur de Florida con una reducción del 72 % del total de hidrocarburos halogenados en un proceso inicial y de un 90 % en una segunda aplicación del proceso. Por último, el proceso BIOX® requiere ser realizado a temperatura ambiente y a pH neutro para tratar aguas subterráneas. Este proceso patentado se aplica en el suelo y debe haber presente H_2O_2, Sulfato Ferroso, óxido de calcio o magnesio, entre otros y degrada sustancias orgánicas tóxicas a otras menos tóxicas.

En Colombia existe una gran variedad de empresas encargadas del tratamiento y potabilización de aguas (PRAXAIR, aguas de Colombia, Valrex, NyF de Colombia, entre otras). Sin embargo, la implementación de este tipo de tecnología es poco utilizada aunque según la oferta nacional unas pocas empresas ofrecen este tipo de procedimientos ya que los tratamientos ofrecidos en el mercado para aguas residuales industriales están diseñados como tratamientos primarios y secundarios con procesos de coagulación, floculación, sedimentación, reducción metálica, neutralización, estabilización de pH, cribado, trampa para grasas, tratamientos biológicos de tipo aerobio o con lodos activados, filtración por percolador y/o por membranas entre otros. Ya en los tratamientos terciarios o avanzados ofrecen microfiltración, ósmosis inversa, biorreactor de membranas (MBR), adsorción y desinfección y los que ofrecen AOPs, los ofertan como: “unidades para tratamiento de aguas residuales industriales por tecnología de oxidación avanzada, generando en sitio radicales oxidrilos mediante la utilización de Reactivos como el peróxido de hidrógeno irradiados con (UV-C) 254 nm, en complemento con la ultrafiltración”, no aclaran la técnica específica a utilizar, el tipo de agua a tratar o las condiciones en que puede ser tratada, las concentraciones y el tipo de contaminante.

A continuación se presentan en la tabla 2.0.6 las patentes asociadas al método Electro-Fenton y Foto Electro-Fenton, encontradas a nivel mundial:

Patente	**Codigo**
1. Electro-Fenton reaction waste water treatment equipment	CN 102139938 B
2. Waste water treatment device using electro-Fenton reaction	CN 201932937 U (Modelo de Utilidad)
3. Electrolytic apparatus, methods for purification of aqueous solutions and synthesis of chemicals	US 6328875 B1
4. Electrolytic purification of contaminated waters by using oxygen diffusion cathodes.	US 6224744 B1
5. Method for organic wastewater electro-fenton treatment adopting bentonite	CN 102942241 B
6. Groundwater remediation method by Electro-Fenton reaction using iron cathode	CN 102976472 B
7. Multi dimensional electro-Fenton device and method for treating industrial wastewater by using same	CN 103951018 A (Modelo de utilidad)
8. Integrated device for treatment of industrial wastewater	CN 203904118 U
9. Method for processing organic wastewater by electro-fenton	CN 104326611 A
10 Method for removing organic matters in water by utilizing three-dimensional electrode electro-fenton and device thereof	CN 102070230 A
11. Mineralized refuse participating organic wastewater electro-Fenton treatment method	CN 102897921 B
12. Novel hydrogen peroxide generator, and method for of electro-Fenton treatment of organic wastewater	CN 104372371 A
13. Preparation method of supported FeOOH catalyst, and Electro-Fenton wastewater treatment system	CN 102218319 B
14. Pretreatment method for pesticide larvin wastewater	CN 104098208 A
15. Procedimiento para tratar aguas residuales que comprende oxidación fenton y oxidación biológica	WO2014083224 A1
16. Sewage treatment method coupled with organic membrane and electro-Fenton catalytic technology.	CN 103193297 A
17. Solar photoelectric - Fenton treatment method for H acid wastewater of dye immediate	CN 101723489 A
18. Three Dimensional electro-Fenton water treatment device	CN 203820510 U (Modelo de Utilidad)
19. Wastewater treatment method based on electro-Fenton reaction	CN 101798130 A
20. Wastewater treatment method by combination of three-dimensional electrode and electro-Fenton	CN 101811758 A

Tabla 2.0.6: Patentes Asociadas a procesos Electro-Fenton

Capítulo 3

Justificación

El incremento indiscriminado en el consumo de fármacos prescritos y no prescritos en humanos y animales con fines médicos y su descarte inadecuado, así como el uso de sustancias psicoactivas (SPA), es una preocupación para las autoridades de salud a nivel mundial [65, 66], pues es un tópico sobre el cual hay poca información, en especial por los posibles riesgos ecológicos derivados de su liberación al ambiente. La dificultad se encuentra bien fundamentada porque mucha del agua superficial es empleada como fuente para consumo humano (previo a tratamientos convencionales) o para la irrigación de cultivos [67].

El aumento de los niveles en la concentración de fármacos en los ecosistemas acuáticos ha llevado a su persistencia aún cuando hayan pasado por sistemas de tratamiento de aguas residuales, por tanto pueden acumularse en los cuerpos de agua o en los lodos por encontrarse en concentraciones muy pequeñas, son difíciles de tratar [68]. Por ejemplo, la liberación de antibióticos al ambiente es un riesgo potencial, cuya presencia puede promover procesos de selección de genes y bacterias resistentes a los antibióticos disponibles[69], al igual que el aumento en el uso de hormonas, actuando como agentes de disrupción endocrina y pueden presentar un impacto potencial en la salud reproductiva y la supervivencia de diferentes especies de peces y anfibios, alterando los ciclos de reproducción y, por tanto, la sostenibilidad de las comunidades aledañas a los cuerpos de agua[70].

Entonces es necesario llevar a cabo la identificación y cuantificación de fármacos lícitos como ilícitos en las PTAR, para adquirir el conocimiento de los porcentajes de remoción en las mismas. Desde hace algunos años, este monitoreo se viene realizando en países europeos y se ha fundamentado en metodologías multiresiduo, las cuales se basan en el uso de (LC -MS/MS). Los análisis pueden limitarse a un número concreto de compuestos, a partir de un barrido amplio de los contaminantes de mayor interés para definir metodologías puntuales de cuantificación, monitoreo y remoción acordes con el entorno y tipología de PID's consumidas en un lugar en particular.

A pesar de la detección de estas sustancias, las normativas vigentes no regulan la presencia de estos contaminantes en las aguas residuales, aunque son candidatos a una regulación futura y evidencian la falta de tratamientos eficientes para en su eliminación. Teniendo en cuenta la necesidad de restaurar los cuerpos de agua residuales para nuevas aplicaciones y con el conocimiento de cuales son los principales contaminantes presentes en los efluentes, como lo han reportado Hernández (2015) y Bijlsma (2016) en Colombia. En estos trabajos se estudió la viabilidad de los procesos EF y PEF en la eliminación de CEs. Por las razones anteriores, en el presente trabajo se plantea la siguiente pregunta de investigación: ***¿Son los procesos avanzados de oxidación, específicamente los procesos EF y PEF, eficientes en el tratamiento de CEs persistentes en las PTAR, para reducir su concentración en las aguas residuales?***

Capítulo 4

Publicaciones y Resultados

En este capítulo se presentan cinco trabajos para dar respuesta a la metodología propuesta: En el primero se desarrolla un método multiresiduo para la determinación y cuantificación de un grupo de 32 fármacos en varios puntos geográficos y diferentes fuentes hídricas de Colombia, de los cuales se confirmó la presencia de 16. Las muestras investigadas fueron aguas residuales urbanas, recolectadas durante una semana, del efluente en la PTAR salitre de Bogotá. Además, del departamento de Antioquia, de aguas residuales sin tratar de un Hospital en Tumaco (Nariño) y de la ciudad de Florencia (Caquetá). El análisis fue realizado mediante (LC-MS/MS QqQ) mostrando una alta prevalencia de productos farmacéuticos en todas las muestras analizadas. Los fármacos antihipertensivos, VAL y LOS, estaban comúnmente presentes en las aguas residuales en niveles superiores a 1 µg/L, por lo cual fueron seleccionados para los estudios adicionales. Esto demostró que el tratamiento aplicado en las PTAR no elimina eficientemente los compuestos seleccionados, resaltando la pertinencia del desarrollo de nuevas y mejores tecnologías para su eliminación.

En el segundo artículo se muestra la oxidación del antihipertensivo VAL por los procesos EF y PEF, utilizando un ánodo DSA de Ti/IrO_2 dopado con SnO_2 y un cátodo GDE, evaluando la influencia de variables como el electrolito soporte, la densidad de corriente y el pH. La eficiencia del proceso se determinó de acuerdo a la eliminación del contaminante y la tasa de mineralización. Los procesos se llevaron a cabo en modo batch, en una celda de 250 mL. Se realizaron ensayos con diferentes electrolitos, usando NaCl como electrólito soporte a pH (3,0) y una densidad de corriente de 3,46 mA/cm^2 añadiendo 3,6x10^{-5} mol/L de Fe^{2+}, se observó una degradación total de VAL después de 45 minutos. A los 120 minutos, sólo se obtuvo el 25 % de la mineralización. También, pruebas sin modificación de pH y en presencia de ácido oxálico (4,6x10^{-5} mol/L) con resultados comparables a los obtenidos a pH 3,0. Los compuestos intermedios aromáticos fueron identificados mediante (UPLC/Q - QTOF MS/MS) y se propuso una ruta de degradación inicial. Ademas, para determinar la biodegradabilidad de los productos de degradación fue acoplado el proceso a un sistema biológico aeróbico, demostrando la viabilidad de los procesos EF y PEF para degradar el VAL sin modificación del pH.

En el tercer artículo se presentó la remoción, degradación y/o mineralización de dos fármacos antihipertensivos VAL y LOS con el proceso PEF usando un ánodo de DSA de Ti/IrO_2 dopado con SnO_2 y un cátodo GDE bajo radiación con LEDs de luz blanca. Además, se utilizaron ácidos orgánicos (ácidos cítrico, tartárico y oxálico) como agentes complejantes de iones Fe^{2+}/Fe^{3+} con el fin de mantener el rendimiento de la reacción Fenton sin modificación de pH. Los resultados mostraron una degradación de VAL y LOS de 70 % y 100 % respectivamente a 3.42 mA/cm^2 después de 90 min de tratamiento con EF. Igualmente la degradación total de VAL y LOS se alcanzó con el proceso PEF a 60 minutos de tratamiento para ambos compuestos. La mineralización para ambos compuestos fue de 30 % después de 2 horas de tratamiento en ambos procesos. Así mismo, cuando se usaron los ácidos cítrico, tartárico y oxálico, se obtuvieron resultados similares, es decir, degradación total de ambos compuestos, después de 90 minutos de tratamiento a pH cercanos al neutro. El rendimiento de la degradación en presencia de los ácidos orgánicos podría atribuirse al aumento de hierro disuelto en el sistema, facilitando la redución de de Fe^{3+}a Fe^{2+} en la reacción PEF y en consecuencia, la producción de radicales $\bullet OH$. Igualmente, el aumento de la fotoactividad de los complejos podría estar asociado con la alta capacidad de complejo Fe^{3+} promoviendo la transferencia de carga del ligando al metal, clave para alimentar Fe^{2+} al proceso Fenton. Los resultados muestran un sistema evaluado más eficiente para eliminar los compuestos utilizando iluminación LED en comparación con las lámparas UV-A tradicionales en este tipo de trabajos. Adicionalmente, tres (3) productos de transformación de VAL y dos (2) de LOS se identificaron mediante (UPLC/Q - QTOF MS/MS) al final del proceso PEF. Finalmente, los compuestos orgánicos acumulados y no mineralizados, se trataron eficazmente con un sistema biológico aerobio posterior.

El cuarto trabajo (esta pendiente de publicación) se basa en la aplicación de los sistemas EF y PEF para el tratamiento de muestras de agua de la PTAR salitre de Bogotá utilizando dos materiales ánodicos: un ánodo DSA de Ti/IrO_2 dopado con SnO_2 y un ánodo BDD de diamante dopado con boro y un cátodo de difusión de gas GDE. Se utilizó NaCl y Na_2SO_4 como electrólito de soporte con los anodos DSA y BDD, respectivamente. las condiciones del sistema utilizadas fueron: pH (3,0), una densidad de corriente de 3,46 mA / cm^2 y 3,6x10^{-5} mol/L de Fe^{2+}. Los resultados muestran un efecto positivo en la propiedades organólepticas del agua y una disminución en la concentración de los compuestos. Adicionalmente, 2 poster como complemento al trabajo realizado en los artículos presentados.

Por último, se propone un documento de propiedad intelectual de un producto y un proceso basados en el proceso EF (patente de invención) como resultado de los conocimientos generados durante el desarrollo de este trabajo.

A continuación se anexa una tabla con el listado de productos de propiedad intelectual realizados en el marco de este proyecto de I+D+i:

Clase de producto	**Titulo**	**Medio de publicación**	**Clasificación**	**Fecha**	**Estado**
Artículo 1	An investigation into the occurrence and removal of pharmaceuticals in Colombian wastewater	Science of the Total Environment	Q1	Junio 2018	Publicado
Artículo 2	Photo-electro-Fenton process applied to the degradation of valsartan: effect of parameters, identification of routes and combination with a biological system	Environmental Chemical Engineering	Q1	Mayo 2018	Sometido
Artículo 3	Advanced oxidation of antihypertensives losartan and valsartan by photo-electro-Fenton at near-neutral pH using natural organic acids and a dimensional stable anode-gas diffusion electrode (DSA-GDE) system under light emission diode (LED) lighting	Environmental Science and pollution Reserche	Q2	Julio 2018	Publicado
Artículo 4	Eliminación de contaminantes emergentes en aguas residuales urbanas mediante diferentes sistemas Electro-Fenton				Por someter
Poster 1	Removal of Sartans (Losartan and Valsartan) by Electro-Fenton and Photo-Electro-Fenton using a BDD Anode: Identification of Transformation Products.	3rd Iberoamerican Conference on Advanced Oxidation Technologies (III CIPOA) and 2nd Colombian Conference on Advanced Oxidation Processes (II CCPAOX)		Noviembre 2017	Presentado. Artículo en proceso de escritura

Poster 2	Inactivation of Microorganisms from Effluents of Wastewater Treatment Plant of Bogotá by Electrochemical Oxidation and Photo-Electro-Fenton Process using a DSA Anode and GDE Cathode	3rd Iberoamerican Conference on Advanced Oxidation Technologies (III CIPOA) and 2nd Colombian Conference on Advanced Oxidation Processes (II CCPAOX)	Noviembre 2017	Presentado Artículo en proceso de escritura
Presentación Oral	Removal of Sartans (Losartan and Valsartan) by Advanced Electrochemical Oxidation Process Photo-Electro- Fenton using a BDD Anode. Identification of Transformation Products.	3rd Iberoamerican Conference on Advanced Oxidation Technologies (III CIPOA) and 2nd Colombian Conference on Advanced Oxidation Processes (II CCPAOX)	Noviembre 2017	Presentado
Patente de invención			2018	En Desarrollo: (Financiado por Colciencias)

Pasantía:

Institución	País	Año	Actividades realizadas
Universidad Jaume I (UJI) Institut Universitari de Plaguicides i Aigües (IUPA)	Castellon - España	2017	• Capacitación en el uso de cromatografía de alta resolución acoplada a masas (por Triple cuádrupolo y QTOF). • Capacitación en el tratamiento estadístico de los datos obtenidos por cromatografía. • Identificación y seguimiento de intermediarios. Planteamiento de mecanismos de reacción. • Análisis de resultados y complementación de la escritura y publicación de Artículos científicos.

De igual manera se resalta el apoyo de Colciencias con recursos para el desarrollo de la fase experimental:

Nombre del proyecto	Entidad	Participación en	Año	Valor Total
Aproximación a la Remoción Eficiente de Drogas Ilícitas y Farmacéuticas Presentes en Aguas Residuales Mediante Procesos Avanzados de Oxidación.	Colciencias	715 - 2015 Convocatoria para proyectos de investigación y desarrollo en Ingenierías.	2015	$ 729,924,412

Artículo 1:

An investigation into the occurrence and removal of pharmaceuticals in Colombian wastewater

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'An investigation into the occurrence and removal of pharmaceuticals in Colombian wastewater'

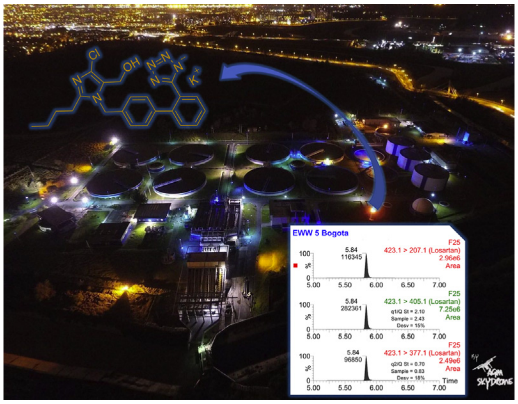
A.M. Botero-Coy [a], D. Martínez-Pachón [b], C. Boix [a], R.J. Rincón [b], N. Castillo [b], L.P. Arias-Marín [c], L. Manrique-Losada [d], R. Torres-Palma [e], A. Moncayo-Lasso [b,*], F. Hernández [a,*]

[a] Research Institute for Pesticides and Water (IUPA), University Jaume I, Castellón, Spain
[b] Grupo de Investigación en Ciencias Biológicas y Químicas, Facultad de Ciencias, Universidad Antonio Nariño, Bogotá D.C., Colombia
[c] Grupo Bioprocesos Microbianos (Biomicro), Escuela de Microbiología, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia
[d] Grupo de Investigación en Materiales, Ambiente y Desarrollo (MADE), Facultad de Ciencias Básicas, Universidad de la Amazonia, Florencia, Colombia
[e] Grupo de Investigación en Remediación Ambiental y Biocatálisis (GIRAB), Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia

HIGHLIGHTS

- Pharmaceuticals were present at ppb levels in urban and hospital wastewaters from Colombia.
- Effluent wastewater from conventional WWTPs contained concentrations similar to raw influent wastewater.
- Both IWW and EWW are directly discharged in the aquatic ecosystem in some locations.
- Removal efficiency of pharmaceuticals in WWTPs is incomplete, therefore additional tertiary treatments are needed.
- The use of LC-MS/MS QqQ allowed reliable quantification supported by quality control analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the presence of 20 pharmaceuticals in wastewater from Colombia is investigated. Several widely consumed compounds have been detected in wastewater samples from different origins and geographical areas in Colombia. The studied pharmaceuticals included antibiotics, analgesics and anti-inflammatories, cholesterol lowering statin drugs, lipid regulators, and anti-depressants. The investigated samples were urban wastewater collected during one whole week before (influent) and after treatment (effluent) in the wastewater treatment plants (WWTPs) of Bogotá and Medellin. Raw wastewater from the Hospital of Tumaco and from the city of Florencia were also collected. Analyses performed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) revealed that most of the target analytes were present in all the wastewater samples. The highest concentrations (up to 50 μg/L) corresponded to acetaminophen, but several antibiotics, such as azithromycin, ciprofloxacin and norfloxacin, and antihypertensive drugs, such as losartan and valsartan, were commonly present in influent wastewater (IWW) at levels above 1 μg/L. Moreover, the treatment applied in WWTPs seemed to not efficiently remove the compounds under study, because most pharmaceuticals were also present in effluent wastewater (EWW) at concentrations close to those of the IWW. Special emphasis was made in this work on the quality of data reported, performing a detailed study of quality control (QC) samples.

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* Corresponding authors.
E-mail addresses: amoncayo@uan.edu.co (A. Moncayo-Lasso), felix.hernandez@uji.es (F. Hernández).

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The analytical approach used –direct injection of 5-fold diluted samples without any additional treatment – is simpler and faster than the commonly applied solid phase extraction (SPE). The use of 12 isotope-labelled internal standards ensured the satisfactory correction of matrix effects for the corresponding analytes. For the remaining 8 compounds, no drastic matrix effects were observed, and only four compounds (cloxacillin, doxycycline, losartan, tetracycline) presented QC recoveries near or slightly below 60%, revealing ionization suppression, particularly in the IWW. Data on the occurrence of pharmaceuticals reported in this paper are the basis for current studies that aim to develop efficient systems for the degradation/removal of these compounds from the aquatic environment.

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1. Introduction

Currently, there is special concern about the presence and potential hazardous effects of emerging contaminants (EC) in the aquatic environment. ECs are widely used compounds that are not regulated yet (or only a few of them); however, they are commonly found in wastewater and surface water at concentrations that may be higher than classical persistent and/or priority substances; therefore, they can be harmful to aquatic ecosystems and become a hazard for human public health (Daughton, 2004; Gracia-Lor et al., 2012a; Hernández et al., 2015a; la Farré et al., 2008). Within the wide group of ECs, pharmaceuticals are among the most frequently detected compounds in the aquatic environment (Hughes et al., 2013). Antibiotics are of particular concern due to the potential risks associated with the development of microorganisms resistant to antibiotics (Makowska et al., 2016; Manaia et al., 2016). The evaluation of the hazards of emerging contaminants, such as pharmaceuticals and personal care and disinfection by products, is a current priority in regulatory water quality monitoring (Loos et al., 2009; Brack et al., 2012; Brack et al., 2017).

It was approximately 40 years ago when pharmaceuticals were first considered environmental contaminants in the aquatic environment (Hignite and Azarnoff, 1977; Richardson and Bowron, 1985). Several pioneer works highlighted the interest in studying the occurrence and impact of pharmaceuticals in the aquatic environment (Daughton and Ternes, 1999; Daughton, 2004; Kolpin et al., 2002). From then, there has been an impressive increase in the number of publications reporting the presence of pharmaceuticals in the water environment. The development of sophisticated analytical techniques played a key role in their emergence (Hernández et al., 2015b; Richardson and Kimura, 2016). Data reported by many environmental laboratories around the world reveal that pharmaceuticals are omnipresent in the aqueous environment (e.g., wastewater influent and effluent, manure, industrial effluent, surface water, groundwater, and drinking water (aus der Beek et al., 2016; Monteiro and Boxall, 2010)). Liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) has played a prominent role in this process. LC-MS/MS is the most widely applied technique for the determination of emerging contaminants in water, due to its excellent sensitivity, selectivity and robustness, together with reliability in the identification of the compound detected. For the successful application of LC-MS/MS, at least two MS/MS transitions need to be monitored and their ion ratios evaluated (Hernández et al., 2018; García-Galán et al., 2016; Gracia-Lor et al., 2014; Bayen et al., 2014; van Nuijs et al., 2010; Pozo et al., 2006a; Pozo et al., 2006b).

As expected from the wide human consumption, the main source of pollution for pharmaceuticals is urban wastewater, and it is rather common to find high pharmaceuticals concentrations (up to hundreds of ppb) in influent wastewater (IWW). Unfortunately, conventional wastewater treatment plants (WWTP) do not efficiently remove these compounds, and they can remain in effluent wastewater (EWW) at concentrations similar, or even higher, than in IWW (Gracia-Lor et al., 2012a; Gros et al., 2010; Jelic et al., 2011; Lacey et al., 2008). In addition to the inefficient removal in WWTPs, some pharmaceuticals are also persistent and can bioaccumulate in living organisms (Daughton and Ternes, 1999; Yang et al., 2014). As a consequence, these compounds can easily reach surface water (Dai et al., 2015; Kasprzyk-Hordern et al., 2008; Fatta-Kassinos et al., 2011; Liu et al., 2015; Matamoros et al., 2012) and even drinking water (Boyd et al., 2003; Carmona et al., 2014; Kumar and Xagoraraki, 2010; Sodré et al., 2010; Vulliet et al., 2011).

Although much data are available around the world, revealing the presence of pharmaceuticals in different aquatic scenarios, little information is available from Latin America. This is a particular worry, because in some areas, the discharge of raw sewage into rivers, lakes and reservoirs is rather common (De Paula et al., 2007; Gracia-Lor et al., 2012b; Montagner and Jardim, 2011; Thomas et al., 2014). Concern over the presence of these contaminants is well founded, because these water resources not only flow through tropical areas rich in biodiversity, but surface waters are also often used as a source for human consumption (Aristizabal-Ciro et al., 2017).

Recently, we performed a wide-scope qualitative screening of organic contaminants, including pharmaceutical, veterinary drugs, X-ray agents, personal care products, sweeteners, illicit drugs, and a notable number of metabolites in wastewater and receiving surface waters from the area surrounding Bogotá (Hernández et al., 2015a). The use of high resolution MS, specifically liquid chromatography coupled to quadrupole-time-of-flight (LC-QTOF MS) allowed us to identify a notable number of pharmaceuticals in both EWW and in surface water, emphasizing acetaminophen, carbamazepine, clarithromycin, diclofenac, lincomycin, losartan and valsartan, among others, together with several metabolites. As a consequence of that work, future monitoring, based on quantitative analyses, was recommended to focus on those compounds found in the screening.

In this work, we have performed a quantitative analysis, based on LC-MS/MS with triple quadrupole, for selected pharmaceuticals in Colombian wastewater. Raw wastewater samples from the Hospital of Tumaco (Nariño), as well as from the city of Florencia (Caquetá), which are currently discharged directly in two rich biodiversity regions in Colombia (the Pacific and Amazonian regions), were analysed. In addition, influent and effluent wastewater samples collected during one week in the cities of Bogotá and Medellin (department of Antioquia) were also analysed. The aim of this work was 1) to estimate the removal efficiency of WWTPs from analysis of IWW and EWW; 2) to have better knowledge on the compounds present in effluent wastewater that potentially reaches the surface waters receiving discharges from WWTPs; 3) to allow the design of complementary treatments, such as the advanced oxidation processes, that we are investigating at present for the efficient removal of the pharmaceuticals most commonly found in wastewater.

2. Experimental

2.1. Characteristics of the wastewater treatment plants and studied areas

The analysed samples were collected in two of the main cities of Colombia (Bogota D.C. and Medellin, department of Antioquia), in the young city located in southeast Colombia (Florencia – Caquetá) and in one coastal pacific city (Tumaco). In the case of Bogotá and the department of Antioquia, a total of 28 samples were taken from the wastewater treatment plants (WWTP). The samples included influent wastewater (IWW) and effluent wastewater (EWW). In the case of Tumaco, three raw composite samples were analysed in three different campaigns and were collected directly from the local Hospital (San Andrés - Hospital). In Florencia, two composite samples were taken from a municipal wastewater discharge.

The WWTP "Salitre" in Bogotá treats wastewater from approximately 2.5 million inhabitants. It is located in the northwest of Bogotá, and collects water from several districts (Fig. 1). After treatment, the effluent wastewater is discharged in the Bogotá River. The average flow rate of wastewater treated by the WWTP over one year is 4 m^3/s (ca. 350,000 m^3/day), with a removal efficiency of 40% BOD and 60% of suspended solids. The WWTP "Salitre" is strategically located at the entry of the "Juan Amarillo" river in order to catch wastewater from the downtown and northern areas of Bogotá. This WWTP uses assisted chemical treatment (ACT) and includes a bar screen to filter solids and large objects. Fat and grease is also removed before the primary treatment of sewage. Likewise, ACT includes a primary treatment based on the partial removal of suspended solids and organic matter through coagulation, flocculation and sedimentation (http://www.acueducto.com.co/). In the case of Antioquia, the study was carried out using wastewater samples from one WWTP of this department. The average flow rate of wastewater treated by the WWTP over 1 year is 1.8 m^3/s (ca. 150,000 m^3/day), with a removal efficiency of 80% BOD and 85% suspended solids. Due to its location, the WWTP collects wastewater from several schools, universities, hospitals, business offices, shops and clubs, and some industries. This plant has a primary treatment coupled to a stabilization process with sludge (http://www.epm.com.co/).

Tumaco does not have treatment plants for wastewater, so contaminated water (e.g., hospital water) is discharged directly to the surface water sources and to the sea. In the case of Florencia, it does not have any WWTPs and currently has 30 discharges on three rivers (Rio Hacha, Quebrada la Perdiz and Quebrada la Sardina) in the city. Quebrada la Perdiz receives a discharge of 254.31 L/s, which consists of 42.15% of the total wastewater flow of the city. The pollutant load due to domestic, agroindustrial and hospital wastewater is 3150.95 kg/day of BOD and 1418.11 kg/day of SST (SERVAF, 2013). In this way, "Quebrada la Perdiz" is affected by anthropic intervention and has become an aquatic ecosystem with poor water quality not suitable for consumption and recreation, and only after treatment can it be used for agriculture, livestock, flora and fauna (Manrique-Losada and Pelaez-Rodriguez, 2010).

Fig. 1 shows the location of the cities of Tumaco and Florencia and the catchment areas of WWTP "Salitre" – Bogotá and WWTP – Antioquia.

2.2. Sample collection

The influent (IWW) and effluent (EWW) wastewater samples (24-h composite) from Bogotá and Medellín were collected daily over seven consecutive days in 2016. In Bogotá, samples were taken using a volume-proportional sampling mode (every 2500 m^3) approximately every 10 min, starting on Wednesday, March 11th and ending on Tuesday, March 17th (auto-sampler Endress-Hauser). In the case of Antioquia, sample collection was performed using a time proportional sampling mode (every 30 min) starting on Monday, October 17th and ending on Sunday, October 23rd. In Tumaco, daily composite samples

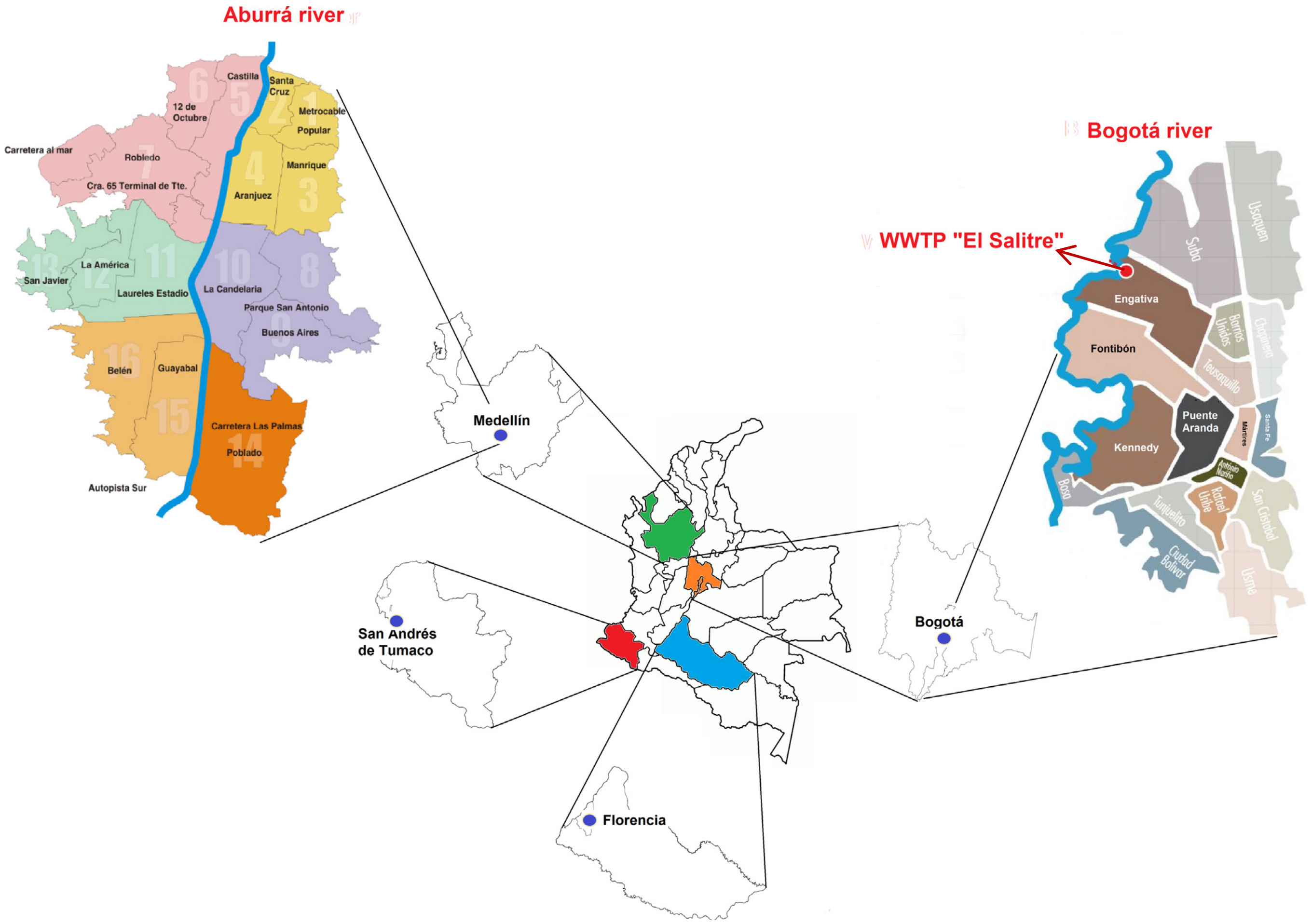

Fig. 1. Location of Tumaco and Florencia cities, and catchment areas of WWTP El Salitre – Bogotá and WWTP – Medellín, Antioquia.

(every 30 min) were collected directly from hospital effluents on three different days: 3rd October 2016, 28th April and 5th July 2017. In all cases, samples were collected in high-density polyethylene bottles and transported to the corresponding laboratories for sample treatment. Upon reception in the laboratory, samples were immediately stored in the dark at −20 °C until filtration. Concentrations of chemical oxygen demand (COD), biological oxygen demand (BOD) and total iron were routinely measured in each sample. In Florencia (Caquetá), the samples were taken from representative effluent located in the Raicero neighbourhood. They were obtained using a volume-proportional sampling mode approximately every 1 h during 24 h on two dates (August 29th and September 30th, 2016) with different weather conditions (rainy and non-rainy day).

2.3. Target compounds

In total, 20 compounds were selected for this study. The target compounds corresponded to: 1 antiepileptic drug, 3 analgesics, 12 antibiotics, 1 antidepressant and 3 antihypertensive drugs.

Table 1 shows the compounds investigated, with the LC-MS/MS conditions and the quality control (QC) recovery values.

2.4. Reagents and chemicals

Pharmaceutical reference standards were acquired from Sigma-Aldrich, LGC Promochem, Toronto Research Chemicals, Across Organics, Bayer Hispania, and Aventis Pharma. All reference standards were of 93% purity or higher.

Individual standard stock solutions were prepared at concentrations between 50 at 500 mg/L. Intermediate solutions of 10 mg/L were prepared by dilution with methanol. Mixed working solutions containing all analytes at the μg/L level were prepared weekly from intermediate solutions by appropriate dilutions with water and were used for preparation of the aqueous standard calibrations and for spiking samples used as quality control.

Isotopically labelled internal standard (ILIS) acetaminophen-d4, diclofenac-d4, valsartan-d8, erythromycin-13C-d3, irbesartan-d6, venlafaxine-d6, carbamazepine 10,11-epoxide-d10 were from CDN Isotopes (Quebec, Canada); sulfamethoxazole-13C6, azithromycin-d3, ciprofloxacin-d8, norfloxacin-d5 and trimethoprim-13C3 were from Cambridge Isotope Laboratories (Andover, MA, USA). Individual ILIS stock solutions between 50 and 500 mg/L were prepared in MeOH. Intermediate mix ILIS between 1 and 0.1 mg/L were prepared by dilution with MeOH. A working mix ILIS solution at 2 μg/L was prepared in MeOH for its use in the analysis of samples. All solutions were stored in amber glass bottles at −20 °C.

HPLC-grade methanol (MeOH), HPLC-grade acetonitrile (ACN), formic acid (HCOOH, content >98%) and ammonium acetate (NH_4AC, reagent grade), were purchased from Scharlab (Barcelona, Spain). HPLC-grade water was obtained from distilled water that was passed through a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.5. Instrumentation

A Waters Acquity UPLC system was interfaced to a triple quadrupole mass spectrometer Xevo TQS (Waters, Milford, MA, USA) equipped with an orthogonal *Z*-spray electrospray ionization interface (ESI) operated in positive mode. Nitrogen (Praxair, Valencia, Spain) was used as a cone gas as well as a desolvation gas at 250 L/h and 1200 L/h, respectively. For operation in MS/MS mode, the collision gas was argon 99.995% (Praxair, Spain) with a pressure of 4 × 10–3 mbar in the collision cell (0.15 mL/min). The capillary voltage was 3.5 kV, source temperature was 150 °C and the desolvation temperature was 650 °C. Cone voltage was selected at 10 V for all compounds. Dwell times were automatically selected in order to obtain enough points per peak and could be decreased down to 3 ms.

Chromatographic separation was performed using an Acquity UPLC BEH C18, 1.7 μm, analytical column, 100 mm × 2.1 mm (Waters). The mobile phase was A = H_2O, B = MeOH, both with 0.01% HCOOH and 1 mM NH_4Ac. The percentage of organic modifier (B) was changed as follows: 0 min, 5%; 7 min, 90%; 8 min, 90%; 8.1 min, 5%; and 10 min, 5%. The flow rate was 0.4 mL/min. The column was kept at 40 °C, and sample manager was maintained at 5 °C. The analysis run time was 10 min.

All data were acquired and processed using Masslynx v 4.1 software (Waters).

2.6. Analytical methodology

The wastewater composite samples were unfrozen and filtered under a vacuum through 0.45-μm membrane filters (mixed cellulose ester, Whatman ME 25) (Whatman, Manchester, UK). Then, aliquots of these samples were collected in centrifuge tubes of 50 mL and

Table 1
Compounds investigated and analytical LC-MS/MS conditions for determination. LOQs and Quality Control data (recovery, %).
All compounds were analysed in ESI positive mode. Q, quantification transition; q1 and q2 confirmation transitions; ILIS, isotope-labelled internal standard; LCL, lowest calibration level.

Compound	Family/Function	Q	q1	Average q1/Q ratio	q2	Average q2/Q ratio	ILIS	QC rec (%) 0.1 μg/L IWW/EWW	QC rec (%) 1 μg/L IWW/EWW	LCL (μg/L)
Acetaminophen (ACET)	Analgesic	152 > 110	152 > 65	0.11	152 > 93	0.17	YES	[a]/[a]	[a]/[a]	0.05
Azithromycin (AZIT)	Antibiotic	749 > 83	749 > 116	0.76	749 > 591	0.39	YES	[a]/[a]	[a]/[a]	0.05
Carbamazepine (CARB)	Antiepileptic	237 > 194	237 > 192	0.24	237 > 179	0.06	YES	88/91	121/87	0.001
Ciprofloxacin (CIPR)	Antibiotic	332 > 314	332 > 231	0.29	332 > 288	0.16	YES	[a]/[a]	98/93	0.05
Clarithromycin (CLAR)	Antibiotic	590 > 158	590 > 116	0.25	590 > 98	0.11		110/107	106/106	0.001
Clindamycin (CLYN)	Antibiotic	425 > 126	425 > 377	0.06	425 > 389	0.02		110/117	105/104	0.001
Cloxacillin (CLOX)	Antibiotic	436 > 160	436 > 277	0.31	436 > 114	0.27		42/51	60/81	0.05
Diclofenac (DICL)	Analgesic	294 > 250	294 > 214	0.05	294 > 178	0.01	YES	105/108	99/99	0.001
Doxycycline (DOXY)	Antibiotic	445 > 428	445 > 154	0.13	445 > 98	0.12		51/53	72/79	0.001
Erythromycin (ERYT)	Antibiotic	734 > 158	734 > 576	0.37	734 > 558	0.03	YES	94/109	83/103	0.001
Irbesartan (IRBE)	Antihypertensive	429 > 207	429 > 195	0.28	429 > 180	0.05	YES	108/104	98/134	0.001
Losartan (LOSA)	Antihypertensive	423 > 207	423 > 405	2.1	423 > 377	0.70		[a]/[a]	67/91	0.001
Metronidazole (METR)	Antibiotic	172 > 128	172 > 82	0.49	172 > 56	0.06		80/88	71/82	0.01
Naproxen (NAPR)	Analgesic	185 > 169						[a]/[a]	96/70	0.001
Norfloxacin (NORF)	Antibiotic	320 > 302	320 > 276	0.16	320 > 281	0.10	YES	[a]/83	75/91	0.05
Sulfamethoxazole (SULF)	Antibiotic	254 > 92	254 > 156	1.58	254 > 108	0.93	YES	[a]/101	124/108	0.001
Tetracycline (TETR)	Antibiotic	445 > 410	445 > 154	0.81	445 > 425	0.71		56/61	92/81	0.001
Trimethoprim (TRIM)	Antibiotic	291 > 123	291 > 230	1.14	291 > 261	0.70	YES	108/125	58/71	0.001
Valsartan (VALS)	Antihypertensive	436 > 207	436 > 235	1.04	436 > 261	0.009	YES	[a]/[a]	87/105	0.001
Venlafaxine (VENL)	Antidepressant	278 > 58	278 > 260	0.62	278 > 121	0.33	YES	101/102	86/104	0.001

[a] Recovery could not be calculated due to the presence of the analyte in the “blank” samples used for preparation of the QC at concentration above that the fortification level.

transported in cool containers to Spain, within a maximum period of 24 h. Once in the laboratory, they were frozen at ≤−18 °C. Water samples were thawed at room temperature the same day of the analysis; an aliquot was transferred to a 2-mL Eppendorf and centrifuged at 12,000 rpm for 3 min. The procedure applied for sample analysis was based on our previous work, where direct injection of the samples, without any pre-concentration step (e.g., SPE), was used. This was possible thanks to the excellent sensitivity of the LC-MS/MS instrument (Boix et al., 2015). In the present work, we included a simple dilution ×5 with Milli-Q water in order to reduce the matrix complexity; a 200 μL-aliquot of wastewater sample was taken and then 750 μL Milli-Q water and 50 μL of a mix ILIS solution (2 μg/L) were added (final ILIS concentration in the samples injected was 0.1 μg/L). Finally, 100 μL of the diluted sample was directly injected into the UHPLC-MS/MS system.

Quality control (QCs) samples consisted of IWW and EWW from Bogota (day 7), spiked with the target pharmaceuticals at 0.1 and 1 μg/L. To this aim, 650 μL of Milli-Q water were taken, and 200 μL of a sample, 100 μL of the mix standard solution (1 or 10 μg/L) and 50 μL of the mix ILIS (2 μg/L) were added.

Quantification of analytes was made using the quantification transition (Q) and external calibration with standards in solvent. In those cases in which the analyte ILIS was available (12 out of 20 compounds analysed), relative areas were used for quantification. In this way, potential matrix effects were corrected, as shown by the acceptable QC recoveries obtained.

The reliable identification of compounds in the samples was carried out by calculating the ion ratios (peak area) between the quantification (Q) and confirmation (q_1 and q_2) transitions. To this aim, three MS/MS transitions were acquired, and two intensity ion-ratios were available for confirmation of the identity (q1/Q and q2/Q). The finding was considered positive when at least one experimental ion ratio and the retention time of the compound in the sample were within the tolerance ranges (±30% for ion ratio, ±0.1 min for retention time) in comparison with the reference standards injected in the calibration (SANTE, 2015).

3. Results and discussion

3.1. Selection of target compounds

A total of 28 compounds were initially selected on the basis of the following information: 1) previous findings in a wide-scope screening performed in wastewater from Bogotá (Hernández et al., 2015a); 2) our previous experience on the determination of pharmaceuticals in effluent wastewater by direct injection of the sample (Boix et al., 2015); and 3) information on the consumption of pharmaceuticals in Colombia (Conpes, 2015; INAS, 2014; Jaramillo et al., 2005; Machado and Moncada, 2012; Mendoza-Ruiz et al., 2017; ODC, 2013;)

The selected compounds corresponded to pharmaceuticals from different therapeutic classes. Twelve of these compounds had been previously found by QTOF MS screening in effluent wastewater and surface water from Bogotá (Hernández et al., 2015a), and 11 compounds were previously tested in different water types with satisfactory analytical figures using direct injection of the samples (Boix et al., 2015). Altogether, there were 14 compounds: 9 were included in both lists, 3 were only in the screening list (Hernández et al., 2015a), and 2 were only in the second list (Boix et al., 2015). In addition, 14 more compounds were added to the target list of the present work based on the consumption data, making a total of 28 selected analytes.

The results obtained for the QCs were not satisfactory for 8 out of the 28 compounds. Some of these 8 compounds could be detected in the samples, but no quantitative data are reported in this paper due to the low recoveries of the QCs. In other cases, the low sensitivity did not allow the targets to be quantified at the concentrations present in the samples, or the method was not robust and/or reproducible. Some examples are ceftriaxone, amoxicillin and meropenem, which were identified in several samples, but could not be quantified. The 8 compounds eventually discarded due to the non-reliability of the data were: amoxicillin, ampicillin, cefotaxime, ceftriaxone, imipenem, meropenem, oxacillin and oxytetracycline.

In summary, considering the QC values, in this work we report data for the remaining 20 compounds. QCs were prepared and analysed for all of them using the "blank" samples under study, which were spiked at 0.1 and 1 μg/L. ILIS were available for 12 of the compounds selected.

3.2. Pharmaceuticals in urban wastewater

A total of 28 wastewater 24-h composite samples were collected from the WWTPs serving Bogotá (14 samples) and Medellín (14 samples). The 14 samples collected at each WWTP corresponded to 7 influent wastewater (IWW) and 7 effluent wastewater (EWW) samples, collected during one whole week. Analyses of IWW and EWW allowed us to roughly estimate the removal efficiency in the WWTP, comparing the concentrations found in the IWW with those obtained in the EWW. Although some compounds (particularly those of low polarity) can be sorbed to the solid particles, and consequently can remain in the sludge, the comparison between IWW and EWW is commonly used for an assessment of the efficiency of the WWTP to remove emerging contaminants (Gracia-Lor et al., 2012a; Bijlsma et al., 2014).

Table 2 shows the daily concentrations of the pharmaceuticals and average weekly concentrations in IWW from Bogota and Antioquia, while Table 3 shows the data obtained for the EWW. It can be seen that all compounds investigated were present in both IWW and EWW, with the exception of tetracycline in some samples, illustrating the wide presence of pharmaceuticals in wastewaters, even after treatment in the WWTPs. In general, the IWW samples from Bogotá contained higher drugs levels than those from Antioquia, with the highest concentrations being found for the widely used analgesic acetaminophen (39.2 and 9.2 μg/L for Bogotá and Antioquia) and the antibiotic azithromycin (6.3 and 5.8 μg/L for Bogotá and Antioquia). Acetaminophen is widely consumed in Colombia due to factors such as the pressure of the pharmaceutical industry, the ease of taking these medications when a pain arises due to it being sold without a prescription, and the lack of knowledge about the implications of its high consumption (Conpes, 2012; Jaramillo et al., 2005). The database (IMS) of the private national pharmaceutical market shows that between April 2010 and April 2011, the country bought USD $ 10,850 in paracetamol, which was higher than the budget for ibuprofen (USD $ 8500) and acetylsalicylic acid (USD $ 4300) (Vásquez Velásquez et al., 2010). Apart from these two major compounds, other pharmaceuticals were found at levels above 1 μg/L in the IWW, such as the antibiotics norfloxacin and ciprofloxacin, the antihypertensives losartan and valsartan, and the analgesic naproxen in the Bogotá samples. However, none of these drugs exceeded an average concentration of 1 μg/L in Antioquia.

All compounds detected in the influent samples were also present in treated EWW, which illustrates the poor removal efficiency of the WWTPs. Similarly to the IWW, the major compounds in treated wastewater were acetaminophen and azithromycin, although the former was found at low levels in the Antioquia samples. Losartan, valsartan and naproxen were at concentrations commonly above 1 μg/L (Table 3).

Daily concentrations for both IWW and EWW were rather consistent throughout the whole week, showing similar consumption patterns of pharmaceuticals, without a significant increase on the weekend. This steady behaviour differs from that of illicit drugs of abuse, which sees concentrations commonly increase on the weekend (Thomas et al., 2012; Bijlsma et al., 2014, 2016). Particularly in Bogotá, the daily levels were quite constant for each compound throughout the week, which is illustrated by coefficients of variation (CV) that were usually below 30%, with a few exceptions (e.g., valsartan). In the samples from Antioquia, the concentrations throughout the week showed the same trend as in Bogotá. Although CVs were higher in Antioquia, this was more due to

Table 2
Pharmaceuticals in 24-h influent wastewater samples collected along one week.

Compound	IWW 1	IWW 2	IWW 3	IWW 4	IWW 5	IWW 6	IWW 7	Average	CV (%)
Bogotá IWW (conc. in µg/L)									
Acetaminophen	38.5	45.7	44.2	36.7	34.1	29.1	46.6	**39.25**	**17**
Azithromycin	6.41	6.13	5.92	6.81	6.37	6.27	6.31	**6.32**	**4**
Carbamazepine	0.073	0.073	0.085	0.060	0.046	0.043	0.082	**0.07**	**25**
Ciprofloxacin	3.35	2.74	2.56	2.09	2.14	1.49	1.69	**2.29**	**28**
Clarithromycin	0.432	0.313	0.393	0.268	0.242	0.212	0.377	**0.32**	**26**
Clindamycin	0.031	0.025	0.023	0.018	0.016	0.013	0.024	**0.02**	**28**
Diclofenac	0.368	0.437	0.717	0.289	0.245	0.331	0.427	**0.40**	**39**
Doxycycline	0.159	0.157	0.136	0.110	0.082	0.092	0.093	**0.12**	**27**
Erythromycin	0.039	0.050	0.051	0.036	0.027	0.032	0.056	**0.04**	**26**
Irbesartan	0.184	0.499	0.140	0.105	0.071	0.110	0.121	**0.18**	**83**
Losartan	2.89	2.41	2.44	1.90	1.36	1.50	2.73	**2.18**	**27**
Metronidazole	0.385	0.363	0.327	0.264	0.264	0.186	0.378	**0.31**	**24**
Naproxen	3.72	3.32	3.28	2.85	2.41	2.21	3.07	**2.98**	**18**
Norfloxacin	2.01	1.53	1.58	1.28	1.13	1.07	0.983	**1.37**	**26**
Sulfamethoxazole	0.729	0.704	0.827	0.609	0.442	0.439	0.662	**0.63**	**23**
Tetracycline	–	0.383	0.341	–	0.276	–	–	**0.33**	**16**
Trimethoprim	0.432	0.315	0.341	0.375	0.241	0.211	0.345	**0.32**	**24**
Valsartan	5.09	1.50	1.33	0.853	0.757	0.702	1.11	**1.62**	**96**
Venlafaxine	0.038	0.034	0.034	0.030	0.030	0.032	0.032	**0.03**	**9**
Medellin IWW (conc. in µg/L)									
Acetaminophen	5.37	11.6	4.65	5.85	1.39	8.20	27.2	**9.19**	**93**
Azithromycin	5.68	5.68	6.21	6.15	5.82	6.07	5.24	**5.84**	**6**
Carbamazepine	0.095	0.041	0.026	0.069	0.451	0.161	0.226	**0.153**	**98**
Ciprofloxacin	1.37	1.04	0.921	0.827	0.898	0.766	1.03	**0.980**	**20**
Clarithromycin	0.238	0.136	0.103	0.123	0.076	0.143	0.172	**0.141**	**37**
Clindamycin	0.009	0.005	0.004	0.003	0.003	0.008	0.007	**0.006**	**45**
Diclofenac	0.556	0.212	0.205	0.081	0.128	0.214	0.256	**0.236**	**65**
Doxycycline	0.159	0.111	0.089	0.095	0.063	0.067	0.075	**0.094**	**35**
Erythromycin	0.056	0.033	0.025	0.020	0.016	0.035	0.028	**0.030**	**44**
Irbesartan	0.045	0.027	0.006	0.012	–	0.032	0.048	**0.028**	**60**
Losartan	1.45	0.941	0.543	0.664	0.434	0.789	0.975	**0.828**	**41**
Metronidazole	0.232	0.267	0.096	0.156	0.072	0.184	0.346	**0.193**	**50**
Naproxen	1.08	1.32	0.735	0.622	0.519	0.847	1.31	**0.919**	**35**
Norfloxacin	1.15	0.799	0.729	0.633	0.714	0.715	0.898	**0.806**	**22**
Sulfamethoxazole	0.441	0.558	0.227	0.203	0.123	0.160	0.379	**0.299**	**54**
Tetracycline	–	–	–	–	–	–	–	–	–
Trimethoprim	0.125	0.110	0.078	0.026	0.013	0.065	0.108	**0.075**	**57**
Valsartan	0.179	0.164	0.062	0.111	0.049	0.114	0.220	**0.128**	**49**
Venlafaxine	0.074	0.052	0.039	0.044	0.052	0.057	0.072	**0.056**	**23**

Average concentration for the seven days (EWW1-EWW7). CV is the variation coefficient in percentage.

the low concentrations present than to the very different concentration levels (see Tables 2 and 3).

In addition to the samples from Bogotá and Antioquia, two samples of raw wastewater were collected from the city of Florencia, Caquetá Province (August and September 2016). The aim was to confirm the presence of the compounds under study in these samples that are directly discharged to the river La Perdiz. The results of analyses (Supporting information, Table S1) revealed high concentrations of acetaminophen (12 and 15 µg/L) and the antibiotic azithromycin (6.5 and 7.0 µg/L) as the major compounds in these samples. All the remaining target compounds were also found, with the exceptions of clindamycin, doxycycline, tetracycline and irbesartan, supporting the wide consumption of most of the compounds investigated in this work.

The data obtained in this work are in general agreement with other papers that have reported the presence of pharmaceuticals in influent and effluent wastewater around the world (Alder et al., 2010; Alidina et al., 2014; Anumol and Snyder, 2015; Campanha et al., 2015; Carmona et al., 2014; Ghoshdastidar et al., 2015; Gracia-Lor et al., 2012a; Gros et al., 2010; Jelic et al., 2011; Lacey et al., 2008; Liu and Wong, 2013; van Nuijs et al., 2015; Wu et al., 2015), although concentrations of acetaminophen and the antibiotic azithromycin in the samples from Colombia seem slightly higher, revealing the high consumption of these compounds in this country.

3.3. Removal efficiency in WWTPs

Removal efficiencies (RE) were estimated by comparing effluent concentrations (C_{EWW}) from day (x + 1) with influent concentrations (C_{IWW}) from day (x), considering a residence time of 24 h (Bijlsma et al., 2014). RE were calculated as:

$$RE(\%) = \left(1 - \frac{C_{EWW}\ (x+1)}{C_{IWW}(x)}\right) \times 100$$

In this way, daily RE were calculated, as well as the average RE for the whole week, estimated from the daily values. Using this approach, the lower levels commonly found in effluents are assumed to be the result of removal in the WWTP, due to microbial degradation, or other transformation processes (Gracia-Lor et al., 2012a). However, the analysis of suspended particulate matter (SPM) has also been suggested to prevent under-reporting. The analysis of both aqueous phase (influent and effluent) and SPM would surely provide a better estimation of the removal and environmental impact of compounds by WWTPs, since removal from wastewater does not necessarily imply degradation (Baker et al., 2012; Baker and Kasprzyk-Hordern, 2013). Some micropollutants can be notably sorbed to SPM, especially those of low polarity, and thus, even good removal rates obtained in the aqueous phase (i.e., comparison of influent and effluent wastewater concentrations)

Table 3
Pharmaceuticals in 24-h effluent wastewater samples collected along one week.

Compound	EWW 1	EWW 2	EWW 3	EWW 4	EWW 5	EWW 6	EWW 7	Average	CV (%)
Bogotá EWW (conc. in μg/L)									
Acetaminophen	35.1	32.8	30.7	32.7	27.5	19.5	29.2	**29.66**	**17**
Azithromycin	4.12	3.95	4.09	4.66	3.55	3.68	3.91	**3.99**	**9**
Carbamazepine	0.078	0.068	0.071	0.067	0.058	0.041	0.069	**0.065**	**19**
Ciprofloxacin	1.07	0.822	0.824	0.766	0.839	0.677	0.668	**0.81**	**17**
Clarithromycin	0.402	0.299	0.271	0.284	0.257	0.216	0.406	**0.31**	**24**
Clindamycin	0.032	0.021	0.014	0.016	0.014	0.009	0.020	**0.018**	**40**
Diclofenac	0.446	0.312	0.332	0.338	0.296	0.225	0.415	**0.34**	**22**
Doxycycline	0.079	0.075	0.062	0.064	0.063	0.059	0.058	**0.066**	**12**
Erythromycin	0.050	0.046	0.036	0.043	0.041	0.031	0.062	**0.044**	**23**
Irbesartan	0.172	0.663	0.167	0.110	0.091	0.077	0.100	**0.20**	**106**
Losartan	2.76	2.14	2.05	1.92	1.66	1.27	2.01	**1.97**	**23**
Metronidazole	0.450	0.372	0.293	0.308	0.297	0.187	0.358	**0.32**	**25**
Naproxen	2.81	3.16	2.42	2.38	2.02	1.69	2.33	**2.40**	**20**
Norfloxacin	0.606	0.453	0.482	0.430	0.504	0.394	0.417	**0.47**	**15**
Sulfamethoxazole	0.831	0.767	0.640	0.680	0.542	0.446	0.624	**0.65**	**20**
Tetracycline	0.126	0.107	0.167	0.106	0.090	0.079	0.090	**0.11**	**27**
Trimethoprim	0.417	0.328	0.456	0.358	0.318	0.168	0.315	**0.34**	**27**
Valsartan	1.42	1.65	0.963	0.894	0.900	0.619	0.889	**1.05**	**34**
Venlafaxine	0.019	0.015	0.012	0.013	0.011	0.011	0.013	**0.014**	**22**
Medellin EWW (conc. μg/L)									
Acetaminophen	0.025	0.058	0.134	0.072	0.410	0.165	0.249	**0.16**	**84**
Azithromycin	4.57	4.10	4.00	3.02	4.08	3.80	3.57	**3.88**	**13**
Carbamazepine	0.102	0.033	0.049	0.054	0.342	0.212	0.179	**0.14**	**81**
Ciprofloxacin	0.654	0.446	0.579	0.758	0.685	0.692	0.526	**0.62**	**17**
Clarithromycin	0.165	0.082	0.117	0.089	0.060	0.078	0.081	**0.096**	**36**
Clindamycin	0.010		0.003	0.004		0.003	0.006	**0.004**	**87**
Diclofenac	0.359	0.127	0.131	0.149	0.111	0.134	0.152	**0.17**	**52**
Doxycycline	0.133	0.086	0.062	0.076	0.069	0.064	0.060	**0.078**	**33**
Erythromycin	0.050	0.021	0.029	0.027	0.021	0.020	0.024	**0.028**	**38**
Irbesartan	0.041	0.006	0.028	0.040	0.006	0.016	0.040	**0.025**	**62**
Losartan	1.41	0.820	1.08	1.15	0.761	0.848	0.945	**1.00**	**23**
Metronidazole	0.381	0.187	0.301	0.315	0.164	0.205	0.272	**0.26**	**30**
Naproxen	0.480	0.502	0.653	0.540	0.477	0.432	0.459	**0.51**	**14**
Norfloxacin	0.529	0.350	0.499	0.540	0.503	0.515	0.429	**0.48**	**14**
Sulfamethoxazole	0.348	0.279	0.358	0.434	0.311	0.348	0.357	**0.35**	**14**
Tetracycline	0.231	0.095	0.185	0.152	0.084	0.079	0.104	**0.13**	**44**
Trimethoprim	0.155	0.051	0.090	0.119	0.066	0.065	0.089	**0.091**	**40**
Valsartan	0.086	0.044	0.085	0.089	0.051	0.049	0.056	**0.066**	**30**
Venlafaxine	0.049	0.021	0.034	0.040	0.030	0.032	0.039	**0.035**	**26**

Average concentration for the seven days (EWW1-EWW7). CV is the variation coefficient in percentage.

might not imply degradation to the same extent (Jelic et al., 2011). In the particular case of pharmaceuticals studied in the present work, it is expected that poor sorption on SPM is due to the medium-high polar nature of most of the selected compounds.

The results obtained in this paper for average removal efficiencies are shown in Fig. 2. Most of the compounds were partially removed (Fig. 2, left), while five drugs were not removed and/or their concentrations in EWW were even higher than in IWW, leading to a negative RE.

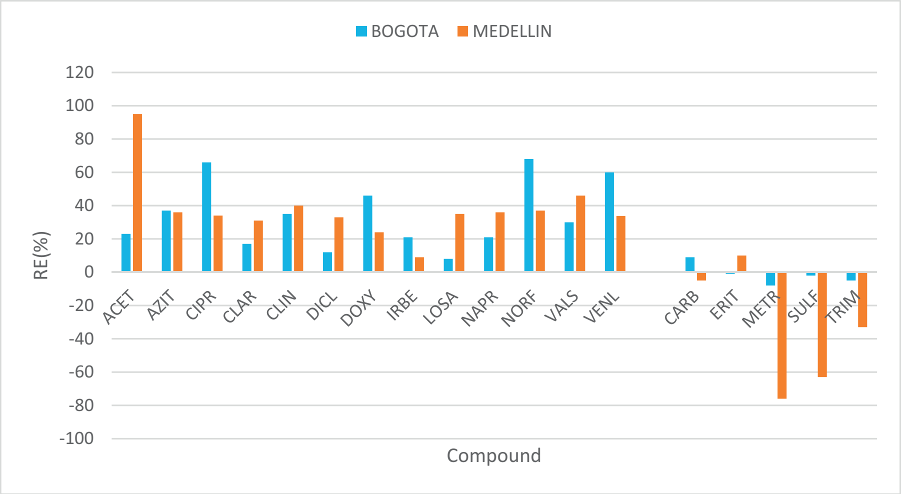

Fig. 2. Estimated removal efficiency of pharmaceuticals in the WWTPs of Bogotá and Medellin. Average values for one week.

The latter was only observed for 3 compounds, all being antibiotics (metronidazole, sulfamethoxazole, trimethoprim) (Fig. 2, right). This is in agreement with previous studies where some compounds were reported to be more abundant in effluents than in influents (Lacey et al., 2008; Gros et al., 2010; Jelic et al., 2011; Gracia-Lor et al., 2012a). The higher complexity of the influents leads to strong matrix effects (commonly ionization suppression), which would lead to reporting lower concentrations if the correction for the matrix effects is not fully satisfactory. In addition, the enzymatic cleavage of the compound glucuronides and other conjugated metabolites and the subsequent release of the parent compound during the treatment process might also lead to higher levels in the effluent samples (Vieno et al., 2007; Lacey et al., 2008; Gros et al., 2010).

In general, the results for the two WWTPs were rather coherent, showing similar trends in the RE, although acetaminophen seemed to be almost completely removed in the Medellin WWTP (RE, 95%) and just partially removed in Bogotá (RE, 23%). This difference might be due to the treatment applied in these plants: only physico-chemical processes in Bogotá, and physico-chemical plus biological processes were applied in Medellin (see Experimental section). The data obtained in this paper in relation to RE are consistent with previous works, which reported that the majority of emerging contaminants were partially or not removed in WWTPs (Gros et al., 2010; Heberer, 2002; Jelic et al., 2011; Gracia-Lor et al., 2012a; Bijlsma et al., 2014).

3.4. Pharmaceuticals in raw hospital wastewater

The analysis of raw wastewater from the Hospital San Andrés in Tumaco revealed the presence of high concentrations of several pharmaceuticals (Table 4). In total, 3 composite samples were analysed in three different campaigns (see "Experimental"). The results showed a high variability in concentrations, which might be explained by the different treatments applied to patients during the days of sampling. With the exception of acetaminophen, the highest levels were generally found for antibiotics, specifically azithromycin, ciprofloxacin, clarithromycin, clindamycin and norfloxacin, with concentrations above 10 μg/L in several samples. This is of particular concern due to the negative effects that antibiotics may have on ecosystems, even leading to bacterial resistance (Boxall et al., 2012; Marti et al., 2013; Marti et al., 2014). Ceftriaxone, amoxicillin and meropenem were also detected in some raw samples from Tumaco hospital, but no quantification was made due to the problems observed in the QC samples.

Table 4
Concentrations of pharmaceuticals (μg/L) in raw wastewater samples from the hospital of Tumaco, Nariño.

Compound	Raw hospital wastewater 3-Oct-16	Raw hospital wastewater 28-April-2017	Raw hospital wastewater 5-July-2017
Acetaminophen	50.9	78.1	10.8
Azithromycin	6.93	d	26.1
Carbamazepine	1.39	–	0.07
Ciprofloxacin	5.56	14.9	20.2
Clarithromycin	11.8	0.11	26.8
Clindamycin	8.34	17.5	24.1
Diclofenac	3.04	1.08	1.72
Doxycycline	–	–	–
Erythromycin	1.85	–	0.31
Irbesartan	1.41	0.24	0.03
Losartan	1.19	4.79	7.65
Metronidazole	3.54	2.40	n.c.
Naproxen	5.74	2.66	n.c.
Norfloxacin	0.853	1.34	10.1
Sulfamethoxazole	0.415	1.30	d
Tetracycline	–	–	–
Trimethoprim	1.71	0.93	0.06
Valsartan	1.93	0.04	2.34
Venlafaxine	0.018	0.07	d

n.c. not confirmed, the identity could not be confirmed by q/Q ratio agreement.
d: detected, concentration below LCL.

3.5. Quality control data

In this work, special emphasis was made on the quality of analysis. To ensure the reliability of the data reported, several quality control samples (QCs) were included in every sample sequence. QCs consisted of IWW or EWW samples spiked at two concentrations, 0.1 and 1 μg/L. They were prepared randomly by selecting one of the "blank" wastewater samples analysed within the batch and were analysed following the same analytical procedure as the samples. When the sample used for QC preparation contained any of the compounds under study, the concentration calculated in that "blank" sample was subtracted from that calculated in the spiked sample. Percentage recoveries for QCs were calculated, and a tolerance range between 60 and 140% was applied to consider recovery as acceptable for individual recoveries, similarly to other analytical fields, such as pesticide residue analyses (SANTE, 2015). When the concentration in the "blank" sample was similar or even higher than the QC, the calculation was subjected to high error, and the recovery could not be reported. In addition to the analysis of QCs, the calibration curve was injected twice, at the beginning and the end of the sample batch.

The confirmation of positive findings was carried out by evaluating q1/Q and q2/Q ion ratios and the retention time of the compound in the sample in comparison with the reference standard (for more details see "Analytical Methodology").

The results obtained for the analysis of QCs are summarized in Table 1. Most QC recoveries were satisfactory, in both IWW and EWW, with the wide majority within the range 70–120% at the 0.1 and 1 μg/L levels. The fact that up to 12 ILIS were used for 20 target analytes was undoubtedly of help in order to get satisfactory quantification for most of the compounds. It is well-known that the use of analyte-labelled internal standards is one of the best ways to correct matrix effects in this type of complex sample.

In contrast, analyte-ILIS was not available at our laboratory for 8 out of 20 pharmaceuticals, which might compromise their quantification. However, acceptable recoveries were obtained for three of them (clarithromycin, clindamycin, metronidazole), as shown in Table 1. Another four compounds (cloxacillin, doxycycline, losartan, tetracycline) presented recoveries at approximately or slightly below 60%, revealing ionization suppression. The matrix effect for these four compounds was more marked in IWW, as illustrated by the lower recoveries in comparison with EWW. A special case was naproxen, for which only one transition was available, compromising its reliable identification in samples. This compound was considered as tentatively identified, and would need additional analysis for unequivocal confirmation.

QC recoveries could not be calculated for two compounds at any of the two levels tested, due to the high analyte concentration in the "blank" sample used for QC preparation (sample 7 from Bogotá). This was the case for acetaminophen (47 μg/L IWW; 27 μg/L EWW) and azithromycin (6.3 μg/L IWW; 4.0 μg/L EWW). Similarly, for some other compounds, QCs could not be calculated at the lowest level tested due to the presence of the analyte at concentrations notably higher than 0.1 μg/L (Table 1).

In the light of our data, it can be concluded that direct injection of 5-fold diluted wastewater samples helps to lowering matrix effects and is a satisfactory approach for most analytes in wastewater samples. This is interesting, since our strategy is the opposite to the most widely applied based on pre-concentration of samples by SPE. The excellent sensitivity of modern LC-MS/MS instruments allows the use of this approach, making sample treatment by SPE unnecessary. It is clear that SPE leads to the pre-concentration of analytes, but not necessarily to a minimization of matrix effects. In our opinion, SPE does not always eliminate or minimize matrix effects, as only those matrix components co-eluting with the analytes would be able to produce ionization suppression or ionization enhancement, and therefore, they might not easily be removed by SPE. With the direct injection of 5-fold diluted samples, it was possible to determine the pharmaceuticals under study in a reliable way, supporting the usefulness of the approach selected for quantification of frequently consumed drugs. Surely, after SPE it would have been possible to determine lower concentrations, which would have been of help in order to quantify less consumed pharmaceuticals, with the drawback, however, of more sample manipulation and potential losses in the SPE step.

As an illustrative example, Fig. 3 shows selected chromatograms for several compounds identified in IWW and EWW, including the 3 transitions acquired and the q/Q ion ratios.

3.6. Selection of target compounds for future degradation studies

In the light of data reported in this work, we selected some model compounds to evaluate the feasibility of complementary degradation studies in the near future. We considered those compounds present at higher concentrations in EWW as well as those that were less removed by conventional treatments plants (i.e., with lowest elimination percentages).

The highest amounts discharged in the effluents of WWTP "Salitre"-Bogotá (Table 3) corresponded to: a) analgesics: acetaminophen and naproxen, with average concentrations of approximately 30 and 2.5 μg/L, respectively; b) antihypertensives: valsartan and losartan, with concentrations between 1.0 and 2.0 μg/L; and c) antibiotics: azithromycin (4.0 μg/L), and ciprofloxacin, clarithromycin, norfloxacin and sulfamethoxazole, the last four in the range of 0.3 to 0.8 μg/L. In the effluents of Antioquia (Table 3), the antibiotic azithromycin and the antihypertensive losartan, with average concentrations of 3.9 and 1.0 μg/L, respectively, were the compounds present at the highest concentrations; the antibiotics ciprofloxacin, norfloxacin and sulfamethoxazole were also found at concentrations similar to the EWW from Bogotá (0.6, 0.5 and 0.4 μg/L, respectively). The results of hospital raw wastewater showed that the antibiotics azithromycin, clindamycin and ciprofloxacin were in all samples at concentrations above 5 μg/L, and in some cases, reached values higher than 20 μg/L.

In relation to the elimination percentages, we found that none of the 20 compounds tested was completely removed by the treatment plants (Fig. 2), even when biological treatment was applied, as in the WWTP of Antioquia. Losartan, valsartan and irbesartan were among the most difficult compounds for WWTP to eliminate, and no removal was observed for carbamazepine, erythromycin, metronidazole, sulfamethoxazole

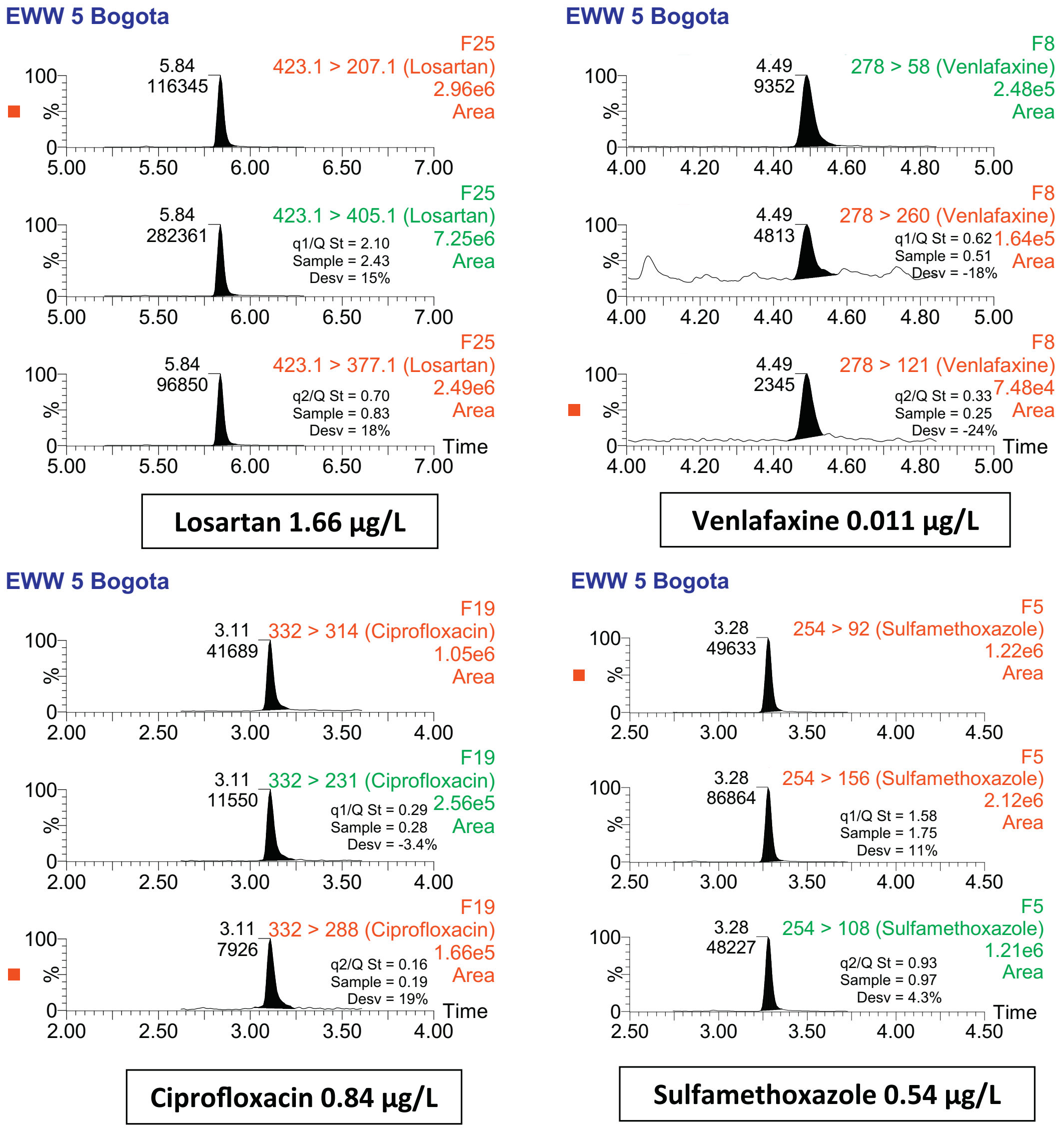

Fig. 3. LC-MS/MS chromatograms of positive effluent (EWW 5 from Bogota) and influent (IWW 6 from Medellin) samples. Ion ratios q1/Q and q2/Q are shown (deviations tolerance ± 30%).

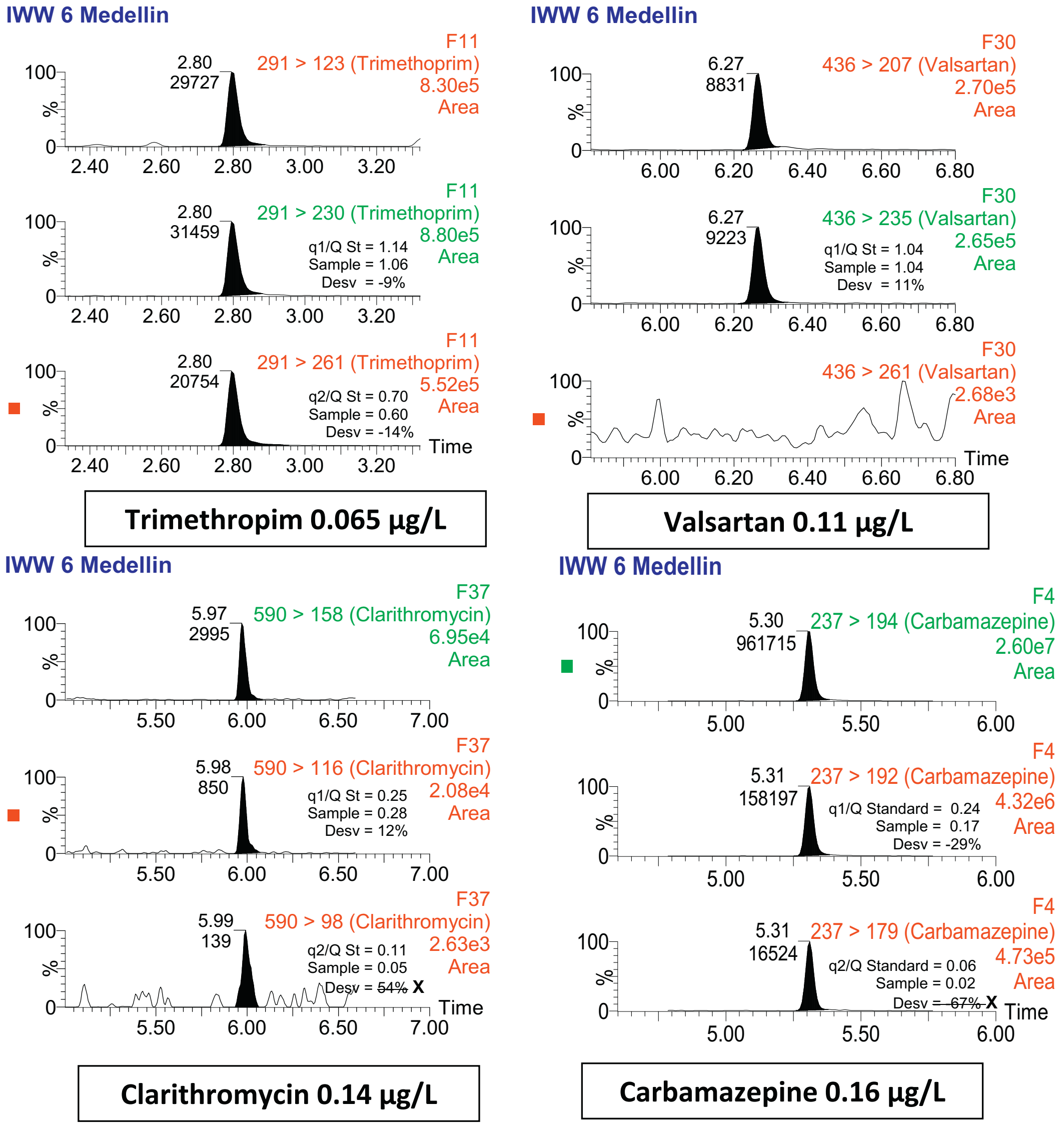

Fig. 3 (*continued*).

and trimethoprim. These results confirm that additional tertiary treatments are required for the elimination of pharmaceuticals. Some studies have shown similar results, where despite having activated sludge treatments in the WWTP, these were not sufficient for the complete elimination of emerging contaminants (de la Cruz et al., 2012). Advanced oxidation processes (AOP) have been shown to be suitable for the degradation of some of these compounds at the laboratory and pilot scales (Liu et al., 2013; Padilla-Robles et al., 2015). As illustrative examples, AOP have been applied to acetaminophen (de Luna et al., 2012), ciprofloxacin (An et al., 2010), norfloxacin (Jojoa-Sierra et al., 2017), carbamazepine, (Komtchou et al., 2015), and penicillin antibiotics (Serna-Galvis et al., 2016).

Our current research is focused on the optimization of AOPs using processes such as electro-Fenton, photo-electro-Fenton and ultrasounds, applied to real-world wastewater matrices, where pharmaceuticals are present at ppb levels and competition may occur between the degradation of organic matter and microorganisms. The data obtained in the present work reveal that most studied compounds are present in influent and effluent wastewater, with poor removal efficiency of WWTPs. Thus, the elimination of pharmaceuticals in wastewater seems a general need and is not limited to only a few compounds. Therefore, the vast majority of compounds studied in the present work are being evaluated in AOP processes applied to wastewater samples, as well as under laboratory controlled conditions. The final objective is to seek more sustainable wastewater management, safeguarding the aquatic environment by minimizing harmful impacts, and fulfilling future legal requirements that will surely be stricter in terms of the maximum pharmaceutical concentrations allowed in water.

4. Conclusions

In this work, the presence of pharmaceuticals, particularly antibiotics such as azithromycin, ciprofloxacin, norfloxacin, has been detected in different types of wastewater from Colombia. Raw wastewater from the cities of Bogotá, Medellín and Florencia contained levels of several pharmaceuticals above 1 μg/L. After treatment in the WWTPs, most of the compounds were not completely removed, still remaining at significant concentrations in the effluents. Raw hospital wastewater was also analysed from the city of Tumaco. As expected, the concentrations for several compounds, usually antibiotics (e.g., azithromycin, ciprofloxacin, norfloxacin, erythromycin and clindamycin), were commonly above 5 μg/L, higher than those found in urban wastewater. The fact that raw wastewater is sometimes directly discharged to surface waters (the case of Florencia and Tumaco), and the presence of most pharmaceuticals investigated in the treated wastewater (Bogotá and Medellín), may suppose a risk for the aquatic environment, provoking bacterial resistance, among other effects. Therefore, there is an urgent need to implement efficient treatments that are able to remove pharmaceuticals in wastewater. Our current research is directed towards the degradation of pharmaceuticals, selected in the light of data reported in this paper, using advanced oxidation systems, such as photo-Fenton, electro-Fenton, photo-electro-Fenton or ultrasonic cavitation, which have demonstrated high removal percentages at the laboratory scale and under controlled conditions.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.06.088.

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Artículo 2:

Photo-electro-Fenton process applied to the degradation of valsartan: effect of parameters, identification of routes and combination with a biological system

Photo-electro-Fenton process applied to the degradation of valsartan: effect of parameters, identification of routes and combination with a biological system

Diana Martínez-Pachón[a]; María Ibáñez[b], Félix Hernández[b], Ricardo A. Torres-Palma[c]*; Alejandro Moncayo-Lasso[a]*

[a] Grupo de Investigación en Ciencias Biológicas y Químicas, Facultad de Ciencias, Universidad Antonio Nariño, Bogotá, Carrera 3 Este # 47 A – 15. Bogotá D.C., Colombia.
[b] Research Institute for Pesticides and Water (IUPA), University Jaume I, Castellón, Spain.
[c] Grupo de Investigación en Remediación Ambiental y Biocatálisis (GIRAB), Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia.

*Co-authors for corresponding
Alejandro Moncayo-Lasso (e-mail: amoncayo@uan.edu.co)
Ricardo Torres-Palma (e-mail: ricardo.torres@udea.edu.co)

Abstract

In this work, the oxidation of the antihypertensive drug valsartan by Electro-Fenton (EF) and Photo-Electro-Fenton (PEF) processes was studied using a Ti/IrO_2 doped with SnO_2 as anode, and a carbon felt air diffusion electrode as cathode. Initially, the influence of variables such as supporting electrolyte type, current density, and pH on EF and/or PEF processes was evaluated. The processes were carried out in batch mode, in an open and undivided cell of 200 cm^3. The efficiency of the systems was evaluated in terms of the removal of the initial contaminant and rate of mineralization. When NaCl was used as a supporting electrolyte at pH (3.0) and current density 3.46 mA/cm^2 adding 3.6×10^{-5} mol/L of Fe^{2+}, total valsartan (2 ppm) degradation was observed after 45 minutes. After 120 min, even if total removal of valsartan was reached, only 25% of mineralization was obtained. Interestingly, valsartan degradation tests at near neutral pH in presence of oxalic acid

($4.6x10^{-5}$ mol/L) lead to comparable results with those obtained at pH 3.0. Primary aromatic intermediates were identified by high resolution mass spectrometry (HRMS) using hybrid quadrupole- time-of-flight (QTOF) MS, from which an initial degradation pathway was proposed. At the end of the PEF system, several aliphatic acids were accumulated and observed, which were effectively removed in a subsequent aerobic biological system. The results demonstrate the feasibility of photo-electro-Fenton and biological coupling process to completely mineralize emerging pharmaceutical pollutants, such as valsartan, at natural pH.

Keywords: Electrochemical advanced oxidation processes; Oxalic Acid; Antihypertensives Elimination; Emergent Pollutant Degradation

Highlights

- Degradation of Valsartan by electro-Fenton and photoelectro-Fenton was assessed.
- Presence chlorides ions favored the valsartan degradation
- Effects of current density, initial pH and oxalic acid addition were also evaluated.
- Four aromatics and three aliphatic by-products were identified.
- Mineralization is reached combining photoelectro-Fenton with a biological step.

1. Introduction

The indiscriminate increase in the consumption of non-prescription drugs for human or animal purposes, as well as the use of psychoactive substances, is a concern for health authorities worldwide [1]. Medicines and other substances unassimilated entirely by the human body, which are excreted in feces or urine [2], [3], are directly discarded into the toilet or thrown away in the trash. Then, they can reach sewage, and remain in these effluents, even after undergoing several depuration treatments [4].

Recent studies about wastewaters in different cities around the world have reported the presence of valsartan (VAL), a pharmaceutic widely used to treat diseases related to blood pressure (World Health Organization, 2013), at high concentrations compared to other commonly used drugs. For instance, in Valencia (Spain) [5]–[7] concentrations up to 6.3 μg/L of VAL have been reported in effluent wastewater (EWW); others authors [8] reported an average of 92 ng/L in the Bay of San Francisco (USA), and in the Bay of Santos - Brazil the VAL concentration ranged between 11.8 and 32 ng/L [9]. In the case of Colombia (Bogotá) the concentration found in the influent wastewater (IWW) and the effluent (EWW) of WWTP (Salitre), were 1.62 μg/L and 1.05 μg/L, respectively [10]. This findings not only highlight the risk associated to the presence of VAL in the environment, but also that WWTPs are not efficient to eliminate this pharmaceutic. As a consequence, the developing of alternative treatments to remove VAL is a need.

Advanced oxidation processes (AOP) have shown a high efficiency in the degradation of a broad spectrum of organic pollutants, including emerging contaminants [11]–[14]. Within the AOP, the electrochemical processes (EAOPs), electro-Fenton (EF) and photo-electro-Fenton (PEF) are typical examples. In the EF process, hydrogen peroxide is electro-generated on the cathode, commonly using a gas diffusion electrode (GDE), via oxygen electro-reduction (Eq. 1). Then, H_2O_2 generated can react with ferrous salts added to the systems yielding radicals •OH through the typical Fenton reaction (Eq. 2) [15]–[17].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (2)$$

Electrochemical oxidation methods for water treatment applications has been improved in recent years with the development of highly efficient and relatively inexpensive anodes, such as dimensionally stable anodes (DSA), which are based on mixtures of metal oxides [18], [19]. These anodes present high surface area, high catalytic activity, high stability to anodic corrosion, and excellent mechanical and chemical resistance even at high current densities and in strong acidic media [20]–[23]. On the other hand, EF can be stimulated with the introduction of UVA irradiation (PEF), which increases the regeneration rate of Fe^{2+} and promotes the formation of extra •OH due to the photolysis of $[Fe(OH)]^{2+}$ (Eq.3) [24], [25].

$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (3)$$

In this work, the degradation of VAL in aqueous medium by EF and PEF processes using a DSA (Ti/IrO_2 doped with SnO_2) anode and a GDE cathode is evaluated sistematically. The influence of variables such as current density, electrolyte type, pH, and in particular the addition of oxalic acid on EF and PEF processes was studied for the first time. The efficiency of the process was evaluated in terms of the removal of the initial pollutant, mineralization extent, and oxidizing species formation. The monitoring of the occurrence and disappearance of the main aromatic degradation by-products formed during the PEF process was performed by ultra-high-performance liquid chromatography coupled to a high resolution mass spectrometry (UHPLC-HRMS), using a QTOF instrument. Finally, in order to evaluate the biodegradability of the obtained byproducts, the evolution of the main aliphatic organics acids was studied and the feasibility of combining the PEF system with an aerobic biological system was assessed.

2. Materials and methods

2.1 Chemicals

Valsartan (99% purity) was purchased from Sigma Aldrich. Iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$), potassium phosphate dibasic (K_2HPO_4), orthophosphoric acid (H_3PO_4), potassium hydrogen phthalate ($C_8H_5KO_4$), sodium sulfate (Na_2SO_4), and sodium chloride (NaCl) were analytical grade from Merck. The pH of the solutions was set using chlorhydric acid (HCl, 98% purity). Methanol (MeOH) and acetonitrile (CH_3CN) HPLC grade were obtained from Panreac. All solutions were prepared with ultrapure water produced by a Millipore Milli-Q system with resistivity >18 MΩ cm at 25 °C.

For UHPLC-HRMS analysis, HPLC-grade water was obtained by purifying demineralized water in a Milli-Q plus system from Millipore (Bedford, MA, USA). HPLC-grade methanol (MeOH), formic acid (HCOOH) and sodium hydroxide (NaOH > 99%) were acquired from Scharlau (Barcelona, Spain).

2.2 Standard stock solution and calibration standards

A standard stock solution was prepared by dissolving 50 mg of VAL in 50 mL of water, and stored protected from daylight at 4ºC until use. This solution was prepared freshly every week. Calibration standards for VAL (0.1, 0.5, 2.0, 5.0, 10.0, 20.0 and 50.0 mg/mL) were prepared daily from standard stock solutions by appropriate dilution processes using Milli-Q water.

2.3 Electrolytic systems

All experiments were carried out in an open undivided electro-Fenton reactor operated in batch mode at room temperature. It consisted of a 250 mL glass beaker, which was filled with 200 mL of 4.6×10^{-5} mol/L Valsartan (VAL) solution, containing 0.050 mol/L sodium chloride as supporting electrolyte and 3.6×10^{-5} mol/L Fe^{2+}. The reactor was equipped with a 2 cm^2 carbon-felt air diffusion cathode (GDE) and a 2.89 cm^2 Ti/IrO_2 doped with SnO_2 anode (DSA). The electrodes were located in the center of the reactor at a distance of 2.0 cm and the system was operated at constant current mode (3.46 mA/cm^2).

The electrochemical cell was bubbled with air obtained from an air compressor in order to saturate the solution with oxygen. When necessary, the pH value was adjusted at 3.0 with 0.1 mol/L sulfuric acid solution and set with a pH meter (HI 2212 pH meter by HANNA Instruments). The solution was stirred continuously throughout the process using a magnetic bar at a speed of 400 rpm on a magnetic stirrer (AREC.T by VELP Scientifica). In photo-electro-Fenton process (PEF), the solution was irradiated with a Toshiba FL4BLB/4W fluorescent black-light blue tube of max 365 nm, placed on one side of the reactor inside the solution (photoionization energy input of 1.4 W/m^2).

2.4 Biological system

The biological process (BP) was carried out over a period of 8 days using aerobic microorganisms (mixed liquor) from the purge of a food processing plant in Bogotá (Colombia). 10 mL of mixed liquor (4000 mg/L of biomass) was added to 900 mL of treated VAL solutions, in order to obtain a ratio biomass:test compound between 2.5:1 and 4:1. This system was slowly aerated with an aquarium pump (AP-005 XILONG). The system was stirred and the temperature was kept at 37 °C in a Shaker (Wise Shake SHO-1D Digital Orbital Shaker). Before being subjected to the BP, the pH of the samples was adjusted to 7.0 using sodium hydroxide (1.0 mol/L). Finally, residual hydrogen peroxide and active chlorine species were eliminated using sodium bisulphite (0.1 mol/L).

2.5 Instruments and analytical procedures

2.5.1. HPLC-DAD and UHPLC-HRMS instrumentation

A Shimadzu LC-20AT equipped with a photodiode array detector SPD-M20A was used. Valsartan determination was carried out on a C18 column (Waters Spherisil ODS 2, 250 mm x 4.6 mm i.d., 5 μm particle sizes). The mobile phase was composed of phosphate buffer (pH 3.5, 0.01 mol/L)/ acetonitrile/ methanol (44/46/10 v/v/v) at 25 °C, at isocratic conditions). The mixture was pumped at 1.0 mL/min flow rate and the detector was set up at 254 nm. Under these conditions, VAL was eluted at 6.9 min.

Water soluble carboxylic acids were detected at 210 nm using an Aminex HPX-87H, Bio-Rad (300 mm × 7.8 mm) column. The mobile phase was a 1.0 mmol/L H_2SO_4 solution, eluting at 0.6 mL/min at 25°C. Well-defined peaks with retention times of 7.9 min, 9.3 min, and 14.3 min were obtained for oxalic, malic, and succinic acids, respectively.

UHPLC-HRMS analysis was carried out as reported in Supporting Material (Text SM 1).

2.5.2. Total organic carbon (TOC) analysis

The mineralization, transformation of the pollutant in water, CO_2 and inorganic ions, of treated samples was monitored by the abatement of TOC, which was measured using a Shimadzu LCSH TOC analyzer. The TOC was determined by combustion with catalytic oxidation at 680 °C using high-purity oxygen as the carrying gas at a flow rate of 190 mL/min with a non-dispersive infrared detector. Calibration of the analyzer was attained with standard potassium hydrogen phthalate (99.5%) solution.

3. Results and discussion

3.1. Electro-Fenton system applied to the removal of valsartan

3.1.1. Effect of supporting electrolyte in the valsartan degradation

The effect of the supporting electrolyte during the EF process was evaluated by determining the percentage of removal of VAL ($4.6x10^{-5}$ mol/L (20 mg/L)) as a function of time in different matrices (sodium sulfate, sodium nitrate and sodium chloride) using a DSA anode and a GDE cathode in the presence of $3.6x10^{-5}$ mol/L of Fe^{2+} and at pH 3.0 (Fig. 1a). When the DSA-GDE system was used in the presence of NaCl, in addition of hydrogen peroxide, chlorine oxidizing species can be electro-generated on the DSA anode surface. Control experiments in absence of both VAL and iron ions (Fig. 1b) demonstrated that in the presence of chloride ions, higher quantities of oxidizing species are generated.

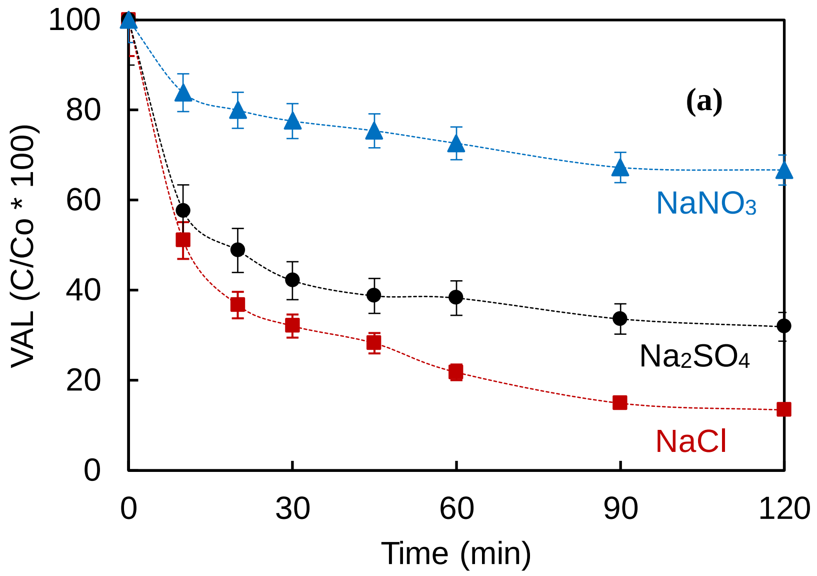
The electro-generation of chlorine oxidizing species was demonstrated using the system (DSA anode - stainless steel cathode (inactive cathode)) (Inset in Fig. 1b). The absence of GDE as cathode in the control experiments precludes the formation and accumulation of hydrogen peroxide in the media, and only chlorinated oxidizing species can be generated. In fact, as seen in Figure 1b, *ca.* 0.44 mmol/L of chlorinated oxidizing species are accumulated after 2 h of treatment in the DSA-stainless steel system, which are half of the oxidized species generated using the DSA-GDE system. As it has been shown previously, due to the high catalytic activity of DSA in conductive media in presence of chloride, a large number of active chlorine species, i.e. Cl_2, HClO and ClO^-, can be produced (Eq. 4-6) [26]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (4)$$

$$Cl_2 + H_2O \rightleftarrows HClO + H^+ + Cl^- \quad (5)$$

$$HClO \rightleftarrows H^+ + ClO^- \quad (6)$$

The predominant specie produced by DSA anodes in the presence of NaCl (at pH < 3.0) is chlorine (E°: 1.36 V/SHE), which promotes the formation of HClO (E°: 1.49 V/SHE) at 3 < pH < 7.5 and ClO^-(E°: 0.89 V/SHE) at pH > 7.5 [27]. In it turn, the electro-generation of hydrogen peroxide (Eq. 1) at the cathode was verified using a Graphite-GDE system (Inset in Fig. 1b). From the aforementioned, in the EF system in presence of chloride ions, VAL molecules are probably not only attacked by hydroxyls radicals from the Fenton reaction but also by the reactive chlorine species generated on the surface of the DSA. According to the pH of the experiment, which only changed from 3.0 to 3.6 after 2 h, Cl_2 and HClO were the chlorinated species participating in the VAL elimination. Such species are able to attack particular sites found in VAL structure such as nitrogen, sulfur, or aromatic systems, through addition reactions to unsaturated bonds or electrophilic substitution reactions to nucleophilic sites [28], [29]



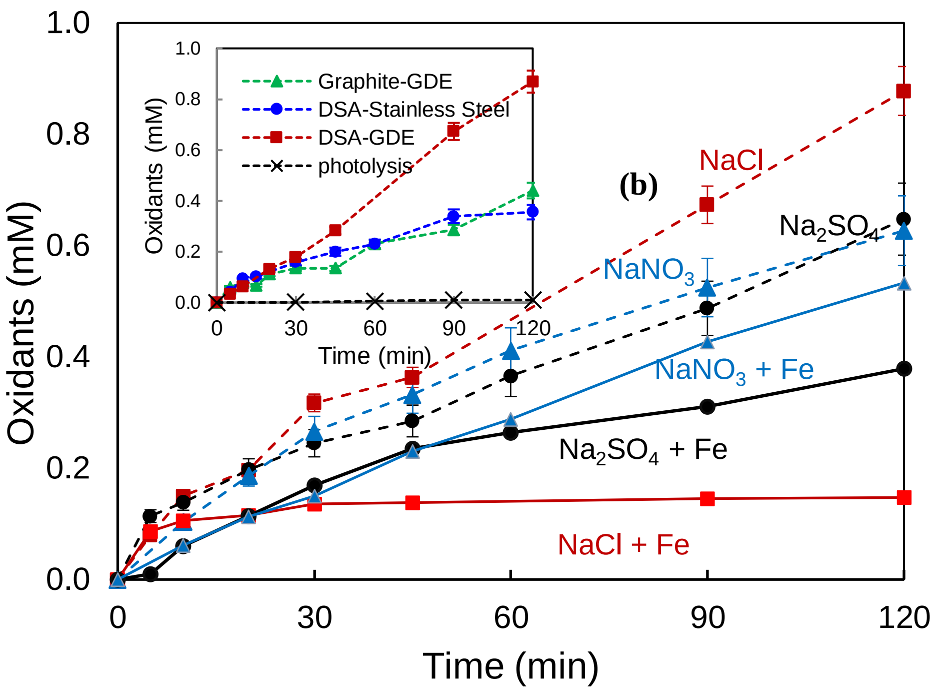


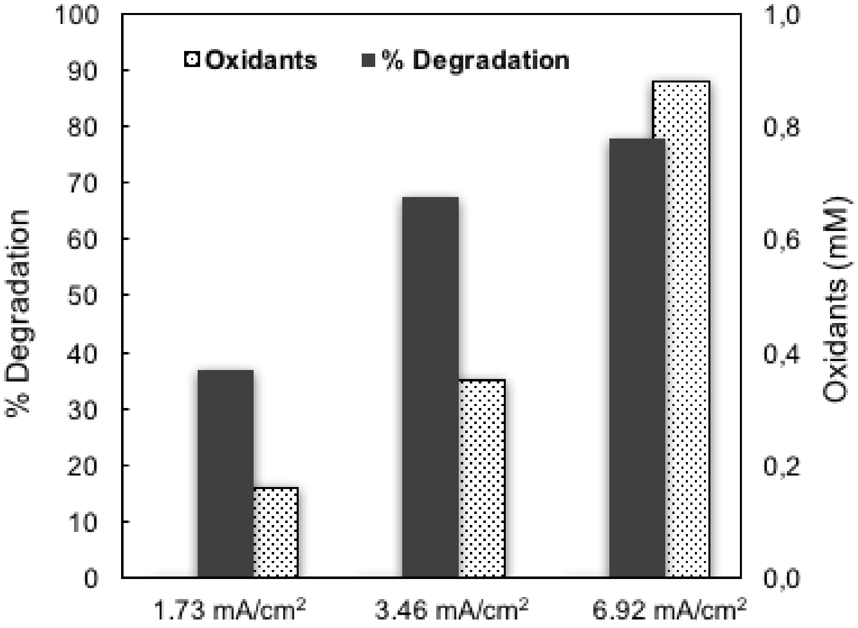
Figure 1. a) Effect of support electrolyte on evolution of VAL during the EF process. DSA anode and GDE cathode. $[VAL]_o$: 4.6×10^{-5} mol/L; $[Fe^{2+}]_o$: 3.6×10^{-5} mol/L, pH 3.0; *j*: 3.46 mA/cm^2; [NaCl]: 0.05 mol/L, $[Na_2SO_4]$: 0.05 mol/L and $[NaNO_3]$: 0.05 mol/L. **b)** Oxidizing species evolution controls: distilled water plus support electrolyte (NaCl (-■-) or Na_2SO_4 (-•-) or $NaNO_3$ (-▲-)) in the absence of Valsartan. Inset figure: Controls of oxidizing species evolution. Photolysis (-X-); only H_2O_2 electro-generated (graphite-GDE) (-▲-); chlorinated species electro-generated (DSA - Stainless steel) (-•-). Relative standard deviation for the data is less than 5%.

On the other hand, when sodium sulfate was used as supporting electrolyte in the DSA-GDE system, the degradation percentage is lower than in NaCl essays, reaching approximately 68% of removal in 120 min. The lower percentage obtained in Na_2SO_4 can be due to the fact that this time the oxidant electro-generated is exclusively hydrogen peroxide, which is produced at the GDE cathode. Then, under such conditions, VAL oxidation occurs by hydroxyl radicals from the Fenton reaction. Interestingly, the evolution of VAL degradation in Na_2SO_4 is approximately equal to that obtained when an inert electrode (graphite sheet) was used as anode and GDE as cathode in the presence of Fe^{2+} and NaCl as a supporting electrolyte (See Supporting Material, Figure SM 1). These results suggest that direct oxidation of VAL on the DSA surface is negligible. Therefore, despite having a DSA electrode as anode in the EF system, in presence of Na_2SO_4 it acts similar to an inert electrode.

Finally, using $NaNO_3$ as electrolyte, a lower degradation percentage was obtained (33%) compared with the results obtained when Na_2SO_4 was used; even if the amount of oxidants produced in presence of Na_2SO_4 and $NaNO_3$ (in absence of VAL and iron ions) was quite similar: 3.6×10^{-4} mol/L with sulfate and 4.1×10^{-4} mol/L with nitrate after 1 h (Fig. 1b). The above can be attributed to the fact that the reaction between Fe^{2+} and H_2O_2 (Eq. 2) could be 2 - 3 times slower in the presence of nitrate ions than in the presence of sulfate or chloride ions [30]. In order to verify this, the oxidants generated on the cathode (DSA-GDE system) were monitored using SO_4^{2-}, Cl^- or NO_3^- as supporting electrolyte and in the presence of Fe^{2+}. It was clearly observed that the hydrogen peroxide is more available in the presence of nitrate and Fe^{2+} than in presence of sulfate and Fe^{2+}or chloride and Fe^{2+} (Fig. 1b), indicating a limited reaction between iron and hydrogen peroxide in presence of nitrate. Therefore, during EF process the supporting electrolyte has a a strong impact on both the nature and concentration of the oxidizing species electro-generated [31], [32].

3.1.2. Effect of current density in the valsartan degradation

Typically, the oxidation efficiency of the electro-Fenton system is proportional to the quantity of oxidizing species generated. As reported by many researchers, the production rate of H_2O_2 on the cathode, depends on current density [33], [34]. As presented in previous sections, an advantage of the proposed system with DSA anodes is that in presence of chloride ions it generates reactive chlorine species. The production of these species is also related to the current density applied [35]. To evaluate the effect of the current density, VAL degradation was tested at three different current densities: 1.73, 3.46, and 6.92 mA/cm^2 using a DSA anode - GDE cathode system at pH 3.0 and NaCl 0.05 mol/L during 120 min of treatment (Figure SM2). Figure 2a shows that using the highest current density (6.92 mA/cm^2), both the degradation of VAL and the oxidants formation was superior. Different studies report that the higher the current density, the greater the oxidizing species production and greater degradation of the contaminant is expected [33].



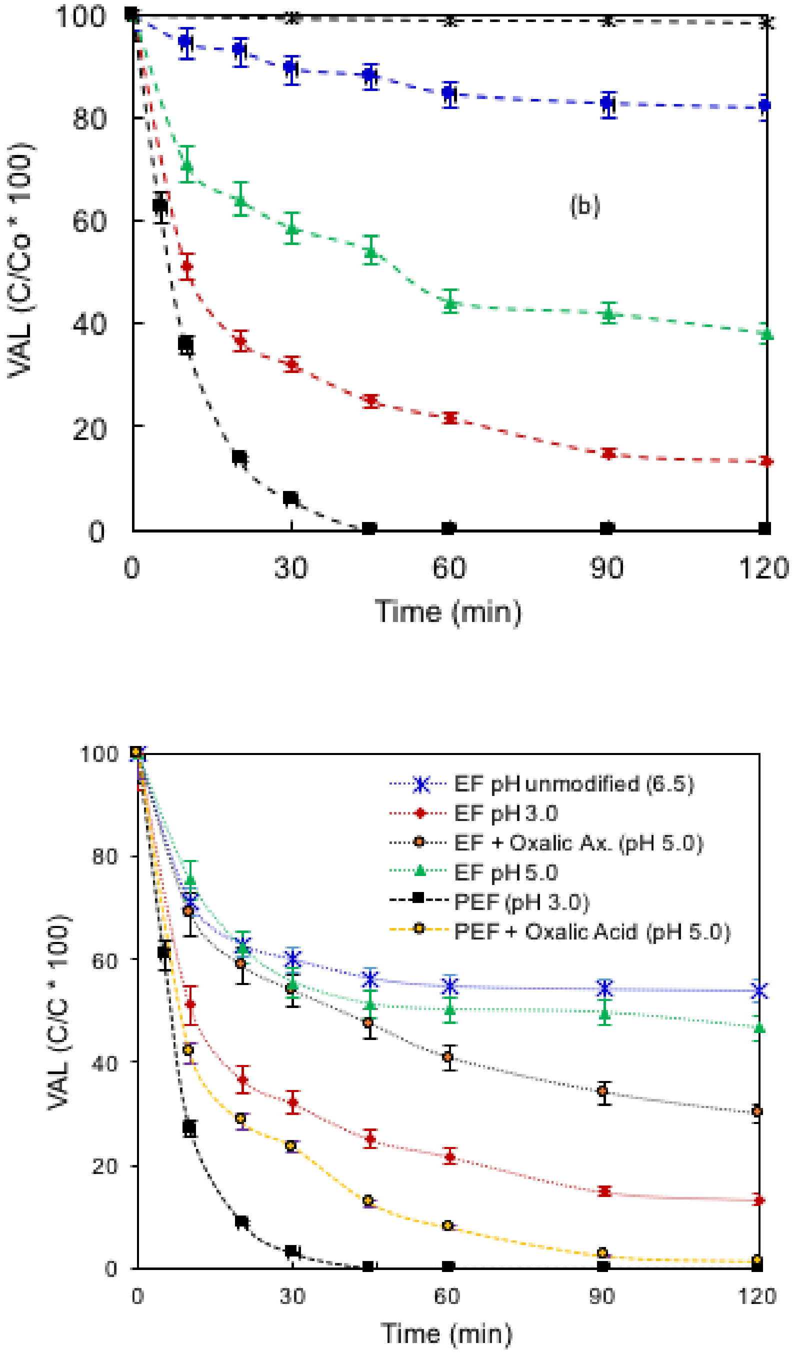


Figure 2. (a) Effect current density on VAL degradation of and oxidizing species accumulated during 60 min under EF process. **(b)** Degradation of VAL by Photo-Electro-Fenton and its former process: Photo-Electro-Fenton (-●-), Electro-Fenton (-■-), Photolysis (-*-), Anodic Oxidation + H_2O_2 electro-generated without adding Fe^{2+} (-▲-) and Anodic Oxidation (Stainless steel cathode and DSA anode) (-•-). **(c)** Effect of pH and presence of oxalic acid during VAL degradation by PEF. Electrodes: DSA anode and GDE cathode. $[VAL]_0$: 4.6 x 10^{-5} mM , [NaCl]: 0.05 M, $[Fe^{2+}]_0$: 1.8 x 10^{-5} M at pH 3.0.

Nevertheless, as the current is raised, electrode polarization is more likely to happen, that is, the charge accumulates in the electrode/solution interface, thus enhancing the cathodic decomposition of H_2O_2 to H_2O (Eq. 7). Likewise, factors such as the increase in temperature and high currents can decrease the solubility of oxygen [15], [33], which could also affect the production of oxidants and therefore the efficiency of the system [36], [37].

$$H_2O_2 + 2e^- + H^+ \rightarrow 2\ H_2O \tag{7}$$

The energy consumption is another important factor in the evaluation of the effect of the current density, since this can affect the possibilities of application of the developed system. The energy consumption per volume of electrolyzed solution can be obtained from Eq. 8:

$$KWhm^{-3} = \frac{\mathrm{I}E_{Cell}\ t}{V_s} \tag{8}$$

Where I is the applied current (A), E_{cell} is the average cell voltage (V), t is the electrolysis time (hours), and V_S is the volume of the treated solution (m^3) [12], [38].

As can be seen in Figure SM2, when 6.92 mA/cm^2 was used in the EF system, 78% of VAL degradation after 60 minutes was reached, which implies an energy consumption of 0.3 kWh/m^3. When a current density of 3.46 mA/cm^2 was applied, the energy consumption was 2.5 times lower (0.12 kWh/m^{-3}) at the same degradation extend of the contaminant, which required 120 minutes of treatment (Figure SM2). Therefore 3.46 mA/cm^2 was the current density selected for the next sections of this work.

3.2. Photo Electro-Fenton system applied to the removal of valsartan

Figure 2a shows that only 45 min were needed to completely remove VAL during the application of PEF at 3.46 mA/cm^2 of current density, pH 3.0 and NaCl 0.05 mol/L. In it turn, in absence of light (EF), 75% of VAL degradation was reached at the same time. As seen in inset of Fig. 1b, photolysis of VAL at 365 nm is not plausible. Therefore, the positive effect of UV light in the PEF system is explained by its ability to regenerate Fe^{2+} from aqua-complexes of iron (III) (Eq. 3).

As described above, in the degradation of the VAL by EF, oxidizing species electro-generated at both the DSA anode and the GDE cathode can also be involved. To verify this, VAL degradation by both anodic oxidation (OA, DSA anode-stainless steel cathode) and anodic oxidation with hydrogen peroxide (OA-H_2O_2, DSA anode-Graphite cathode) were tested. Fig. 2b, show that a difference of photolysis, both systems are able to eliminate the pharmaceutical VAL and themselves, contribute significantly to the VAL elimination by PEF. In fact, after 45 min, 12% of VAL is eliminated by the chlorinated oxidation species electro-generated at the anode (OA system). and 41% in the (OA-H_2O_2 system) due to the incorporation of hydrogen peroxide.

Therefore, as depicted in Fig. 2b, during PEF process, VAL is eliminated by several routes: (i) via chlorinated oxidizing species generated at the anode, mainly Cl_2 and HOCl; (ii) via hydrogen peroxide generated at the cathode; (iii) via hydroxyl radicals from Fenton and photo-Fenton reactions. In this process, complete elimination of VAL was observed after 45 minutes with an energy consumption of 0.135 kWh/m^{-3} (Eq. 8), which includes the energy consumption of the lamp.

3.3. Effect of pH and oxalic acid addition during EF and PEF systems

Solution pH is clearly an important parameter in EF and PEF systems. Several authors [37], [39], [40], [30] have reported that the maximum degradation efficiency is reached at around pH 3.0, when maximum •OH production in the Fenton reaction is observed. Figure 2c shows the effect of solution pH on VAL degradation in EF and PEF systems. The effect of the initial pH of VAL solutions was tested at pH 3.0, 5.0 and pH natural (~ 6.5). As expected, best performances were observed at pH 3.0. However, in order to better interpret these results, several factors need to be considered. The oxidation of chlorine on the surface of the anode at pH 3.0 produces mainly Cl_2, which presents a standard oxidation potential of 1.36 V vs. SHE, while at a pH close to the neutral value, the formation of hypochlorous acid or hypochlorite ions (E° = 1.49 V and 0.89 V vs. SHE, respectively) is privileged [20]. It is important to consider that the reaction between hypochlorous acid or hypochlorite ion with hydrogen peroxide (Eq. 9), [27] is favored at near neutral values, which explains the lower quantity of oxidizing species electro-generated (Figure SM3). This factor also contribute to the better degradation observed at the more acidic values of pH.

$$HOCl + H_2O_2 \rightarrow H_2O + O_2 + H^+ + Cl^- \quad (9)$$

On the other hand, when the pH increases, it produces the precipitation of iron as iron hydroxides, which decreases the free iron concentration in the solution [41], [42] and then negatively affects the efficiency of the Fenton reaction. As early reported organic acids (Oxalic, Oxamic, Tartaric among others) form complexes with iron, type ferroxylate [43], [44], thus avoiding the formation of insoluble iron hydroxides [45]. The iron complexes can be photocatalyzed by UVA light, generating a greater degradation of the contaminant by PEF system at near neutral pH [46]. In order to confirm this hypothesis, several experiences were performed by adding oxalic acid ($4.0x10^{-5}$ mol/L) to the VAL solution. Under this conditions, 70% of VAL was eliminated by the EF process after 120 min of treatment (Fig. 2c), and practically total removal of VAL was observed after 90 min using the PEF system. As it has been showed, the results suggests that the ferryoxalate complexes (Eq. 10), which can keep the iron in solution, are able to react with hydrogen peroxide and absorbe photons (Eq. 11) with wavelengths in the visible region. This is of special interest because the use of oxalic acid could limit the pH adjustment pre- and/or post-treatment.

$$Fe^{3+} + 3\ H_2C_2O_4 \rightarrow Fe^{3+}[(C_2O_4)_3]^{3-} + 6\ H^+ \quad (10)$$

$$2\ Fe^{3+}[(C_2O_4)_3]^{3-} + h\nu \rightarrow 2\ Fe^{2+} + 5\ C_2O_4^{2-} + 2\ CO_2 \quad (11)$$

3.4 Identification of the main aromatic degradation products (DPs) of VAL degradation during PEF treatment

In order to study the formation of possible degradation products, an approach based on common fragmentation pathway was applied [47] assuming that most DPs share the fragmentation pathway with the parent drug. Specific narrow-window extracted ion chromatograms (nw-XICs) at the expected exact-mass *m/z* of the fragments were obtained from high-energy full-spectrum TOF MS acquisitions. Every chromatographic peak with a retention time different than the parent drug was treated as a potential DP. The combined spectrum at the same retention time in the Low Energy (LE) function allowed for establishing the accurate mass of the potential DP, which was studied in order to determine its molecular formula. Finally, QTOF MS/MS experiments were performed and the results compared with the behavior of valsartan. Based on all this information, a derived structure for each DP was established.

An in-depth study of the fragmentation behavior of the parent drug was essential as a first step, in order to obtain structural information of each fragment ion. VAL showed ionization in both positive and negative ion modes with prominent $[M+H]^+$/$[M-H]^-$ at *m/z* 436.2351 and 434.2178, respectively. The High Energy (HE) spectra for VAL produced a rich spectrum providing abundant structural information. As an example, Figure 3a shows the HE spectra for valsartan in positive ion mode as well as the proposed fragmentation pathway (Fig. 3b). Thus, nw-XICs (0.02 Da mass window) corresponding to the *m/z* of the main VAL fragment ions (*m/z* 180.0813, 190.0657, 207.0922, 235.0984, 291.1497 in positive; 116.0712, 156.1388, 179.0861, 192.0813, 276.1501, 350.1603 in negative) were extracted from the TIC of the HE function in the degraded sample.

When the nw-XIC at *m/z* 207.0917 in the HE function was performed, 4 chromatographic peaks were observed, corresponding to valsartan (at 10.87 min) but also to three possible DP at 8.86 min (DP1), 9.98 min (DP2), and the fourth at 11.31 min (DP3) only visible after 30 min (Fig. 4). Regarding DP1, the HE spectra of this peak was extracted as well as the LE spectra, in order to known its accurate mass (Fig. 4b). DP1 showed a $[M+H]^+$ at *m/z* 336.1825 corresponding to an elemental composition of $C_{19}H_{22}N_5O_2$ (0.3 ppm), i.e. $C_2H_8O_2$ atoms less than valsartan. The HE spectra in positive mode was similar to the one obtained for VAL. The presence of the ions at *m/z* 235.0975, 207.0913, 190.0654, and 180.0800 indicated an unaltered 5-(4'-methyl-[1,1'-biphenyl]-2-yl)-2H-tetrazole group. DP1 did not show ionization in negative mode suggesting the loss of the carboxylic acid group. Based on these data, N-((2'-(1H-tetrazol-5-yl)-[1,1'-biphenyl]-4-yl)methyl)-pentanamide was proposed as structure for DP1.

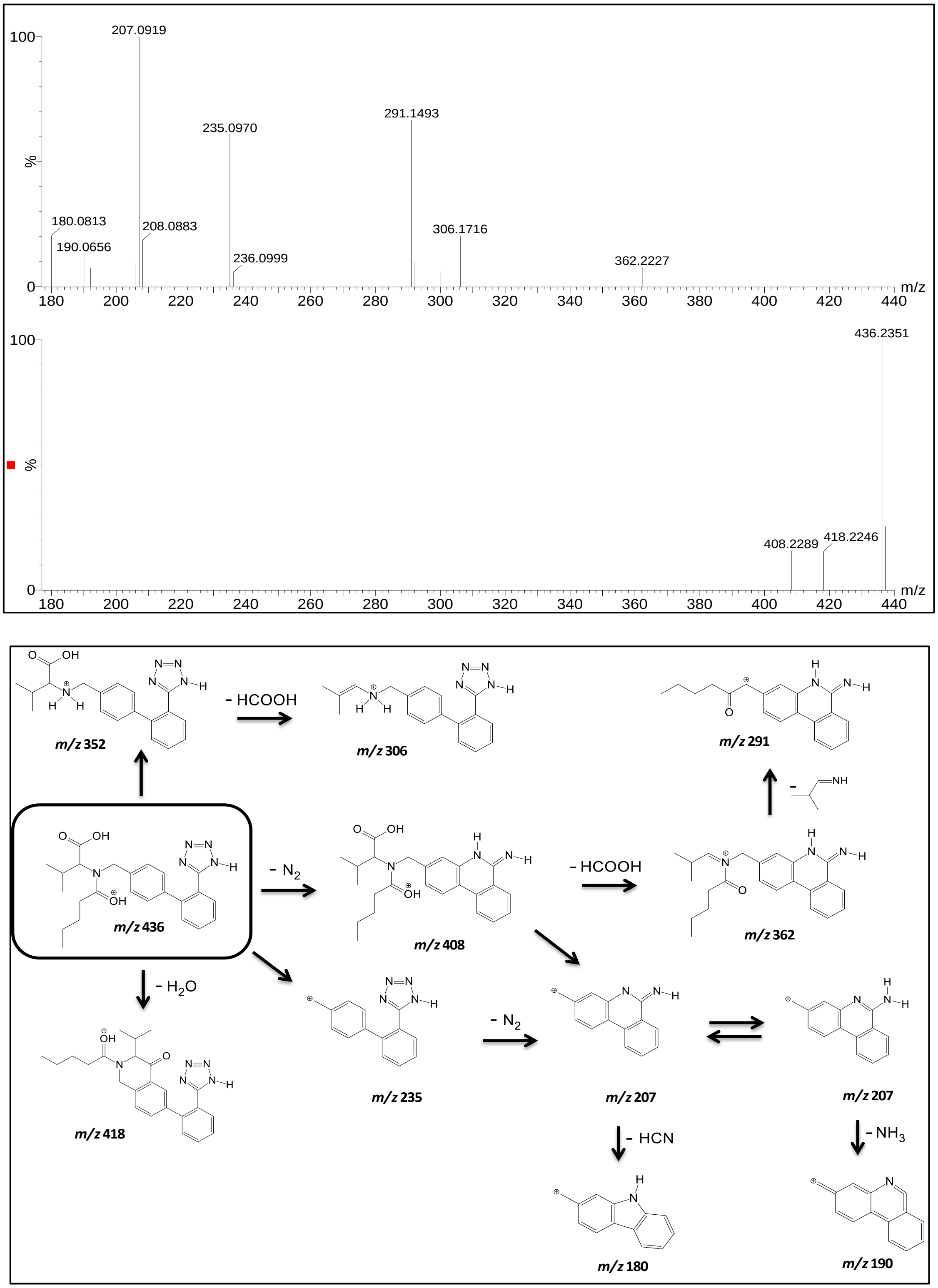


Figure 3. (a) Low-energy (bottom) and high-energy (top) accurate-mass spectra for VAL in positive ion mode; (b) Proposed fragmentation pathway.

The chromatographic peak at 10 min (DP2) showed a $[M+H]^+$ at *m/z* 364.1765 ($C_{20}H_{22}N_5O_2$, -2.2 ppm) (Fig. 4c), this is, C_4H_8O atoms less than valsartan. The HE spectra showed peaks at *m/z* 235.0976, 207.0912, 190.0659, and 180.0801, all of them common to the valsartan, indicating that the 5-(4'-methyl-[1,1'-biphenyl]-2-yl)-2H-tetrazole group remained intact. The product ion at *m/z* 280.1193 ($C_{15}H_{14}N_5O$) corresponded to the loss of C_5H_8O, indicating that this group also remained unaltered. The DP2 was proposed to be N-((2'-(1H-tetrazol-5-yl)-[1,1'-biphenyl]-4-yl)methyl)-N-formylpentanamide.

DP3, eluting at 11 min, corresponded to an elemental composition of $C_{20}H_{20}N_5O_2$, this is 2H less than DP2 (Figure 4). However, the fragmentation observed was completely different. The product ions at *m/z* 207.0906 and 180.0798 were the minority, being the most outstanding at *m/z* 250.0968 ($C_{15}H_{12}N_3O$) and 195.0911 ($C_{13}H_{11}N_2$). After studying the fragmentation, the compound was tentatively identified as 6-(2-(1H-tetrazol-5-yl) phenyl)-2-pentanoylisoindolin-1-one.

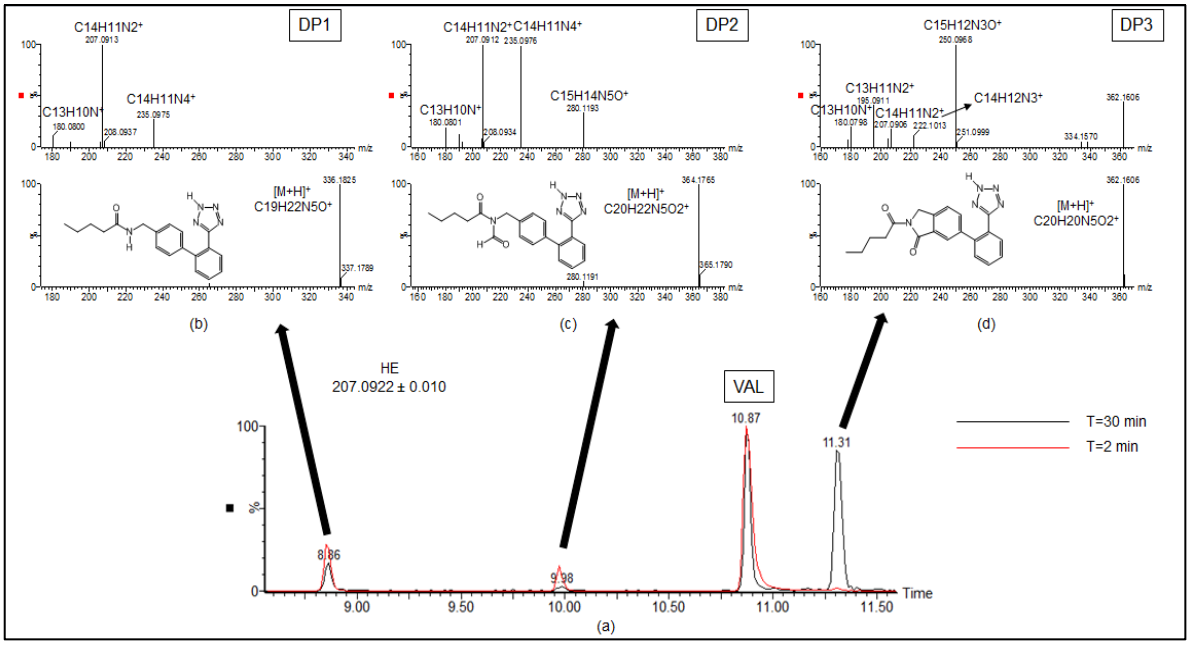


Figure 4. Extracted ion chromatograms (20 mDa absolute mass window) for m/z 207.0922 in the high-energy spectra, for samples collected at 2 and 30 minutes of treatment. Low energy spectrum (bottom), high energy spectrum (top) and proposed structure for: (b) DP1, (c) DP2 and (d) DP3.

In negative mode, when the nw-XIC at *m/z* 116.07 in the HE function was performed, two chromatographic peaks were observed, corresponding to valsartan (at 10.87 min) but also to one possible DP at 6.99 min (DP4). DP4 showed a $[M-H]^-$ at *m/z* 200.1279, which corresponded to an elemental composition of $C_{10}H_{18}NO_3$. The HE spectra showed only a predominant ion at *m/z* 116.0703 ($C_5H_{10}NO_2$) and a minor fragment at 156.1350 ($C_9H_{18}NO$). Finally, a tentative degradation pathway for the degradation of VAL during PEF is proposed in Figure 5.

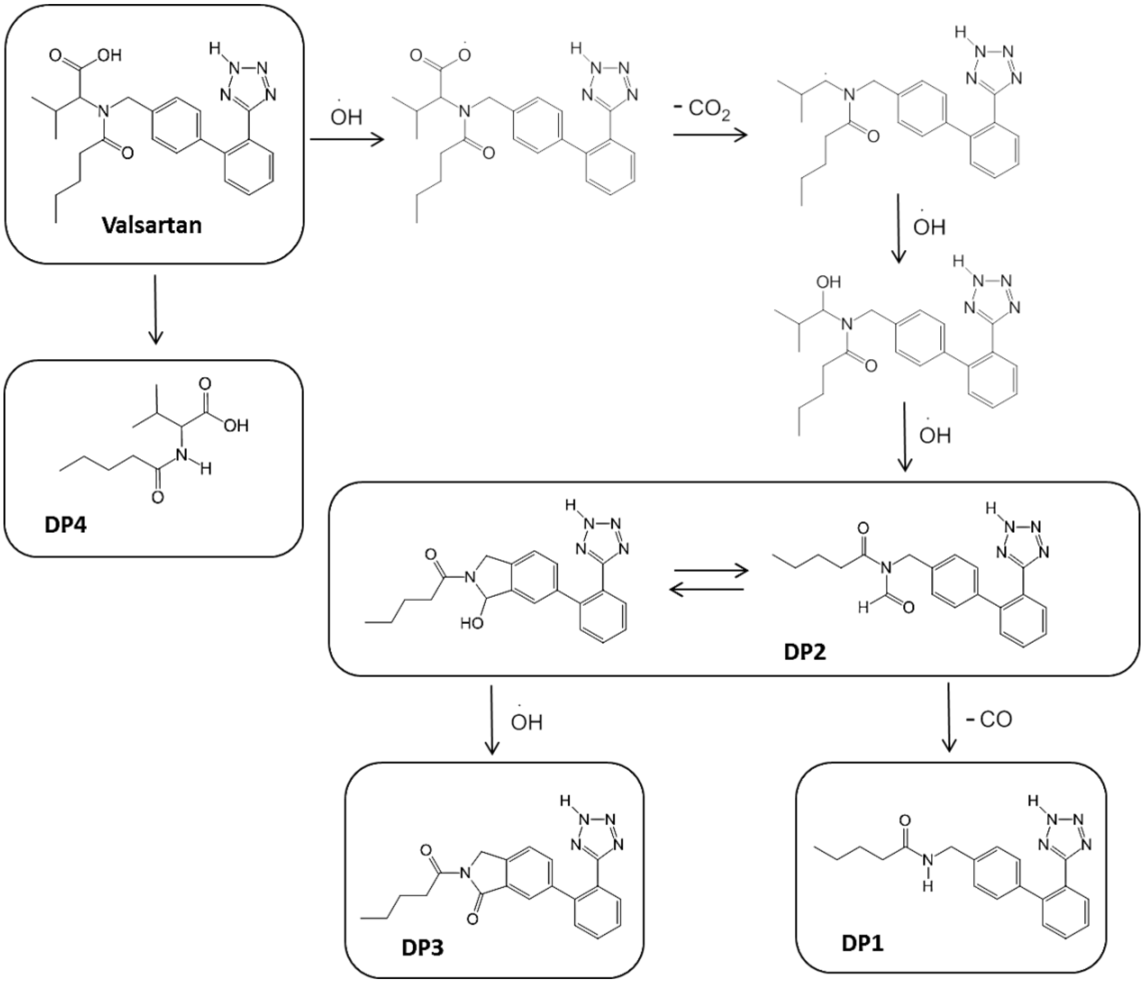


Figure 5. Proposed degradation pathway for Valsartan degradation during PEF system.

3.5 Analysis of mineralization extend and aliphatic by-products evolution during PEF

The four initial VAL by-products identified during the PEF system (DP1-DP4), were it in turn eliminated after 5 h of treatment (data not showed). To investigate the mineralization degree, the TOC evolution in the course of the PEF treatment was measured. As seen in

Figure 6, TOC abatement is fast during the first 60 minutes, achieving 20% elimination. However, TOC removal becomes slow for longer treatment times, since after 5 hours only 35% of TOC elimination is reached (Figure 6). There is only a slight increase of 5% in the mineralization of VAL when the PEF system is used in comparison with the EF system. The results also show that, at difference of the observed during VAL removal, addition of oxalic acid did not enhance the mineralization extend. The results suggest that organic compounds coming from DP1-DP4 transformation, usually small molecules that would reduce the oxygen demand in the treated solution [48], are more recalcitrant to the •OH action.

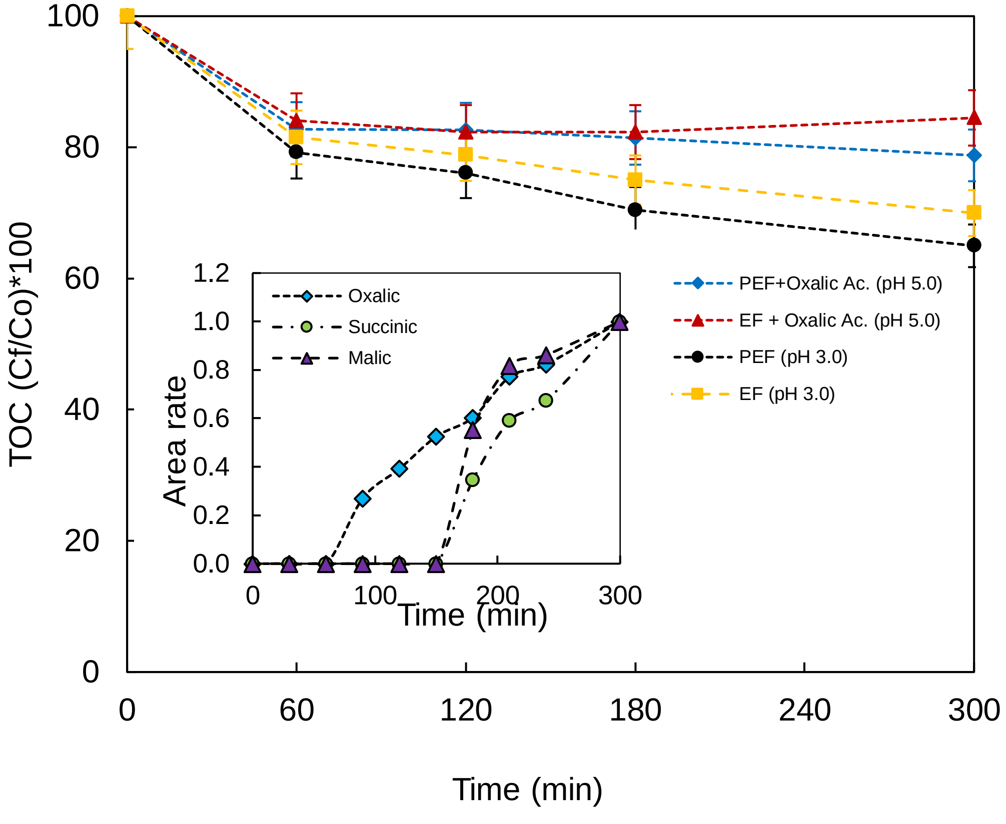


Figure 6. Effect of presence of oxalic acid (pH ~ 5.0) on mineralization of VAL by EF and PEF processes using DSA-GDE system. $[VAL]_0$: $4.6\text{x}10^{-5}$ mol/L, [NaCl]: 0.05 mol/L, $[Fe^{2+}]$: $1.8\text{x}10^{-5}$ mol/L; *j*: 3.46 mA/cm^2, Volume: 0.2 L at room temperature. Inset: Aliphatic acids species generated during PEF; oxalic acid ($C_2H_2O_4$) (-◆-); succinic acid ($C_4H_6O_4$) (-●-) and malic acid ($C_4H_6O_5$) (-▲-)

It is known that oxidation of aromatic compounds via •OH ends up in opening rings to form aliphatic acids [27]. Therefore, the formation of aliphatic acids during the treatment was investigated. As seen in the inset of Figure 6, after 1 h of treatment, oxalic, succinic, and malic acid accumulated in the process, and under work conditions they are not eliminated even after 5 h of treatment.

3.6 Evaluation of the biodegradability of the Valsartan treated solutions by combined photo-electro-Fenton and biological system (PEF-BP)

As the photo electro-Fenton system was not able to transform totally the pollutant into water, carbon dioxide and inorganic ions, the determination of the biodegradability of treated solutions is crucial to discard the accumulation of more dangerous by-products. This is of high relevance because toxic chlorinated organic compounds could be formed during the process. Therefore, a biological process (BP), with non-adapted microorganisms obtained from a food processing plant in Bogotá (Colombia) was carried out. The biological system was applied to solutions treated at different times of PEF process (0; 90 and 300 min). Figure 7 show that for non-treated solutions the initial TOC is poorly removed (~10% removal), even after 8 days of biological treatment. This is in agreement with a previous report that highlight the low biodegradability of VAL [49]. Interestingly, VAL solutions treated during 90 min using the PEF treatment, can be easily mineralized in the subsequent biological step. In fact, more than 80% of initial TOC is removal after 8 days. Further application of PEF process during 300 min increase the efficiency of the subsequent biological treatment (~90% of TOC removal). Thus, confirming the high biodegradable character or the electrochemically-treated solutions.

Considering the differences between the biological process and the photoelectron-Fenton process acting alone, a complete mineralization of the antihypertensive VAL could be reached in a sequential PEF-BP system. In such a combined system, the photo-electrochemical process transforms the recalcitrant pharmaceutical VAL into biodegradable compounds that are treatable in a conventional biological system, without previous adaptation and/or optimization. It is expected that in a biological system previously adapted and optimized the total conversion of the initial pollutant to CO_2, water and inorganic ions could be achieved within the residence time of conventional biological reactors (48 h).

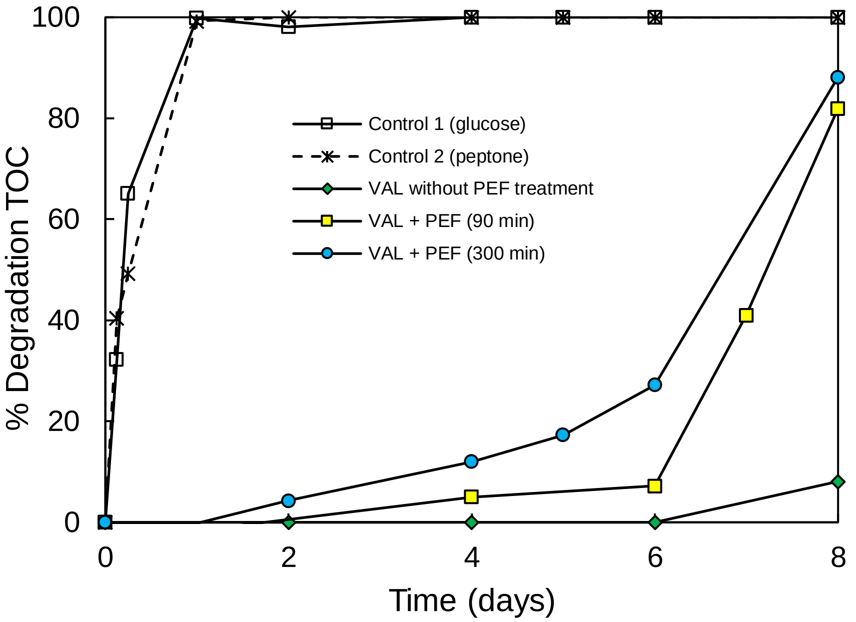


Figure 7. Biological degradation test of the treated (by PEF process) and non-treated effluents. Test conditions: 14 mg/L of initial TOC, 900 mL of solution, pH 7.0, 37 °C.

Conclusions

This work shows that PEF process with a Dimensionally Stable Anode (Ti/IrO_2 doped with SnO_2) and a gas diffusion electrode combined with a biological process is a promising system for the complete mineralization of the pollutant valsartan. The supporting electrolyte composition and the initial pH of solutions play a key role during the EF and PEF processes. It has been demonstrated that in the presence of NaCl as supporting electrolyte, reactive chlorine species are produced, which together with the $^{\bullet}OH$ radicals carry out the degradation of the VAL. However, at pH close to neutral, the HClO produced could reacts with hydrogen peroxide yielding a decrease in the efficiency of the process. It has been demonstrated that the process at natural pH can be significantly improved if it is carried out in presence of oxalic acid. In fact, using oxalic acid, VAL was completely removed within 120 min; while 40% of VAL degradation was observed without pH modification in absence of oxalic acid.

Four (4) VAL degradation compounds were identified and an initial degradation route was proposed. In addition, three short linear carboxylic acids were identified and their evolution was monitored during treatment, observing that these compounds may remain after the application of the PEF treatment.

Concerning the biological treatment, the results showed that VAL solutions without PEF treatment cannot be removed by the biological process, even after 8 days of treatment under favorable conditions of pH and temperature. Interestingly, after only 90 min of treatment, microorganisms of the biological treatment eliminated more than 80% of the initial TOC. Therefore, the PEF system combined with a biological process is a promising alternative for the complete mineralization of the pollutant valsartan.

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Text SM 1

UHPLC-HRMS instrumentation

An Acquity ultra-performance liquid chromatography (UPLC) system (Waters, Milford, MA, USA) was interfaced to a QTOF mass spectrometer (QTOF Xevo G2, Waters Micromass, Manchester, UK) using an orthogonal Z-spray electrospray interface. The LC separation was performed using Acquity UPLC BEH C18 1.7 µm particle size analytical column of 100 x 2.1 mm (from Waters), at a flow rate of 0.3 mL/min. The mobile phases used were H2O (A) and MeOH (B), both with 0.01% (v/v) HCOOH. The proportion of MeOH was linearly increased as follows: 0 min, 10%; 14 min, 90%; 16 min, 90%; 16.01 min, 10% and 18 min, 10%. The injection volume was 20 µL. Nitrogen (Praxair, Valencia, Spain) was used as both the drying gas and the nebulizing gas. The gas flow rate was set at 1000 L/h. The resolution of the TOF mass spectrometer was approximately 20.000 at full width half maximum (FWHM) at m/z 556. MS data were acquired over a m/z range of 50–1000 in a scan time of 0.3 s. The MCP detector potential was set to 3700 V. Capillary voltages of 0.7 kV and -2.0 kV were used in positive and negative ionization modes, respectively. A cone voltage of 20 V was applied. The collision gas was argon (99.995%, Praxair). The interface temperature was set to 600 ºC and the source temperature to 130 ºC. The column temperature was set to 40 ºC and the samples to 5 ºC.

For MSE experiments, two acquisition functions with different collision energies were created: the low-energy function with a collision energy of 4 eV, and the high energy function with a collision energy ramp ranging from 15 to 40 eV. MS/MS experiments were also performed, using a cone voltage of 20 V and collision energies of 10, 15, 20, 30 and 40 eV. Calibration of the mass-axis from m/z 50 to 1000 was conducted with a 1:1 mixture of 0.05M NaOH/5% (v/v) HCOOH diluted (1:25) with water/ACN (20:80 v/v). For automated accurate mass measurement, the lock-spray probe was performed, using as lock mass leucine enkephalin (2 mg/L) in ACN/water (50/50) at 0.1% HCOOH, pumped at 20 µL/min through the lock-spray needle. The leucine enkephalin [M+H]+ ion (m/z 556.2771) for positive ionization mode, and [M-H]- ion (m/z 554.2615) for negative ionization, were used for recalibrating the mass axis and to ensure a robust accurate mass measurement over time. MS data were acquired in centroid using MassLynx v 4.1 (Waters Corporation).

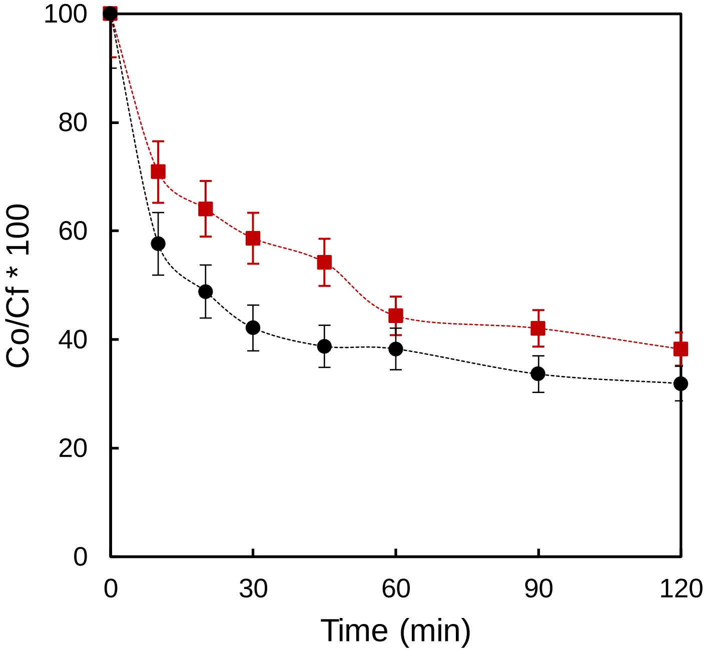

Fig. SM 1. Degradation of VAL using DSA – GDE system in presence of Fe^{2+} ($3.6x10^{-5}$ mol/L) and Na_2SO_4 (0.05 mol/L) as supporting electrolyte (-•-) and using Graphite sheet – GDE system in presence of Fe^{2+} ($3.6x10^{-5}$ mol/L) and NaCl (0.05 mol/L) as supporting electrolyte (-■-). Relative standard deviation for the data is less than 5%.

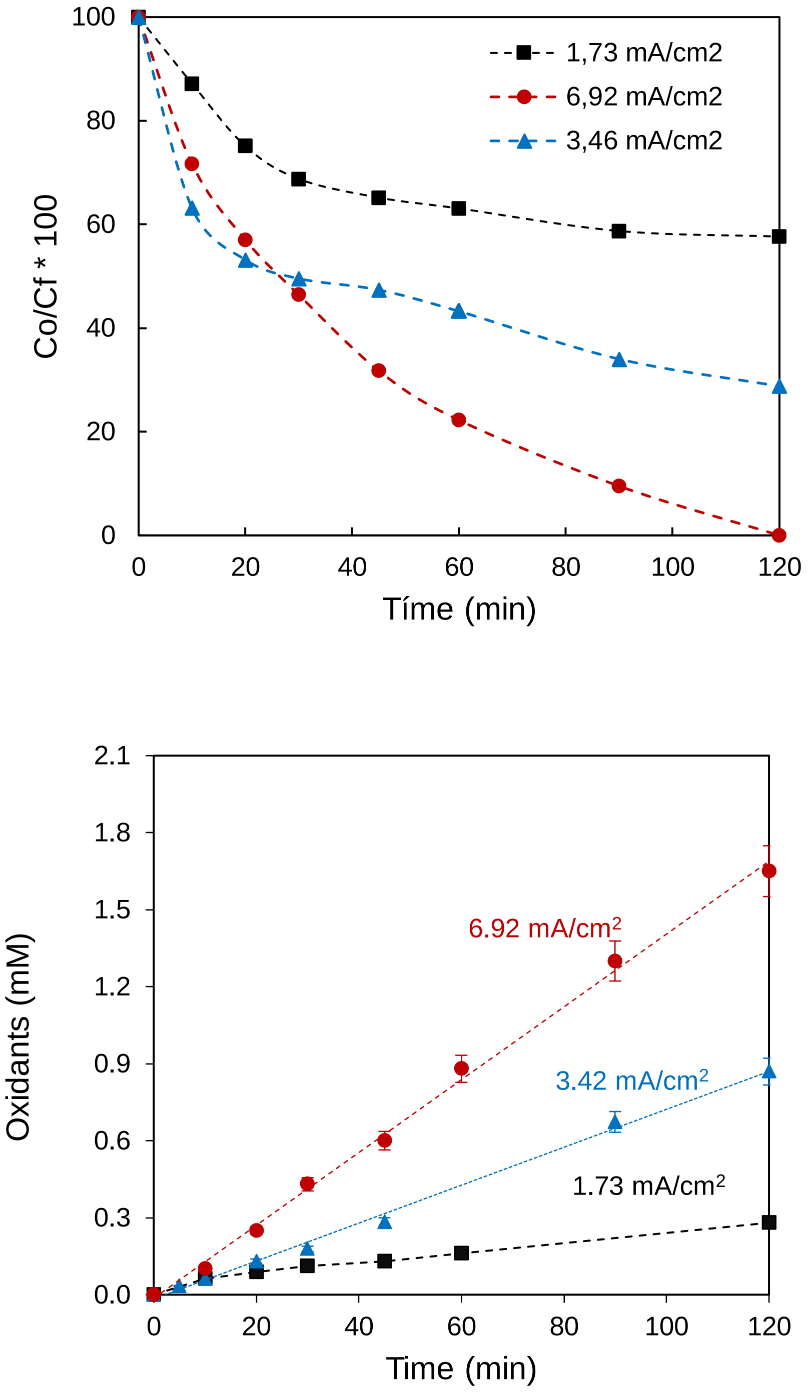

Fig. SM 2. Effect of current density on VAL degradation (a) and oxidizing species evolution (b) using NaCl as supporting electrolyte: 6.92 mA/cm^2 (-•-); 3.46 mA/cm^2 (-▲-); 1.73 mA/cm^2 (-■-). Relative standard deviation for the data is less than 5%.

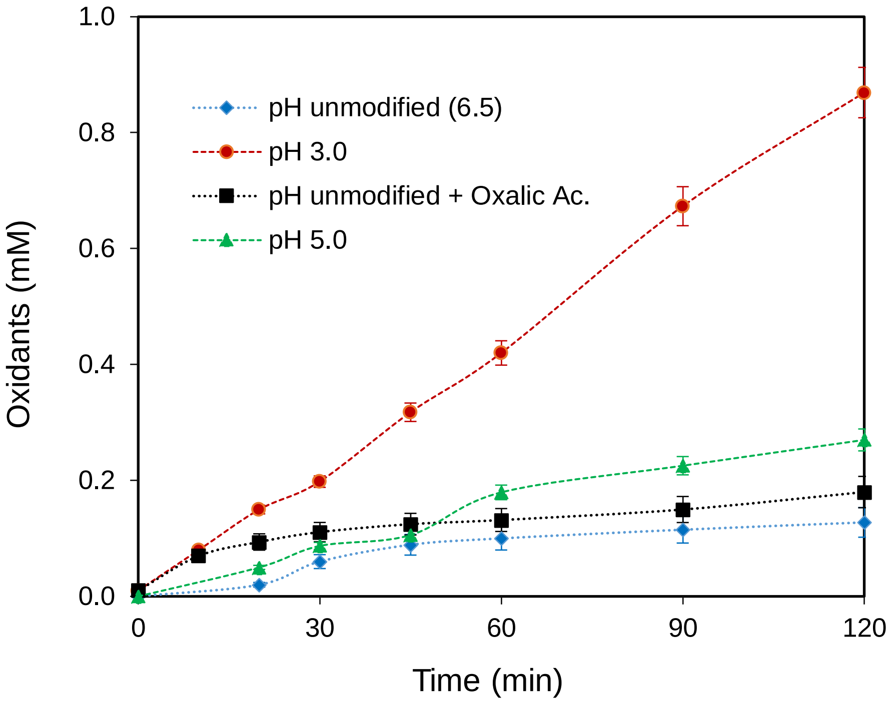

Fig. SM3. Effect of pH on the evolution of oxidizing species using DSA – GDE system in presence of NaCl (0.05 mol/L) as supporting electrolyte (-●-). Relative standard deviation for the data is less than 5%.

Artículo 3:

Advanced Oxidation of Losartan and Valsartan via Photo-Electro-Fenton Process at near-neutral pH using natural organic acids and a Dimensional Stable Anode - Gas Diffusion Electrode (DSA-GDE) System under Light Emission Diode (LED) Lighting

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ADVANCED OXIDATION TECHNOLOGIES: STATE-OF-THE-ART IN IBERO-AMERICAN COUNTRIES

Advanced oxidation of antihypertensives losartan and valsartan by photo-electro-Fenton at near-neutral pH using natural organic acids and a dimensional stable anode-gas diffusion electrode (DSA-GDE) system under light emission diode (LED) lighting

Diana Martínez-Pachón[1] · Paula Espinosa-Barrera[1] · Javier Rincón-Ortíz[2] · Alejandro Moncayo-Lasso[1]

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Abstract

In this work photo-electro-Fenton (PEF) processes using a dimensionally stable anode-gas diffusion electrode (DSA-GDE) system under light emission diodes (LED)-type radiation were used in the degradation of the angiotensin-II-receptor antagonists (ARA II), valsartan (VAL), and losartan (LOS), which are used in the treatment of hypertension diseases, and are considered among the emerging contaminants (ECs). Organic acids as citric, tartaric, and oxalic acids were used as complexing agents of iron ions in order to maintain the performance of the Fenton reaction at near-neutral pH value. The results show that at 3.42 mA/cm^2 after 90 min of electro-Fenton (EF) treatment, degradation of 70% of VAL and 100% of LOS were observed. Total degradation of VAL and LOS was reached with a PEF process at the same time with mineralization of 30%. When citric and tartaric acids were used instead of oxalic acid, similar results were obtained, i.e., total degradation of both compounds, LOS and VAL, after 90 min of treatment. The degradation performance can be attributed to the increase of the initial dissolved iron in the system, facilitating the Fe^{3+}/Fe^{2+} turnover in the catalytic photo-Fenton reaction and consequently, hydroxyl radical ($^{\bullet}OH$) production. In addition, the increased photo-activity of the complexes can be associated with their high capability to complex Fe^{3+} and to promote ligand-to-metal charge transfer, which is of key importance to feed Fe^{2+} to the Fenton process. The results show that the system evaluated was more efficient to eliminate sartan family compounds using LED lighting in comparison with traditional UV-A lamps used in this kind of work. Moreover, three transformation products of VAL degradation and two transformation products of LOS degradation were identified by high-resolution mass spectrometry (HRMS) using hybrid quadrupole-time-of-flight (QTOF) MS and, at the end of the PEF system, the several organic compounds accumulated and no mineralized were effectively treated in a subsequent aerobic biological system.

Keywords Electro-Fenton · Photo-electro-Fenton · Photo-electro-Fenton with organic acids · Emerging contaminants · Sartans · Wastewater treatment · Losartan · Valsartan

Introduction

The antihypertensives of the sartan family are considered as emerging contaminants (ECs) since they are not regulated, and they are present in aqueous media at very low concentrations (ng/L–μg/L). In recent years, their consumption has increased significantly (Hiltunen et al. 2015). Most pharmaceutical compounds are not completely metabolized after their consumption and consequently are excreted via urine and feces (Jurado et al. 2012). The presence of those kinds of compounds may act as disruptors of endocrine systems and affect the development of aquatic and wildlife (Zhang et al. 2015;

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✉ Alejandro Moncayo-Lasso
amoncayo@uan.edu.co

[1] Grupo de Investigación en Ciencias Biológicas y Químicas, Facultad de Ciencias, Universidad Antonio Nariño, Bogotá, D.C., Colombia

[2] Grupo de Investigación Fundamental y Aplicada en Materiales, Facultad de Ciencias, Universidad Antonio Nariño, Bogotá, D.C., Colombia

Tejada et al. 2014; Wang et al. 2016). In recent studies, losartan (LOS), valsartan (VAL), and irbersartan (IRB) have been detected in many wastewater treatment plants (WWTP) around the world (Klosterhaus et al. 2013; Pereira et al. 2016). In the affluent (AWW) and effluent (EWW) of wastewater treatment plants (WWTP) in Bogotá and Medellín (two of the major cities of Colombia), VAL and LOS have also been found (Bijlsma et al. 2016; Hernández et al. 2015). The values of VAL concentration in the AWW and EWW from WWTP (Salitre-Bogotá) were 1.6 and 1.1 μg/L, respectively. In the case of LOS, concentrations of 2.20 μg/L in the AWW and 2.00 μg/L in the EWW were found. Lower concentrations of IRB were also detected in those wastewater samples (0.18 and 0.20 μg/L). Those ECs were detected among other pharmaceutical products that remain in the water even after it passes through WWTPs.

The deficient elimination of these ECs by conventional treatments suggests that complementary treatments are needed to remove these types of contaminants.

Among the tertiary treatments, advanced oxidation processes (AOPs) appear as an excellent alternative to upgrade WWTPs and minimize the discharge of pharmaceutical ECs into water bodies, improving the quality of effluent, and the possibility that, in some cases, treated water may be reused (De la Cruz et al. 2012). AOPs are based on hydroxyl radical production ($^{\bullet}OH$) by different ways. These radicals are highly reactive and powerful oxidizing species ($E° = 2.80$ V) and could lead to the chemical oxidation of pollutants, even up to complete mineralization (generation of CO_2 and H_2O as final products). Among the AOPs, the Fenton reagent is one of the processes with great application potential. In this process, environmentally friendly reactants are used, such as hydrogen peroxide (H_2O_2) and ferrous ion at low amounts, which catalyze the breaking down of H_2O_2 molecules yielding hydroxyl radicals (Eq. 1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \qquad (1)$$

When the Fenton reaction and electrochemical cells are combined, electrochemical advanced oxidation processes (EAOPs) are obtained (Sirés et al. 2014; Martínez-Huitle et al. 2015). Among the EAOPs, the electro-Fenton process (EF) is recognized. In this process, H_2O_2 is generated in situ on cathode via a two-electron reduction of oxygen in an acidic medium (Eq. 2) (Qiu et al. 2015) and the Fe^{2+} ions can be added to the electrochemical cell-reactor to produce the $^{\bullet}OH$ radicals. Dimensional stable anodes (DSA) are generally titanium electrodes with metal oxides (Rao and Venkatarangaiah 2014). They are recognized as common electrodes to generate high quantities of chlorinated species in the presence of chloride ions (Eqs. 3–5), which could degrade and mineralize organic contaminants and may even be used in disinfection treatments (Deborde and Von Gunten 2008):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$

$$2\ Cl^- \rightarrow Cl_2 + 2e^- \qquad (3)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad (4)$$

$$HOCl \rightarrow H^+ + ClO^- \qquad (5)$$

The EF process can be enhanced under UV-Vis light (photo-electro-Fenton process; PEF) and, in the presence of an organic acid such as oxalic acid or citric acid; the need to regulate the pH in the range of 2.8–3.0 can be eliminated since iron-organic acid complexes are formed, and so maintain the iron ions in the solution (Isarain-Chávez et al. 2011). The irradiation of the reactor with UV-Vis light releases Fe^{2+} to the solution from hydroxyl-aqueous-Fe^{3+} complexes and organic acids-Fe^{3+} complexes (Eqs. 6–8) (Ma et al. 2016; Palma-Goyes et al. 2016; Santana-Martínez et al. 2016).

$$[Fe(OH)]^{2+} + h\upsilon \rightarrow Fe^{2+} + \bullet OH \qquad (7)$$

$$[Fe(OOCR)]^{2+} + h\upsilon \rightarrow Fe^{2+} + CO_2 + R\bullet \qquad (8)$$

$$2Fe(C_2O_4)n^{(3\text{-}2n)} + h\upsilon \rightarrow 2\ Fe^{2+}(2_{n\text{-}1})C_2O_4{}^{2-} + 2CO_2 \qquad (9)$$

Some works have focused on exploring the degradation of drugs using different electrolytic cells, electrodes, and stoichiometric ratios of reactants in the presence of different organic acids (Brillas et al. 2009; Graça et al. 2017; Pignatello et al. 2006; Safarzadeh-Amiri et al. 1996; Souza et al. 2014), showing, in most cases, a low efficiency under dark conditions in comparison with results obtained under light conditions. In this case, the $^{\bullet}OH$ radical formation is improved because of the breaking up of the Fe^{3+}- carboxylate complexes, which makes it possible to keep the Fe^{2+} available longer in the system.

With respect to the type of lamps used in the photocatalytic processes, LED lighting is employed as an alternative to the traditional lamps of Hg and Xe for the elimination of pollutants from water (Yeh et al. 2014), since LED lamps have low energy consumption and can address different photo-reactors' configurations to solve the problem of artificial light energy consumption (Izadifard et al. 2013). The operation of LED lighting is based on the electrons coupling in specific electron holes. This keeps the lamps stable and allows converting almost all of the electrical energy into light. The light emitted is considered monochromatic because all the emitted photons have the same energy (by the electroluminescence phenomenon determined by the energy band gap) and consequently, similar wavelengths are obtained (Natarajan et al. 2011). This type of light source has the advantage of selective wavelength application and durability of about 100 times greater than traditional lamps, although the efficiency of these processes can be affected by the temperature (Rodríguez-Chueca et al. 2016; Rojviroon et al. 2012). LEDs are more robust, they can be compacted, they have a lifetime of

10,000 h of low released heat, stable linearity for irradiation-current, and they can be operated with pulsed illumination (Jo and Rajesh 2014).

The aim of this work was to study the degradation of LOS and VAL antihypertensives in an aqueous medium by EF and PEF processes using a DSA-GDE system in the presence of oxalic acid and white LED lighting. The effect of pH and the presence of organic acids added (citric acid and tartaric acid) to the removal rate and degree of mineralization of LOS and VAL by EF and PEF processes were evaluated. Finally, the monitoring of the occurrence and disappearance of the degradation of the intermediates of VAL and LOS formed during the PEF process was studied by ultra-high performance liquid chromatography coupled with high-resolution mass spectrometry (UHPLC-HR MS), and the biodegradability of the final VAL and LOS solutions treated by PEF was evaluated using an aerobic biological system.

Materials and methods

Chemicals

Valsartan and losartan potassium (99% purity) were purchased from Sigma-Aldrich. Iron(II) sulfate heptahydrate ($FeSO_4.7H_2O$), dibasic potassium phosphate (K_2HPO_4), orthophosphoric acid (H_3PO_4), potassium hydrogen phthalate ($C_8H_5KO_4$), sulfuric acid (H_2SO_4), oxalic acid ($C_2H_2O_4$), citric acid ($C_6H_8O_7$), tartaric acid ($C_4H_6O_6$), sodium sulfate (Na_2SO_4), and sodium chloride (NaCl) were analytical grade from Merck. The pH of the solutions was set using hydrochloric acid (HCl, 98% purity). Methanol and acetonitrile (HPLC grade) were obtained from Panreac. All solutions were prepared with ultrapure water produced by a Millipore Milli-Q system with a resistivity of > 18 MΩ cm at 25 °C.

Solutions of electrochemical cell

It consisted of a 250-mL glass beaker, which was filled with 200 mL of 4.5×10^{-5} mol/L of a valsartan (VAL) solution and 4.7×10^{-5} mol/L of a LOS solution which contained sodium chloride 0.050 mol/L as supporting electrolyte and Fe^{2+} ions 3.6×10^{-5} mol/L. The pH was adjusted to 3.0 ± 0.1 with 0.1 mol/L hydrochloric acid solution and set with a pH meter HI 2212 by HANNA Instruments. In the case of systems with oxalic, citric, or tartaric acids, the pH remained unchanged and organic acid was added (4.0×10^{-5} mol/L) (Hislop and Bolton 1999; Pignatello et al. 2006; Graça et al. 2017). The solution was stirred continuously throughout the process with a bar magnet at a speed of 400 rpm on a ARECT magnetic stirrer from VELP Scientifica to assure appropriate mixing and reactant transport from/towards the electrodes.

Experimental procedure

Electrolytic system

All experiments were carried out in batch mode using an open, undivided electro-Fenton reactor at room temperature. It consisted of a 250-mL glass beaker. The reactor was equipped with cathode of carbon 2.00 cm^2 GDE and DSA anode 2.89 cm^2 of Ti/IrO_2-doped SnO_2. The electrodes were located in the middle of the reactor at an inter-electrode distance of 2.0 cm, and the system was operated with direct current (j 3.46 mA/cm^2). The electrochemical cell was bubbled with air from an air compressor to saturate it with oxygen solution and ensure its presence during the process, supplemented with magnetic stirring between 400 and 600 rpm. In the PEF process, the solution was irradiated with a Toshiba FL4BLB/4W fluorescent 368 nm black blue maximum tube light from Japan, which was placed inside of the reactor in contact within the solution. The alternative source of radiation was a white LED light wrapped around the beaker (UK; 4.8 V).

Instrumentation and analytical measurements

Measurement of oxidants

The production of total oxidizing species in the system was determined by the metric iodine method. Aliquots of 30 µL, containing the oxidizing agent in a spectrophotometer cell, were taken. Subsequently, 1920 µL of the 0.1-mol/L potassium iodide solution and 50 µL of the ammonium heptamolybdate solution were added. The sample was homogenized, and the absorbance of solution was measured at a wavelength of 350 nm after 15 min in the dark.

HPLC-DAD instrumentation

As a result of the relatively low polarity of VAL and LOS, an HPLC system equipped with an RP C18 column (Waters Spherisil ODS 2, 250 mm × 4.6 mm i.d., 5 µm particle size) was used for the separation. The concentration of VAL and LOS was determined on a Shimadzu LC-20AT with a SPD-M20A photodiode array detector set at 254 nm. The mobile phase was composed of phosphate buffer (pH 3.5; 0.01 mol/L)/ acetonitrile/methanol (44:46:10/*v*/*v*/*v*) at 25 °C under isocratic conditions. The mixture was pumped at a flow rate of 1.0 mL/min. Under these conditions, VAL and LOS were eluted at 6.9 and 5.23 min, respectively.

UHPLC-HRMS instrumentation

An Acquity ultra-performance liquid chromatography (UPLC) system (Waters, Milford, MA, USA) was interfaced with a QTOF mass spectrometer (QTOF Xevo G2, Waters

Micromass, Manchester, UK) using an orthogonal Z-spray electrospray interface. The LC separation was performed using an Acquity UPLC BEH C18 1.7 μm particle size analytical column of 100 × 2.1 mm (from Waters), at a flow rate of 0.3 mL/min. The mobile phases used were H_2O (A) and MeOH (B), both with 0.01% (*v*/*v*) HCOOH. The proportion of MeOH was linearly increased as follows, 0 min, 10%; 14 min, 90%; 16 min, 90%; 16.01 min, 10%, and 18 min, 10%. The injection volume was 20 μL. Nitrogen (Praxair, Valencia, Spain) was used as both the drying gas and the nebulizing gas. The gas flow rate was set at 1000 L/h. The MCP detector potential was set to 3700 V. Capillary voltages of 0.7 and − 2.0 kV were used in positive and negative ionization modes, respectively. A cone voltage of 20 V was applied. The collision gas was argon (99.995%, Praxair). The interface temperature was set to 600 °C and the source temperature to 130 °C. The column temperature was set to 40 °C and the samples to 5 °C. For MSE experiments, two acquisition functions with different collision energies were created: the low-energy function with a collision energy of 4 eV, and the high energy function with a collision energy ramp ranging from 15 to 40 eV. MS/MS experiments were also performed, using a cone voltage of 20 V and collision energies of 10, 15, 20, 30, and 40 eV. For automated accurate mass measurement, the lock-spray probe was performed, using as lock mass leucine enkephalin (2 mg/L) in ACN/water (50/50) at 0.1% HCOOH, pumped at 20 μL/min through a lock-spray needle. The leucine enkephalin $[M + H]^+$ ion (m/z 556.2771) for positive ionization mode, and [M-H]-ion (m/z 554.2615) for negative ionization, were used for recalibrating the mass axis and to ensure a robust accurate mass measurement over time. MS data were acquired in centroid using MassLynx v 4.1 (Waters Corporation).

Total organic carbon analysis

The mineralization of untreated and treated (by EF and PEF processes) samples was monitored by the abatement of the total organic carbon content, measured using a Shimadzu LCSH TOC analyzer. The total organic carbon (TOC) was measured by combustion with catalytic oxidation at 680 °C using high-purity compressed air as a carrying gas at a flow rate of 190 mL/min. A non-dispersive infrared detector was used in the system to determine the TOC amount in the samples. Calibration of the analyzer was obtained with a standard potassium hydrogen phthalate (99.5%) solution. The injection volume was 50 μL.

Biological system

The biological process (BP) was carried out over a period of 8 days using aerobic microorganisms (mixed liquor) from the purge of a food processing plant in Bogotá. Ten milliliters of mixed liquor (4000 mg/L of biomass) was added at 900 mL of the treated VAL and LOS solutions in order to obtain a rate biomass/test compound between 2.5:1 and 4:1. This system was slowly aerated with an aquarium pump (AP-005 XILONG). The system was stirred and the temperature was kept at 37 °C in a Shaker (Wise Shake SHO-1D Digital Orbital Shaker). Before being subjected to the BP, the pH of the samples was adjusted to 7.0 and residual hydrogen peroxide was eliminated using sodium hydroxide (1.0 mol/L) and sodium bisulfite (0.1 mol/L).

Energetic consumption calculation

The energy consumption per volume of electrolyzed solution was obtained from:

$$KWhm^{-3} = \frac{\left(IE_{Cell} + Watts_{lamp}\right).\ t}{V_s} \tag{10}$$

where I is the applied current (A), E_{cell} is the average cell voltage (V), t is the electrolysis time (hours), $\text{Watts}_{\text{lamp}}$ is the power light of the lamp used, and V_s is the volume of the treated solution (L) (Brillas et al. 2009; Salazar et al. 2016).

Results and discussion

Evaluation of oxidizing species generated in the DSA-GDE system

In an electrochemical system, it is important to establish the accumulation of electro-generated oxidizing agents and determine their role in the degrading process. The DSA-GDE electrochemical system was used in the presence of NaCl and, therefore, due to the high catalytic activity of DSA in conductive media in the presence of chloride, active chlorine species, i.e., Cl_2, HClO, and ClO^-, can be electro-generated on the anode surface of the DSA (Eqs. 3–5), which are able to react with VAL and LOS, in addition to the Fenton reagent (hydrogen peroxide generated in the cathode plus iron ions added).

The electro-generation of chlorine oxidizing species on the DSA anode, and hydrogen peroxide on the GDE cathode, separately was demonstrated. In the first case, a system DSA anode-stainless steel cathode (inactive cathode) (Fig. 1a) was used. In these experiments, the absence of GDE as cathode precludes the formation and accumulation of hydrogen peroxide in the media, and only chlorinated oxidizing species can be generated. In fact, as seen in Fig. 1a, ca. 0.35 mmol/L of chlorinated oxidizing species are accumulated after 2 h of treatment in the DSA-stainless steel system, which are half of the oxidized species generated using the DSA-GDE system. In the case of hydrogen peroxide evolution, the graphite-GDE system was used, and the 0.44 mmol/L of this oxidant

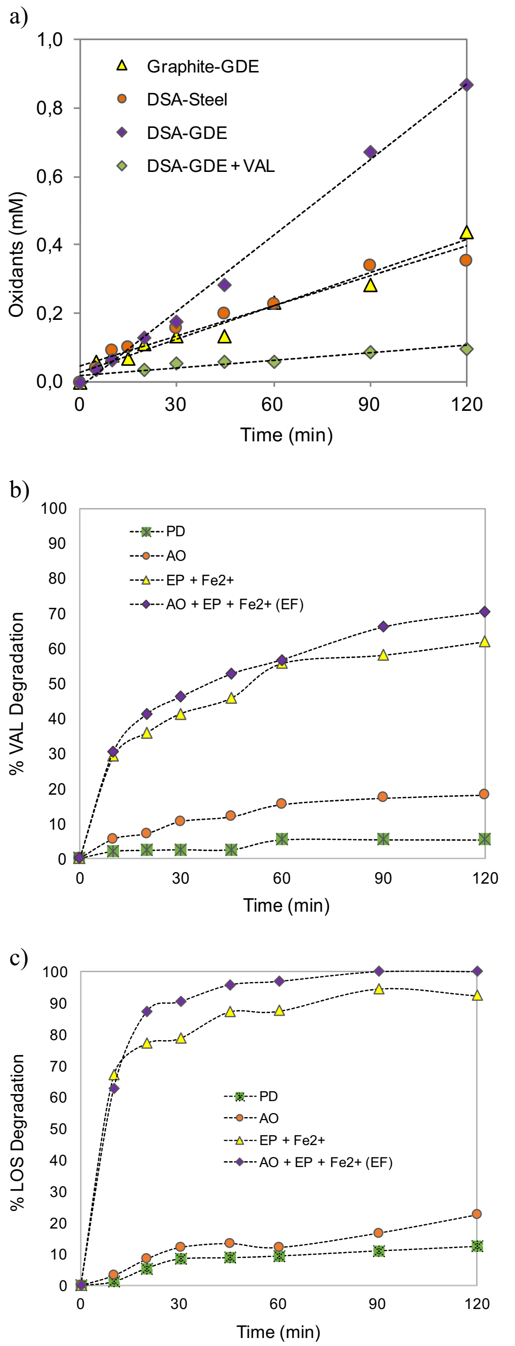


Fig. 1 **a** Controls of oxidizing species evolution: H_2O_2 and chlorinated species electro-generated (DSA-GDE), only H_2O_2 electro-generated (graphite-GDE), chlorinated species electro-generated (DSA-stainless steel), and H_2O_2 and chlorinated species electro-generated (DSA-GDE) in the presence of valsartan. **b** Degradation of valsartan by EF (DSA-GDE) controls: photolysis (PD); anodic oxidation (AO; DSA-stainless steel); H_2O_2 electro-generated (EP; graphite-GDE) in the presence of Fe^{2+}. $[VAL]_0$ 4.6×10^{-5} mol/L, [NaCl] 0.05 mol/L, $[Fe^{2+}]_0$ 3.6×10^{-5} mol/L, j 3.46 mA/cm^2, volume 0.2 L, pH 3.0, at room temperature. In the case of PD test, a white LED light 4.8 W was used. The results correspond to average of two replicates and relative standard deviation for the data is less than 5%

was accumulated after 2 h of treatment. In addition, the active chlorine species and hydrogen peroxide accumulation in the absence and in the presence of VAL and LOS was followed. Figure 1a exemplifies the VAL case. In the VAL presence, the accumulation profile of the total oxidizing species is lower than in its absence, suggesting a reaction between the VAL and the oxidizing total species. Additionally, in the VAL and LOS degradation experiments (Fig. 1b-c), the contribution of only active chlorine species was evidenced (DSA-stainless steel system), around 15% for VAL and 22% for LOS. When EP (graphite-GDE system) was combined with iron ions added, 62% of VAL and 92% of LOS were degraded. This percentages were enhanced because of the use of the DSA anode (DSA-GDE system), reaching 70% of VAL degradation in 120 min of treatment and total removal of LOS in 90 min This results show the contribution of separate systems to the global degradation of antihypertensives by using the DSA-GDE system.

The effect of pH on the degradation of VAL and LOS by EF

The decrease of the VAL and LOS concentration during the EF and PEF was monitored at different pH values and in the presence or absence of three different organic acids (oxalic, citric, and tartaric) in order to evaluate the effect of the Fe(III)-carboxylate complexes formed (Fe(III)–oxalate, Fe(III)–citrate, and Fe(III)–tartrate) in the degradation and mineralization of VAL and LOS. Other conditions such as the current density, the concentration of Fe^{2+}, the supporting electrolyte, and the organic acids used in the tests were established according to parameters evaluated in a previous works (Martínez-Pachón 2018).

Figure 2 shows the degradation of LOS and VAL using different pH values, in the presence and absence of oxalic acid by the EF process using the DSA/GDE system. The highest percentages of degradation of LOS (total removal after 20 min) and VAL (85% after 90 min) were obtained, as was expected, at pH 3.0. During the tests, an increase of pH above 3.5 is not observed. At this pH value, the high concentration of oxidizing species (0.75 mmol/L after 120 min) was also observed (Fig. 2). The degradation of the contaminants could be carried out by (a) the reaction with oxidizing species formed on the DSA anode (chlorinated species; Eqs. 2–5), where at pH 3.0, the predominant specie is the Cl_2 ($E°$= 1.36 V/SHE) (Panizza 2010; Serna-Galvis et al. 2017); (b) the reaction with the hydrogen peroxide formed on GDE cathode, and (c) the attack of $^{\bullet}OH$ radicals produced during the reaction between the Fe^{2+}, added to the system, and the hydrogen peroxide electro-generated (Fenton reaction, Eq. 1). When the process was evaluated at higher pH values, the process was affected and lower degradation percentages were observed. At pH values close to neutral (pH ~6.5 unmodified), 40% of

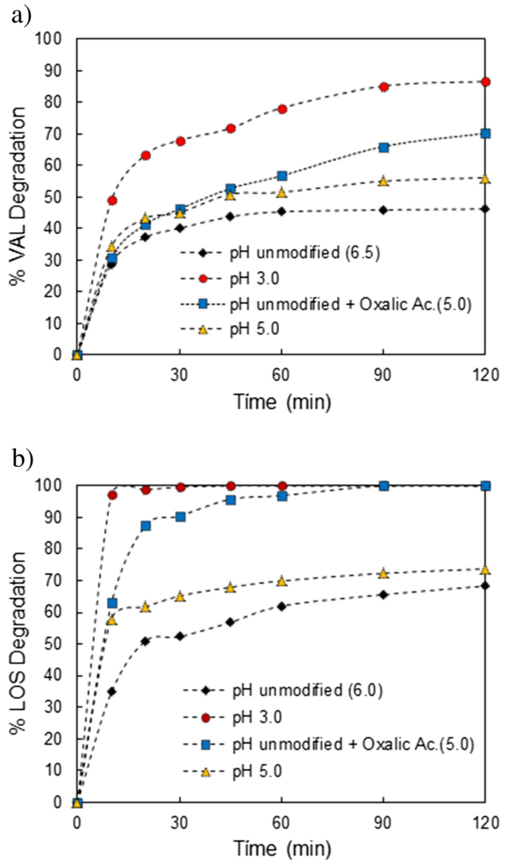


Fig. 2 Effect of pH and the presence of oxalic acid (4.0×10^{-5} mol/L) on the degradation of valsartan (**a**) and losartan (**b**) by the EF process using a DSA anode and GDE cathode at 3.42 mA/cm^2 and sodium chloride (5.0×10^{-2} mol/L) as support electrolyte

degradation for VAL and 60% of degradation for LOS, in 60 min, was obtained. The poor degradation is due possibly to low concentration of Fe^{2+} ions free to react with the hydrogen peroxide electro-generated. The degradation observed could be due mainly to the presence of other electro-generated oxidizing species such as chlorinated species (Serna-Galvis et al. 2017). At pH 5.0, a lower percentage of degradation is observed compared with the results obtained at pH 3.0 (50% VAL and 70% LOS), but higher than when pH was unmodified (~ 6.0). It is clearly related to the low availability of Fe^{2+} free at higher pH values and with a lower concentration of total oxidizing species in the system (see Fig. 3; 0.4 mmol/L after 120 min). At these pH values, the formation of hypochlorous acid and hypochlorite is favored. These species can react directly with the hydrogen peroxide electro-generated (Eq. 10) decreasing the concentration of the oxidizing species generated. At pH 3.0, the formation of Cl_2 is favored, which has a low rate reaction with the hydrogen peroxide (De Luna et al. 2012; Zhu et al. 2008); therefore, higher concentrations of total oxidants were observed. Also, at pH 5 and pH 6, no significant pH modification was observed.

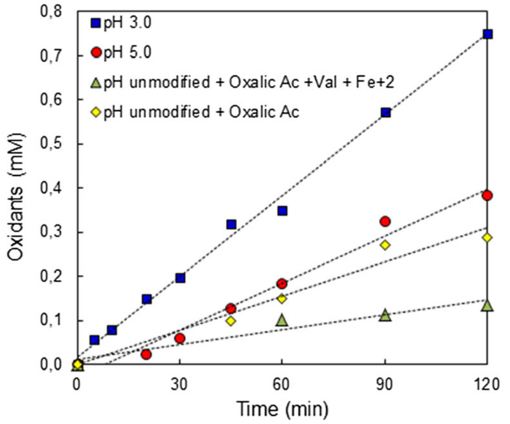


Fig. 3 pH effect in the electro-generated oxidizing species without contaminant at pH 3.0; pH 5.0, in the presence of oxalic acid (4.0×10^{-5} mol/L) without pH modification and in the presence of contaminant (VAL), Fe^{2+} (3.6×10^{-5} mol/L), and oxalic acid (4.0×10^{-5} mol/L) without pH modification during 120 min of treatment using sodium chloride (5.0×10^{-2} mol/L) as support electrolyte at 3.42 mA/cm^2

$$H_2O_2 + HClO/ClO^- \rightarrow H_2O + H^+/Cl^- + O_2 \qquad (11)$$

Near-neutral electro-Fenton process in the presence of oxalic acid

The influence of the oxalate ligand on VAL and LOS degradation by EF without pH modification was evaluated. The stoichiometry of Fe(III)–oxalate complexes was 1:3, which has been reported as optimal by several authors (Glebov et al. 2011; Moreira et al. 2015; Souza et al. 2014). To understand the formation of such complexes, it is necessary to understand the speciation of oxalic acid in aqueous solution, which includes two ionization reactions ($pK_{a1} = 1.25$; $pK_{a2} = 4.27$) and three species: $H_2C_2O_4$, $HC_2O_4^-$, and $C_2O_4^{2-}$, which coexist in equilibrium (Stumm and James 1996). At pH values close to neutral, it has been identified that the $C_2O_4^{2-}$ ion is the predominant species in equilibrium. This has two oxygen atoms with unshared pairs of electrons, and in the presence of Fe^{3+} and Fe^{2+} ions, oxalate ions can generate five-membered rings and form different complex ions, where the Fe(III)–oxalate complexes are more stable than the Fe(II)–oxalate complexes (Villegas-Guzman et al. 2017). Thereby rendering it more likely to outcompete hydroxide ions for complexation with Fe^{3+}/Fe^{2+} in aqueous solution at high pH (Feng et al. 2012). Therefore, the solution pH for •OH production can be extended at near-neutral pH.

Figure 2 shows the VAL (Fig. 2a) and LOS (Fig. 2a) degradation in the presence of Fe(III)-oxalate without pH modification (pH ~ 5.0). It is demonstrated that the EF process was able to degrade completely the LOS molecule after 90 min of treatment, and approximately 70% of VAL was removed after

120 min. These degradation percentages were higher in comparison with those obtained at pH 5.0 in absence of Fe(III)-oxalate, in which 70% of LOS and 50% of VAL was eliminated after 90 min. These results demonstrated the positive effect of the presence of oxalic acid on the EF process although it is known that some anodic materials can be deactivated by dirtiness generated in the surface by the chemisorptive interaction of polymeric products derived from aliphatic acids and aromatic byproducts (Bock and MacDougall 1999). No deactivation of the anode was evidenced because the results were consistently reproducible in the degradation of pollutants after many runs. The use of carboxylic acids solve two of the main limitations of the EF process: (a) it allows the iron to be available in solution at higher pH that 3.0, thus extending the reaction optimal pH range from acid to near-neutral values and enabling the treatment of contaminated waters without acidification and neutralization (Batista and Nogueira 2012), and (b) the formation of Fe(III)–sulfate and Fe(III)–chloride complexes (Moreira et al. 2017) and some Fe(III)–pollutants complexes (Silva et al. 2010) is limited, since these compounds exhibit lower formation constants than Fe(III)–carboxylate complexes. In addition, the reaction rate of Fe(III)–oxalate complexes with hydrogen peroxide is higher than with Fe(III)-aquo complexes (2.4×10^9 and 586 M^{-1} s^{-1}, respectively), which indicates that the use of oxalic acid could favor the Fenton reaction (non-photo-catalyzed system) (Graça et al. 2017; De Laat et al. 2004).

EF process under light irradiation, PEF (LED and UV-A (368 nm) lamps)

The degradation of VAL and LOS by the EF process was evaluated with two light sources: (a) UV-A irradiation (blue tube with black fluorescent light, 4 W, 15 cm, and 365 nm) which are commonly used in these processes, but have a high energy requirement associated to the high input power, low photonic efficiency resulting in high energy consumption, a short lifetime, and problems related to end-of-life disposal for the mercury content in the lamp (Autin et al. 2013) and (b) LED irradiation (white light, 4.8 W per 60 LED, 80 cm with 48 LEDs), as there is growing interest in using (LEDs) as alternative to traditional mercury lamps, due to their low energy consumption, potential for high efficiency, and long lifetime. Also, different authors have found that have high penetration and coverage of the light emitted in the solutions to be treated (Würtele et al. 2011; Villegas- Guzman et al. 2017).

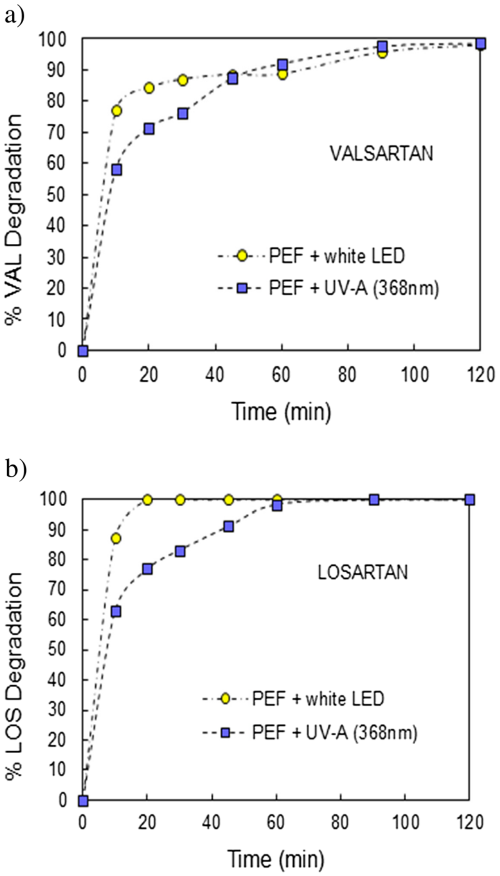


Fig. 4 Effect of type of lamp (white LED and UV-$A_{368\ nm}$) on the degradation of valsartan (**a**) and losartan (**b**) by the PEF process using DSA - GDE at 3.42 mA/cm^2 and sodium chloride (5.0×10^{-2} mol/L) as support electrolyte and in the presence of oxalic acids (4.0×10^{-5} mol/L) without pH modification

As shown in Fig. 4, the VAL was totally degraded after 120 min using UV-A (365 nm) lamp or LED indistinctly. However, the total energy consumption calculated (Eq. 9), was slightly lower using the LED system, 0.29 KW/h than using UV-A (365 nm) lamp, 0.3 KW/h. It is important to note that all energy consumption calculations were made taking into account the power of the lamps used.

In the case of LOS, the degradation of this compound is achieved after 20 min of treatment using the LED system, while using the UV-A (360 nm) lamp, the total LOS removal was obtained after 60 min of treatment, so the LED lighting system has a lower energy consumption than UV-A (365 nm) lamp (4 times less: LED 4.8 KW/h and UV-A lamp 4.0 KW/h). These results could be due to the fact that the PEF system is favored by the use of radiation in the UV-Vis range, since the Fe(III)-carboxylates and aqua-complexes of Fe(III), present in the solution, are dissociated by absorbing radiation in the range of 200 and 500 nm of wavelength (Eqs. 6–8) (Moreira et al. 2015), yielding Fe^{2+} ions free and available to react with hydrogen peroxide in the Fenton reaction.

In addition, it is known that most of $C_2O_4^{2-}$ ions, resulting from light absorption by the ferrioxalates complexes (Eqs. 11–12), decompose to carbon dioxide radical anion and carbon dioxide (Eqs. 13–14) (Souza et al. 2014). Besides, the photodecarboxylation of ferrioxalates provides a quicker pathway for regeneration to Fe^{2+} from Fe^{3+} and further reaction with H_2O_2 yielding additional $^{\bullet}OH$ radicals (Eq. 15). The H_2O_2 can also react with $^{\bullet}$ OH and generate superoxide radical ($HO_2^{\bullet}$). Thus, ferrioxalate photolysis in the presence of H_2O_2 provides a continuous source of $^{\bullet}OH$ radicals through the Fenton reaction (Silva et al. 2010):

$$Fe^{3+}(C_2O_4)_2^{-} + h\nu \rightarrow Fe^{-2+}(C_2O_4) + C_2O_4^{\bullet-} \quad (12)$$

$$Fe^{3+}(C_2O_4)_3^{3-} + h\nu \rightarrow Fe^{2+} + 2\ C_2O_4^{2-} + C_2O_4^{\bullet-} \quad (13)$$

$$C_2O_4^{\bullet-} \rightarrow CO_2^{\bullet-} + CO_2 \quad (14)$$

$$CO_2^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + CO_2 \quad (15)$$

$$Fe^{2+} + H_2O_2 + 3\ C_2O_4^{2-} \rightarrow Fe^{3+}(C_2O_4)_3^{3-} + \bullet OH + OH^{-} \quad (16)$$

Electronic excitation is also produced, decreasing the activation energy for the decomposition of the proposed compounds (Eqs. 11–14), accelerating the production of •OH (Monteagudo et al. 2010; Oturan and Jean-Jacques 2014), and therefore the oxidation of VAL and LOS.

These results demonstrated that, in the case of the PEF proposed system, the LED as radiation source is an economical and a viable alternative for the PEF treatments, since it covers wavelengths within the visible, ultraviolet, and infrared spectra (especially the white LED, since it has a more ambiguous emission range than the others: between 400 and 700 nm) (Vargas-Hernández and Rengifo-Morocho 2012) and it has longer durability and versatility.

PEF degradation in the presence of other Fe(III)–carboxylate complexes using citric and tartaric acids

The ability of the oxalate ligand to obtain good results in the degradation of VAL and LOS at near-neutral pH has been demonstrated, although it is not the only complex that has been reported to have the ability to improve these results in PEF systems (Abrahamson et al. 1994; Nogueira et al. 2017; Rodríguez et al. 2009; Villegas-Guzman et al. 2017). Therefore, the degradation of VAL and LOS in the presence of Fe(III)-oxalate, Fe(III)-citrate, and Fe(III)-tartrate at near-neutral pH was studied. Figure 5 shows the total degradation of VAL and LOS, after 120 and 20 min, respectively, in the presence of the three carboxylates evaluated indistinctly. When the mineralization of VAL and LOS was evaluated in the presence of the citric, oxalic, or tartaric acids, approximately 30% of TOC was removed in all cases (see Fig. 5). This suggests that organic compounds coming from the transformation of VAL and LOS (see Table 1) are more recalcitrant to the $^{\bullet}OH$ action. In addition, as it is well known, these processes lead to the formation of the other aliphatic acids such as malic and succinic, causing a slower degradation rate.

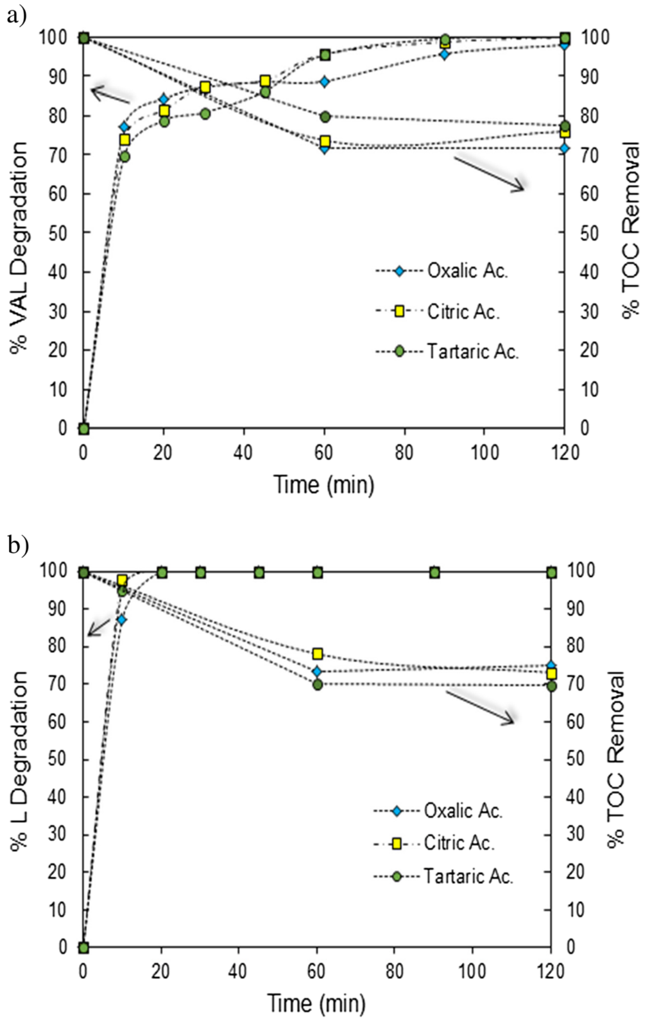
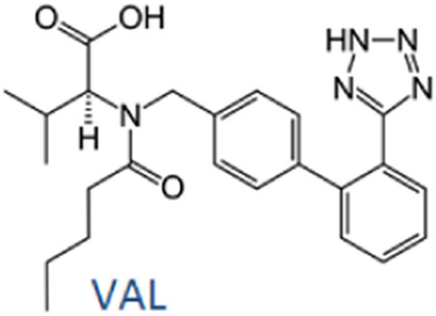
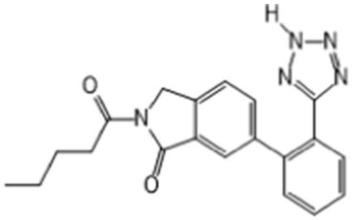
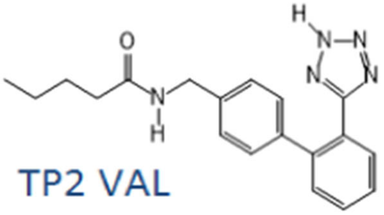
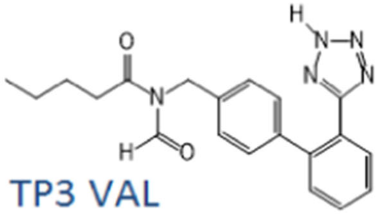
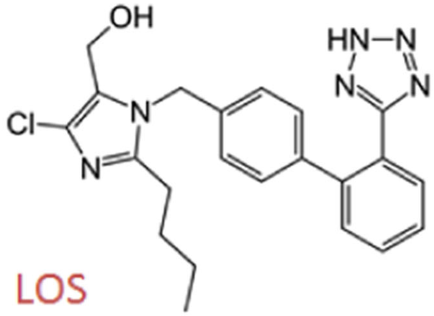
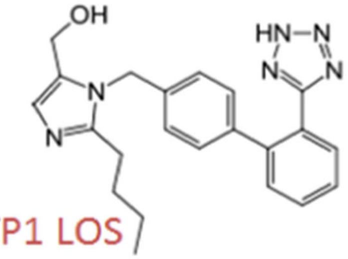
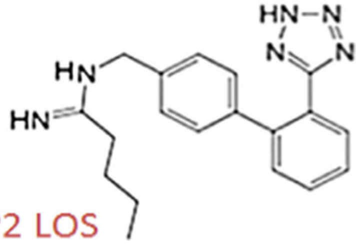


Fig. 5 Degradation and mineralization of valsartan (**a**) and losartan (**b**) by the PEF process using white LED (DSA-GDE) system at 3.42 mA/cm^2; sodium chloride (5.0×10^{-2} mol/L) as support electrolyte and in the presence of organic acids (4.0×10^{-5} mol/L): oxalic acid, citric acid, and tartaric acid

However, despite of the good results achieved with the use of Fe(III)-carboxylate complexes, the use of carboxylic acids should be taken with precaution because the presence of an excess of oxalate ions, which is not complexed with the Fe^{3+} ions present in solution, could act as an extra carbon source (only 0.96 mg/L, in this work), explaining the difficulty for the TOC elimination (Glebov et al. 2011), but also due to a decrease of light penetration throughout the solution and the necessity to support higher costs, so it should not overcome this stoichiometric relationship (Brillas et al. 2009).

Table 1 Transformation products for the degradation of valsartan and losartan by the photo-electro-Fenton (DSA-GDE) system at 3.42 mA/cm^2, sodium chloride (5.0×10^{-2} mol/L) as support electrolyte by UHPLC/MS-MS based on the common fragmentation method

Structure of the compounds	Structure of transformation products
 VAL	 TP1 VAL  TP2 VAL  TP3 VAL
 LOS	 TP1 LOS  TP2 LOS

Structure-reactivity relationship in the degradation of LOS and VAL by the PEF process

The higher percentages of degradation of LOS compared with those obtained for VAL (Fig. 5) by PEF using the DSA/GDE system could be due to their chemical composition. LOS and VAL structures present a common skeleton of two aromatic rings bonding to tetrazole groups and only differ in the substituents (Table 1). The VAL structure is relatively more stable to the attack with $^{\bullet}$OH radicals than the LOS structure. The quicker transformation at 120 min when using the Cl^{-} medium can be related to the faster reaction of LOS with chloride reactive species, especially HClO. This is one of the active chlorine species, which is electro-generated by the direct oxidation of chloride ions as shown in Eq. 3 (Salazar et al. 2016). Also, the hydroxyl radical acts by electrophilic addition on the -C=C- bonds, and in the case of LOS, will attack the imidazole ring, which will be more prone to breakage. Recent results of our research group have demonstrated the formation of transformation products (Table 1) after 2.0 min of PEF treatment. Regarding the other oxidizing species generated, the Cl^{-} is rapidly hydrolyzed to hypochlorous acid which is in equilibrium with chloride ion (Eqs. 4 and 5). On the other hand, the rupture of the imidazole ring is more difficult to occur in VAL structure since it does not have the “instability” in its structure. The presence of the ketone and the carboxylic acid groups promote the electrophilic addition on those groups (Brillas and Martínez-Huitle 2015; Díez et al. 2017).

Identification and evolution of oxidation products and its biodegradability

The proposed PEF system using organic acids and LEDs allowed the total degradation of VAL and LOS. However, these compounds have not reached total mineralization, which implies the production of transformation products (TPs), which have been identified by UHPC/MS-MS based on the common fragmentation method. Assuming that most TPs share the fragmentation pathway with the parent drug, specific narrow-window extracted ion chromatograms (nw-XICs) at the expected exact-mass m/z fragments were obtained from high-energy full-spectrum TOF-MS acquisitions. Every chromatographic peak with a retention time different than the parent drug was treated as a potential TP. The combined spectrum at the same retention time in the LE function allowed for establishing the accurate mass of the potential TP, which was studied in order to determine its molecular formula. Based on this information, possible structures for some transformation products are proposed (Table 1). However, some additional analytical assays are necessary to propose any oxidation pathway for the LOS and the VAL.

Once these TPs have been identified, the determination of their biodegradability is crucial to rule out that they are dangerous. To evaluate the PEF system capability to transform the initial pollutant in more biodegradable compounds, a biological process was carried out using non-adapted microorganisms obtained from the purge of a food processing plant in Bogotá (data not showed). The biological system was applied to solutions submitted after different times of PEF system treatment (0, 90, and 300 min) for VAL and (0, 60, and 300 min) for LOS. For the case of VAL, the TOC remains practically unchanged after 5 days of BP. However, after 8 days of BP, a high degradation (80%) was observed, and in the case of LOS after 3 days of BP, it already reached a degradation of 50% for the treated sample of 5 h and 30% for the 1-h sample. On the fifth day of BP, a total degradation was observed (see Table 2). Controls were made; VAL and LOS solutions without PEF treatment were also summited to BP. No decrease of TOC was observed after 8 days, which indicates that these compounds, VAL and LOS, are highly recalcitrant to the action of microorganisms.

Table 2 Evolution of TOC removal by biological degradation test of the treated (by PEF process) and non-treated solutions of valsartan and losartan. Test conditions, 14 mg/L of TOC for VAL and 12.7 mg/L of TOC for LOS initial, 900 mL of solution, pH 7.0, 37 °C

Time	% Degradation			
	Control (glucose)	VAL without PEF treatment	VAL + PEF (90 min)	VAL + PEF (300 min)
Day 2	100.0%	0.0%	2.0%	6.0%
Day 4	100.0%	0.0%	10.0%	13.0%
Day 6	100.0%	0.0%	45.0%	30.0%
Day 8	100.0%	10.0%	80.0%	87.0%
Time	% Degradation			
	Control (glucose)	LOS without PEF treatment	LOS + PEF (60 min)	LOS + PEF (300 min)
Day 2	100.0%	0.0%	6.7%	27.0%
Day 4	100.0%	0.0%	19.0%	36.0%
Day 6	100.0%	2.0%	61.0%	100.0%
Day 8	100.0%	11.0%	100.0%	100.0%

Conclusions

The EF and PEF processes by using DSA anode and GDE cathode and based on the use of organic acids and LED lights demonstrate to be adequate for efficient degradation of the antihypertensives VAL and LOS. The synergic combination of photolysis, anodic oxidation on the DSA surface, the generation of hydrogen peroxide by the cathode, the subsequent generation of hydroxyl radicals by the Fenton reaction in presence of iron ions, and the breakdown of iron complexes formed with the organic acids under with LED lighting, permits obtaining a system with high efficiency in the degradation and mineralization of the compounds in the study. During the EAOP obtained, three aromatic compounds of VAL and two aromatic compounds of LOS were characterized as the main transformation products. The results show that these kind of systems can be an interesting alternative to removing emerging contaminants present in surface water and wastewater from WWTPs. Concerning the biological treatment, the solutions of VAL and LOS treated during 90 and 300 min by the PEF process were eliminated approximately 80% of the initial TOC by microorganisms in the biological treatment. Therefore, the PEF system combined with a biological process is a promising alternative for the complete mineralization of the pollutants.

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Eliminación de contaminantes emergentes en aguas residuales urbanas mediante diferentes sistemas Electro-Fenton

Eliminación de contaminantes emergentes en aguas residuales urbanas mediante diferentes sistemas Electro-Fenton

Diana Martínez-Pachón[a]*; Ana Botero-Coy*[b]*, Ricardo A. Torres-Palma*[c]*, Félix Hernández*[b]*;*

Alejandro Moncayo-Lasso[a]***

[a] Universidad Antonio Nariño; Facultad de Ciencias; Grupo de Investigación en Ciencias Biológicas y Químicas; Bogotá D.C. – Colombia.

[b] Research Institute for Pesticides and Water (IUPA), University Jaume I, Castellón, Spain.

[c] Universidad de Antioquia; Instituto de Química; Grupo de Investigación en Remediación Ambiental y Biocatálisis; Medellín. – Colombia

*Co-author for corresponding

Alejandro Moncayo-Lasso (e-mail: amoncayo@uan.edu.co)

Resumen:

Este estudio se centró en la eliminación de 16 compuestos farmacéuticos identificados en muestras del efluente de la PTAR Salitre de Bogotá. Los tratamientos probados para evaluar la eliminación de los compuestos farmacéuticos fueron: EF (sin Fe^{+2}), EF (Fe^{+2}), PEF (Fe^{2+}/ luz (365 nm)) y PEF (Fe^{2+}/ luz (365 nm) / ácido oxálico). Las muestras utilizadas tenían un contenido inicial de carbono orgánico de 38,8 mg/L y la masa total de los fármacos fue de 9,73 μg/L. Todos los ensayos se realizaron a pH natural (6,8), con dos materiales anódicos (DSA y BDD) usados de forma independiente. El sistema Electro-Fenton utilizado en los ensayos mostró una degradación de los contaminantes aproximadamente del 40 % después de

3 horas de tratamiento. La implementación de luz reveló una mejoría hasta del 50 % utilizando DSA como material anódico en el sistema PEF con respecto al proceso EF. En cambio, el sistema PEF, cuando se adicionó ácido oxálico, presentó mejores resultados, demostrando la eliminación del 66% de los fármacos encontrados. Se pudo establecer como esta condición estimula la formación de complejos Fe(III)-oxalato que a valores de pH cercanos al neutro producen Fe^{2+} aumentando su disponibilidad en el sistema y por ende su eficiencia. En consecuencia, el aspecto más importante de este trabajo, es la alta capacidad que mostraron estos sistemas para eliminar contaminantes emergentes, confirmando su viabilidad para ser utilizados en el tratamiento de aguas residuales reales, sin modificación de pH.

Palabras Clave: Electro-Fenton, Foto-Electro-Fenton, Foto-Electro-Fenton con ácido oxálico, contaminantes emergentes, aguas residuales

Introducción

Los compuestos farmacéuticos son uno de los muchos contaminantes que pueden llegar a los cuerpos de agua, debido a su uso indiscriminado y su eliminación continua, generando riesgos para la salud humana, los animales y el ambiente (Jurado et al. 2012), como lo son, la resistencia a los antibióticos y el resurgimiento de diferentes microorganismos con efectos indeseables (Alalm, Tawfik, and Ookawara 2015; Zhang, Ghali, and Houlachi 2017). Estos compuestos pueden ser desechados directamente en el inodoro, en la basura o como sustancias no asimiladas completamente por el cuerpo humano (metabolitos), excretadas en heces u orina, llegando a las aguas residuales y permaneciendo en los efluentes (Mackuľak et al. 2015), incluso después de someterse a varios tratamientos de depuración (Barceló 2003).

Identificarlos no ha sido tarea fácil, requirió de mejoras en las técnicas analíticas, lo cual permitió avances en ese campo con la identificación de un nuevo tipo de contaminante ambiental, denominado contaminantes emergentes (CEs), y prendió las alarmas de las comunidad científica para su análisis y estudio (Catalá et al. 2015).

De este tipo de contaminantes, no hay información veraz sobre datos toxicológicos, riesgo en los ecosistemas y su posible impacto, por lo cual es difícil establecer sus efectos sobre el ambiente (Fick et al. 2010; Gómez-canela et al. 2016). Algunos estudios han establecido la presencia en los cuerpos de agua de sustancias como antibióticos, analgésicos, anticonvulsivos, β-bloqueadores, anticonceptivos, esteroides y antidepresivos, entre otros (Hernando et al. 2006; Ibáñez et al. 2013). De igual manera, como consecuencia en el aumento del consumo de drogas de abuso como marihuana y cocaína, en Latinoamérica, también se ha observado su presencia en los cuerpos de agua.

En Colombia, en el año 2015 se realizó un Screening en la PTAR “Salitre” de Bogotá (Hernández et al. 2015) identificando la presencia de más de mil compuestos, dentro de los que se encuentran fármacos, productos de cuidado personal, drogas de abuso, pesticidas, entre otros y se desconoce su destino e impacto ambiental, pero puede predecirse o evaluarse sobre la base de sus características químicas y biológicas (Fatta-Kassinos, Meric, and Nikolaou 2011), como los son el polimorfismo, su introducción en el ambiente como metabolitos y su estructura químicamente compleja (Kummerer 2009), por lo cual pueden presentar fenómenos de adsorción en los suelos y sedimentos, complejarse con metales y compuestos orgánicos, oxidarse, sufrir fotólisis, volatilización y biodegradación. De igual manera, estos compuestos pueden ser considerados contaminantes en su forma elemental o como metabolitos (Feng et al. 2014; Valcárcel et al. 2012), según estudios realizados en 2013, el 64% de los fármacos son excretados en la orina y un 35% en las heces. A su vez, se determinó que el 42% de estas sustancias se excretan también como metabolitos secundarios (Tejada, Quiñonez, and Peña 2014).

Como se presenta en múltiples trabajos, incluyendo algunos realizados por nuestro grupo de investigación, se ha demostrado que las plantas de tratamiento de aguas residuales, a nivel mundial, no están en capacidad de eliminar en su totalidad este tipo de contaminantes (Hernández et al. 2015; Mackuľak et al. 2015; Martínez-Huitle and Brillas 2009; Oturan and Aaron 2014). Por lo cual, se requiere de nuevos y mejores procesos que estén en capacidad de eliminarlos.

Los procesos avanzados de oxidación (AOPs) han demostrado ser una alternativa para la remoción de estos contaminantes (Klamerth et al. 2010), siendo eficientes en la eliminación de una gran variedad de CEs (Annabi et al. 2016; Jojoa-Sierra et al. 2017; Liu et al. 2013; Padilla-Robles et al. 2015; Salazar, Contreras, Mansilla, Yáez, et al. 2016), a través, de una serie de reacciones donde se generan los radicales $^{\bullet}OH$, para atacar la materia orgánica.

Dentro de los AOPs los procesos electroquímicos (EAOPs) permiten la electrólisis del contaminante de forma directa “oxidación anódica (AO)” o indirecta “Electro-Fenton (EF)”. El proceso EF es el más conocido y se fundamenta en la electro-generación continua de H_2O_2 (Ec. 1) sobre la superficie de un cátodo, generalmente, de grafito en presencia de gas O_2, que junto con la adición de Fe^{2+} generan la reacción Fenton (Ec. 2) para producir el oxidante $^{\bullet}OH$, un compuesto altamente oxidante que ataca de manera no selectiva dichos contaminantes.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (2)$$

En este proceso son utilizados diversos materiales como electrodos, los más comunes en el cátodo para la producción del peróxido son: el grafito, el carbón vítreo reticulado, filtros o fieltros de carbono y los de difusión de gas. De los materiales utilizados en el ánodo están: el diamante dopado con boro sobre platino o borosilicato (BDD), los electrodos dimensionalmente estables (DSA), hechos a base de óxidos de metales, y los ánodos de platino (Pt) (Brillas et al. 2009).

Los ánodos de BDD son reconocidos como un excelente ánodo (no activo) para ser utilizado en el tratamiento electroquímico de contaminantes orgánicos (Comninellis 1994). Sobre la superficie del BDD se generan radicales $^{\bullet}OH$, los cuales al ser fisiadsorbidos $BDD(^{\bullet}OH)$ (Ec. 3) permanecen estables, haciéndolos disponibles para reaccionar fácilmente con los contaminantes orgánicos en la solución (representados como R. Ec. 4), dando como resultado la degradación y en el mejor de los casos la mineralización completa a dióxido de carbono (Panizza 2010).

$$BDD + H_2O \rightarrow BDD(^{\bullet}OH) + H^+ + e^- \qquad (3)$$

$$BDD(^{\bullet}OH) + R \rightarrow BDD + CO_2 + H_2O \qquad (4)$$

De igual manera, los ánodos dimensionalmente estables (DSA) basados en mezclas de óxidos metálicos como IrO_2, RuO_2, TiO_2 y Ta_2O_5, y, en algunos casos, dopados con SnO_2, Sb_2O_5 y PbO_2, también han sido probados en el tratamiento de aguas residuales y han demostrado su alta eficacia en la degradación de compuestos orgánicos (Malpass et al. 2010; Ricardo E. Palma-Goyes et al. 2016). Estos ánodos presentan una gran área superficial, alta actividad catalítica, estabilidad a la corrosión y excelente resistencia mecánica y química incluso a alta densidad de corriente y en medios fuertemente ácidos. Además, en presencia de cloruros como electrolito soporte, especies de cloro activo como Cl_2, HClO y el ClO^- (Zhu et al. 2008), pueden producirse adicionalmente en el sistema (Ec. 5-7) los cuales también son reconocidos oxidantes y pueden eliminar la materia orgánica :

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{5}$$

$$Cl_2 + H_2O \rightleftarrows HOCl + H^+ + Cl^- \tag{6}$$

$$HOCl \rightleftarrows H^+ + ClO^- \tag{7}$$

Esto motivo el seguimiento de un grupo de compuestos de especial interés por su amplio consumo en Colombia y por sus posibles afectaciones a los ecosistemas y la salud humana (DPN 2012; Vásquez Velásquez, J., Gómez Portilla, K., & Rodríguez Acosta 2010) en muestras de aguas residules del efluente de la PTAR Salitre de Bogotá para evaluar su eliminación a partir de una serie de EAOPs propuestos, utilizando UHPLC acoplado a espectrometría de masas con triple cuadrupolo.

Materiales and Métodos

Reactivos:

Los reactivos metanol (MeOH), acetonitrilo (ACN) y acetato de amonio (NH_4AC) son de calidad HPLC y el ácido fórmico (HCOOH) con pureza mayor al 98% de Scharlab (Barcelona, España). Se obtuvo agua de grado HPLC a partir de agua destilada a través de un sistema de purificación de agua Milli-Q (Millipore, Bedford, MA, EE. UU.).

Los estándares de referencia farmacéutica son Sigma-Aldrich, LGC Promochem, Toronto Research Chemicals, Across Organics, Bayer Hispania y Aventis Pharma. Todos con una pureza superior al 93%. Se prepararon soluciones madre de los estándares a concentraciones entre 50 y 500 mg/L, para preparar soluciones intermedias de 10 mg/L por dilución con metanol. Las soluciones de trabajo que contienen todos los analitos al nivel de µg/L se prepararon semanalmente a partir de soluciones madre mediante diluciones con agua, y se usaron para la preparación de estándares de calibración y para ser utilizadas como muestras en el control de calidad (QCs).

Los estándares internos isotópicamente marcados (ILIS) utilizados fueron: acetaminofén-d4, diclofenaco-d4, valsartan-d8, erytromicina-13C-d3, irbesartan-d6, venlafaxina-d6, carbamazepina 10,11-epóxido-d10 eran de isótopos provienen de CDN (Quebec, Canadá); sulfametoxazol-13C6, azitromicina-d3, ciprofloxacina-d8, norfloxacina-d5 y trimetoprima-13C3 son de Cambridge Isotope Laboratories (Andover, MA, EE. UU.). Se prepararon soluciones madre de ILIS entre 50 y 500 mg/L individuales en MeOH. Se prepararon mezclas intermedias de ILIS entre 1 y 0,1 mg/L por dilución con MeOH. Posteriormente se preparó una solución mezclada de ILIS a 2 µg/L en MeOH para su uso en el análisis de muestras. Todas las soluciones se almacenaron en botellas de vidrio ámbar a -20ºC.

Toma de muestras:

Las muestras del efluente de la PTAR “Salitre” de Bogotá, fueron recolectadas, diariamente, durante siete días consecutivos en 2017, de forma compuesta durante 24 horas, recolectando muestras cada 10 minutos para un volumen total de 2500 mL/dia con un automuestreador Endress-Hauser, comenzando el miércoles de marzo 11 y terminando el martes 17 de marzo. Las muestras se recogieron en botellas de polietileno de alta densidad y se transportaron a los laboratorios para su tratamiento. Tras la recepción en el laboratorio, las muestras se almacenaron inmediatamente en oscuridad a -20 °C hasta la filtración.

Carbono Orgánico Total (TOC):

La transformación del contaminante en CO_2, iones inorgánicos y agua se midió en muestras tratadas y no tratadas, mediante combustión catalítica a 680 °C usando gas O_2 de alta pureza a un caudal de 190 mL/min, usando un analizador TOC Shimadzu LCSH. Se usó un detector infrarrojo no dispersivo en el sistema para determinar la cantidad de TOC en las muestras. La calibración del analizador se logró con una solución estándar de ftalato de potasio al (99.5%) y el volumen de inyección fue de 50 μL.

Procedimiento Experimental

Sistema Electroquímico:

Todos los experimentos se llevaron a cabo en un reactor electroquímico en batch que consistía en un beaker de vidrio pyrex de 250 mL, el cual se llenó con 200 mL de muestra homogenizada del efluente de la PTAR “Salitre” de Bogotá a temperatura ambiente. Todos los ensayos fueron realizados con un cátodo de difusión de gas con fieltro de carbono (GDE) y con un ánodo (DSA) de Ti/IrO_2 dopado SnO_2 o un (BDD) de diamante dopado con Boro los cuales usaron como electrolito soporte 0,050 mol/L de (Cloruro de sodio (NaCl) y Sulfato de sodio (Na_2SO_4), respectivamente. Los electrodos se ubicaron en el centro del reactor a una distancia de 2,0 cm y el sistema se hizo funcionar en modo de corriente constante. Se adicionó $3.6x10^{-5}$ mol/L de Fe^{2+} como sulfato ferroso. La celda se burbujeó con aire para saturar la solución con oxígeno y se agitó continuamente a una velocidad de 400 rpm (AREC.T por VELP Scientifica).

Se realizaron diferentes ensayos de los sistemas: EF (sin Fe^{+2}), EF (Fe^{+2}), PEF (Fe^{2+}/ luz (365 nm)) y PEF (Fe^{2+}/ luz (365 nm) / ácido oxálico). El sistema PEF se irradió con un tubo de luz fluorescente negro-azul de 365mn FL40BLB/4W y el ácido oxálico se adiciono en una concentración de $4.0x10^{-5}$ mol/L.

Instrumentación y métodos Analíticos:

Instrumentación UHPLC-HRMS

Los compuestos fueron identificados y cuantificados utilizando UHPLC acoplado a espectrometría de masas con triple cuadrupolo Xevo TQS (Waters) equipado con un Z-spray ortogonal de interfaz de ionización por electrospray en modo positivo. (ESI). El nitrógeno (Praxair, Valencia, España) se usó como gas de cono y gas de desolvatación a 250 L/h y 1200 L/h, respectivamente. Para la operación en modo MS/MS, el gas de colisión fue argón de 99.995% de puereza (Praxair, España) con una presión de $4x10^{-3}$ mbar en la celda de colisión a 0.15 mL/min. La tensión capilar fue de 3.5 kV, la temperatura de la fuente de 150 ºC y la temperatura de desolvatación de 650 ºC. El voltaje del cono se seleccionó a 10 V para todos los compuestos. Los tiempos de retención se seleccionaron automáticamente para obtener suficientes puntos por pico y podrían reducirse a 3 ms.

La separación cromatográfica se realizó usando una columna analítica Acquity UPLC BEH C18, 1,7 µm, 100 mm x 2,1 mm (Waters). La fase móvil fue A: H_2O, B: MeOH, ambos compuestos con 0.01% de HCOOH y 1 mM de NH_4Ac. El solvente (B) uso un gradiente de elución de la siguiente manera: 0 min, 5%; 7 min, 90%; 8 min, 90%; 8.1 min, 5%; 10 min, 5%. El flujo fue de 0,4 ml/min. La columna se mantuvo a 40 ºC y el automuestreador se mantuvo a 5 ºC. El tiempo de análisis fue de 10 min. Todos los datos fueron adquiridos y procesados utilizando el software Masslynx V 4.1 (Waters).

Método Analítico:

Se tomaron alícuotas de las muestras tratadas con los diferentes sistemas electroquímicos a 60, 120 y 300 minutos de tratamiento y sin tratar en tubos de centrífuga de 15 mL, las cuales fueron enviadas en contenedores fríos al Instituto Universitario de Plaguicidas y Aguas (IUPA) de la Universidad Jaume I (UJI) Castellon-España, en un plazo máximo de 24 h. Una vez en el laboratorio, se congelaron a -20 ºC y se descongelaron a temperatura ambiente el mismo día del análisis; se transfirieron alícuotas en Eppendorf de 2 mL y centrifugaron a 12000 rpm durante 3 min. El procedimiento multiresiduo aplicado para el análisis de las muestras se basó en un trabajo previo del grupo, donde se requirió la inyección directa de las muestras, sin ningún paso de preconcentración, debido a la excelente sensibilidad del instrumento utilizado (Boix et al. 2015). Se tomarón alícuotas de 1000 µL de las muestras y 100 µL de ILIS de 2 µg/L (concentración final de ILIS en las muestras inyectadas, 0.1 µg/L). el volumen de inyección al equipo fue 100 µL.

Las muestras de control de calidad (QCs) estaban constituidas por alícuotas del efluente de la PTAR, enriquecidas con los productos farmacéuticos objetivo a 0.1, 1 y 10 µg/L. Para este fin, se tomaron 1000 µL de muestra, 100 µL de solución estándar (10 µg/L) y 100 µL de ILIS 2 µg/L. La cuantificación de los analitos se realizó usando la transición Q y la calibración externa con estándares. En aquellos casos donde el analito ILIS estaba disponible, se usaron áreas relativas para la cuantificación. De esta forma, se corrigieron los posibles efectos de la matriz, como lo muestran las recuperaciones obtenidas en las muestras de control de calidad (QCs).

La identificación confiable de los compuestos en las muestras se llevó a cabo calculando las relaciones iónicas (área del pico) entre las transiciones de cuantificación (Q) y confirmación (q1 y q2). A medida que se adquirieron tres transiciones, dos relaciones de iones de intensidad estaban disponibles para la confirmación de la identidad (q1/Q y q2/Q). El hallazgo se consideró positivo cuando al menos una relación iónica experimental y el tiempo de retención del compuesto en la muestra estuvieron dentro de los rangos de tolerancia (± 30% para relación iónica, ± 0,1 min para tiempo de retención) en comparación con los estándares de referencia inyectados en la calibración (Commission and Safety 2015).

Resultados y Discusión

De 32 compuestos farmacéuticos seleccionados inicialmente para este estudio en aguas residuales de la PTAR "Salitre" - Bogotá, 16 se lograron identificar y cuantificar. Los compuestos diana correspondieron a 1 analgésico, 1 droga ilícita y su metabolito, 9 antibióticos, 1 antidepresivo, 1 anticonvulsivo y 2 antihipertensivos, en concentraciones entre 0,13 y 2,03 µg/L (**Ver tabla 1**). Estos compuestos fueron sometidos a diferentes sistemas EF ya que diversos estudios han demostrado una gran efectividad de los EAOPs en la degradación y mineralización de múltiples sustancias farmacológicas ya sea en soluciones sintéticas (Annabi et al. 2016; Feng et al. 2014; Olvera-Vargas et al. 2015; Santana-Martínez et al. 2016; Soni et al. 2017) o en aguas residuales (Catalá et al. 2015; De la Cruz et al. 2012; Valcárcel et al. 2012). Los sistemas EF evaluados comprenden el uso de 2 materiales anódicos: DSA y BDD por separado en presencia de NaCl (Lacasa et al. 2012; Ricardo E. Palma-Goyes et al. 2016) y Na_2SO_4 (Ganzenko et al. 2015; Salazar, Contreras, Mansilla, Yañez, et al. 2016), como electrolito soporte, respectivamente. En ambos casos se emplearon las mismas condiciones de trabajo: pH natural (6,8), 3.6×10^{-5} mol/L de Fe^{2+} y *j*: 3.46 $mA/cm^{2.}$ En las **Tablas 2 y 3** se presentan los porcentajes de degradación de los 16 compuestos después de 3 horas de tratamiento en todos los sistemas propuestos.

Tabla 1. Concentración 16 compuestos encontrados en el efluente de la PTAR "Salitre" de Bogotá-Colombia

Compuesto	**Concentración µg/L**
Diclofenaco	0,68
Cocaína	0,32
Benzoilecgonina	0,67
Carbamazepina	0,13
Venlafaxina	0,08
Irbesartan	0,13
Losartan	1,72
Metronidazol	0,19
Sulfametoxazol	0,66
Trimetoprim	0,34
Clindamicina	1,33
Ciprofloxacina	2,03
Norfloxacina	0,91
Claritromicina	0,27
Eritromicina	0,04
Azithromicina	0,23

Tabla 2: Seguimiento de la degradación de 16 fármacos utilizando un ánodo BDD y cátodo GDE, con los siguientes parámetros: [Na_2SO_4]: 0.05 mol/L, [Fe^{2+}]$_0$: 1.8x10^{-5} mol/L; *j*: 3.46 mA/cm^2, Volumen: 0.2 L; pH: 6,8, TOC inicial 38,8mg/L ∑ Micro contaminantes inicial 9,73 y en presencia de ácido oxálico (4.0x10^{-5} mol/L, pH 6,7).

Familia	**Compuesto**	**Tiempo**	**BDD**							
			without Fe^{2+} + Light.	**% Deg**	**Fe^{2+}**	**% Deg**	**Fe^{2+} + Light.**	**% Deg**	**Fe^{2+} + Light + Oxalic Ac.**	**% Deg**
Analgesico	**Diclofenac**	0	0,68		0,68		0,68		0,68	
		60 min	0,75	-10,29	0,84	-23,53	0,81	-19,12	n.d.	100,00
		120 min	0,61	10,29	0,71	-4,41	0,38	44,12	n.d.	100,00
		180 min	0,72	-5,88	0,49	27,94	0,34	50,00	n.d.	100,00
Ilícitas	**Cocaine**	0	0,32		0,32		0,32		0,32	
		60 min	0,24	25,00	0,29	9,38	0,36	-12,50	0,30	6,25
		120 min	0,22	31,25	0,26	18,75	0,33	-3,13	0,26	18,75
		180 min	0,22	31,25	0,20	37,50	0,24	25,00	0,19	40,63
	Benzoylecgonine	0	0,67		0,67		0,67		0,67	
		60 min	0,79	-17,91	0,86	-28,36	0,83	-23,88	0,85	-26,87
		120 min	0,69	-2,99	0,81	-20,90	0,73	-8,96	0,73	-8,96
		180 min	0,69	-2,99	0,63	5,97	0,57	14,93	0,52	22,39
Anticonvulsivo y Antidepresivo	**Carbamazepine**	0	0,13		0,13		0,13		0,13	
		60 min	0,08	38,46	0,12	7,69	0,14	-7,69	0,07	46,15
		120 min	0,07	46,15	0,09	30,77	0,09	30,77	0,04	69,23
		180 min	0,07	46,15	0,06	53,85	0,05	61,54	0,03	76,92
	Venlafaxine	0	0,08		0,08		0,08		0,08	
		60 min	n.d.	100,00	0,01	87,50	0,01	87,50	0,01	87,50
		120 min	n.d.	100,00	0,01	87,50	0,01	87,50	0,01	87,50
		180 min	n.d.	100,00	0,01	87,50	0,01	87,50	0,01	87,50
Antihipertensivos	**Irbesartan**	0	0,13		0,13		0,13		0,13	
		60 min	0,13	0,00	0,15	-15,38	0,17	-30,77	0,11	15,38
		120 min	0,09	30,77	0,15	-15,38	0,16	-23,08	0,03	76,92
		180 min	0,08	38,46	0,13	0,00	0,14	-7,69	0,03	76,92
	Losartan	0	1,72		1,72		1,72		1,72	
		60 min	1,81	-5,32	2,17	-26,16	2,47	-43,76	2,69	-56,40
		120 min	1,67	2,92	1,88	-9,30	2,34	-36,05	2,55	-48,26
		180 min	1,46	15,21	1,64	4,65	1,58	7,91	2,15	-25,00
Bactericida	**Metronidazole**	0	0,19		0,19		0,19		0,19	
		60 min	0,00	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00
		120 min	0,00	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00
		180 min	0,00	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00
Sulfonamidas	**Sulfamethoxazole**	0	0,66		0,66		0,66		0,66	

		60 min	0,74	-12,12	0,87	-31,82	0,75	-13,64	0,80	-21,21
		120 min	0,68	-3,03	0,75	-13,64	0,64	3,03	0,69	-4,55
		180 min	0,66	0,00	0,62	6,06	0,45	31,82	0,45	31,82
	Trimethoprim	0	0,34		0,34		0,34		0,34	
		60 min	0,31	8,82	0,29	14,61	0,31	8,82	0,19	44,57
		120 min	0,27	20,59	0,31	9,60	0,27	20,59	0,27	21,85
		180 min	0,26	23,53	0,22	34,53	0,18	47,06	0,19	44,57
Lincomicinas	**Clindamycin**	0	1,33		1,33		1,33		1,33	
		60 min	n.d.	100,00	0,00	100,00	0,08	94,32	n.d.	100,00
		120 min	n.d.	100,00	0,00	100,00	0,04	97,35	n.d.	100,00
		180 min	n.d.	100,00	0,00	100,00	0,01	98,98	n.d.	100,00
Quinolonas	**Norfloxacine**	0	0,91		0,91		0,91		0,91	
		60 min	1,23	-35,16	0,33	63,74	0,68	25,27	0,34	62,64
		120 min	1,00	-9,89	0,32	64,84	0,50	45,05	0,40	56,04
		180 min	0,94	-3,30	0,44	51,65	0,46	49,45	0,42	53,85
	Ciprofloxacin	0	2,03		2,03		2,03		2,03	
		60 min	1,22	39,90	0,58	71,43	0,77	62,07	0,73	64,04
		120 min	0,86	29,51	0,52	10,34	0,68	11,69	0,69	5,48
		180 min	0,78	61,58	0,71	65,02	0,66	67,49	0,91	55,17
Macrolidos	**Clarithromycin**	0	0,27		0,27		0,27		0,27	
		60 min	0,09	65,68	0,20	25,93	0,25	6,95	n.d.	100,00
		120 min	0,09	88,60	0,16	77,46	0,19	71,86	n.d.	100,00
		180 min	0,05	81,78	0,07	74,07	0,12	55,84	n.d.	100,00
	Erithromycin	0	0,04		0,04		0,04		0,04	
		60 min	n.d.	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00
		120 min	n.d.	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00
		180 min	n.d.	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00
	Azithromycin	0	0,23		0,23		0,23		0,23	
		60 min	0,14	38,12	0,12	47,83	0,21	8,98	0,18	21,74
		120 min	0,14	40,47		100,00	0,15	33,35	0,14	39,13
		180 min	0,11	52,10	0,06	73,91	0,10	54,80	0,06	73,91
∑ Micro contaminantes (mg /L) después del Tratamiento			6.04		5,28		4,92		4,96	
TOC mg/L después de los tratamientos			33,63		26,58		23,91		28,83	
pH después del Tratamiento			8,02		8,3		7,64		6,9	

* n.d. no detectado

Tabla 3: Seguimiento de la degradación de 16 fármacos utilizando un ánodo DSA y cátodo GDE, con los siguientes parámetros: [Na_2SO_4]: 0.05 mol/L, [Fe^{2+}]$_0$: $1.8x10^{-5}$ mol/L; *j*: 3.46 mA/cm^2, Volumen: 0.2 L; pH: 6,8, TOC inicial 38,8mg/L $\sum$ Micro contaminantes inicial 9,73 y en presencia de ácido oxálico ($4.0x10^{-5}$ mol/L, pH 6,7).

Familia	Compuesto	Tiempo	DSA							
			without Fe^{2+} + Light.	**% Deg**	**Fe^{2+}**	**% Deg**	**Fe^{2+} + Light.**	**% Deg**	**Fe^{2+} + Light + Oxalic Ac.**	**% Deg**
Analgésico	**Diclofenaco**	0	0,68		0,68		0,68		0,68	
		60 min	0,37	45,59	0,71	-4,41	0,89	-30,88	n.d.	100,00
		120 min	0,23	66,18	0,37	45,59	0,33	51,47	n.d.	100,00
		180 min	0,15	77,94	0,49	27,94	0,03	95,59	n.d.	100,00
Ilícitas	**Cocaine**	0	0,32		0,32		0,32		0,32	
		60 min	0,27	15,63	0,28	12,50	0,37	-15,63	0,20	37,50
		120 min	0,17	46,88	0,28	12,50	0,36	-12,50	0,11	65,63
		180 min	0,15	53,13	0,23	28,13	0,32	0,00	0,16	50,00
	Benzoylecgonine	0	0,67		0,67		0,67		0,67	
		60 min	0,80	-19,40	0,90	-34,33	0,90	-34,33	0,77	-14,93
		120 min	0,50	25,37	0,96	-43,28	0,93	-38,81	0,43	35,82
		180 min	0,61	8,96	0,90	-34,33	0,93	-38,81	0,38	43,28
Anticonvulsivo y Antidepresivo	**Carbamazepine**	0	0,13		0,13		0,13		0,13	
		60 min	0,12	7,69	0,13	0,00	0,12	7,69	0,05	61,54
		120 min	0,04	69,23	0,09	30,77	0,11	15,38	0,04	69,23
		180 min	0,04	69,23	0,08	38,46	0,08	38,46	0,06	53,85
	Venlafaxine	0	0,08		0,08		0,08		0,08	
		60 min	n.d.	100,00	0,00	100,00	0,01	87,50	0,01	87,50
		120 min	n.d.	100,00	0,01	87,50	0,01	87,50	n.d.	100,00
		180 min	n.d.	100,00	0,00	100,00	0,01	87,50	0,00	100,00
Antihipertensivos	**Irbesartan**	0	0,13		0,13		0,13		0,13	
		60 min	0,18	-38,46	0,14	-7,69	0,33	-153,85	0,08	38,46
		120 min	0,11	15,38	0,14	-7,69	0,38	-192,31	0,06	53,85
		180 min	0,10	23,08	0,12	-7,69	0,32	-146,15	0,11	15,38
	Losartan	0	1,72		1,72		1,72		1,72	
		60 min	2,12	-23,52	2,46	-43,02	2,58	-49,85	1,74	-1,16
		120 min	0,96	44,24	1,80	-4,65	2,58	-50,08	0,95	44,77
		180 min	0,85	50,83	1,71	0,58	2,24	-30,38	1,26	26,74
Bactericida	**Metronidazole**	0	0,19		0,19		0,19		0,19	
		60 min	0,00	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00
		120 min	0,00	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00
		180 min	0,00	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00

Sulfonamidas	**Sulfamethoxazole**	0	0,66		0,66		0,66		0,66	
		60 min	0,53	19,70	0,72	-9,09	0,81	-22,73	0,33	50,00
		120 min	0,18	72,73	0,39	40,91	0,69	-4,55	0,16	75,76
		180 min	0,08	87,88	0,36	45,45	0,60	9,09	0,29	56,06
	Trimethoprim	0	0,34		0,34		0,34		0,34	
		60 min	0,26	23,53	0,28	16,53	0,33	2,94	0,14	57,37
		120 min	0,14	58,82	0,22	36,03	0,30	11,76	0,10	71,26
		180 min	0,12	64,71	0,18	47,88	0,31	8,82	0,16	52,94
Lincomicinas	**Clindamycin**	0	1,33		1,33		1,33		1,33	
		60 min	n.d.	100,00	0,00	100,00	0,08	94,30	n.d.	100,00
		120 min	n.d.	100,00	0,00	100,00	0,08	93,65	n.d.	100,00
		180 min	n.d.	100,00	0,00	100,00	0,08	93,99	n.d.	100,00
Quinolonas	**Norfloxacine**	0	0,91		0,91		0,91		0,91	
		60 min	0,86	5,49	0,33	63,74	0,44	51,65	0,25	72,53
		120 min	0,80	12,09	0,27	70,33	0,41	54,95	0,23	74,73
		180 min	0,79	13,19	0,26	71,43	0,41	54,95	0,25	72,53
	Ciprofloxacin	0	2,03		2,03		2,03		2,03	
		60 min	0,65	67,98	0,55	72,91	0,69	66,01	0,62	69,46
		120 min	0,48	26,15	0,46	16,36	0,67	2,90	0,60	3,23
		180 min	0,48	76,35	0,43	78,82	0,57	71,92	0,57	71,92
Macrolidos	**Clarithromycin**	0	0,27		0,27		0,27		0,27	
		60 min	0,18	33,26	0,13	51,85	0,32	-17,89	0,08	70,37
		120 min	0,05	89,79	0,09	79,07	0,31	46,09	0,01	98,25
		180 min	0,02	94,03	0,13	51,85	0,31	-13,80	n.d.	100,00
	Erithromycin	0	0,04		0,04		0,04		0,04	
		60 min	n.d.	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00
		120 min	n.d.	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00
		180 min	n.d.	100,00	n.d.	100,00	n.d.	100,00	n.d.	100,00
	Azithromycin	0	0,23		0,23		0,23		0,23	
		60 min	0,18	22,48	0,17	26,09	0,30	-29,11	0,12	47,83
		120 min	0,10	57,36	0,13	43,48	0,27	-19,19	0,08	65,22
		180 min	0,08	65,78	0,12	47,83	0,25	-10,75	0,11	52,17
∑ Micro contaminantes (mg /L) después del Tratamiento			5,21		6,26		3,46		3,35	
TOC mg/L después de los tratamientos			30,9		29,45		32,24		34,45	
pH después del Tratamiento			8,12		7,67		7,8		6,87	

* n.d. no detectado

Sistema EF en el tratamiento de muestras del efluente de la PTAR "Salitre" de Bogotá utilizando DSA vs. BDD como materiales anódicos:

Los resultados muestran que cuando se utilizó BDD como material anódico, compuestos como metronidazol, clindamicina y eritromicina fueron degradados totalmente después de 1 hora de tratamiento (**Ver figura 1**), no obstante, otros compuestos presentaron porcentajes de degradación entre un 52 y 87% en el mismo intervalo de tiempo, entre los que se encuentran venlafaxina, ciprofloxacina, norfloxacina, claritromicina y azitromicina, otros compuestos como cocaína, carbamazepina y trimetoprim mostraron una degradación inferior al 25% y finalmente un grupo de compuestos presentaron un aumento en su concentración, por lo que sus porcentajes de degradación son negativos, entre los que se encuentran diclofenaco, benzoylecgonine, irbesartan, losartan, y sulfametoxazol (**ver figura 2a**).

En los ensayos realizados empleando DSA como material ánodico, el metronidazol, clindamicina, eritromicina y venlafaxina fueron degradados totalmente. Por otra parte, para compuestos como la ciprofloxacina, norfloxacina y claritromicina se alcanzaron porcentajes de degradación entre un 52 y 79% y compuestos como, cocaína, carbamazepina, irbesartan, losartan, trimetoprim, sulfametoxazol y azitromicina fueron degradados entre el 2 y 45% (**Ver fig 2a**) después de 1 hora de tratamiento. El diclofenaco, benzoylecgonine, irbesartan, losartan, y sulfametoxazol, presentan el mismo comportamiento que usando el ánodo BDD, es decir, presentan un aumento de su concentración.

Estos resultados son interesantes, considerando que la presencia de materia orgánica (38,80 mg/L inicial de TOC), puede competir con los fármacos evaluados por los radicales hidroxilo durante el proceso EF (Radjenović, J., Jelić, A., Petrović, M., & Barceló 2009; Valcárcel et al.

2012). De hecho, esta puede contener contaminantes refractarios, compuestos húmicos relacionada con su existencia en las fuentes de agua potable y material biológico provenientes del metabolismo de microorganismos (Shon et al., 2006) y se puede suponer que sea parte de la fracción activa en el proceso de degradación por parte de los PAOs. Sin embrago, se espera que gran parte de su eliminación esté relacionada con la formación de floculos producto de la adición de coagulantes durante el tratamiento, especialmente de las moléculas de gran tamaño (Giannakis et al. 2015). Otro resultado interesante es que la electroproducción de peróxido en el sistema alcanza una concentración entre 0,30 y 0,41 mM a la hora de tratamiento usando un ánodo DSA y uno BDD respetivamente, que sumado a la presencia de Fe^{2+} en las plantas de tratamiento de origen natural o antrópico (1.8×10^{-5} mol/L) y el adicionado en los sistemas garantiza que la reacción Fenton se lleve a cabo.

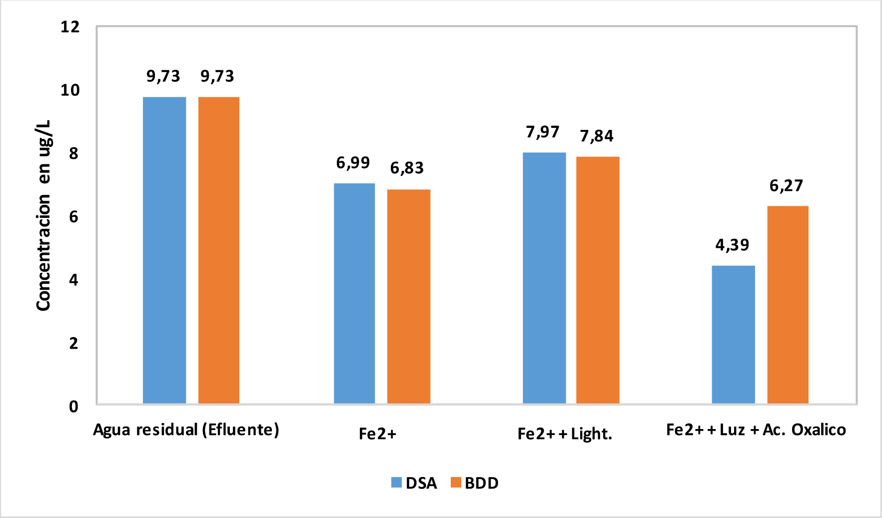
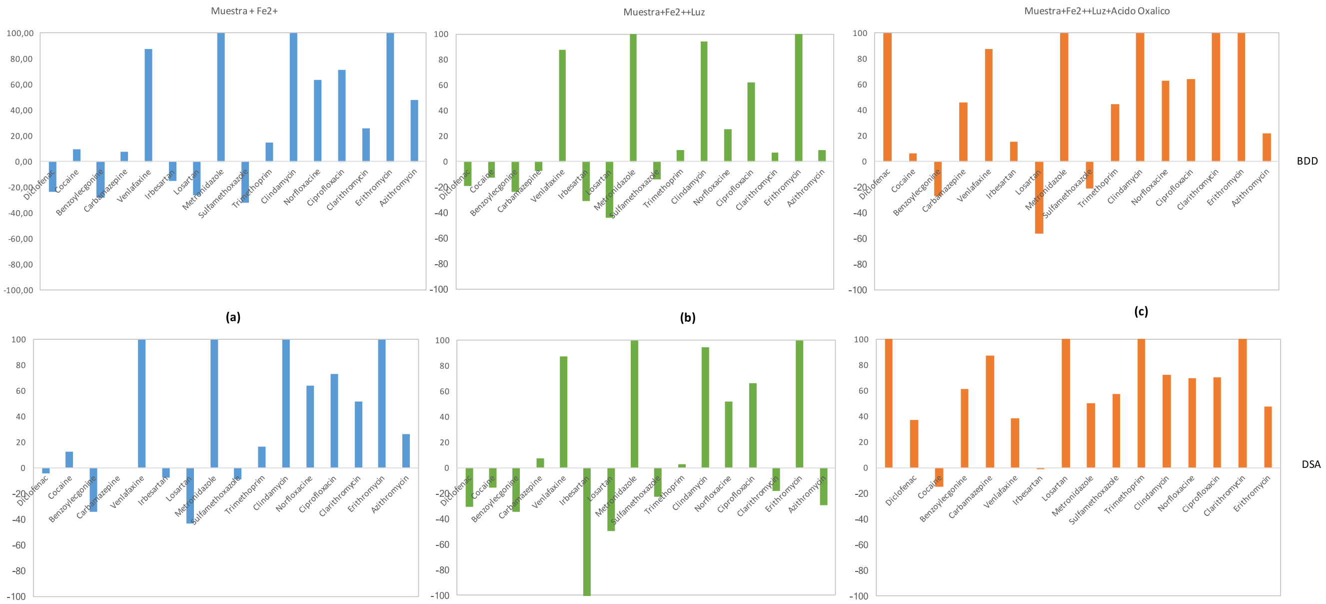


Figura 1: Remoción de fármacos en μg/L usando el sistema EF, PEF y PEF con ácido oxálico usando dos materiales anódicos (a) BDD y (b) DSA en 1 hora de tratamiento.

Si tenemos en cuenta que la degradación de la sumatoria total de los compuestos es del 25% usando ambos materiales anódicos después de 1 hora de tratamiento, condición que se ve levemente favorecida, aumentando el tiempo de tratamiento, aumentando tan solo un 15% después de 3 horas de tratamiento (**Ver tablas 3 y 4**). Este leve aumento puede deberse a que el hierro se limita en ambos sistemas, debido a que se puede precipitar como hidróxidos a valores de pH cercanos al neutro, disminuyendo su concentración después de 1 hora de tratamiento. **(Ver tabla 2)**.

Figura 2: Concentración de Microcontaminantes después de 1 hora de tratamiento a) EF con Fe^{+2}, b) PEF con Fe^{+2} + Luz y PEF con Fe^{+2} + Luz + Ácido Oxálico.



PEF en el tratamiento de aguas residuales para la degradación de CEs

Si bien el proceso EF presenta buenos resultados en la oxidación de los compuestos identificados en las aguas residuales, este puede mejorarse considerablemente si la solución se irradia simultáneamente con luz en longitudes de onda de emisión en el rango visible y el ultravioleta (proceso PEF) (Pignatello, Oliveros, and MacKay 2006).

Tabla 4: Seguimiento de la concentración de Fe^{+2} en los sistemas propuestos

Muestra	Tiempo	mg/L
Agua residual	0 min	**0,65**
	30 min	**0,69**
	60 min	**0,67**
	90 min	**0,69**
Agua residual + Fe^{+2}	0 min	**2,29**
	30 min	**1,95**
	60 min	**2,05**
	90 min	**2,01**
Agua residual+ Fe^{+2} + Luz	0 min	**2,13**
	30 min	**1,08**
	60 min	**0,72**
	90 min	**0,58**
Agua residual+ Fe^{+2} + Luz + Ác.Oxalico	0 min	**2,15**
	30 min	**2,66**
	60 min	**2,97**
	90 min	**2,98**

Sin embargo, los resultados no muestran esa mejora ya que, compuestos como el diclofenaco, cocaína, benzoilcgocnina, carbamazepina, irbesartan, losartan y sulfametoxazol presentan un aumento en su la concentración, reportando porcentajes de degradación negativos aún mayores que los observados en el proceso EF (**Ver figura 2b**). Cabe notar que los porcentajes de degradación aumentan significativamente con tiempos mayores de tratamiento (**Ver tabla 3**).

El aumento de la concentración de algunos fármacos después del tratamiento, podría explicarse por la formación de complejos entre estos compuestos con sulfatos o glucoronidos presentes en las muestras de agua evaluadas, que al ser sometidas al tratamiento EF o PEF se rompen y dejan disponibles en solución estos compuestos, reportando concentraciones mayores a la inicial (Bijlsma et al. 2013). Por otro lado, es bien conocido que algunos de estos compuestos son metabolitos o productos de transformación de otros, por ejemplo, la benzoilecognina es un conocido metabolito de la cocaína (Bijlsma et al. 2013; Mathieu et al. 2011), por lo que, al disminuir la concentración de la cocaína, aumenta la benzoilecognina. Otro caso es la posible formación de losartan como producto de transformación del valsartan (Ibañez et al. 2013) .

Si se analizan los resultados a partir de la degradación de la sumatoria total de los contaminantes (9,73 μg/L), después de 3 horas de tratamiento los compuestos se degradan un 15% más utilizando un ánodo DSA que utilizando BDD, llegando a concentraciones de (3,46 μg/L), y (4,92 μg/L) respectivamente (**Ver tabla 2 y 3**), lo que se podría explicar por la formación adicional de compuestos reactivos de cloro en este sistema (Ec. 5-7). Adicionalmente, en el caso del DSA los resultados muestran después de 3 horas de tratamiento, una mejora aproximadamente del 50% en el sistema PEF con respecto al proceso EF. Es bien conocido que esto puede d deberse a: (i) estimulación de la regeneración catódica del Fe^{3+} a Fe^{2+} (Ec. 8), (ii) la producción de $^{\bullet}OH$ a partir de la fotólisis de hidróxidos formados a pH cercanos al neutro (Ec. 9) y (iii) la fotodescarboxilación de complejos de Fe(III)-carboxilato (Ec. 10), que pueden generarse por la presencia de materia orgánica natural, hecho que es corroborado por la presencia continua de Fe^{2+} en el sistema (**Ver tabla 4)** el cual se mantiene constante durante todo el proceso.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (8)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+}_{(ac)} + {}^{\bullet}OH \qquad (9)$$

$$[Fe^{3+}\text{- AOCC}] + h\nu \rightarrow Fe^{2+} + CO_2 \qquad (10)$$

Efecto del Ácido oxálico en el proceso PEF en el tratamiento de compuestos farmacéuticos:

Se sabe que durante el proceso EF, a pH 6,8, los iones $Fe^{2+/}Fe^{3+}$ se precipitan en forma de hidróxidos y por ende, disminuye el Fe^{2+} disponible en el sistema y la reacción se puede ver desfavorecida. Sin embargo, la materia orgánica presente, especialmente ácidos alifáticos de cadena corta, pueden actuar como ligandos, para formar complejos Fe(III)-carboxilatos, (Santana-Martínez et al. 2016) que a pH> 4 y en presencia de suficiente ligando generaría Fe^{2+} y así continuar la reacción Fenton (Ec. 11). Estos complejos presentan coeficientes de absorción molar más altos en las regiones cercanas a la luz visible y ultravioleta que otros complejos (Ma et al. 2016; R E Palma-Goyes et al. 2016).

$$[Fe(OOCR)]^{2+} + h\upsilon \rightarrow Fe^{2+} + CO_2 + R\bullet \tag{11}$$

Ejemplos de ácidos orgánicos empleados son el oxálico succínico o tartárico (Villegas- Guzman et al. 2017), los cuales han demostrado interesantes resultados en el aumento de la degradación de algunos contaminantes emergentes con respecto al proceso PEF (Abrahamson, Rezvani, and Brushmiller 1994; Moreira et al. 2015). Al adicionar ácido oxálico en el sistema PEF los porcentajes de degradación mejoraron un 20% comparado con el sistema PEF sin adicionar ácido oxálico, aumentando considerablemente la concentración de Fe^{+2} disponible (**ver tabla 4**) y por ende la eficiencia del proceso (Ec. 12-13).

$$Fe^{2+} + H_2O_2 + 3\ C_2O_4^{2-} \rightarrow Fe^{+3}(C_2O_4)_2^{3-} + \bullet OH + OH^- \tag{12}$$

$$Fe^{+3}(C_2O_4)_2^{-3} + h\upsilon \rightarrow Fe^{+2} + 2C_2O_4^{2-} + C_2O_4^{\bullet -} \tag{13}$$

En consecuencia, compuestos como diclofenaco y claritromicina utilizando un ánodo BDD se degradan por completo después de 3 horas de tratamiento, otros como carbamacepina, venlafaxina, irbesartan, ciprofloxacina, norfloxacina y azitromicina presentan degradaciones hasta del 87%. De modo similar la cocaína, benzoilcgocnina, sulfametoxazol, trimetropin mejoran su degradación con respecto al tratamiento PEF sin adición de ácido oxálico (**Ver figura 3**). Por último, cabe resaltar el caso del losartan, compuesto que durante todo el proceso presenta porcentajes de degradación negativos, lo que demuestra que es un compuesto altamente recalcitrante a los procesos electroquímicos.

En el caso del DSA los resultados son similares a los obtenidos con el electrodo BDD, ya que el diclofenaco, claritromicina y venlafaxina presentan una degradación total. Los demás compuestos presentan degradaciones por encima del 50% a excepción del losartan e irbesartan que son del 27 y 15% respectivamente (**Ver tablas 2 y 3**).

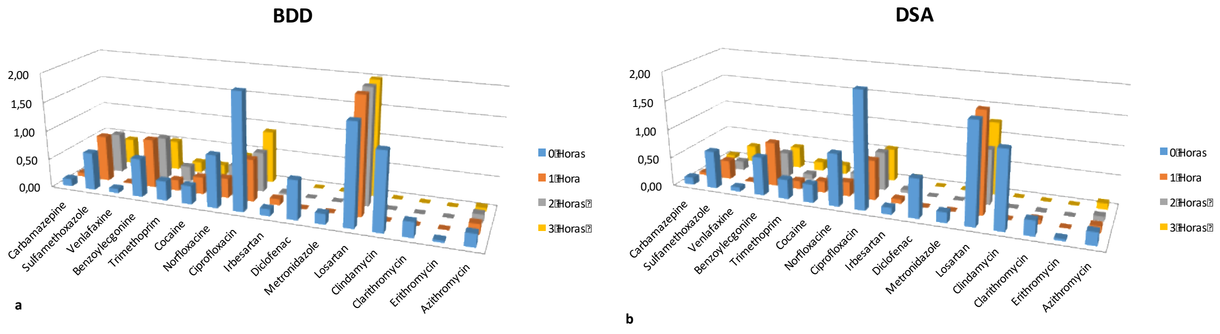


Figura 3: Remoción de fármacos usando PEF / Fe^{+2} / Luz / ácido oxálico, durante 3 horas de tratamiento (a) BDD y (b) DSA

En consecuencia, este sistema logra eliminar el 66% de los compuestos farmacéuticos encontrados en concentraciones de μg/L a pesar de la presencia de materia orgánica presente en dichas muestras (38,8mg/L), lo que demuestra que la materia orgánica no compite de manera significativa con los microcontaminantes por los compuestos oxidantes (ver figura 4).

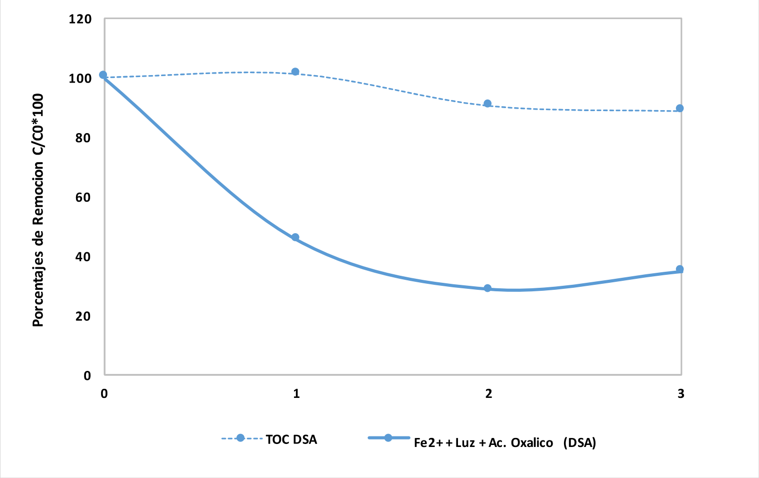


Figura 4: (Sistema PEF + Fe^{+2} + Luz + ácido oxálico) Porcentajes de remoción en la sumatoria de los contaminantes y el TOC

Conclusiones

Se identificaron 16 compuestos en el efluente de la PTAR "Salitre" de Bogotá, utilizando UHPLC-MS/MS. Diclofenaco, Carbamazepina, Venlafaxina, Irbesartan, Losartan, Metronidazol, Sulfametoxazol, Trimetoprim, Clindamicina, Ciprofloxacina, Norfloxacina, Claritromicina, Eritromicina y Azithromicina, igualmente 2 drogas ilicitas: Cocaina y Benzoilecgonina. Las concentraciones más altas corresponden al losartan y ciprofloxacina, de los cuales el losartan presenta los menores índices de degradación en todos los sistemas utilizados.

Se utilizaron varios AEOPs para determinar su potencial en la eliminación de estos compuestos obteniendo resultados positivos. El metronizazol, clindamicina y eritromicina se degradaron por completo en todos los sistemas. Se demostró que a pH natural es posible realizar el proceso EF sin necesidad de acidificar como se recomienda en las reacciones Fenton, ya que parte de la materia organiza fue usada para la formación de complejos con el hierro que hizo posible mantenerlo soluble en el sistema, puesto que las muestras contenían una cantidad suficiente de Hierro para no requerir su adición en el proceso.

A pesar de los buenos resultados y la alta viabilidad que estas técnicas presentan para la eliminación de este tipo de contaminantes, cabe resaltar que no todos los compuestos son susceptibles a su ataque, ya que compuestos como el Losartan son claramente más recalcitrantes y aporta al sistema hasta el 20% de la masa sin degradar, dificultando llegar al 100% de la degradación de estos compuestos en el sistema optimizado.

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Poster 1 (Presentado CIPOA 2017):

Removal of Sartans (Losartan and Valsartan) by Electro-Fenton and Photo-Electro-Fenton using a BDD Anode: Identification of Transformation Products.

Removal of Sartans (Losartan and Valsartan) by Electro-Fenton and Photo-Electro-Fenton using a BDD Anode: Identification of Transformation Products.

D. Martínez-Pachón[1], M. Ibañez[2], R.Torres-Palma[3], F. Hernández[2] , A. Moncayo-Lasso[1]

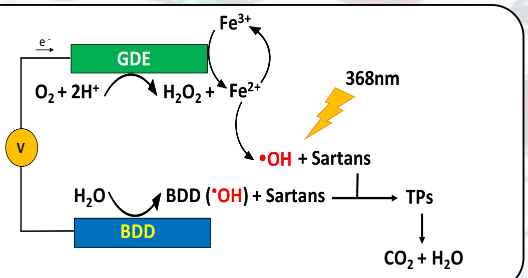
1. Universidad Antonio Nariño; Facultad de Ciencias; Grupo de Investigación en Ciencias Biológicas y Químicas; Bogotá D.C. – Colombia.
dianamartine@uan.edu.co

2. Research Institute for Pesticides and Water (IUPA), University Jaume I, Castellón, Spain.

3. Universidad de Antioquia; Instituto de Química; Grupo de Investigación en Remediación Ambiental y Biocatálisis; Medellín. – Colombia

Introduction

The degradation of Valsartan (VAL) and Losartan (LOS) were carried out by photo electro-Fenton (PEF) process using a cell with a BDD anode and a GDE cathode. High mineralization (80%) of LOS was observed at pH 3.0 and current density of 3.46 mA/cm^2 in presence of 0.018 mM of Fe^{2+} and 50 mM of Na$_2$SO$_4$ under UV-A radiation (wavelength 368 nm). LOS and VAL were totally removed after 45 and 90 minutes of treatment respectively, due to the oxidation by hydroxyl radical (•OH) from Fenton's reaction between Fe^{2+} added and H$_2$O$_2$ electro-generated on cathode and BDD(•OH) physisorbed on anode. Transformation products of LOS and VAL were identified by using UHPLC/MS-MS.



Results

Degradation Vs Mineralization by Electro-Fenton and photo-Electro Fenton process

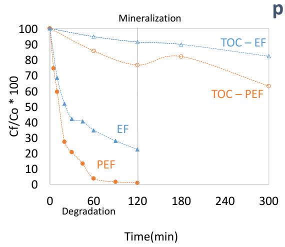


Fig. 1. Degradation (close symbols) and mineralization (open symbols) of VAL by EF (-▲-) and PEF (-●-) process

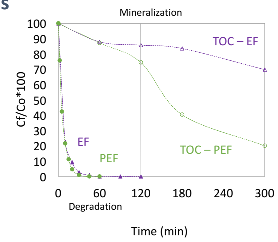


Fig. 2. Degradation (close symbols) and mineralization (open symbols) of LOS by EF (-▲-) and PEF (-●-) process

Compound	Photolysis	Anodic oxidation	Electro peroxidation	Electro Fenton	(EF) TOC	Photo Electro Fenton	(PEF) TOC
VAL	2,90 %	16,6 %	67,18 %	77,61 %	17,86 %	99,10 %	30,15 %
LOS	7,12 %	19,94 %	62,21 %	100,00 %	37,03 %	100,00 %	79,94 %

Table 1. Percent of degradation and mineralization of antihypertensives after 120 min using different electrochemical systems with BDD Anode.

Effect of other Anodic material (DSA)

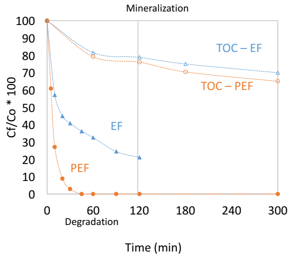


Fig. 3. Degradation (close symbols) and mineralization (open symbols) of VAL by EF (-▲-) and PEF (-●-) process

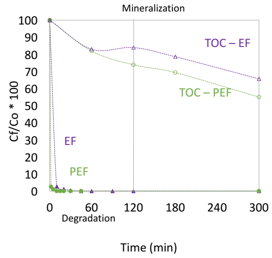


Fig. 4. Degradation (close symbols) and mineralization (open symbols) of LOS by EF (-▲-) and PEF (-●-) process

Transformation Products of VAL and LOS

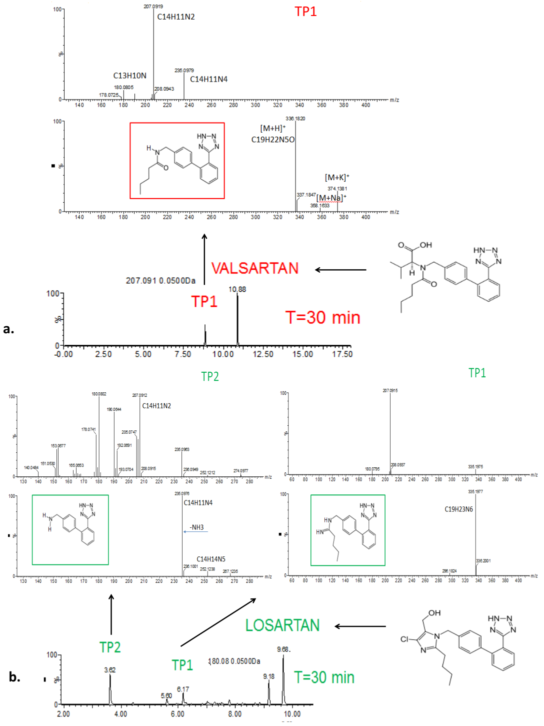


Fig 5. Extracted ion chromatograms (20 mDa absolute mass window) for samples collected at 30 minutes; Low energy spectrum (bottom), high energy spectrum (top) and proposed structure for TPs for VAL (a) and LOS (b)

Conclusions

- The ability of PEF process to degrade totally LOS and VAL was demonstrate. High percentages of mineralization, in the LOS case, had been also demonstrated.
- Principal TPs were identified for each compound obtained as result of the attack of hydroxyl radicals on the aromatic rings and the cleavage of either the N=N or the C-N bond by the fenton reaction, physisorbed BDD(•OH) and a possible direct oxidation.

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Poster 2 (Presentado CIPOA 2017):

Inactivation of Microorganisms from Effluents of Wastewater Treatment Plant of Bogotá by Electrochemical Oxidation and Photo-Electro-Fenton Process using a DSA Anode and GDE Cathode

Inactivation of Microorganisms from Effluents of Wastewater Treatment Plant of Bogotá by Electrochemical Oxidation and Photo-Electro-Fenton Process using a DSA Anode and GDE Cathode

L. Bonilla-Velásquez[1], D.Martínez-Pachón[1], P. Espinosa[1], R. Torres-Palma[2], N.I. Castillo[1], A. Moncayo-Lasso[1]

1. Universidad Antonio Nariño; Facultad de Ciencias; Grupo de Investigación en Ciencias Biológicas y Químicas; Bogotá D.C. – Colombia nancastillo@uan.edu.co

2. Universidad de Antioquia; Instituto de Química; Grupo de Investigación en Remediación Ambiental y Biocatálisis; Medellín. – Colombia

Introduction

Nowadays the reuse of effluents is an alternative to provide water sources for industrial, agricultural or municipal applications, but the purity of the same must be ensured. AOPs such as electro-Fenton, have shown effectiveness both for the degradation of organic substances and for the inactivation of microorganisms.

The objective of the present study was to evaluate the bacteria disinfection of effluents from WWTP El Salitre-Bogotá via photo-electro-Fenton process by using DSA anode and GDE electrodes in the one undivided electrolytic cell.

In addition, the inactivation of a phytopathogenic fungus, *Fusarium sp*., in Milli-Q water intentionally contaminated with the propagules of the fungus, by the same PEF process was also evaluated.

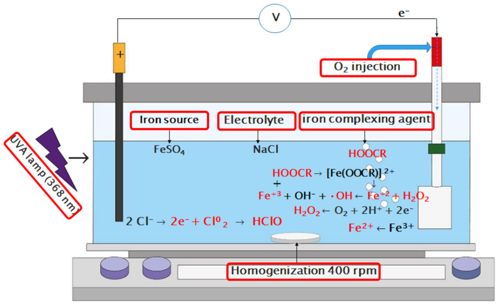
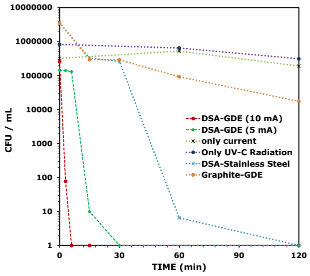


Figure 1. Experimental set up.

Results and Discussion

Electrochemical disinfection systems based on the photo-electro-Fenton process - Bacteria inactivation

Bacteria Inactivation by PEF

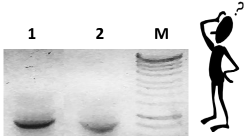


Inactivation of bacteria naturally present in the effluent from WWTP by PEF process using DSA and GDE electrodes system.

CONDITION GENERAL TO TESTS:

Photo-Electro-Fenton (DSA-GDE) system at 3.42 mA/cm² (10 mA) or 1,73 mA/cm² (5 mA) and sodium chloride (5.0×10^{-2}mol/L) as support electrolyte. pH value remain unchanged (pH 4,6) oxalic acid ($4,6\times10^{-5}$mol/L) and Fe^{2+} ($1,8\times10^{-5}$mol/L).

Are the bacteria completely eliminated?



PCR product of bacteria naturally present in the effluent from WWTP sample:
Line 1: At 120 min of treatment with PEF – 5mA.
Line 2: At 120 min of treatment with PEF – 10mA.
Lane M: HyperLadder 1kb DNA.
Run 0,8% agarose gel electrophoresis at 85V for 45 min.

Total DNA from water was extracted and with the product obtained from the extraction, a PCR was performed in order to amplify a constitutive gene (16s rRNA) and to determine if there is at least a minimum amount of bacteria in the water, observing the gene amplification, which indicates residual permanence of microorganisms or genes afterward 120 minutes of treatment.

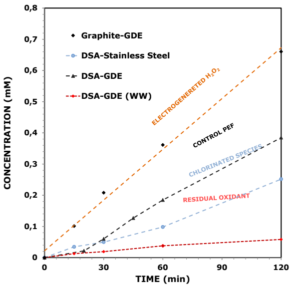
Mineralization in wasterwater

Time	60 min			120 min		
Condition	ED (DSA-Stainless steel)	PEF (Graphite -GDE)	PEF (DSA-GDE)	ED (DSA-Stainless steel)	PEF (Graphite-GDE)	PEF (DSA-GDE)
TOC Remove	10%	12%	17%	14%	17%	25%

Table 1. TOC evolution during ED and photo-electro-Fenton (PEF) disinfection at 10mA, in presence of oxalic acid without pH modification. TOC initial 52 mg/L.

About of organic matter removal was noted that the main TOC removal occurred during the early 60 min of treatment (Table 1) measurements show a low mineralization, ~ 10% during 120 min of treatments. Whit PEF using DSA/GDE system, higher TOC removal was observed (25%), indicating that this system is more efficient to organic matter remove that ED and PEF(only GDE) systems, without affect the bacterial inactivation. It is possible that oxidizing species produced in the bulk firstly trends to react whit easily oxidable organic matter and a second step attack the bacteria.

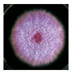
Oxidizing species formed



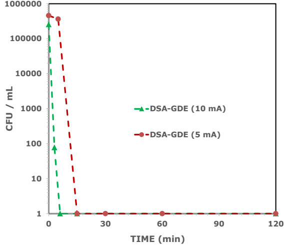
Oxidizing species formed during the PEF processes.

Fusarium inactivation by PEF process using DSA-GDE electrodes system

Different species of Fusarium cause diseases in plants and therefore large economic losses. Irrigation waters are not usually reused for fear of the presence of pathogenic microorganisms which can infect plants.



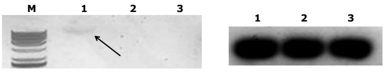
Fusarium Inactivation by PEF



When a current of 5 mA is applied, Fusarium inactivation begins after 5 minutes of treatment but at 15 minutes there is a inactivation of 5 orders of magnitude; the latter occurs when the current applied is 10 mA but in the first 5 minutes of treatment, which indicates that PEF treatment is equally effective in both current conditions.

The synergistic effect observed in bacterial inactivation assays was probably the main reason of efficient the fungus inactivation but is important mentioned that in these samples there is no competition of the oxidants by organic matter reason why the PEF system seem to be so efficient. Molecular tests indicate that the fungus was not completely removed from the treated waters.

Is fusarium completely eliminated?



Genomic DNA **PCR product**

Line 1: Positive control.
Line 2: Before of treatment - 10^5-10^6 UFC/mL.
Line 3: At 120 min of treatment with PEF – 10 mA.
Lane M: Vc 1kb DNA ladder
Run 0,8% agarose gel electrophoresis at 85V for 45 minutes.

At the left, in line 1 total DNA above 10,000 bp and at the right, amplicons below 500 bp ladder marker is observed.

Conclusions

At these conditions of the photo-electro-Fenton system, inactivation of the bacteria and Fusarium was observed in the first 3 minutes of treatment (at 10 mA)

This is perhaps due to the synergistic effect of anodic oxidation, electrochemical disinfection by chlorinated species formed on the anode, hydrogen peroxide produced on the cathode and hydroxyl radicals formed in the Fenton and electro-Fenton reactions.

These results shown that EAOPs potentially can be used as a complementary treatment to traditional processes of water purification in order to diminish chemical and biological risks, since as has been demonstrated, organic compounds are also eliminated.

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Patente de Invención

(Propuesta aceptada para ser financiada en la convocatoria 793

de Colciencias para el fomento a la protección de Invenciones)

(Propuesta) Patente de Invención:

Título de la invención:

Sistema de eliminación de contaminantes emergentes presentes en aguas residuales.

Definición del problema técnico que resuelve la invención:

Actualmente, la contaminación del agua generada por diversos orígenes, establece una necesidad creciente de técnicas de descontaminación, más económicas, accesibles, eficientes y especificas para las diversas comunidades. En Colombia y en el mundo se implementan una serie de tratamientos primarios y secundarios para la descontaminación de aguas residuales. No obstante, en muchas ocasiones, este procedimiento es insuficiente para tratar o eliminar diferentes contaminantes en bajas concentraciones y resistentes a las metodologías descontaminantes utilizadas. Por este motivo, países industrializados optan por implementar procesos complementarios que les permitan alcanzar los grados de pureza en el agua requeridos, recurriendo a diferentes tecnologías como las AOPs. Estas metodologías pueden ser implementados en aguas a pequeña o mediana escala y se basan en la generación del radical hidroxilo, el cual es extraordinariamente reactivo y poco selectivo, además, es conocido por su capacidad para oxidar y mineralizar casi cualquier contaminante orgánico, pero las algunas características técnicas del sistema EF, han impedido que estos procesos sean ampliamente aplicados a nivel industrial. Dentro de estas problemáticas se encuentran:

- Su alto consumo energético en sistemas como los basados en UVC o el ultrasonido.
- Requieren cantidades relativamente grandes de oxidantes y catalizadores (por ejemplo, ozono, peróxido de hidrógeno o cloro y los sistemas que requieren modificación en el pH). Porque deben ser adicionados constantemente y su manipulación puede ser peligrosa.
- Requieren materiales de manufactura costosos (titanio, paladio, platino, diamante dopado con boro, entre otros)

Esto implica un aumento en los costos de operatividad, dificultades de manipulación y uso del sistema a gran escala, haciendo estos tratamientos poco eficientes.

Palabras clave:

Fenton, electrodos de grafito, contaminantes emergentes, aguas residuales, procesos avanzados de oxidación.

Estado de desarrollo de la invención:

Validado a Nivel de laboratorio con pequeños volúmenes en aguas reales: Se construye un modelo original que presenta todas las cualidades técnicas y características de funcionamiento del nuevo producto o proceso, aunque no se ha probado en condiciones reales.

Estado de la técnica asociado a la invención:

En el estado de la técnica encontramos 4 patentes relacionadas con el sistema electro-Fenton de tratamiento de aguas residuales, con similitudes al sistema propuesto, como se muestra en la tabla 4.0.1:

Patente	**Código**	**Campo de acción**	**Características**
Special equipment for treating organic sewage by utilizing electro-Fenton reaction	CN102674505 (A)	Equipo especial para el tratamiento de aguas residuales orgánicas mediante la utilización de la reacción electro-Fenton	El equipo especial para tratar aguas residuales orgánicas utilizando la reacción de Fenton, caracterizado porque: el cátodo está hecho de chatarra producida por procesamiento de metales y se lava con una solución diluida de ácido clorhídrico de 10 % de masa concentración minutos para eliminar el aceite de la superficie, y luego se lavó con agua hasta el valor de pH del agua de lavado de 6-8, y luego se electro deposita Ag o Ti en la superficie. La densidad aparente es de 2.0T / m3 a 2.5T / m3. 3. El ánodo es una varilla de grafito de 1cm ~ 5cm, ubicada en una torre interna en la parte central de la celda. La pared de la torre interior está provista de agujeros de guía de desviación y agujeros de derivación de diámetro de 1 cm ~ 5 cm, tasa de apertura total de 10 % a 20 %.
Semi-coke waste water pretreatment method based on Electro-Fenton oxidization technology	CN102633322 (A)	La presente invención se refiere al campo del tratamiento de aguas residuales industriales, en particular a un método de pretratamiento de aguas residuales Lancaster basado en la tecnología de oxidación por electro función.	Un método de pretratamiento de aguas residuales de Lancaster basado en el proceso de oxidación Fenton se caracteriza porque un electrodo de difusión de gas de grafito se usa como cátodo y una placa de acero inoxidable como un ánodo. El H2O2 se genera burbujeando aire en la región del cátodo que en reacción con Fe2+ constituye un reactivo de Fenton, dando como resultado un fuerte agente oxidante (hidroxilo) que degrada los contaminantes orgánicos. El pretratamiento del agua residual es caracterizado porque la tasa de flujo de aire de la zona del cátodo de 2.5L / min, la densidad de corriente de 5.2 mA/cm2, el valor de pH del agua residual debe controlarse entre 3.0 ±1.5, espacio entre las placas del electrodo mantenido a 2cm. El electrodo de difusión de gas de grafito y el ánodo de acero inoxidable están conectados por múltiples grupos de electrodos en paralelo o en serie.

Waste water treatment device using electro-Fenton reaction	CN201932937 (U)	La invención pertenece al campo de la ingeniería y tecnología ambiental y se refiere principalmente a un nuevo reactor de Fenton penetrante y a un método para el tratamiento de aguas residuales orgánicas.	El primer ánodo es un ánodo dimensionalmente estable con un catalizador de óxido compuesto de estaño, antimonio, iridio y tántalio revestido sobre una superficie de titanio, y la segunda placa de ánodo es una placa de acero. Cuando el dispositivo está en funcionamiento, el aire genera H_2O_2 sobre el cátodo y Fe2+ en un segundo ánodo, H_2O_2 , Fe^{2+} y agua se someten a una reacción electro-Fenton, y los contaminantes orgánicos contenidos en las aguas residuales se degradan con un hidroxilo radical generado por la reacción. La reacción electro-Fenton continúa cuando las aguas residuales ingresan al reactor de profundidad, lo que garantiza el tiempo de residencia de la reacción y la realización de una gran cantidad de reflujo.
Wastewater treatment device with coupled Electro-Fenton and electrocatalytic oxidation without solid waste generation	CN105884091 (A)	La presente invención se refiere al campo del tratamiento de aguas residuales	El dispositivo de tratamiento de aguas residuales requiere: Dos electrolizador de membrana, un tanque de reacción, un tanque de sedimentación de coagulación y un tanque de disolución de lodo de hierro, donde el primer electrolizador de membrana comprende más de una celda donde un primer ánodo y un primer cátodo, estando ubicados en la primera membrana en el medio de la primera celda, el primer ánodo y el primer cátodo, están respectivamente ubicados a ambos lados de la primera membrana para formar una cámara de ánodo y una cámara de cátodo. La placa de aireación está conectada con una bomba de aire dispuesta fuera del segundo electrolizador de membrana, el compartimento de ánodo del primer electrolizador de membrana está en comunicación con el compartimiento anódico del segundo electrolizador de membrana; el compartimento de cátodo del segundo electrolizador de membrana está en comunicación con el tanque de reacción de Fenton.

Tabla 4.0.1: Estado de la Técnica

Sector tecnológico relacionado con la invención

Ambiental.

Sectores de mayor interés para explotar comercialmente la invención:

- Ambiental - Manufactura - Industrial - Salud

Tipo de empresas posiblemente interesadas en la invención.

Empresas generadoras de aguas contaminadas con sustancias orgánicas, durante o al final de la cadena productiva ya sea para su reúso o para alcanzar niveles óptimos por ley para su eliminación, y empresas de tratamiento de aguas a pequeña escala.

Posibles usos o aplicaciones futuras.

Obtención de aguas de alta calidad para reúso en diversos sistemas productivos. Descontaminación de aguas con niveles altos de contaminación como aguas residuales domésticas, aguas industriales o aguas hospitalarias.

Capítulo 5

Conclusiones Generales y Perspectivas

La presencia de productos farmacéuticos ha sido demostrada en el efluente de la PTAR "Salitre de Bogotá" por encima de 1 µg/L. Entre los farmacos encontrados están: Diclofenaco, Carbamazepina, Venlafaxina, Irbesartan, Losartan, Metronidazol, Sulfametoxazol, Trimetoprim, Clindamicina, Ciprofloxacina, Norfloxacina, Claritromicina, Eritromicina y Azithromicina, igualmente 2 drogas ilícitas: Cocaína y Benzoilecgonina. Después del tratamiento en la PTAR, se observa que permanecen en concentraciones significativas, demostrando una baja eliminación. Como es de esperar, esto suponen un riesgo para el ambiente acuático, lo cual puede provocar resistencia bacteriana, entre otros efectos. Por tanto, a la luz de los datos presentados es evidente que existe una necesidad de implementar tratamientos eficientes y capaces de eliminar compuestos farmacéuticos en las aguas residuales como lo son los procesos Electro Fenton y Foto Electro Fenton.

El proceso EF utilizando un ánodo dimensionalmente estable (DSA) de (Ti/IrO_2 dopado con SnO_2) y un electrodo de difusión de gas (GDE) combinado con un proceso biológico, demostró ser un sistema prometedor para la mineralización completa de VAL (Compuesto modelo presente en el afluente y efluente de la PTAR Salitre de Bogotá). Así mismo, la composición del electrólito soporte y el pH inicial de las soluciones juegan un papel clave durante los procesos EF y PEF. Esto demostró que en presencia de NaCl como electrólito de soporte, se producen especies de cloro reactivo junto con los radicales $^{\bullet}OH$, participando en la degradación del VAL. Sin embargo, a un pH cercano al neutro, el HClO producido podría reaccionar con el H_2O_2 generando una disminución en la eficiencia del proceso. Esta desventaja se puede superar si el proceso es llevado a cabo en presencia de ácido oxálico para formar el complejo Fe(III)-Oxalato que en presencia de luz permite tener el Fe^{2+}disponible en el medio. De hecho, usando ácido oxálico y luz el VAL se eliminó por completo en 120 min de tratamiento; en cambio, tan solo se observó un 40 % en la degradación de VAL sin modificación del pH en ausencia de ácido oxálico.

Estudios adicionales, basados en los procesos EF y PEF demuestran ser adecuados también para la degradación eficiente del antihipertensivo LOS, utilizando un ánodo dimensionalmente estable (DSA) de (Ti/IrO$_2$ dopado con SnO$_2$) y un electrodo de difusión de gas y (GDE) con en el uso de ácidos orgánicos y LEDs. La combinación sinérgica de fotólisis, oxidación anódica en la superficie de DSA, la generación de peróxido de hidrógeno por el cátodo, la posterior generación de radicales hidroxilo por la reacción Fenton en presencia de iones de hierro y compuestos reactivos de cloro, al igual quen la descomposición de los complejos de hierro formados con los ácidos orgánicos bajo radiación incidente, permitieron obtener un sistema con alta eficiencia en la degradación y mineralización de los compuestos de estudio. Durante los tratamientos, tres compuestos de VAL y dos compuestos de LOS se caracterizaron como los principales productos de transformación. Con respecto al tratamiento biológico, en las soluciones de VAL tratadas por proceso de PEF se eliminó aproximadamente el 80 % del TOC después de 300 minutos, garantizando la biodegradación de los productos de transformación, generando un impacto ambiental menor. Sin embargo, se considera importante en trabajos futuros realizar ensayos de toxicidad adicionales.

Ensayos realizados utilizando: EF (sin Fe+2), EF (Fe+2), PEF (Fe2+/ luz (365 nm)) y PEF (Fe2+/ luz (365 nm) / ácido oxálico) muestran una mejora significativa en las propiedades organolépticas de las muestras de agua del efluente de la PTAR “Salitre” de Bogotá y lograron la eliminación hasta del 66 % de los compuestos farmacéuticos encontrados con el sistema PEF con ácido oxálico, a pesar de la presencia de materia orgánica en dichas muestras (38,8mg/L), lo que demuestró que la materia orgánica no compite de manera significativa con los microcontaminantes por los compuestos oxidantes.

además la eliminan de un 90 % los compuestos en comparación con otros AOPs como la Oxidación Anódica (AO), la Electro Peroxidación (AO-H$_2$O$_2$) o el Ultrasonido. Los resultados obtenidos en los ensayos realizados muestran que este tipo de sistemas puede ser una alternativa interesante para eliminar los contaminantes emergentes presentes en las aguas residuales de las PTAR salitre de Bogotá.

El sistema PEF en las condiciones propuestas, demostró la inactivación de las bacterias en los primeros 3 minutos de tratamiento (a 3.42 mA/cm^2). Posiblemente se debido al efecto sinérgico de la oxidación, la desinfección electroquímica por especies cloradas formadas en el ánodo, el peróxido de hidrógeno producido en el cátodo y los radicales hidroxilo formados en las reacciones Fenton. Gracias a estos resultados los EAOPs pueden usarse potencialmente como un tratamiento, complementario, a los procesos tradicionales de purificación de agua con el fin de disminuir los riesgos químicos y biológicos, ya que, como se ha demostrado, que también elimina los compuestos orgánicos.

Todos los estudios utilizando el sistema EF demostraron tener un amplio potencial para eliminar y/o remover contaminantes emergentes y microorganismos en muestras de agua real, por lo cual la propuesta de un sistema que permita su eliminación a bajo costo y altamente eficiente es una necesidad abordada desde los principios básicos del DCA, en consecuencia se plantea un producto de alto valor agregado (patente de invención) para la eliminación de contaminantes emergentes en aguas residuales a nivel de laboratorio.

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