

UNIVERSIDAD AUTÓNOMA DE MADRID

FACULTAD DE CIENCIAS

Departamento de Ingeniería Química



**APPLICATION OF PHOTOCATALYTIC PROCESSES  
FOR WATER TREATMENT**

**APLICACIÓN DE PROCESOS  
FOTOCATALÍTICOS AL TRATAMIENTO DE AGUAS**

Tesis Doctoral

ÁLVARO TOLOSANA MORANCHEL

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**APLICACIÓN DE PROCESOS  
FOTOCATALÍTICOS AL TRATAMIENTO DE AGUAS**

MEMORIA

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presentada por:

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HACEN CONSTAR:

que el presente trabajo, titulado “Aplicación de procesos fotocatalíticos al tratamiento de aguas”, presentado por D. Álvaro Tolosana Moranchel, ha sido realizado bajo su dirección, en los laboratorios del Departamento de Ingeniería Química, en la Universidad Autónoma de Madrid, y laboratorios del Instituto de Catálisis y Petroleoquímica del CSIC que a su juicio reúne los requisitos de originalidad y rigor científico necesarios para ser presentado como Tesis Doctoral.

Y para que conste a efectos oportunos, firmamos el presente informe en Madrid, a 25 de Marzo de 2019.

José Antonio Casas de Pedro

Ana M<sup>a</sup> Bahamonde Santos

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# Capítulo 1:

Introducción y objetivos

## **1.1. CONTAMINACIÓN HÍDRICA Y MARCO LEGAL**

La ausencia de recursos naturales y la competencia por un recurso limitado puede estimular conflictos y generar tensiones. El caso del agua es todavía más singular, ya que además de ser vital para la vida en el planeta su importancia para el desarrollo económico es cada vez mayor. El desarrollo industrial, el crecimiento demográfico que lleva asociado una mayor producción y consumo, así como una mayor urbanización provocan un aumento continuo de la demanda de agua de calidad [1, 2]. En este contexto, otro problema a tener en cuenta es el cambio climático, cuyos efectos ya están repercutiendo directamente en el ciclo del agua, causando importantes impactos negativos distribuidos de manera irregular dentro de cada continente.

Como consecuencia, hoy en día la crisis hídrica está estrechamente ligada a las crisis de cambio climático, económica, energética y alimentaria. Por tanto, los impactos de estas crisis se intensificarán hasta que se logre encontrar una solución a la crisis del agua, pudiendo en extremo llegar a generar inseguridad política y conflictos tanto locales como nacionales [3]. Por este motivo, el Foro Económico Mundial ha clasificado a la crisis del agua y a la incapacidad para adaptarse al cambio climático como dos de los grandes riesgos con mayor impacto en la mejora económica y en la estabilidad social de los próximos 10 años [4]. Por ello, resulta imprescindible una adecuada gestión de los recursos hídricos, así como una buena inversión en infraestructuras, para lograr los Objetivos de Desarrollo Sostenible (ODS) marcados por la ONU para el milenio [5]. Estos ODS (17 en total) se plantearon en la Conferencia de las Naciones Unidas sobre el Desarrollo Sostenible, celebrada en Río de Janeiro en 2012, y adoptados en 2015 con el fin de proteger el planeta, reducir la pobreza y conseguir un desarrollo y crecimiento más equitativo. Entre todos ellos, el ODS 6 está relacionado directamente con el agua y tiene como objetivo un uso sostenible de la misma, mejorar la eficiencia de su uso, una reducción de su contaminación y una mejora del acceso al saneamiento integral. Sin embargo, como el agua es un elemento crucial para la vida y el desarrollo interconecta con la mayoría de los ODS; siendo necesaria para una producción segura de los alimentos (ODS 2), es vital disponer de agua limpia e instalaciones de saneamiento que permitan garantizar una vida sana (ODS 3) y se requiere tanto para la producción de energía asequible y sostenible, como para la mejora de la situación económica y laboral (ODS 7 y 8). Al mismo tiempo, la consecución de los objetivos anteriores resultará imposible si no se dispone de recursos hídricos suficientes y con una calidad adecuada para preservar el medio ambiente (ODS 13, 14 y 15) [5, 6].

La evolución demográfica implica un aumento de la demanda y consumo de agua que afecta no solo a la disponibilidad de los recursos hídricos, sino también a su calidad como consecuencia de su uso y contaminación. Por tanto, la contaminación hídrica se define como *“la acción y el efecto de introducir materia o formas de energía, o inducir condiciones en el agua que, de modo directo o indirecto, impliquen una alteración perjudicial de su calidad en relación con usos posteriores, con la salud humana, o con los ecosistemas acuáticos o terrestres directamente asociados a los acuáticos; y que causen daños a los bienes; y deterioren o dificulten el disfrute y los usos del medio ambiente”* [7].

De acuerdo con su origen se pueden distinguir diferentes tipos de aguas residuales: de origen agrícola, doméstico e industrial. Las escorrentías pluviales, las aguas residuales domésticas y las aguas residuales industriales se mezclan antes de ser gestionadas y tratadas en conjunto en una estación depuradora de aguas residuales (EDAR). En las EDAR se lleva a cabo el tratamiento de prácticamente todos los vertidos líquidos urbanos de los países más desarrollados con el fin de evitar o minimizar su impacto en el medio ambiente. Un esquema general de los tratamientos llevados a cabo en una EDAR convencional puede ser el siguiente: un pre-tratamiento físico, donde se eliminan fundamentalmente sólidos de gran tamaño; un tratamiento primario, consistente en utilizar operaciones físico-químicas de separación para disminuir la cantidad de sólidos en suspensión, y un tratamiento secundario, en el que se suele utilizar un tratamiento biológico aerobio o anaerobio para reducir la materia orgánica y los nutrientes. Además, hay que añadir un tratamiento de los lodos generados en el tratamiento secundario y un tratamiento terciario cuando se plantee reutilizar el agua tratada [8, 9]. En este contexto, la depuración de las aguas residuales es imprescindible para su posterior reutilización, o para devolverla al medio natural con una calidad y características que cumplan la normativa vigente de calidad del agua [9, 10].

Con el objetivo de proteger y regular la gestión de los recursos hídricos se ha producido una continua evolución del marco legislativo. Conviene destacar la Directiva 2000/60/CE del Parlamento Europeo y del Consejo de la Unión Europea conocida como Directiva Marco del Agua. Esta directiva integró las directivas de diferentes generaciones para prevenir o reducir la contaminación, promover un uso más sostenible del agua y lograr una mejora de los medios acuáticos [11]. La Directiva 2000/60/CE fue posteriormente modificada por la Directiva 2013/39/CE, en la que se introdujeron cambios relativos a los contaminantes incluidos en la lista de sustancias

prioritarias en el ámbito de la política de agua, estándares de control y en la que se actualizaron las normas de calidad ambiental de los diferentes tipos de aguas mediante el establecimiento de concentraciones máximas admisibles [12]. La Directiva 39/2013 se transpuso al marco jurídico español a través del Real Decreto 817/2015 [13]. Como consecuencia de la falta de regulación de los denominados contaminantes emergentes, tales como por ejemplo, pesticidas, hormonas o fármacos, y ante la necesidad de información para asignar el riesgo asociado de estas sustancias se publicó la Decisión de Ejecución de la Comisión (UE) 2018/840, del 5 de junio de 2018, por la que se establece una lista de observación de este tipo de sustancias, a efectos de seguimiento a nivel de la Unión Europea, en el ámbito de la política de aguas [14].

Ante la falta de una legislación que regulara la reutilización de aguas depuradas, en España se publicó el Real Decreto 1620/2007 [15], en el que se denomina aguas regeneradas a las *“aguas residuales depuradas que, en su caso, han sido sometidas a un proceso de tratamiento adicional o complementario que permite adecuar su calidad al uso al que se destinan”*. En función del uso al que se quiera destinar el agua regenerada, se establecen unos valores límite admisibles con los que se fija la calidad del agua.

Es precisamente la existencia de una regulación estricta en materia de aguas la que motiva el tratamiento, uso o eliminación de las aguas residuales. La proporción de aguas residuales industriales y municipales tratadas está directamente relacionada con el nivel de ingresos del país. De manera que se estima una proporción de aguas residuales tratadas del 70, 38, 28 y 8% para países con ingresos altos (Europa), medios-altos (Oriente Medio y África del Norte), medios-bajos (América Latina) y bajos (gran parte de África subsahariana), respectivamente [16, 17]. Como consecuencia, es probable que alrededor de un 80% de las aguas residuales no se sometan a un tratamiento adecuado. No obstante, estas aguas residuales son una parte esencial del ciclo del agua, desde la captación del agua dulce hasta que, después de ser tratadas tras su utilización, finalmente son reutilizadas o devueltas al medio ambiente para su posterior captación en un punto posterior al que han sido vertidas. Sin embargo, las aguas residuales siguen siendo consideradas un recurso infravalorado cuya gestión no se lleva a cabo para cumplir con rigor la legislación vigente. Una buena gestión de las aguas residuales puede ayudar a reflejar su auténtico valor, especialmente en una economía circular, en la que existe un equilibrio entre la protección del medio ambiente, la utilización sostenible de los recursos y el desarrollo económico [17]. Por

lo tanto, en países en vías de desarrollo donde se lleva a cabo una mala gestión de las aguas residuales, existe una gran oportunidad para su reutilización y la recuperación de subproductos útiles como calor, nutrientes, metales o biogás. Para lograr la optimización de todos estos recursos es esencial el desarrollo de tecnologías de tratamiento que permitan alcanzar la calidad necesaria para el fin previsto.

En los países desarrollados el continuo desarrollo e innovación de la tecnología provoca una evolución positiva de la gestión de las aguas residuales. A comienzos de este siglo, los avances tecnológicos se han centrado en los procesos avanzados y en la aplicación de nanotecnología en materia de tratamiento de aguas, con el fin de cumplir con los requisitos establecidos en una regulación cada vez más estricta [17, 18].

## 1.2. TRATAMIENTO FOTOCATALÍTICO

Los procesos convencionales de tratamiento de las aguas residuales basados en la aplicación de tratamientos biológicos tienen un amplio rango de aplicación [10]. A pesar de su eficacia, estos procedimientos no son capaces de reducir la concentración de algunos de los contaminantes existentes por debajo de los niveles establecidos por la ley, o los requeridos para su uso posterior. Estas situaciones se dan fundamentalmente por la presencia de compuestos orgánicos tóxicos o biorefractarios [8]. Por ello, se han ido desarrollando los denominados tratamientos terciarios con los que conseguir una depuración más eficaz. Muchos de estos procesos todavía necesitan alcanzar un mayor desarrollo y conocimiento de los mecanismos implicados, de la cinética de las distintas reacciones químicas que tienen lugar y la optimización de las variables operacionales o de los reactores donde se llevan a cabo. Entre ellos conviene destacar los procesos fotocatalíticos, puesto que generalmente conducen a la degradación total de los compuestos orgánicos en condiciones atmosféricas. Además, si se aprovecha la energía solar y se realiza el proceso en condiciones aerobias, se consigue reducir los costes operacionales.

En 1972, K. Honda y A. Fujishima descubrieron la capacidad de llevar a cabo la electrólisis del agua para generar  $H_2$  y  $O_2$ , al utilizar un electrodo de  $TiO_2$  iluminado con radiación ultravioleta y un electrodo de Pt como cátodo [19]. A partir de la publicación de estos resultados se ha producido un crecimiento exponencial del número de publicaciones relacionadas con la fotocatalisis, como se observa en la Figura 1.1. Hoy en día, el interés en la aplicación de la fotocatalisis se ha centrado en diversos campos, como la producción de hidrógeno [20-24], el tratamiento de aguas

residuales, la descontaminación atmosférica [25-31], el desarrollo de materiales fotocatalíticos autolimpiantes [32, 33] e incluso en la fotorreducción de  $\text{CO}_2$  para la producción de combustibles [34].

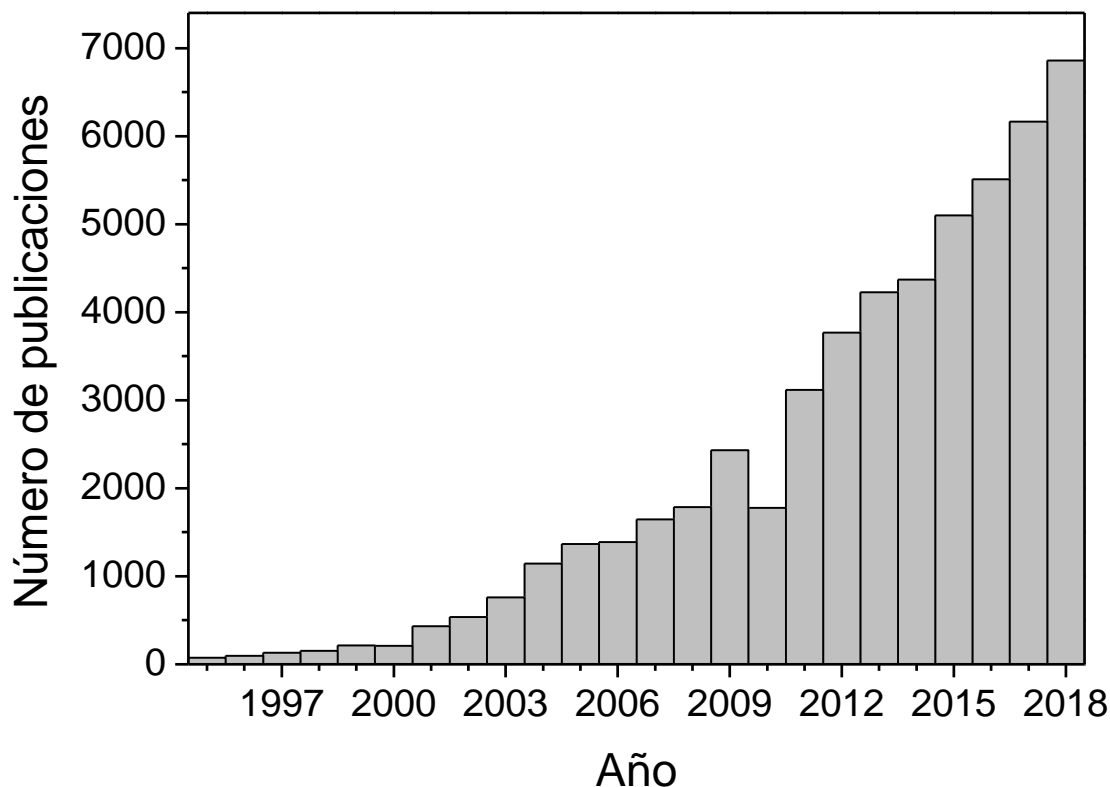


Figura 1.1. Evolución del número de publicaciones relacionadas con fotocatalisis (Fuente: Web of Science; Campo: "Photocatalysis").

La fotocatalisis heterogénea se basa en la absorción de radiación por parte de un sólido semiconductor. En la Figura 1.2, se representa el mecanismo global del proceso de la fotocatalisis heterogénea para la oxidación de materia orgánica, que tiene lugar en una partícula de  $\text{TiO}_2$  suspendida en fase acuosa con un contaminante orgánico R y empleando  $\text{O}_2$  como oxidante. Cuando el fotocatalizador absorbe radiación con una energía igual o superior al band-gap del sólido semiconductor, es decir, igual o superior a la diferencia de energía entre la banda de valencia (BV) y la banda de conducción (BC), se produce la excitación de un electrón ( $e^-$ ) de la banda de valencia a la banda de conducción, dejando un hueco ( $h^+$ ) en la banda de valencia (Ec. 1.1). Los pares electrón-hueco ( $e^-/h^+$ ) fotogenerados pueden migrar a la superficie y participar en las reacciones de oxidación y reducción [35, 36]. Sin embargo, se puede producir la recombinación del par electrón-hueco en la superficie o en el interior del semiconductor (Ec. 1.2), provocando un impacto negativo en el proceso fotocatalítico [35]. Para que tengan lugar las reacciones en la interfase del fotocatalizador-electrolito

es necesario que la diferencia entre los potenciales redox, de la especie dadora de  $e^-$  y la banda de valencia, así como de la especie aceptora de  $e^-$  y la banda de conducción, sea la adecuada [8]. Los huecos de la banda de valencia reaccionarán con especies dadoras de electrones, como agua o con iones hidróxido ( $HO^-$ ) adsorbidos en la superficie del fotocatalizador (Ec. 1.3-1.4). De manera que siempre que la energía de la banda de valencia ( $E_{BV}$ ) sea mayor que el potencial redox del radical hidroxilo ( $E_{HO^\bullet/H_2O}=2.8\text{ V}$ ), se generarán radicales  $HO^\bullet$ , uno de los principales responsables de la degradación de la materia orgánica [37]. Los huecos fotogenerados también pueden reaccionar directamente con el compuesto orgánico, siempre que su potencial de oxidación sea menor que el de la banda de valencia (Ec. 1.5). Por otro lado, los electrones de la banda de conducción pueden reaccionar con especies aceptores de electrones, siendo el  $O_2$  disuelto la especie aceptora más común (Ec. 1.6). La fotorreducción del oxígeno tendrá lugar siempre que su potencial de oxidación sea más negativo que el de la banda de conducción, dando lugar al radical superóxido ( $O_2^{\bullet-}$ ), que puede participar en la oxidación de la materia orgánica o seguir reaccionando para generar peróxido de hidrógeno ( $H_2O_2$ ) (Ec. 1.7-1.8). Ambos,  $O_2^{\bullet-}$  y  $H_2O_2$ , pueden generar a su vez más radicales hidroxilo (Ec. 1.9-1.11) [8, 38].

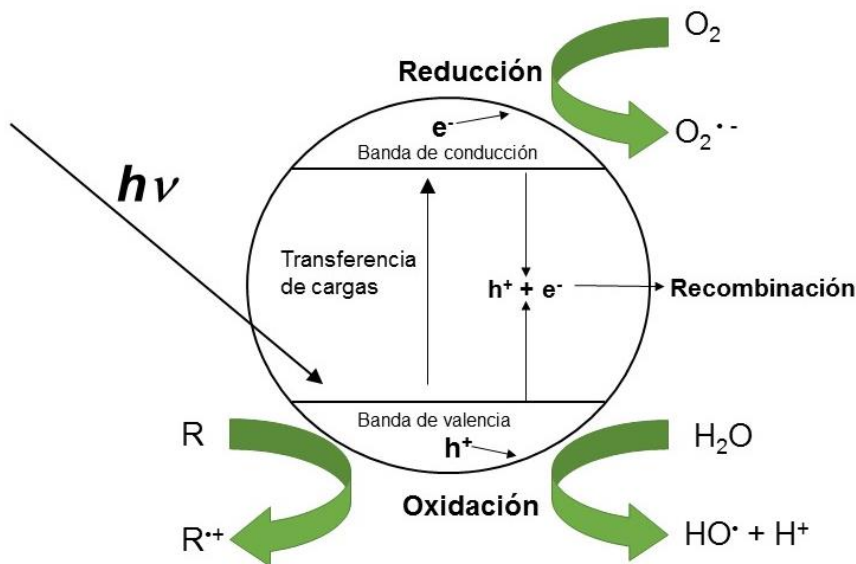
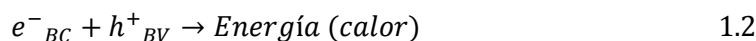
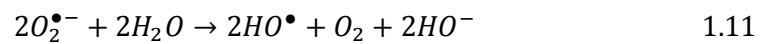
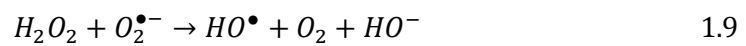
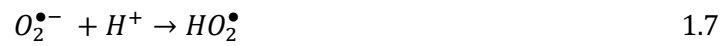


Figura 1.2. Esquema del proceso fotocatalítico durante la de oxidación de materia orgánica en fase acuosa, empleando  $O_2$  como oxidante, en una partícula catalítica de  $TiO_2$ .





Como cualquier proceso de catálisis heterogénea, en fotocatalisis los parámetros operacionales son los que gobiernan la cinética del proceso. Específicamente, cabe destacar: concentración del catalizador, oxígeno disuelto, pH del medio, concentración inicial de sustrato, radiación incidente y temperatura. La optimización de todos estos parámetros conlleva analizar detenidamente su efecto e influencia para cada una de las aplicaciones estudiadas, ya que son dependientes del contaminante y catalizador empleado [26, 36, 39].

### 1.2.1. MECANISMO DEL PROCESO FOTOCATALÍTICO

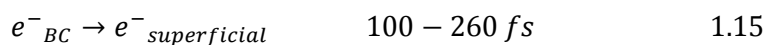
Para lograr un mejor diseño de los sistemas fotocatalíticos, con el consiguiente desarrollo de fotocatalizadores más eficientes, y una mejor comprensión de los mecanismos de reacción, resulta crucial el estudio de los procesos de generación, atrapamiento y relajación, recombinación y transferencia de las cargas fotogeneradas [35, 40].

Como consecuencia de la absorción de radiación con una energía superior a la del band-gap, se produce la fotogeneración de pares  $e^-/h^+$  en el  $TiO_2$ , en la escala de femtosegundos (Ec. 1.12) [35]. Además, debido a la flexión de las bandas, la recombinación de los portadores de carga se retrasa al migrar los electrones libres al bulk y los huecos a la superficie [35, 40, 41].





Los huecos son atrapados por  $O^{2-}$  o aniones  $HO^-$  superficiales dando lugar a la formación de radicales  $O^{\bullet}$  o  $HO^{\bullet}$ , respectivamente. Se ha comprobado que los huecos pueden ser atrapados en diferentes localizaciones, pudiendo clasificarse en dos tipos de trampas (Ec. 1.13-1.14): trampas profundas, en las que los huecos atrapados ( $h^+_{profunda}$ ) son poco reactivos y tienen largos tiempos de vida media, y trampas superficiales en las que los huecos ( $h^+_{superficial}$ ) tienen un elevado potencial de oxidación [42-44]. Estos últimos pueden ser excitados térmicamente y desplazarse a la banda de valencia, teniendo una reactividad comparable a la de los  $h^+$  sin atrapar [40, 42]. Del mismo modo, los electrones son atrapados por  $Ti^{4+}$  o vacantes de oxígeno ( $O_V$ ) localizados en la interfase agua-partícula catalítica (Ec. 1.15) [45]. Los  $e^-$  posteriormente se pueden relajar y localizarse en niveles más profundos (Ec. 1.16) en torno a los 50 ps, teniendo menos movilidad y con una menor probabilidad de recombinarse [35, 44].

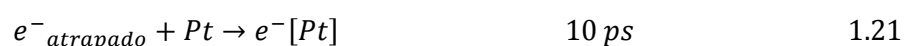


La recombinación de las cargas fotogeneradas puede tener lugar mediante procesos no radiativos, liberando calor, o mediante procesos radiativos (Ec. 1.17 y 1.18). En el caso del  $TiO_2$ , los pares  $e^-/h^+$  se recombinan principalmente mediante procesos no radiativos en el intervalo de los ns. De acuerdo con la bibliografía, mientras que los huecos tienen similares tiempos de vida media (ns) en estructuras anatasa y rutilo, los electrones tienen un mayor tiempo de vida media en la fase cristalina anatasa que en el rutilo ( $\sim$ ms y 24 ns respectivamente) [35]. No obstante, la recombinación depende de diversos factores, como la preparación del catalizador, la temperatura de operación, el atrapamiento y transferencia de las cargas y la intensidad de la luz con la que se excita. Para evitar la recombinación de los portadores de cargas, se tienen que aplicar bajas energías de excitación para evitar un exceso de pares electrón-hueco presentes en la partícula catalítica [35, 46, 47]. Del mismo modo, cuanto menor sea el tamaño de partícula de una suspensión coloidal mayor es la fracción de pares electrón-hueco que se recombinan para un tiempo determinado [58].

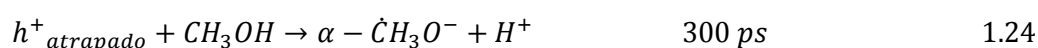
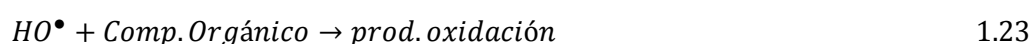
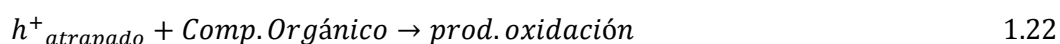




En el caso de las reacciones de reducción foto-inducidas en la superficie del TiO<sub>2</sub>, los e<sup>-</sup> atrapados en la banda de conducción pueden llegar a reaccionar con especies aceptoras de e<sup>-</sup> (O<sub>2</sub>) para formar radicales superóxido (O<sub>2</sub><sup>•-</sup>), en el intervalo de los 100 ns y 10-100 μs, respectivamente (Ec. 1.19-1.20) [40]. La incorporación de Pt en el fotocatalizador, por ejemplo, puede actuar como atrapador (*scavenger*) de e<sup>-</sup> (Ec. 1.21) [42], favoreciendo la separación de los pares e<sup>-</sup>/h<sup>+</sup>, al ser los e<sup>-</sup> transferidos a los 10 ps, y facilitando la reducción fotocatalítica [35, 44].



En el caso de los huecos no existe un consenso en cómo se transfieren. Sin embargo, se ha demostrado que en función de la interacción del compuesto orgánico con el TiO<sub>2</sub>, se puede dar una transferencia directa o indirecta del hueco (Ec. 1.22-1.23) [40, 48]. Por ejemplo, el metanol se oxida por la transferencia directa de un hueco a los 300 ps, después de haberse irradiado el fotocatalizador (Ec. 1.24) [35].



Al comparar los diferentes procesos que pueden llegar a tener lugar, la transferencia interfacial de los portadores de carga, especialmente de los e<sup>-</sup>, es bastante más lenta que la de los procesos de recombinación, tanto en la superficie como en el interior del semiconductor. De hecho, estudios previos han demostrado que la mayoría de los pares e<sup>-</sup>/h<sup>+</sup> (~90%) se recombinan rápidamente después de que el fotocatalizador sea excitado [35]. Por esta razón, se han desarrollado diferentes estrategias para mejorar la separación y transferencia de cargas para alcanzar mayores actividades fotocatalíticas y una mejora en la fotoeficiencia del sistema catalítico.

### 1.3. TiO<sub>2</sub> COMO FOTOCATALIZADOR

Entre los diversos semiconductores que han sido estudiados en los procesos fotocatalíticos (ZnO, WO<sub>3</sub>, MoO<sub>3</sub>), el dióxido de titanio (TiO<sub>2</sub>) es, sin duda, el semiconductor más utilizado por su relativa alta actividad fotocatalítica, estabilidad, baja toxicidad, resistencia a la corrosión y por su bajo coste [26, 35, 49].

El TiO<sub>2</sub> puede presentarse formando diversas estructuras polimorfas, cada una de ellas con estructuras cristalinas y electrónicas distinguibles. Normalmente se definen tres tipos de estructuras cristalinas diferentes: brookita, rutilo y anatasa, siendo las dos últimas las más activas desde el punto de vista fotocatalítico. Sin embargo, en la mayoría de las aplicaciones de descontaminación ambiental se ha comprobado que es su forma cristalina anatasa la que presenta una mayor actividad fotocatalítica. Sin embargo, al ser el band-gap de la anatasa y del rutilo próximos a 3.2 eV y 3 eV respectivamente, estas estructuras cristalinas solo pueden ser activadas mediante radiación ultravioleta hasta 390 nm aproximadamente, pudiendo aprovechar, por tanto, solo un 4-5% de la radiación solar [9].

#### 1.3.1. MODIFICACIONES DEL TiO<sub>2</sub>

Como se ha mencionado en los apartados anteriores, debido al alto valor de su band-gap el TiO<sub>2</sub> solo es capaz de absorber radiación principalmente en la región UV, por lo que no resulta muy eficiente desde el punto de vista de absorción de la energía solar [49, 50]. Además, hay que tener en cuenta los bajos rendimientos cuánticos que alcanza (<10%), definidos como la relación entre la velocidad de degradación de un compuesto y la radiación absorbida por el TiO<sub>2</sub>, como consecuencia de la rápida recombinación de sus pares electrón-hueco [35, 37]. Por ello, se han desarrollado una serie de estrategias, alguna de ellas recogidas en la Figura 1.3, con el objetivo de modificar las posiciones de las bandas de conducción y de valencia, la estructura, la superficie y la interfase del fotocatalizador para alcanzar así una disminución de la recombinación de las cargas fotogeneradas, aumentar la reactividad de la superficie y ampliar el intervalo del espectro solar donde el fotocatalizador sea activo [26, 35, 37, 49-51].

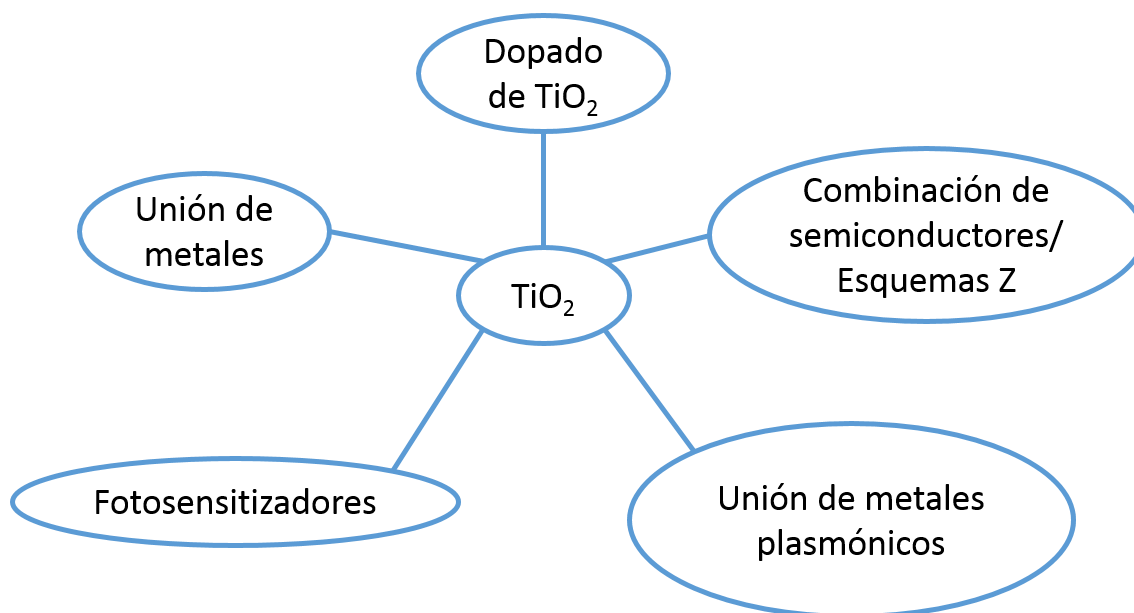


Figura 1.3. Estrategias de modificación del  $\text{TiO}_2$  para mejorar su fotoeficiencia.

El dopado de  $\text{TiO}_2$  consiste en la introducción de iones metálicos y no metálicos en la estructura del  $\text{TiO}_2$  para crear nuevos niveles en el band-gap original del  $\text{TiO}_2$ . Esta estrategia busca reducir el band-gap, para conseguir que el fotocatalizador absorba y presente actividad en el espectro visible. Además, la presencia de aniones o cationes dopantes facilita la separación de cargas, aumentando el tiempo de vida media de los pares  $e^-/h^+$  y la velocidad de los procesos de transferencia de carga [25]. El efecto de la introducción de agentes dopantes metálicos y no metálicos en el band-gap se describe en la Figura 1.4 A.

Otra de las metodologías utilizadas para conseguir catalizadores activos en el espectro visible consiste en unir al  $\text{TiO}_2$  un fotosensibilizador. El fotosensibilizador suele consistir en un colorante, orgánico o inorgánico, capaz de absorber radiación en la región visible, e incluso a veces en la región del infrarrojo cercano del espectro electromagnético. Cuando sobre el sistema incide radiación de una longitud de onda adecuada, se produce la excitación del fotosensibilizador, como se representa en la Figura 1.4 B. A continuación, el fotosensibilizador excitado inyecta un electrón a la banda de conducción del semiconductor, iniciando así las correspondientes reacciones fotocatalíticas. Por tanto, la reacción de reducción ocurre en el semiconductor mientras que la reacción de oxidación tiene lugar en el fotosensibilizador. Si el  $\text{TiO}_2$  es excitado con luz suficientemente energética, la reacción de oxidación tendrá lugar tanto en el semiconductor como en el fotosensibilizador [25, 26, 35, 37].

Otro tipo de sensibilización es la que se da en partículas de  $\text{TiO}_2$  unidas a metales plasmónicos, como ciertos metales nobles (Au, Ag, Pt). A diferencia de otros sistemas fotocatalíticos, este tipo de modificación presenta dos ventajas: la formación de una barrera de Schottky y la resonancia de plasmones superficiales localizados [50, 51]. Las nanopartículas metálicas se caracterizan por ser sensibilizadores al absorber luz visible, debido al efecto de resonancia de plasmones superficiales localizados (RPSL). La RPSL hace referencia a la oscilación colectiva de los electrones libres en las nanopartículas metálicas, en resonancia con el campo eléctrico de la radiación incidente. La resonancia se produce cuando la frecuencia de los fotones coincide con la frecuencia de oscilación de los electrones superficiales. Por tanto, se generará un campo electromagnético muy intenso cuando las partículas metálicas sean iluminadas. La interacción de este campo eléctrico con el semiconductor, induce la formación de portadores de carga en las proximidades de la superficie del  $\text{TiO}_2$  [35, 52, 53]. La generación y separación de los pares  $e^-/h^+$ , al ser estos fotocatalizadores irradiados con luz visible, está descrita con detalle en la Figura 1.4 C.

Una de las estrategias más utilizadas hoy en día para conseguir reducir la velocidad de recombinación de los pares  $e^-/h^+$  consiste en la combinación de distintos semiconductores. La diferencia de potencial inducida por el contacto entre semiconductores con diferentes posiciones de las bandas de conducción y valencia, pueden facilitar la separación y transferencia de cargas [25, 26, 37, 50, 54]. Esta transferencia de portadores de carga está representada en la Figura 1.4 D. No obstante, todavía es posible conseguir una mayor reducción de la recombinación de las cargas fotogeneradas mediante el desarrollo de heterouniones ternarias [37, 54]. Sin embargo, este tipo de sistemas presenta la desventaja de que tanto los electrones como los huecos transferidos sufren una reducción de su potencial redox [50].

Este inconveniente se puede evitar mediante el desarrollo de esquemas Z, consistentes en la utilización de dos semiconductores. Sin embargo, aunque la ventaja que presentan estos sistemas es que se mantienen los electrones y huecos con mayor potencial de reducción y oxidación; se produce la recombinación de los electrones y huecos con menor potencial de reducción y oxidación [37, 51, 55, 56]. Los sistemas fotocatalíticos esquema Z se pueden dividir a su vez en sistemas esquema Z indirecto o directo, descritos en las Figura 1.4 E y F respectivamente, en función de si se utiliza un mediador redox (un par aceptor/donador de electrones) en fase líquida, o si no se utiliza ningún mediador redox [37, 50, 51, 55].

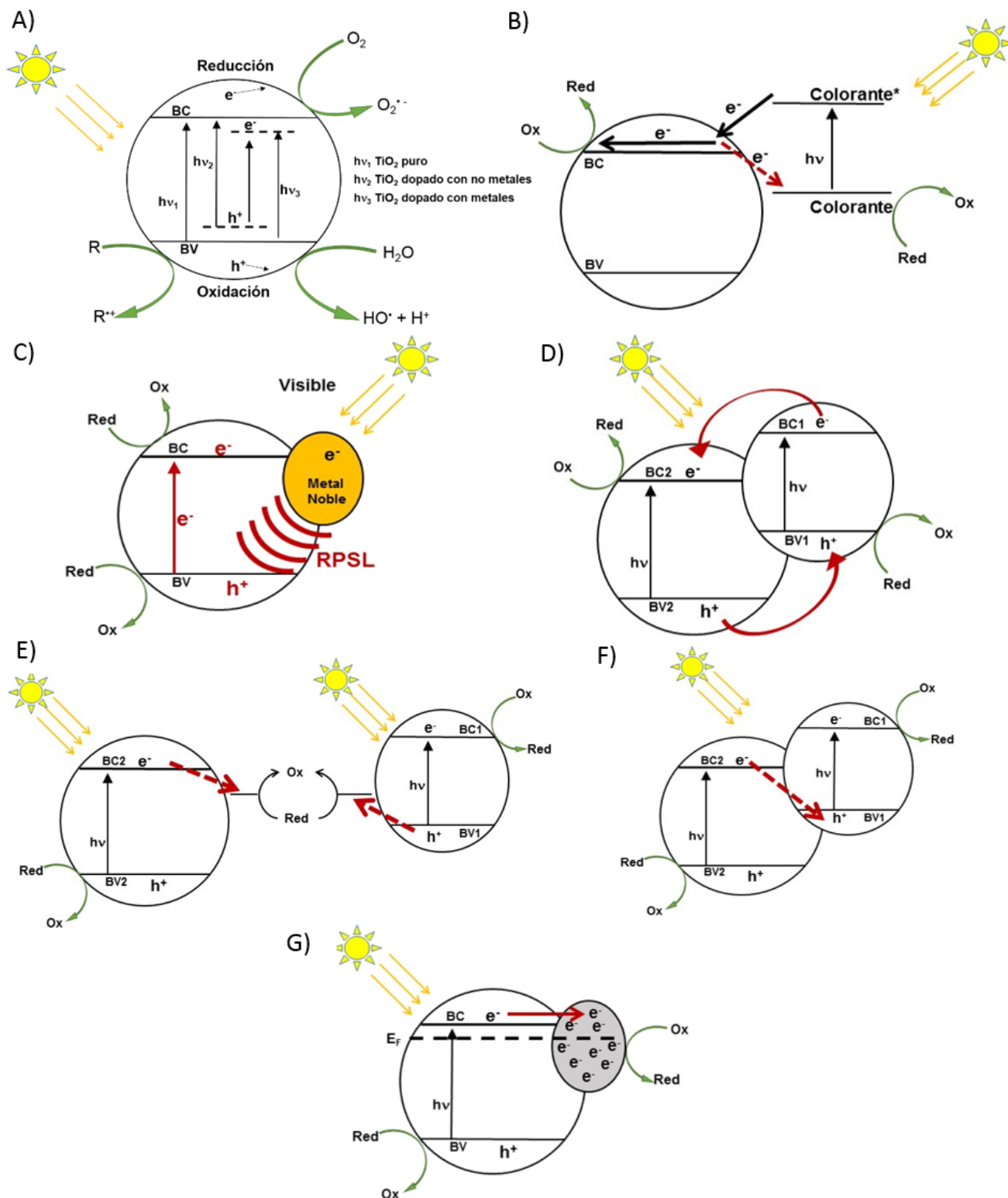


Figura 1.4. Representaciones esquemáticas de los procesos fotocatalíticos que tienen lugar en fotocatalizadores de  $\text{TiO}_2$  modificados: dopados con elementos no metálicos y metálicos (A), sensibilización con un colorante que es fotoexcitado (B), unido a un metal plasmónico (C), heterouniones “p-n” o “n-n” (D), semiconductores combinados para formar un esquema Z indirecto (E), esquema Z directo (F), heterounión formada por un semiconductor y un material conductor (G).

La formación de la barrera de Schottky, al adicionar un metal (Ag, Cu, Au, Pt, Pd) sobre la superficie del semiconductor, también proporciona una mejora destacable de la separación de los electrones y los huecos fotogenerados. Esta mejora se debe principalmente al menor valor del nivel de Fermi ( $E_F$ ) del  $\text{TiO}_2$  comparado con el del metal depositado. Cuando ambos están conectados eléctricamente, se producirá la transferencia de electrones de la banda de conducción del  $\text{TiO}_2$  al metal, hasta que ambos niveles de Fermi alcancen un equilibrio. En la Figura 1.4 G se describe el efecto de la adición de un metal en la separación de las cargas [25, 26, 35, 37, 57, 58].

En los últimos años, debido a las excelentes propiedades que presentan tanto el grafeno como el óxido de grafeno, su utilización ha adquirido cada vez más importancia en la formación y optimización de barreras de Schottky, de heterouniones “n-n” o “p-n” y la formación de esquemas Z [37], para mejorar la eficiencia final del fotocatalizador.

### 1.3.2. SISTEMAS BINARIOS $\text{TiO}_2$ -rGO

En 2004 Andre Geim y Kostya Novoselov publicaron la obtención de láminas bidimensionales de átomos de carbono, denominadas grafeno, que supuso un gran hito y descubrimiento científico, consiguiendo el Premio Nobel de Física en 2010 [59]. El grafeno presenta excelentes propiedades como una gran conductividad térmica ( $\sim 5000 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ), transmitancia óptica ( $\sim 97\%$ ) resistencia mecánica, una excelente movilidad de portadores de carga a temperatura ambiente ( $200000 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ) y una superficie específica teórica muy alta ( $\sim 2630 \text{ m}^2\cdot\text{g}^{-1}$ ) [27, 37, 60, 61].

El grafeno, una forma alotrópica del carbón, consiste en una sola capa de átomos de carbono enlazados mediante hibridación  $sp^2$  con una estructura semejante a la de un panal de abejas debido a su configuración atómica hexagonal. El grafeno puede ser preparado mediante métodos ascendentes (*bottom-up*) y descendentes (*top-down*). Sin embargo, debido a su conveniencia y menor coste los métodos “*top-down*” son los más empleados, especialmente cuando el material resultante va a ser utilizado en fotocátalisis [51, 60]. La técnica más común para su obtención consiste en la síntesis de óxido de grafeno (GO) a partir de grafito y su posterior reducción para obtener óxido de grafeno reducido (rGO). Existen varios métodos para preparar GO a partir de grafito, entre los que caben destacar los publicados por Brodie [62] y Hummers [63]. Posteriormente, han surgido otros métodos alternativos más seguros y eficientes [64, 65]. Las láminas de óxido de grafito, una vez exfoliadas, presentan una gran variedad de grupos funcionales oxigenados como grupos hidroxilo, carbonilo o epoxi. Gracias a



estos grupos funcionales el GO puede ser fácilmente dispersado y exfoliado en agua, facilitando el crecimiento de las nanopartículas del  $\text{TiO}_2$  al interaccionar los cationes con los grupos funcionales [51, 66]. Cuando el grado de oxidación del GO es suficientemente alto, su estructura electrónica es adecuada para actuar como fotocatalizador, haciendo posible la oxidación y reducción del agua para producir  $\text{H}_2$  y  $\text{O}_2$  [51, 67]. La reducción del óxido de grafeno, con una regeneración parcial de la red gráfitica, puede llevarse a cabo mediante diferentes métodos tales como reducción química, térmica, electroquímica, fotocatalítica, sonoquímica o incluso con microondas [51, 61].

En este contexto, los nanocomposites o fotocatalizadores de dióxido de titanio-óxido de grafeno reducido ( $\text{TiO}_2$ -rGO) pueden ser sintetizados mediante diferentes metodologías. El crecimiento *in situ* utilizando GO y un precursor del metal es uno de los procedimientos más usados. De esta forma, se consigue evitar en las láminas de GO/rGO la aglomeración de las nanopartículas del semiconductor correspondiente [68-73]. Otras estrategias utilizadas para sintetizar semiconductores unidos a GO/rGO consisten en la aplicación de procesos hidrotermales o solvotermales. En estos procesos las nanopartículas del semiconductor, o su precursor, se depositan en las láminas del GO al mismo tiempo que se produce su reducción [57, 70, 74-76]. Entre otras metodologías utilizadas para la obtención de este tipo de nanocomposites o fotocatalizadores, cabe destacar su síntesis a partir de la agitación de la mezcla física formada por el  $\text{TiO}_2$  con el rGO, a partir de metodologías fotocatalíticas [27, 77], asistidas por microondas [78-80] o ultrasonidos [65]. Varias de estas metodologías de síntesis han sido comparadas para su aplicación a la degradación de diferentes contaminantes. Por ejemplo, Fan y colaboradores [81] prepararon distintos composites de  $\text{TiO}_2$ -rGO mediante reducción fotocatalítica, reducción química con hidracina y a partir de una síntesis hidrotermal. Todos los fotocatalizadores estudiados presentaron mejor actividad fotocatalítica que el  $\text{TiO}_2$  de partida en la producción de  $\text{H}_2$  a partir de metanol en disolución acuosa. De todos ellos, el que alcanzó las mayores velocidades de generación de  $\text{H}_2$  fue el composite preparado mediante síntesis hidrotermal. Por otro lado, Al-Kandari y colaboradores [82] también evaluaron la influencia que tiene el método de síntesis en fotocatalizadores de  $\text{TiO}_2$ -rGO. Estudiaron tres tipos de síntesis: (1) el GO fue impregnado sobre el  $\text{TiO}_2$  y posteriormente se redujo usando una corriente de  $\text{H}_2$  a 450 °C; (2) a partir de la reducción inicial del GO con hidracina en un horno microondas y su posterior unión al  $\text{TiO}_2$  mediante agitación durante 24 h y (3) mediante reducción inicial del GO en un proceso hidrotermal y la posterior adición de  $\text{TiO}_2$ . En este caso, también detectaron las mayores velocidades de degradación de



fenol con radiación UV al utilizar el composite con GO reducido mediante síntesis hidrotermal.

Actualmente, este tipo de nanocomposites o fotocatalizadores tiene lugar en diversos campos, tales como la producción de  $H_2$  [37, 61, 81, 83], la desinfección [27, 77] y la degradación de contaminantes orgánicos [57, 66, 76, 84, 85]. La mayor actividad fotocatalítica detectada en todos estos sistemas binarios se debe fundamentalmente al papel que juega el rGO como aceptor de electrones, que actúa disminuyendo la recombinación de los portadores de cargas, a su mayor superficie específica con un aumento de la cantidad y calidad de los centros de adsorción y, por último, a la capacidad de modificar el band-gap en función de su grado de oxidación y/o extender el intervalo de absorción de radiación [60, 61]. Además, estos fotocatalizadores tienen la ventaja de sedimentar mucho más rápido que el semiconductor por separado, facilitando su recuperación final mediante sedimentación [86].

#### **1.4. MODELADO DE FOTORREACTORES**

Durante las últimas décadas se ha realizado un gran esfuerzo para entender los procesos fotocatalíticos y desarrollar nuevos materiales fotocatalíticos que permitan alcanzar mayores fotoeficiencias. Sin embargo, para diseñar y escalar los reactores fotocatalíticos donde se llevarán a cabo los diferentes procesos estudiados a escala de laboratorio, es estrictamente necesario el desarrollo de modelos predictivos [87-89]. En el caso de reactores convencionales se requiere la resolución de los correspondientes balances de cantidad de movimiento, de energía térmica y de materia para cada especie. Sin embargo, dado que en los procesos fotocatalíticos la primera etapa consiste en la activación del fotocatalizador, es esencial considerar la ecuación de transferencia radiativa (RTE) y desarrollar modelos que permitan describir la absorción de la radiación en el interior del reactor. Por el contrario, el balance entálpico no se suele tener en cuenta, ya que los perfiles y efectos de la temperatura no suelen ser importantes. Para resolver el balance de materia es necesario e imprescindible la obtención de un modelo cinético que muestre una dependencia explícita de la radiación absorbida (expresada a través de la velocidad volumétrica local de absorción de fotones, LVRPA) [87, 89, 90].

### 1.4.1. FUNDAMENTOS DEL TRANSPORTE DE RADIACIÓN

La radiación puede considerarse como una “fuente” de fotones que se propagan en forma de rayos, caracterizados por su dirección y energía, cuya propiedad asociada es la intensidad específica espectral. Su valor es proporcional al número de fotones que se propagan en la dirección  $\Omega$  con una energía igual a  $h\nu$ . La integración de la intensidad específica espectral, en todas las direcciones posibles, da lugar a la Radiación Incidente Espectral que viene definida por la siguiente expresión:

$$G_\lambda(\underline{x}) = \int_{\Omega} I_\lambda(x, \Omega) d\Omega \quad 1.25$$

Para evaluar la velocidad volumétrica local de absorción de fotones (LVRPA,  $e_\lambda^a(\underline{x})$ ) es necesario conocer la intensidad específica espectral en cada punto del reactor, para lo cual se debe resolver la ecuación de transferencia radiativa (RTE) [89, 90].

La velocidad volumétrica local de absorción de fotones forma parte de la velocidad de reacción por medio de la etapa de activación. Por lo tanto es necesario calcularla, y para ello se requieren dos tareas adicionales: la resolución de la ecuación de transferencia radiativa (RTE) para resolver el balance de fotones; y por otro lado, la determinación de todos los parámetros ópticos del medio.

### 1.4.2. ECUACIÓN DE TRANSFERENCIA RADIATIVA (RTE)

Consideramos un elemento de volumen  $V$  que contiene un medio en el que se produce absorción, emisión y dispersión (*scattering*). Siendo los fotones que nos interesan aquellos que se propagan dentro de un ángulo sólido  $d\Omega$ , y que transportan energía radiante de una determinada longitud de onda  $\lambda$  (fotones  $\Omega, \lambda$ ), el balance de transferencia de fotones se puede representar mediante la siguiente expresión:

$$\left[ \begin{array}{l} \text{Velocidad con la que cambia} \\ \text{la cantidad de fotones } \Omega, \lambda \end{array} \right] + \left[ \begin{array}{l} \text{Flujo neto de fotones } \Omega, \lambda \\ \text{dentro del volumen } V \text{ a} \\ \text{través de la superficie } A \end{array} \right] = \left[ \begin{array}{l} \text{Ganancia neta de} \\ \text{fotones } \Omega, \lambda \text{ debida a} \\ \text{absorción, emisión,} \\ \text{in y out - scattering} \end{array} \right] \quad 1.26$$

La parte derecha del balance incluye los siguientes términos: (1) emisión ( $W_{\Omega, \lambda}^{em}$ ), (2) absorción ( $W_{\Omega, \lambda}^{ab}$ ), (3) *out-scattering* ( $W_{\Omega, \lambda}^{ou-s}$ ) e (4) *in-scattering* ( $W_{\Omega, \lambda}^{in-s}$ ). Por lo tanto:

$$\frac{1}{c} \frac{\partial I_{\Omega, \lambda}}{\partial t} + \nabla \cdot (I_{\Omega, \lambda}) = W_{\Omega, \lambda}^{em} - W_{\Omega, \lambda}^{ab} - W_{\Omega, \lambda}^{ou-s} + W_{\Omega, \lambda}^{in-s} \quad 1.27$$

Asumiendo que el término correspondiente a la emisión de radiación es insignificante a la temperatura de trabajo y que el campo de radiación alcanza el estado estacionario de manera instantánea, ya que el factor  $1/c$  es muy bajo, se obtiene que:

$$\frac{1}{c} \frac{\partial I_{\Omega,\lambda}}{\partial t} = 0 \quad 1.28$$

Entonces, la RTE presenta la siguiente forma matemática:

$$\underbrace{\frac{dI_{\lambda}(x, \Omega)}{ds}}_{\text{Variación sobre la dirección } \Omega} + \underbrace{\kappa_{\lambda}(x)I_{\lambda}(x, \Omega)}_{\text{Pérdida por absorción}} + \underbrace{\sigma_{\lambda}(x)I_{\lambda}(x, \Omega)}_{\text{Pérdida por Out-scattering}} = \underbrace{\frac{\sigma_{\lambda}(x)}{4\pi} \int_{\Omega'=4\pi} p(\Omega' \rightarrow \Omega) I_{\lambda}(x, \Omega) d\Omega'}_{\text{Ganancia por In-scattering}} \quad 1.29$$

Según esta ecuación, un rayo de luz pierde energía debido a la absorción y al *out-scattering*, que se modela mediante los coeficientes de absorción volumétrico ( $\kappa_{\lambda}$ ) y de *scattering* volumétrico ( $\sigma_{\lambda}$ ), respectivamente. La ganancia de energía se debe a la emisión interna, considerada despreciable, y al *in-scattering*. El *in-scattering*, modelado mediante una función de fase  $p(\Omega' \rightarrow \Omega)$ , puede definirse como la contribución de energía que es incorporada a la dirección  $\Omega$  y que proviene de la energía dispersada por algunos rayos debido al *out-scattering* [89-92].

Para resolver la RTE y evaluar la radiación absorbida es necesario conocer el flujo de radiación que llega al fotorreactor. Estas condiciones de contorno se pueden determinar de dos maneras diferentes: mediante medidas experimentales a través de actinometrías o mediante modelos de emisión [87-89].

El transporte de radiación policromática en un medio participativo y reactivo (lo cual implica absorción, *scattering* y reacción química) es de suma complejidad, dado que los modelos bidimensionales-bidireccionales no pueden resolverse analíticamente. Por ello, es necesario utilizar aproximaciones tanto teóricas como numéricas. Entre los diferentes métodos empleados para resolver la RTE se encuentran: el método de la ordenada discreta (DOM) [89, 90, 93, 94], el método de Monte Carlo (MC) [93, 95-99], el modelo de absorción-*scattering* de la radiación de “dos flujos” (TFM) o de “seis flujos” (SFM) [88, 100-102] y otros métodos alternativos [103, 104]. Cabe destacar el Método de la Ordenada Discreta (DOM), que está considerado como el procedimiento numérico más robusto para la solución de este tipo de problemas o cálculos numéricos, el cual fue desarrollado inicialmente en el campo de la ingeniería nuclear para el transporte de neutrones [87, 89, 90, 105-107]. Sin embargo, el método de Monte Carlo ha adquirido más importancia en los últimos años y se utiliza cada vez más, debido a su simplicidad y a que puede ser aplicado en reactores con geometría

compleja. Se trata de un método estocástico que consiste en rastrear fotones desde su generación hasta que son absorbidos o dispersados fuera del sistema de reacción. En los últimos años, programas comerciales basados en modelos de dinámica de fluidos computacional (CFD), son empleados cada vez con más frecuencia para modelar la radiación absorbida [28, 108-111]. Estos métodos de resolución de la RTE han sido aplicados a reactores de geometrías muy diversas, como por ejemplo, reactores anulares [100, 102, 112, 113], cilíndricos [95, 97-99, 106, 114], reactores rectangulares planos [102, 104] o incluso reactores multitubulares [111].

### 1.4.3. PROPIEDADES ÓPTICAS DE LA SUSPENSIÓN

Para la resolución de la RTE es necesario conocer las propiedades determinantes que permitan una caracterización óptica del medio sólido-líquido a estudiar donde tiene lugar el proceso fotocatalítico.

En el caso de trabajar con sistemas heterogéneos, como las reacciones fotocatalíticas con  $\text{TiO}_2$ , es necesario conocer el valor de los coeficientes de absorción y de *scattering* del medio sólido-líquido. Estos coeficientes representan la fracción de radiación incidente que es absorbida o dispersada, respectivamente, por unidad de longitud de camino óptico de la radiación. Para ello, es necesario determinar primero el coeficiente de extinción ( $\beta_\lambda$ ), que incluye los coeficientes anteriores (Ec. 1.30), mediante medidas espectrofotométricas convencionales [87, 115, 116].

$$\beta_\lambda = \sigma_\lambda + \kappa_\lambda \quad 1.30$$

Para determinar el coeficiente de absorción volumétrico ( $\kappa_\lambda$ ) es necesario recurrir a medidas espectrofotométricas, utilizando una esfera integradora que permita detectar los fotones dispersados en el mismo sentido que el de la radiación incidente (*forward scattering*) [87, 115, 116].

Por otra parte, es necesario determinar la función de fase, que incorpora la distribución de direcciones y frecuencias de la radiación dispersada [87, 115, 116]. Existen diferentes modelos empleados con distintos tipos de partículas en suspensión. Al principio, funciones de fase isotrópicas se utilizaron para modelar la distribución de la radiación [115]. Sin embargo, posteriores estudios indicaron que la aplicación de una función de fase anisotrópica, como la función de fase Henyey–Greenstein, permite obtener resultados más precisos [87, 116-118].

$$p_{HG,\lambda}(\cos\theta) = \frac{(1 - g_\lambda^2)}{(1 + g_\lambda^2 - 2g_\lambda \cos\theta)^{\frac{3}{2}}} \quad 1.31$$

donde  $g_\lambda$  es el factor de asimetría, de forma que valores de  $g_\lambda=0$  representa *scattering* isotrópico. Asimismo, valores de  $g_\lambda>0$  y  $g_\lambda<0$  indican una dispersión de la radiación principalmente en la misma dirección y en dirección contraria a la de la radiación incidente, respectivamente.

Las propiedades ópticas dependen en gran medida del tipo de fotocatalizador empleado y de las condiciones de operación en las que tiene lugar el proceso a estudiar. En cuanto al catalizador hay que tener en cuenta desde el tipo de semiconductor, su composición, hasta modificaciones superficiales o incluso la introducción de agentes dopantes. Por último, en cuanto a las condiciones de operación, el pH, agitación, el medio en que se encuentra el fotocatalizador y la forma en que se usa (suspendido o soportado) pueden afectar considerablemente a las propiedades ópticas [87].

#### 1.4.4. VELOCIDAD VOLUMÉTRICA LOCAL DE ABSORCIÓN DE FOTONES (LVRPA)

La solución de la RTE proporciona el campo de radiación dentro del fotorreactor, es decir, se obtienen los valores de las intensidades de fotones de la radiación monocromática para cada dirección y elemento de volumen del reactor. Una vez que estas intensidades son conocidas, la velocidad volumétrica local de absorción de fotones (LVRPA,  $e_\lambda^a(x)$ ) puede ser calculada a partir de la Radiación Incidente Espectral. Frecuentemente, en estos reactores fotocatalíticos sólo el catalizador en suspensión absorbe radiación. En este caso, si el catalizador es ópticamente estable, y su concentración no cambia, el campo de radiación es independiente del avance de la reacción [89, 92, 119].

$$e_\lambda^a(x) = \kappa_\lambda(x)G_\lambda(x) \quad \left[ \frac{\text{Einstein}}{\text{cm}^3 \text{ s}} \right] \quad 1.32$$

En caso de tratarse de radiación policromática, es necesario integrar en el rango útil de longitudes de onda donde convergen tanto el intervalo de emisión de la lámpara como aquel intervalo donde el catalizador absorbe radiación. En este caso la expresión de la LVRPA es la siguiente:

$$e_\lambda^a(x) = \int_{\lambda_{min}}^{\lambda_{max}} \kappa_\lambda(x)G_\lambda(x)d\lambda \quad \left[ \frac{\text{Einstein}}{\text{cm}^3 \text{ s}} \right] \quad 1.33$$

### 1.4.5. EFICIENCIA CUÁNTICA Y EFICIENCIA FOTÓNICA

Uno de los primeros parámetros que permiten estimar la actividad intrínseca del catalizador y la eficiencia en el uso de los fotones en un sistema fotocatalítico, es la relación entre la velocidad inicial de reacción volumétrica molar del proceso  $\langle -r_{CO}(x, t_0) \rangle_{V_R}$  y la velocidad volumétrica de absorción de fotones por el catalizador  $\langle e^a(x) \rangle_{V_R}$ . Esta relación se denomina eficiencia cuántica ( $\eta$ ) en el caso de utilizar radiación policromática [87].

$$\eta = \frac{\langle -r_{CO}(x, t_0) \rangle_{V_R}}{\langle e^a(x) \rangle_{V_R}} \quad 1.34$$

Los valores más comunes de la eficiencia cuántica suelen ser inferiores al 10% [35, 97, 106].

Otro parámetro importante a tener en cuenta es la eficiencia fotónica o eficiencia cuántica aparente, que indica la eficiencia en el uso de fotones de un proceso fotocatalítico con respecto al total de fotones incidentes [89].

$$\xi = \frac{\langle -r_{CO}(x, t_0) \rangle_{V_R} V_R}{q^0 A_{Irr}} \quad 1.35$$

donde  $q^0 A_{Irr}$  es el producto del flujo de fotones que inciden sobre el fotorreactor por el área irradiada. La ventaja es que estos flujos de radiación se pueden determinar fácilmente mediante medidas experimentales (actinometrías) [120] o radiométricas. Además, esta eficiencia fotónica permite tener en cuenta no solo la eficiencia de la reacción fotocatalítica, sino también la eficiencia del catalizador en la absorción de la luz disponible y la eficiencia del diseño del reactor para optimizar la distribución de la radiación [89].

### 1.4.6. MODELADO CINÉTICO

En la literatura científica es común encontrar expresiones de tipo global que no son fácilmente extrapolables a otros tipos de reactores o cambios de escala [26]. Por esta razón, la expresión cinética debe tener siempre desagregadas las contribuciones de todas las variables representativas del proceso y del fotorreactor (expresadas a través de la valoración de la LVRPA) [87]. Por lo tanto, resulta imprescindible la obtención de un modelo cinético intrínseco para describir de manera rigurosa la velocidad de reacción. El punto de partida para la obtención de la expresión cinética consiste en

plantear un mecanismo o esquema simplificado de reacción, como el descrito en la Tabla 1.1, donde es esencial considerar al menos: la activación del catalizador por absorción de la radiación, la recombinación de los pares  $e^-/h^+$ , el atrapamiento de los portadores de carga y la reacción entre los radicales hidroxilo ( $HO^\bullet$ ) y el compuesto orgánico a degradar [87, 90, 95, 121]. Además, otras etapas como la adsorción de los reactivos o la oxidación por los huecos fotogenerados deberían también tenerse en cuenta.

Tabla 1.1. Mecanismo simplificado de la oxidación fotocatalítica de un compuesto orgánico A mediante radicales hidroxilo.

Activación	$TiO_2 \xrightarrow{h\nu} TiO_2 + e^- + h^+$	$r_{gs}$
Recombinación	$e^- + h^+ \rightarrow heat$	$k_2[e^-][h^+]$
Atrapamiento de $e^-$	$O_{2,ads} + e^- \rightarrow O_2^{\bullet-}$	$k_3[e^-][O_{2,ads}]$
Atrapamiento de $h^+$ y generación de $HO^\bullet$	$H_2O_{ads} + h^+ \rightarrow HO^\bullet$	$k_4[h^+][H_2O_{ads}]$
Ataque de $HO^\bullet$	$A_{ads} + HO^\bullet \rightarrow B_{ads}$	$k_{85}[HO^\bullet][A_{ads}]$

En muchos casos la expresión de la velocidad de fotodegradación de un compuesto orgánico A tiene la siguiente forma:

$$-r_A = \alpha_1 \frac{C_A}{(\alpha_3 C_A + 1)} \{-1 + \sqrt{1 + \alpha_2 e^a}\} \quad 1.36$$

donde  $\alpha_i$  son los parámetros cinéticos intrínsecos que engloban las constantes cinéticas y concentraciones de aquellas especies consideradas constantes [87, 90].

En general, la evaluación de los parámetros cinéticos se desarrolla siguiendo el procedimiento esquematizado en la Figura 1.5. Primero, a partir de las condiciones experimentales en que se llevaron a cabo todas las reacciones, se obtiene el flujo de radiación incidente al reactor a partir de las correspondientes medidas de actinometría y el espectro de emisión de las lámparas utilizadas. A partir de la condiciones limite, se determina el campo de radiación dentro del fotorreactor mediante la resolución de la RTE, para lo cual se requieren las propiedades ópticas de cada fotocatalizador. Posteriormente, los valores de la LVRPA son calculados para cada elemento diferencial del reactor. Por último, a partir de los resultados anteriores, se comparan los valores simulados de la concentración del compuesto orgánico con los valores

obtenidos experimentalmente, para estimar los correspondientes parámetros cinéticos ( $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ ) mediante regresiones múltiples no lineales.

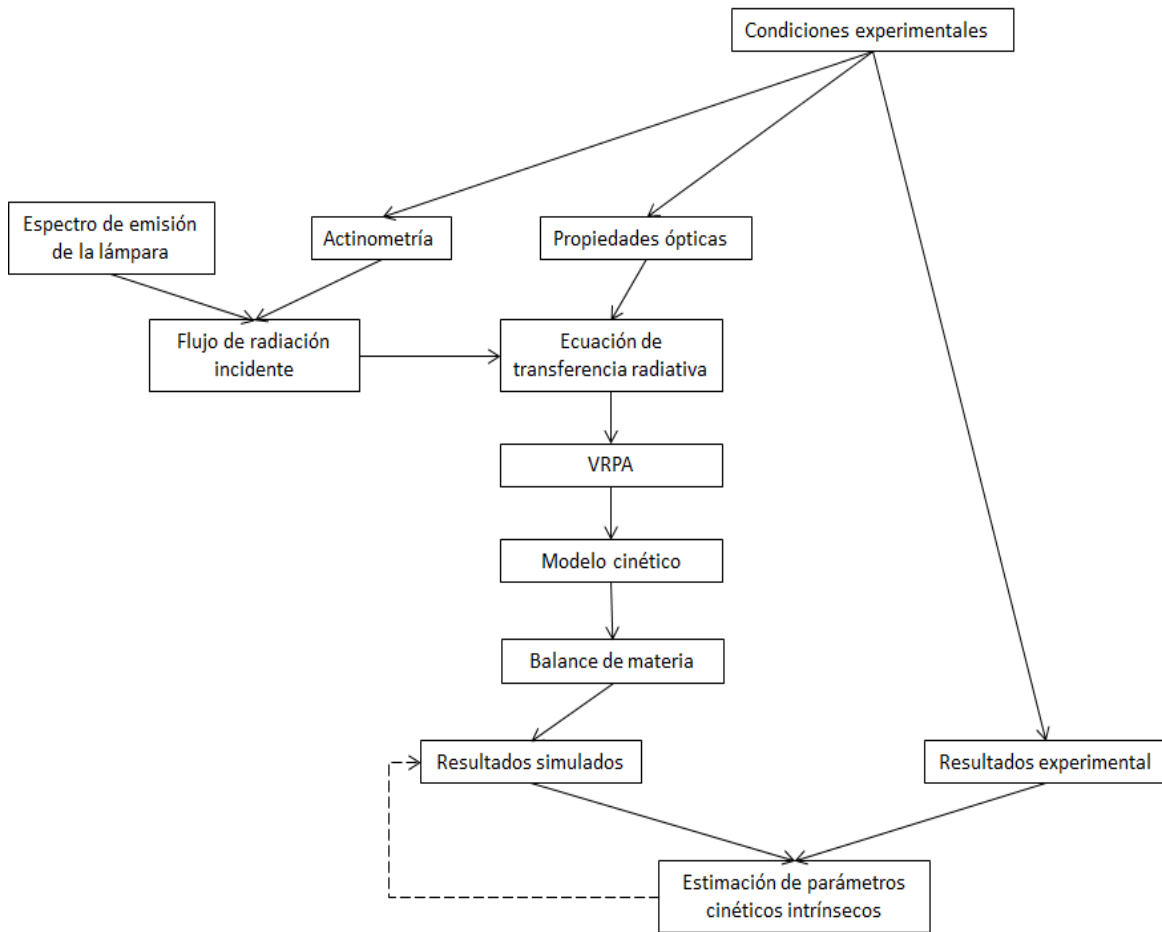


Figura 1.5. Esquema del procedimiento utilizado para la estimación de los parámetros cinéticos intrínsecos.

La ventaja de los parámetros cinéticos intrínsecos es que son independientes de la geometría del reactor, de las condiciones hidrodinámicas y de los perfiles de radiación dentro del reactor [100, 122]. Y por tanto, estos parámetros si pueden ser utilizados para simular la evolución de la concentración de una especie en diferentes reactores. En la bibliografía se han obtenido los parámetros cinéticos intrínsecos correspondientes a la desinfección fotocatalítica de bacterias [112, 113] y a la fotodegradación de diferentes contaminantes orgánicos: fenólicos [88, 105], ácidos orgánicos de cadena corta [100, 104, 123], cianuro [87, 92] e incluso compuestos farmacéuticos [95-97, 124]. Estos parámetros cinéticos intrínsecos también han sido utilizados para simular la concentración de los contaminantes orgánicos o bacterias a lo largo de una reacción. Comparando los valores experimentales y los simulados siempre se obtuvieron errores muy pequeños [87, 88, 113, 124]. De hecho, varias publicaciones demostraron la idoneidad del uso de parámetros cinéticos intrínsecos



obtenidos a escala de laboratorio para diseñar, escalar y optimizar otro tipo de fotorreactores [113, 122, 124-126].

Estos parámetros resultan también útiles para evaluar la fotoactividad y analizar el efecto de las distintas modificaciones del semiconductor en su comportamiento cinético. Entre estas modificaciones cabe destacar: la unión de óxidos metálicos [103], plata [102], o el recubrimiento de diferentes soportes, como partículas de sílice [87, 92], con  $\text{TiO}_2$ . En este sentido, es importante destacar el trabajo realizado por Ballari y colaboradores [127], en el que evaluaron las limitaciones de transferencia de materia interna y externa que tienen lugar en los aglomerados de un fotocatalizador de  $\text{TiO}_2$  en suspensión. Para ello, emplearon modelos rigurosos de transferencia de materia y radiación y definieron un factor de efectividad fotocatalítico. Este factor de efectividad permite separar los efectos del gradiente de concentración y de la penetración de la luz. Concluyeron que limitaciones de transferencia de materia externa eran insignificantes para los tamaños de partículas catalíticas con los que normalmente se trabaja. Sin embargo, limitaciones de transferencia de materia interna siempre existirán en los aglomerados al atenuarse rápidamente la radiación incidente.

## 1.5. OBJETIVOS

La presente tesis doctoral se centrará en el estudio y desarrollo de fotocatalizadores basados en  $\text{TiO}_2$  y composites  $\text{TiO}_2$ -rGO, para su aplicación en la fotodegradación de contaminantes orgánicos en fase acuosa, y en el desarrollo de modelos predictivos para simular la evolución de la fotorreacción catalítica estudiada. Se desarrollarán y estudiarán distintos nanocomposites basados en dióxido de titanio-óxido de grafeno reducido para obtener fotocatalizadores con alto rendimiento fotocatalítico en procesos de eliminación de contaminantes orgánicos en fase acuosa.

El fenol será el contaminante a fotodegradar, debido a que es un compuesto que ha sido ampliamente estudiado como contaminante modelo en procesos de oxidación y, por tanto, los resultados obtenidos en el presente trabajo pueden ser comparados con otros estudios de la bibliografía. Además, para analizar el efecto del tipo de sustituyente en la fotodegradación de compuestos fenólicos, se analizará la influencia de diferentes grupos funcionales sustituyentes en posición *para*:- 4-clorofenol, 4-nitrofenol y metil-4-hidroxibenzoato. En último lugar, se estudiará la fotodegradación de un contaminante emergente, un metabolito de un compuesto farmacéutico, el ácido clofíbrico.

Por lo consiguiente, el objetivo global de esta Tesis Doctoral es estudiar y modelar el proceso fotocatalítico utilizando fotocatalizadores de  $\text{TiO}_2$  y de  $\text{TiO}_2$  modificado con óxido de grafeno reducido para mejorar la fotoactividad. Para poder alcanzar este objetivo se han planteado los siguientes objetivos específicos:

- Analizar la influencia del tamaño de partícula hidrodinámico del fotocatalizador en suspensión acuosa y desarrollar un modelo predictivo de la fotodegradación de fenol con una dependencia explícita de la radiación absorbida para obtener los correspondientes parámetros cinéticos intrínsecos.
- Estudiar la influencia de la adsorción y la naturaleza química de compuestos fenólicos, con diferentes grupos funcionales en la posición para (fenol, 4-clorofenol, 4-nitrofenol y metil 4-hidroxibenzoato), en la actividad fotocatalítica de cinco  $\text{TiO}_2$  comerciales con diferentes propiedades físico-químicas.
- Analizar la importancia de los diferentes mecanismos de fotodegradación (a través de  $\text{h}^+$ , mediante radicales  $\text{HO}^\bullet$  generados en la oxidación del agua o mediante especies oxidantes reactivas formadas a partir de los  $\text{e}^-$ ) en la fotooxidación de los diferentes compuestos fenólicos seleccionados, evaluando, además, la eficiencia cuántica de los catalizadores comerciales de  $\text{TiO}_2$  empleados.
- Síntesis, caracterización y estudio de la fotoactividad de una serie de fotocatalizadores binarios constituidos por  $\text{TiO}_2$  y rGO con diferentes relaciones rGO: $\text{TiO}_2$ .
- Evaluar el efecto que tiene la modificación de  $\text{TiO}_2$  con rGO en las propiedades ópticas de la suspensión y en la eficiencia con la que se usan los fotones absorbidos en la fotodegradación de un metabolito de un compuesto farmacéutico, como es el ácido clofíbrico.
- Desarrollar un modelo cinético con una dependencia explícita de la radiación absorbida, así como obtener los correspondientes parámetros cinéticos intrínsecos, para simular la evolución de ácido clofíbrico y de sus principales intermedios, utilizando  $\text{TiO}_2$ -rGO como fotocatalizador.

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# Capítulo 2:

Resumen / Summary

El desarrollo demográfico e industrial del último siglo ha aumentado el uso indiscriminado de los recursos hídricos hasta niveles insostenibles. Actualmente, la legislación que regula el uso del agua es cada vez más restrictiva. Por otro lado, el crecimiento de la demanda de agua de buena calidad está constantemente aumentando, lo que ha dado lugar a problemas de abastecimiento en determinadas zonas del planeta. Por ello, el desarrollo de nuevas tecnologías que permitan el tratamiento de las aguas residuales para su depuración y/o su posterior reutilización es una de las claves para su uso sostenible, dado que hoy en día el enfoque de la gestión hídrica busca recuperar y regenerar el agua residual que utilizamos y contaminamos.

En este sentido, los Procesos de Oxidación Avanzada (AOPs) han representado una opción eficaz para el tratamiento de aguas contaminadas con materia orgánica. Los AOPs están basados en la generación de especies radicalarias de alto poder oxidante, como el radical hidroxilo ( $\text{HO}^\bullet$ ). Estos radicales interaccionan con los contaminantes provocando la ruptura de sus enlaces estructurales y su oxidación hasta alcanzar su mineralización total.

En este contexto, la fotocatalisis heterogénea se presenta como una Tecnología Catalítica de Oxidación Avanzada muy prometedora. Su eficiencia es notoria en el tratamiento de sustancias difícilmente biodegradables, siendo un claro ejemplo del empleo con éxito de catalizadores sólidos en la degradación de concentraciones moderadas de contaminantes orgánicos. Entre las principales características que hacen que este proceso sea aplicable al tratamiento de efluentes acuosos contaminados, merece destacar que se lleva a cabo en condiciones ambientales, tanto de presión como de temperatura, con el consiguiente ahorro energético. La fotocatalisis heterogénea es un proceso en el cual se generan radicales hidroxilo en cantidad suficiente para oxidar la materia orgánica presente en el agua, hasta su mineralización y consiguiendo su purificación. En líneas generales, el proceso de la reacción de foto-oxidación catalítica está basado en la excitación de un semiconductor sólido por la absorción de luz de una longitud de onda apropiada, dando lugar a pares electrón-hueco y por consiguiente, a centros de oxidación y reducción. El  $\text{TiO}_2$  ha sido uno de los semiconductores más utilizados, debido a sus excelentes propiedades físico-químicas. Sin embargo, presenta algunas limitaciones: (1) solo es capaz de absorber radiación con una longitud de onda inferior a  $\sim 390$  nm y (2) presenta bajas eficiencias cuánticas debido a la rápida recombinación de los pares electrón-hueco. Como consecuencia, en las últimas décadas se han dedicado muchos esfuerzos a extender la respuesta espectral del dióxido de titanio a la zona del visible, mediante

modificaciones de su estructura. Entre las alternativas más implantadas destacan desde el dopaje del  $\text{TiO}_2$  con heterocaciones, hasta su combinación con otros semiconductores, con materiales carbonosos o grafeno.

Por otro lado, para llegar a alcanzar la aplicación industrial de la tecnología de la fotocatalisis al tratamiento de aguas residuales es imprescindible el estudio y desarrollo de modelos cinéticos predictivos concretos para el diseño, optimización y escalado de los correspondientes fotorreactores.

En este contexto, el objetivo principal de esta Tesis Doctoral es el estudio de fotocatalizadores basados en  $\text{TiO}_2$  y nanocomposites de dióxido de titanio-óxido de grafeno reducido ( $\text{TiO}_2$ -rGO), para su aplicación a la fotodegradación de distintos contaminantes orgánicos en fase acuosa, y en el desarrollo de modelos cinéticos predictivos para simular la evolución de las fotorreacciones catalíticas estudiadas. Los diferentes objetivos abordados en cada uno de los capítulos se encuentran esquematizados en la Figura 2.1.

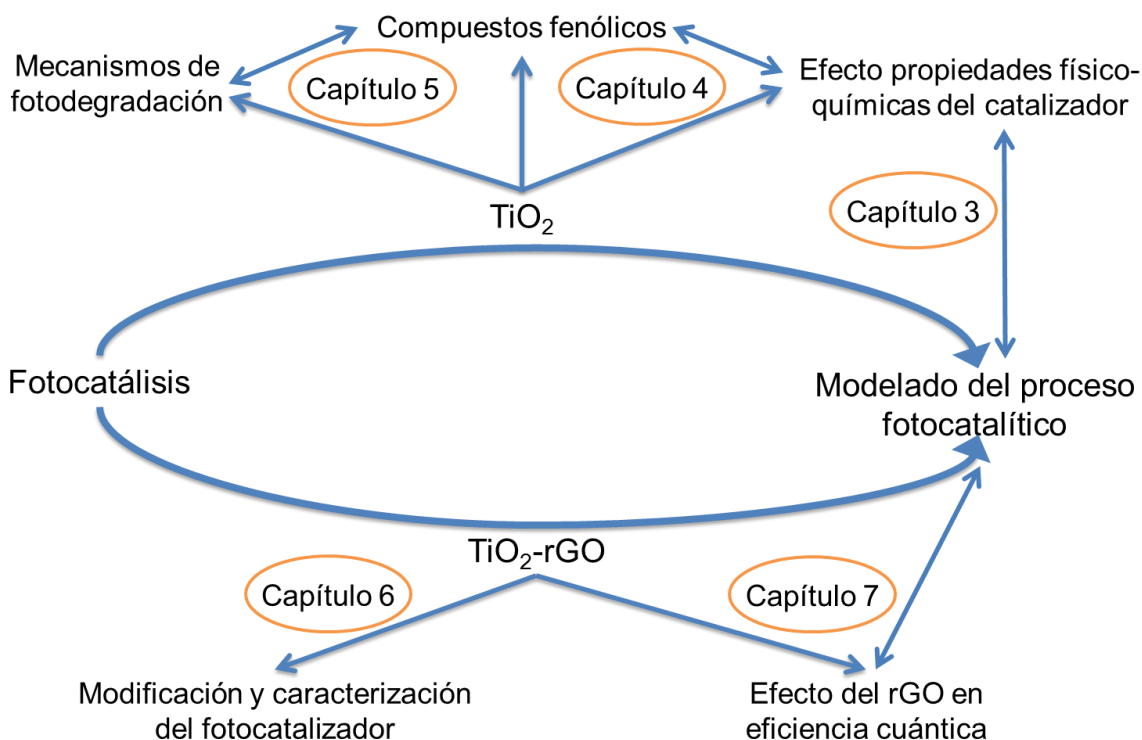


Figura 2.1. Esquema de los principales objetivos desarrollados en cada uno de los capítulos de la Tesis Doctoral.

A lo largo de la Tesis Doctoral se han estudiado diversos catalizadores comerciales de  $\text{TiO}_2$  y se han preparado diferentes nanocomposites de  $\text{TiO}_2$ -rGO, con diferentes relaciones másicas de  $\text{GO}:\text{TiO}_2$ , mediante síntesis hidrotérmica. El estudio de sus

propiedades físico-químicas más relevantes y su correlación con los estudios de fotoactividad catalítica han desempeñado un papel importante en la discusión y las conclusiones alcanzadas en este trabajo. Por tanto, las técnicas de caracterización físico-química utilizadas han sido muy diversas y aportan información acerca de las propiedades estructurales, electrónicas, superficiales y electroquímicas de los fotocatalizadores estudiados. Entre otras se han empleado: Espectroscopía Infrarroja en Reflectancia Difusa (DRIFTS), Difracción Láser (DL), Difracción de Rayos X (DRX), Microscopía Electrónica de Transmisión (TEM), isotermas de adsorción-desorción de nitrógeno, Microscopía Electrónica de Barrido (SEM), isotermas de adsorción-desorción de amoníaco, Espectroscopía de Resonancia Paramagnética (EPR), Espectroscopía UV-Vis de reflectancia difusa, Espectroscopía de Absorción Transitoria (TAS), etc.

Respecto al papel destacado que tiene la radiación absorbida en procesos fotocatalíticos en medio acuoso, en el tercer capítulo de esta Memoria se ha analizado el efecto que las propiedades ópticas de diferentes catalizadores comerciales de TiO<sub>2</sub>, P25 Aeroxide®, P25/20 VP Aeroperl® y P90 Aeroxide®, con idénticas propiedades físicoquímicas pero con distinta morfología y tamaño de partícula hidrodinámico en suspensión acuosa ( $d_{PHD}$ ), ejercen en la foto-oxidación de un contaminante modelo como es el fenol.

Los estudios de fotoactividad catalítica se evaluaron en un fotorreactor cilíndrico discontinuo, tipo *slurry*, de 1 L rodeado por 10 lámparas: 6 Black Light Blue UV-A y 4 day-light, siendo el valor de la radiación incidente, en el intervalo UV-A,  $1,4 \cdot 10^{-8}$  Einstein·cm<sup>-2</sup>·s<sup>-1</sup>.

En este estudio se ha propuesto un modelo cinético, que incluye no solo los parámetros cinéticos convencionales, sino también una dependencia explícita de la radiación absorbida. Se calculó la radiación absorbida para los tres catalizadores de TiO<sub>2</sub> estudiados, con el objetivo de simular los resultados experimentales obtenidos y poder abordar el diseño y escalado de fotorreactores catalíticos.

Con este propósito se estimaron las propiedades ópticas de las suspensiones de TiO<sub>2</sub>, que incluyen los coeficientes volumétricos de extinción ( $\beta_\lambda$ ), absorción ( $\kappa_\lambda$ ) y *scattering* ( $\sigma_\lambda$ ). Una vez obtenidas las correspondientes propiedades ópticas, se determinó la velocidad volumétrica local de absorción de fotones (LVRPA). Posteriormente, se derivó una ecuación cinética a partir de un mecanismo propuesto, según el cual los radicales hidroxilos (HO•) eran los principales responsables de la

fotodegradación de fenol. Por último, los parámetros cinéticos se calcularon mediante regresión múltiple no lineal.

Los fotocatalizadores con menor valor de diámetro de partícula hidrodinámico fueron los que absorbieron mayor radiación a bajas concentraciones de  $\text{TiO}_2$  ( $0-0,1 \text{ g}\cdot\text{L}^{-1}$ ). En todas las condiciones estudiadas el fotocatalizador P25 fue el que presentó una mayor eficiencia en el aprovechamiento de los fotones absorbidos. Únicamente a altas concentraciones de  $\text{TiO}_2$  ( $0,6 \text{ g}\cdot\text{L}^{-1}$ ) el catalizador P25/20 alcanzó fotoeficiencias comparables.

Los parámetros cinéticos estimados permitieron reproducir satisfactoriamente todos los resultados experimentales obtenidos con gran exactitud, con valores de la raíz del error cuadrático medio (RMSE) inferiores al 5%. Estos resultados dieron lugar a la siguiente publicación: A. Tolosana-Moranchel, J.A. Casas, J. Carbajo, M. Faraldos, A. Bahamonde. Influence of  $\text{TiO}_2$  optical parameters in a slurry photocatalytic reactor: kinetic modelling. *Applied Catalysis B: Environmental* 200 (2017) 164-173.

Tras evaluar la influencia del tamaño de partícula hidrodinámico en las propiedades ópticas y en la fotoactividad, en el cuarto capítulo de esta memoria se ha abordado el análisis del efecto del tipo de sustituyente, en la adsorción y fotodegradación.

Se estudiaron 5 catalizadores de  $\text{TiO}_2$  comerciales con diferentes propiedades físico-químicas: P25 Aeroxide®, P25/20 VP Aeroperl®, P90 Aeroxide®, Hombikat UV 100 y PC 105 de Crystal Global. Todos los estudios de fotoactividad catalítica se llevaron a cabo en el fotorreactor discontinuo, tipo *slurry*, rodeado de 10 lámparas fluorescentes descrito anteriormente.

La forma en la que los compuestos fenólicos se adsorbían en la superficie del catalizador se caracterizó utilizando Espectroscopía Infrarroja de Reflectancia Difusa (DRIFTS). Todos los contaminantes aromáticos estudiados, salvo el 4-nitrofenol, se adsorbían mediante interacciones entre los grupos  $-\text{OH}$  de los compuestos fenólicos y el  $\text{TiO}_2$ . Los resultados experimentales obtenidos indicaron que la cantidad adsorbida de contaminante no dependía ni de la naturaleza química del sustituyente, ni de la superficie específica del catalizador.

Los estudios de fotodegradación catalítica no indicaron ninguna dependencia de la foto-oxidación con la superficie específica de cada catalizador (al igual que la capacidad de adsorción). Al analizar detenidamente la velocidad inicial de fotodegradación se obtuvo la siguiente secuencia, independientemente del compuesto

fenólico a oxidar: P25 > P90 > P25/20 > PC105 > Hombikat. Las mayores velocidades iniciales de degradación se obtuvieron con aquellos fotocatalizadores de TiO<sub>2</sub> que presentaban una mezcla de las fases cristalinas (anatasa y rutilo) y tenían un menor tamaño de partícula hidrodinámico en el medio de reacción. Por último, se observó una clara relación entre la velocidad de fotodegradación de los contaminantes estudiados y las constantes de Hammett de los respectivos sustituyentes, según la cual, cuanto mayor fuera la constante de Hammett, menor era la velocidad de foto-oxidación. Estas constantes de Hammett representan el efecto que los sustituyentes tienen en el carácter electrónico de un sistema aromático dado. Estos resultados dieron lugar a la publicación: A. Tolosana-Moranchel, J.A. Anderson, J.A. Casas, M. Faraldos, A. Bahamonde. Defining the role of substituents on adsorption and photocatalytic degradation of phenolic compounds. *Journal of Environmental Chemical Engineering* 5 (5) (2017) 4612-4620.

Una vez determinada la forma en que los compuestos fenólicos se adsorbían sobre la superficie de cada fotocatalizador, en el quinto capítulo de esta Memoria se ha tratado de elucidar y establecer qué tipo de fotomecanismo es el más relevante en la foto-oxidación catalítica de compuestos fenólicos con catalizadores comerciales de TiO<sub>2</sub>. Para ello, se analizó la eficiencia en la fotodegradación de los 4 compuestos fenólicos ya estudiados (fenol, 4-clorofenol, 4-nitrofenol y metil-4-hidroxibenzoato), utilizando en este caso, dos catalizadores comerciales de TiO<sub>2</sub>, Hombikat UV-100 y Aeroxide® P25, con diferencias significativas en sus propiedades físico-químicas. Los estudios de fotoactividad catalítica se realizaron en el mismo sistema de reacción descrito anteriormente.

A partir de los resultados obtenidos se puede concluir que el catalizador P25 fue capaz de absorber mayor radiación que el Hombikat, independientemente del compuesto fenólico estudiado. Se calculó la velocidad volumétrica de absorción de fotones, mediante la resolución de la ecuación de transferencia radiativa utilizando el método de Monte Carlo. Se alcanzaron siempre mayores eficiencias cuánticas con el fotocatalizador P25, salvo en el caso de la fotodegradación del 4-nitrofenol, con conversiones de carbono orgánico total (COT) próximas al 90% (excepto en el caso del 4-nitrofenol) tras 5 horas de reacción.

Para determinar la importancia de los huecos fotogenerados (h<sup>+</sup>), de los radicales hidroxilo (HO<sup>•</sup>) y de los electrones de la banda de conducción (e<sup>-</sup>) en el mecanismo de la fotodegradación de los compuestos orgánicos estudiados, se llevaron a cabo reacciones en presencia de tres tipos diferentes de *scavengers*: ácido fórmico para

capturar los  $h^+$ , metanol para atrapar los radicales  $HO^\bullet$  y nitrato de cobre (II) para capturar los electrones de la banda de conducción. Se pudo concluir que los radicales hidroxilo ( $HO^\bullet$ ), formados a partir de los huecos fotogenerados, fueron los principales responsables de la fotodegradación de todos los contaminantes estudiados, excepto en el caso del 4-nitrofenol. Sin embargo, un mecanismo iniciado por los electrones foto-inducidos parece ser el más relevante en la fotodegradación del 4-nitrofenol, debido a su adsorción mediante la formación de un complejo en la superficie del  $TiO_2$ . De manera que, la velocidad de fotodegradación del 4-nitrofenol aumentó considerablemente cuando se llevó a cabo en presencia de un *scavenger* de  $h^+$ , como ácido fórmico u oxálico que favorecen la disminución del proceso no deseado de la recombinación del par  $e^-/h^+$ . Los resultados obtenidos en este estudio fueron publicados en: A. Tolosana-Moranchel, A. Montejano, J. A. Casas, A. Bahamonde. Elucidation of the photocatalytic-mechanism of phenolic compounds. Journal of Environmental Chemical Engineering 6 (5) (2018) 5712-5719.

Con el objetivo de superar algunas de las limitaciones que presenta el  $TiO_2$  en los procesos fotocatalíticos, en el sexto capítulo de esta Memoria se ha evaluado la influencia que tiene la unión de óxido de grafeno reducido (rGO) en la actividad fotocatalítica de nanocomposites de  $TiO_2$ -rGO. Para ello, a partir del catalizador comercial Aeroxide® P25, que fue con él que se alcanzaron los mejores resultados de fotoactividad y eficiencia en los estudios anteriores, se sintetizaron fotocatalizadores binarios de P25-rGO mediante una metodología hidrotermal. Se sintetizaron varios composites con diferentes relaciones máxicas de GO: $TiO_2$  que se denominaron P25-rGO 0%, P25-rGO 0,1%, P25-rGO 0,5% y P25-rGO 1%. Tras caracterizar los fotocatalizadores preparados, se observó que a pesar del contacto e interacción entre el  $TiO_2$  y el rGO, no se modificó el valor del band-gap (3,1 eV).

La caracterización electroquímica de los fotocatalizadores, realizada mediante medidas de Espectroscopia de Impedancia Electroquímica (EIS), fotocorriente inducida y voltamperometrías de barrido lineales, indicó que la presencia de rGO permitía reducir la resistencia a la transferencia de carga a través de la interfase semiconductor-electrolito. Además, los resultados obtenidos revelaron una mayor eficiencia en la separación de los pares  $e^-/h^+$ .

Para evaluar la actividad fotocatalítica se llevaron a cabo reacciones de fotodegradación de ácido oxálico (1mM) utilizando radiación UV-A ( $I=1,0 \text{ mW}\cdot\text{cm}^{-2}$ ). Sin embargo, aunque el fotocatalizador P25-rGO 0,5% fue el que dio lugar a los mejores resultados de fotodegradación, las diferencias observadas entre las

constantes cinéticas estimadas fueron muy pequeñas. Estos resultados se relacionaron con la influencia de la cantidad de rGO presente en el nanocomposite en la generación de radicales  $\text{HO}^\bullet$  y de radicales superóxido ( $\text{O}_2^{\bullet-}$ ), así como con la recombinación y la transferencia de los pares  $e^-/h^+$ . Para ello se realizaron medidas de Resonancia Paramagnética Electrónica (EPR) y de Espectroscopía de Absorción Transitoria (TAS). Se comprobó que el rGO actuaba como aceptor de electrones, produciéndose la transferencia del  $e^-$  del  $\text{TiO}_2$  al rGO. Esta transferencia facilitaba la separación de cargas en presencia de  $\text{N}_2$ , lo que explica el aumento de la generación de  $\text{HO}^\bullet$  obtenida incluso con el fotocatalizador P25-rGO 0,1%. Sin embargo, en presencia de  $\text{O}_2$ , que también actúa como aceptor de electrones, no es tan inmediata la transferencia de electrones desde el  $\text{TiO}_2$  al rGO. De manera que puede concluirse que, en presencia de  $\text{O}_2$ , la diferencia entre la generación de radicales  $\text{O}_2^{\bullet-}$  y  $\text{HO}^\bullet$  alcanzada tanto por el P25-rGO 0% como con el resto de los nanocomposites de P25-rGO estudiados no fue muy relevante. Los resultados obtenidos dieron lugar a la siguiente publicación: A. Tolosana-Moranchel, J. A. Casas, A. Bahamonde, L. Pascual, L. I. Granone, J. Schneider, R. Dillert, D. W. Bahnemann. Nature and photoreactivity of  $\text{TiO}_2$ -rGO nanocomposites in aqueous suspensions under UV-A irradiation. Applied Catalysis B: Environmental 241 (2019) 375-384.

Debido a la importancia que presenta la absorción de fotones en los procesos fotocatalíticos, en el séptimo capítulo de esta Memoria se ha analizado y estudiado el efecto de la presencia de rGO en los nanocomposites de  $\text{TiO}_2$ -rGO sobre las propiedades ópticas y la eficiencia cuántica de la fotodegradación de un contaminante emergente, como ácido clofíbrico. Se utilizaron fotocatalizadores de  $\text{TiO}_2$ -rGO sintetizados mediante tratamiento hidrotérmico, donde las condiciones de operación se optimizaron para reducir la duración de la metodología de síntesis. Los nanocomposites se sintetizaron con diferentes relaciones másicas de GO: $\text{TiO}_2$ . Estos fotocatalizadores fueron caracterizados mediante diferentes técnicas químico-físicas, observando la reducción del óxido de grafeno (GO) que recubría las partículas de  $\text{TiO}_2$ , lo que parece que favorece la interacción entre el  $\text{TiO}_2$  y el rGO. De nuevo la presencia de rGO en el fotocatalizador no implicó una reducción del valor del band-gap (3,1 eV) ni de la superficie específica del catalizador ( $57 \text{ m}^2 \cdot \text{g}^{-1}$ ).

Se estimaron las propiedades ópticas de las suspensiones de  $\text{TiO}_2$  y  $\text{TiO}_2$ -rGO, que incluyen el factor de asimetría ( $g$ ) y los coeficientes volumétricos de extinción ( $\beta_\lambda$ ), absorción ( $\kappa_\lambda$ ) y *scattering* ( $\sigma_\lambda$ ). Se observó un aumento de los coeficientes de



extinción y *scattering* y la presencia de rGO pareció afectar más al coeficiente de *scattering* que al coeficiente de absorción.

En cuanto a los estudios de fotodegradación catalítica de ácido clofibrico, realizados en un fotorreactor de 1 L con recirculación continua, se observó que la actividad de los fotocatalizadores seguía la siguiente secuencia: P25-rGO 0,5% > P25-rGO 0,1%  $\approx$  P25-rGO 0% > P25-rGO 1%. Se pudo apreciar que un exceso de rGO conllevó un descenso de la velocidad de reacción. Se calculó la eficiencia cuántica obteniendo el valor óptimo al utilizar 100 mg·L<sup>-1</sup> de P25-rGO 0,5%, cuyo valor era un 11% superior al obtenido con P25-rGO 0%.

Se desarrolló también un modelo cinético intrínseco para simular la evolución del ácido clofibrico utilizando el fotocatalizador P25-rGO 0,5%, que fue con el que se alcanzaron los mejores resultados de fotoactividad. Para ello, se estimaron los valores de la velocidad volumétrica local de absorción de fotones (LVRPA) utilizando diferentes concentraciones y niveles de radiación (100%, 62% y 30%). Se observó que incluso cuando se utilizaban bajas concentraciones de fotocatalizador, la mayor parte de la radiación se absorbía cerca de las paredes del fotorreactor.

En último lugar, una vez propuestos los balances de materia y desarrolladas las ecuaciones cinéticas de la fotodegradación de ácido clofibrico, 4-clorofenol y p-benzoquinona (intermedios de reacción), se estimaron los parámetros cinéticos mediante regresiones múltiples no lineales. El modelo con seis parámetros cinéticos fue el que mejor reprodujo los resultados experimentales obtenidos en la fotodegradación de ácido clofibrico con el nanocomposite P25-rGO 0,5%, con un valor de la raíz del error cuadrático medio (RMSE) inferior al 11%. Los resultados obtenidos en este estudio se publicaron en los dos siguientes artículos: A. Tolosana-Moranchel, A. Manassero, M.L. Satuf, O.M. Alfano, J.A. Casas, A. Bahamonde. Influence of TiO<sub>2</sub>-rGO optical properties in the photocatalytic activity and efficiency to photodegrade an emerging pollutant. *Applied Catalysis B: Environmental*. 246 (2019) 1-11; A. Tolosana-Moranchel, A. Manassero, M. L. Satuf, O. M. Alfano, J.A. Casas, A. Bahamonde. "TiO<sub>2</sub>-rGO photocatalytic degradation of an emerging pollutant: kinetic modelling and determination of intrinsic kinetic parameters". Submitted for publication to *Applied Catalysis B: Environmental*, 2019 (APCATB-D-19-01079).

In the last century, demographic and industrial development has increased the indiscriminate use of water resources to an unsustainable level. Nowadays, water management regulations are becoming tougher and tougher. Furthermore, since water resources demand is increasingly rising, along with their quality, serious issues relating to water supply exists in certain areas of the planet. Thus, the development of new technologies able to treat and purify water properly for their subsequent reuse is key to achieve its sustainable use. Nowadays, new approaches in water management aim to reuse and regenerate wastewater that has been used and polluted.

The Advanced Oxidation Processes (AOPs) have emerged in recent decades as an effective solution to remove organic pollutants in wastewater. The AOPs are based on physico-chemical processes able to degrade the organic matter by generating hydroxyl radicals ( $\text{HO}^\bullet$ ), highly reactive species with a high oxidation potential, capable of reacting with most of organic compounds in a non-selective manner.

In this context, heterogeneous photocatalysis is regarded as a promising Advanced Oxidation Catalytic Technology, that operates at atmospheric pressure and temperature conditions and reaches a remarkable efficiency in the treatment of poorly biodegradable substances, being a clear example of the successful use of solid catalysts to degrade moderate concentrations of organic pollutants.

Heterogeneous photocatalysis is a process in which a considerable amount of hydroxyl radicals are generated to oxidize dissolved organic matter to achieve its mineralization, and therefore water purification. Heterogeneous photocatalysis is based on the excitation of a solid semiconductor with light that has sufficient energy.  $\text{TiO}_2$  has been one of the most studied photocatalysts because of its good properties. However,  $\text{TiO}_2$  photocatalysis still have some disadvantages: (1) the photocatalyst is not able to absorb radiation with wavelength longer than  $\sim 390$  nm and (2) low quantum efficiencies are arisen due to fast recombination of electron-hole pairs. As a consequence, several strategies have been developed to modify semiconductors to improve their performance in the visible region. Among that, it can be emphasized doping  $\text{TiO}_2$  or construction of heterojunctions, adding others semiconductors or carbonaceous materials such as graphene.

Moreover, nowadays the lack of industrial applications of this technology is fundamentally due to the necessity of developing simple methods to design, optimize and scale up photoreactors.

In this context, the main objective of this Doctoral Thesis has consisted in the study of different photocatalysts, based on  $\text{TiO}_2$  and titanium dioxide-reduced graphene oxide nanocomposites ( $\text{TiO}_2$ -rGO), in order to photodegrade organic pollutants in aqueous solution. Kinetic models have been developed to simulate the studied photocatalytic process as well. The different goals of this Thesis are outlined in Figure 2.2.

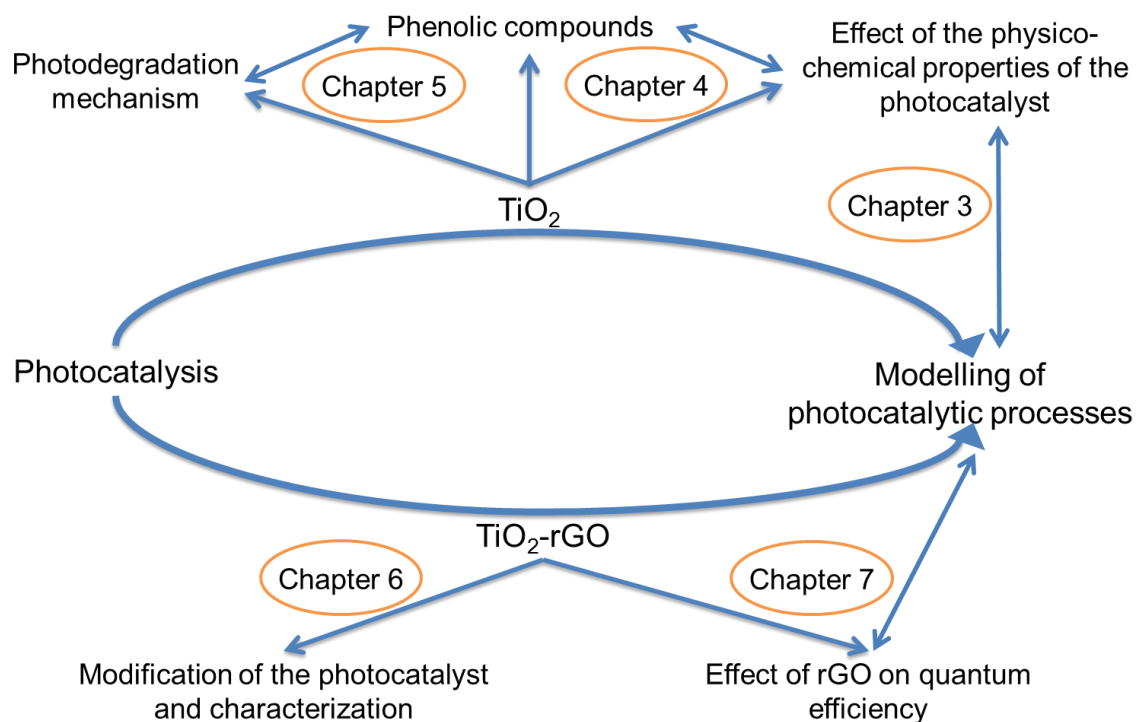


Figure 2.2. Scheme of the specific research conducted in each chapter of the Doctoral Thesis.

For this purpose, several commercial  $\text{TiO}_2$  catalysts have been studied, and different  $\text{TiO}_2$ -rGO nanocomposites, with different GO: $\text{TiO}_2$  ratios, were synthesized by hydrothermal methodology.

The study of the more relevant properties of these photocatalysts ( $\text{TiO}_2$  and  $\text{TiO}_2$ -rGO nanocomposites) and their interrelationship to the photocatalytic activity studies have played an important role on the discussion and conclusions arisen in this work. To do that, the physico-chemical characterization techniques used here have been diverse, and all of them have contributed to achieve significant information about structural, electronic, superficial and electrochemical properties of all studied photocatalysts. Among others, the following techniques have been employed: Diffuse Reflectance Infrared Spectroscopy (DRIFTS), Laser Diffraction (LD), X Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), nitrogen isotherms, Scanning Electron Microscopy (SEM), Ammonia Isotherms, Paramagnetic Resonance Spectroscopy

(EPR), diffuse reflectance UV-Vis spectroscopy, Transient Absorption Spectroscopy (TAS), etc.

Regarding the role played by absorbed radiation in photocatalytic process in aqueous media, in the third chapter of this Memory, the effect of optical properties of different commercial TiO<sub>2</sub> (P25 Aeroxide®, P25/20 VP Aeroperl® and P90 Aeroxide®), with similar structural and electronic properties, but with singular differences in morphology and aggregation particle sizes (hydrodynamic particle size in aqueous suspensions,  $d_{PHD}$ ), have been analyzed on the final photo-efficiencies of organic matter removal in aqueous suspensions, with a model pollutant such as phenol.

The photocatalytic studies were carried out in a cylindrical photoreactor surrounded by 10 fluorescent lamps (6 Black Light Blue UV-A Lamps and 4 day-light lamps), which provided an incident radiation flux of  $1.4 \cdot 10^{-8}$  Einstein·cm<sup>-2</sup>·s<sup>-1</sup> in the UV-A region.

In this study a kinetic model with an explicit dependence of the absorbed radiation was developed to simulate the phenol photodegradation results and address the design and scale-up of catalytic photoreactors.

The first step was to estimate the optical properties of TiO<sub>2</sub> suspensions, which include the extinction ( $\beta_{\lambda}$ ), absorption ( $\kappa_{\lambda}$ ) and scattering ( $\sigma_{\lambda}$ ) coefficients. Once the optical properties were obtained, the local volumetric rate of photon absorption (LVRPA) was calculated. Afterwards, a kinetic equation was derived from a proposed mechanism where hydroxyl radicals (HO<sup>•</sup>) were the main responsible for phenol photodegradation. Finally, the kinetic parameters were estimated by comparing experimental data of phenol concentration and those predicted by the model, applying non-linear regressions.

The photocatalysts with lower hydrodynamic particle sizes were able to absorb more radiation at low photocatalyst concentrations (0-0.1 g·L<sup>-1</sup>). Although P25 photocatalyst was the most efficient on using absorbed photons, P25/20 was able to reach similar values of photo-efficiency when high concentrations were employed (0.6 g·L<sup>-1</sup>).

The estimated intrinsic kinetic parameters allowed simulating experimental results with great accuracy, with a root-mean-square error (RMSE) below 5%. These results led to the following article: A. Tolosana-Moranchel, J.A. Casas, J. Carbajo, M. Faraldos, A. Bahamonde. Influence of TiO<sub>2</sub> optical parameters in a slurry photocatalytic reactor: kinetic modelling. Applied Catalysis B: Environmental 200 (2017) 164-173.

After analyzing the influence of the hydrodynamic particle size on the optical properties and photoactivity, in the fourth chapter of this Memory, adsorption behavior of phenol and other three para-substituted phenolic compounds was analyzed. The influence of the chemical nature of the substituent and adsorption on the photocatalytic activity was also evaluated. Five commercial TiO<sub>2</sub> photocatalysts with different physico-chemical properties were employed: P25 Aeroxide®, P25/20 VP Aeroxide®, P90 Aeroxide®, Hombikat UV 100 and PC 105 from Crystal Global.

To better understand adsorption of these phenolic compounds, Diffuse Reflectance Infrared Spectroscopy (DRIFTS) measurements were carried out to determine the way they were mainly adsorbed on the photocatalyst surface. All the phenolic compounds, except 4-nitrophenol, were adsorbed via interactions between the phenolic –OH group and TiO<sub>2</sub> surface. After the results were analyzed, neither significant influence of the specific surface area nor the chemical nature of the substituent on the uptake capacity was observed.

Regarding photocatalytic activity, it could be noted that catalyst specific surface area did not have an effect on the photodegradation of these phenolic compounds (just like the adsorption uptake). When initial photoreaction rates were calculated, the following sequence was obtained, regardless of the phenolic compound photodegraded: P25 > P90 > P25/20 > PC105 > Hombikat. In this study it was also observed that the fastest initial photodegradation rates were obtained for those photocatalysts consisting of a mixture of crystalline phases (anatase and rutile) and presented the smallest hydrodynamic particle sizes in the reaction media. Finally, a clear dependence of the photodegradation rates on the Hammett constants of the substituents was noted. According to which, the greater the Hammett's constant, the lower the photo-oxidation rate. These results were published in the following article: A. Tolosana-Moranchel, J.A. Anderson, J.A. Casas, M. Faraldos, A. Bahamonde. Defining the role of substituents on adsorption and photocatalytic degradation of phenolic compounds. *Journal of Environmental Chemical Engineering* 5 (5) (2017) 4612-4620.

Once it was studied the way in which phenolic compounds were adsorbed, the fifth chapter of this work aims to clarify which pathway is more relevant to the corresponding photodegradation mechanism of phenolic compounds over TiO<sub>2</sub> catalysts. For that, phenol and other phenolic compounds (4-chlorophenol, 4-nitrophenol and methyl 4-hydroxybenzoate) were selected to investigate their photocatalytic-mechanism with two commercial TiO<sub>2</sub> catalysts: Hombikat UV-100 and

Aeroxide® P25, with different physico-chemical properties. Photocatalytic activity runs were performed in the same photoreaction system previously described above.

Regardless of the pollutant considered, P25 photocatalyst achieved the best results, reaching total organic carbon (TOC) conversions above 90% (except in the case of 4-nitrophenol) after 5 hours of photoreaction. Regarding quantum efficiencies, values three-four times greater were obtained with P25, which indicated that P25 was more efficient in the use of absorbed photons to photodegrade these organic compounds.

To evaluate the importance of photogenerated holes ( $h^+$ ), hydroxyl radicals ( $HO^\bullet$ ) and electrons from the conduction band ( $e^-$ ) on the photodegradation of these organic compounds, reactions were carried out in the presence of different scavengers. Hydroxyl radicals ( $HO^\bullet$ ) formed from photogenerated holes were the main responsible for the photodegradation of all the studied pollutants except for 4-nitrophenol. However, a photo-induced electron mediated mechanism seemed to be more relevant in 4-nitrophenol photodegradation, owing to the fact that 4-nitrophenol can be adsorbed on  $TiO_2$  surface forming a complex. As a consequence, the photocatalytic degradation rate of 4-nitrophenol was accelerated when a  $h^+$  scavenger was present in the reaction media, such as formic acid or oxalic acid, which favored the reduction of the recombination process. The results obtained in this study gave rise to the following article: A. Tolosana-Moranchel, A. Montejano, J. A. Casas, A. Bahamonde. Elucidation of the photocatalytic-mechanism of phenolic compounds. *Journal of Environmental Chemical Engineering* 6 (5) (2018) 5712-5719.

To overcome some of the limitations  $TiO_2$  photocatalysis has, in the sixth chapter of this Thesis the influence of the addition of reduced graphene oxide (rGO) on the photocatalytic activity of  $TiO_2$ -rGO nanocomposites was assessed. Aeroxide® P25 was chosen to synthesize P25-rGO photocatalysts through a hydrothermal method, given that it has been thoroughly studied in the literature for its excellent photocatalytic performance. Various nanocomposites were prepared with different GO: $TiO_2$  ratios that were named P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1%, respectively. By Raman spectroscopy measurements the D and G bands, related to rGO, were detected. After characterization studies of these nanocomposites, it could be noted that the presence of rGO did not alter the band-gap energy (3.1 eV) despite the contact and interaction between  $TiO_2$  and rGO.

Electrochemical characterization of these nanocomposites, which was carried out by performing electrochemical impedance spectroscopy (EIS), photocurrent response and

linear sweep voltammetry, indicated that the presence of rGO led to a decrease of the charge transfer resistance across the semiconductor-electrolyte interface. Moreover, the results revealed a more effective charge separation of the photogenerated electron-hole pairs.

To evaluate photocatalytic activity, oxalic acid (1mM) photodegradation experiments were performed under UV-A irradiation ( $I=1.0 \text{ mW}\cdot\text{cm}^{-2}$ ). Even though the photocatalyst P25-rGO 0.5% yielded the best results, no significant differences among the kinetic constants obtained for all the nanocomposites were detected. These results were related to the influence of the quantity of rGO in the nanocomposite on the  $\text{HO}^\bullet$  and superoxide radical ( $\text{O}_2^{\bullet-}$ ) generation, and on the recombination and transfer of the photogenerated species. In order to do that, Electron Paramagnetic Resonance (EPR) spectroscopy and Transient Absorption Spectroscopy (TAS) measurements were carried out. It was proven that rGO could act as an electron acceptor, occurring the electron transfer from  $\text{TiO}_2$  to rGO. This transfer enhances charge carriers separation in the presence of  $\text{N}_2$ , which explains the increase of  $\text{HO}^\bullet$  generation, even when P25-rGO 0.1% was used. However, under  $\text{O}_2$  atmosphere, which acts as an electron acceptor, the electron transfer from  $\text{TiO}_2$  to rGO is hindered. Thus, the difference of  $\text{O}_2^{\bullet-}$  and  $\text{HO}^\bullet$  radical generation among P25-rGO 0% and the rest of the nanocomposites was not so relevant. These results were published in the following article: A. Tolosana-Moranchel, J. A. Casas, A. Bahamonde, L. Pascual, L. I. Granone, J. Schneider, R. Dillert, D. W. Bahnemann. Nature and photoreactivity of  $\text{TiO}_2$ -rGO nanocomposites in aqueous suspensions under UV-A irradiation. *Applied Catalysis B: Environmental* 241 (2019) 375-384.

Because of the importance that photon absorption has in photocatalytic processes, in the second-to-last chapter the effect of rGO on the optical properties and on the quantum efficiency of the photodegradation of an emerging pollutant, clofibric acid, was evaluated.  $\text{TiO}_2$ -rGO nanocomposites were synthesized via a hydrothermal treatment where the operating conditions were optimized to reduce the duration of the synthesis. These photocatalysts were characterized by employing different techniques. The results revealed that graphene oxide (GO) was reduced and covered the  $\text{TiO}_2$  nanoparticles, favoring interaction between both compounds. It could also be noticed that the presence of rGO in the photocatalyst did not mean any reduction of the band-gap value (3.1 eV) or of the specific surface area of the photocatalysts ( $57 \text{ m}^2\cdot\text{g}^{-1}$ ).

First of all, optical properties of  $\text{TiO}_2$  and  $\text{TiO}_2$ -rGO suspensions, which include the asymmetry factor ( $g$ ) and the extinction ( $\beta_\lambda$ ), absorption ( $\kappa_\lambda$ ) and scattering ( $\sigma_\lambda$ )



coefficients, were estimated. An increase of the extinction and scattering coefficients was observed, and the presence of rGO seemed to have a greater effect on the scattering coefficient than on the absorption coefficient.

Concerning photoactivity studies, which were carried out in a 1 L photoreactor that was part of a batch recirculating system, it was noted that photocatalytic activity followed the following order: P25-rGO 0.5% > P25-rGO 0.1%  $\approx$  P25-rGO 0% > P25-rGO 1%. It was observed that an excess of rGO could lead to a decrease of the reaction rate. Quantum efficiency was determined and the optimum value was obtained when 100 mg·L<sup>-1</sup> of P25-rGO 0.5% were used, whose quantum efficiency value was 11% higher than that obtained with P25-rGO 0%.

Then, an intrinsic kinetic model was developed to simulate the evolution of clofibric acid using P25-rGO 0.5% as photocatalyst, since it provided the best results in the previous study. Local volumetric rates of photon absorption (LVRPA) profiles for different concentrations and different irradiation levels (100%, 62% y 30%) were estimated. It was observed that most of the radiation was absorbed near the walls even when low photocatalyst concentrations were used.

Finally, subsequent to deriving the kinetic equations of clofibric acid, 4-chlorophenol and p-benzoquinone photodegradation and proposing the mass balances, the kinetic parameters were estimated by applying non-linear regressions. A model with six kinetic parameters was able to accurately predict experimental results throughout the whole reaction, with a root-mean-square error (RMSE) below 11%. The results obtained in this study led to the following articles: A. Tolosana-Moranchel, A. Manassero, M.L. Satuf, O.M. Alfano, J.A. Casas, A. Bahamonde. Influence of TiO<sub>2</sub>-rGO optical properties in the photocatalytic activity and efficiency to photodegrade an emerging pollutant. *Applied Catalysis B: Environmental*. 246 (2019) 1-11; A. Tolosana-Moranchel, A. Manassero, M. L. Satuf, O. M. Alfano, J.A. Casas, A. Bahamonde. "TiO<sub>2</sub>-rGO photocatalytic degradation of an emerging pollutant: kinetic modelling and determination of intrinsic kinetic parameters". Submitted for publication to *Applied Catalysis B: Environmental*, 2019 (APCATB-D-19-01079).

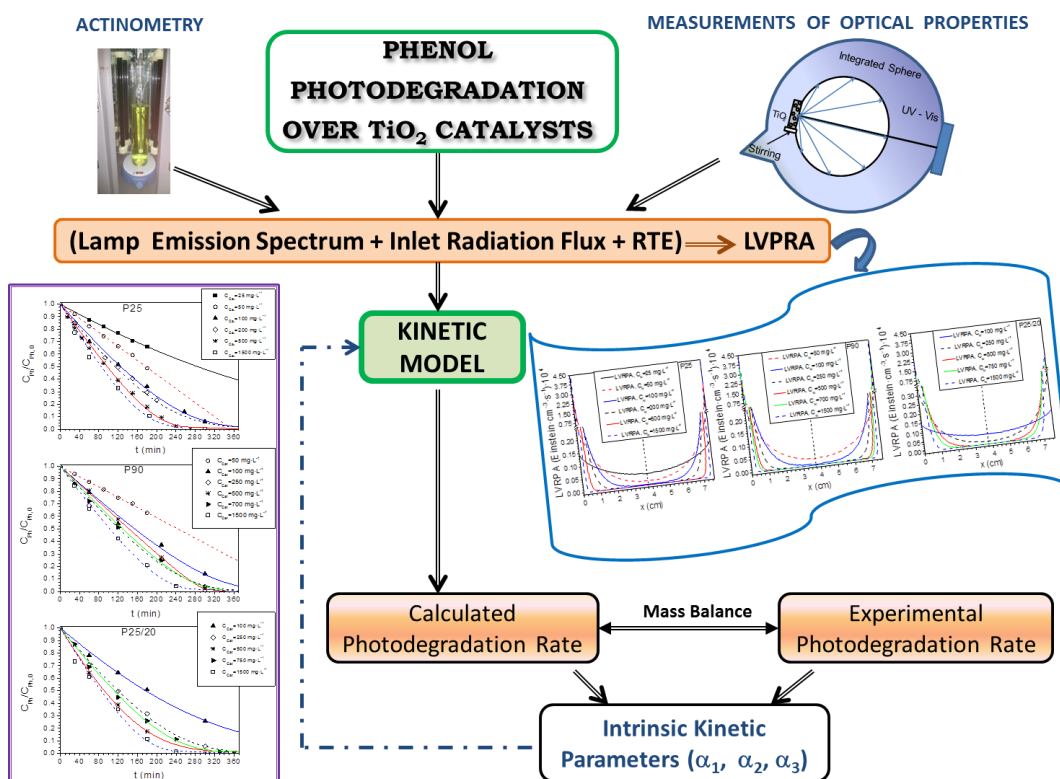


# Capítulo 3:

## Influencia de las propiedades ópticas de catalizadores de $\text{TiO}_2$ en un reactor fotocatalítico tipo *slurry*: Modelado Cinético

"Influence of  $\text{TiO}_2$  optical parameters in a slurry photocatalytic reactor: Kinetic modelling". *Applied Catalysis B: Environmental* 200 (2017) 164-173.

En este capítulo se aborda el primer objetivo de la Tesis Doctoral, que consiste en analizar el efecto que las propiedades ópticas de tres catalizadores comerciales de  $\text{TiO}_2$ , con idénticas propiedades físico-químicas pero con distintos tamaños de partícula hidrodinámico en suspensión acuosa, ejercen en la foto-oxidación de fenol. Con el fin de reproducir satisfactoriamente todos los resultados obtenidos en la foto-oxidación catalítica de fenol, se ha desarrollado un modelo cinético con una dependencia explícita de la radiación absorbida y los correspondientes parámetros cinéticos intrínsecos se han obtenido mediante regresiones múltiples no lineales.



Análogamente a los procesos convencionales de catálisis heterogénea, en fotocatalisis heterogénea los parámetros de operación gobiernan la cinética del proceso y entre otros, caben destacar por ejemplo, concentración inicial de sustrato, concentración de catalizador y pH. Además, en los reactores fotocatalíticos heterogéneos, a diferencia de los reactores catalíticos convencionales, la geometría y los materiales deben favorecer una absorción eficiente de los fotones incidentes en el sistema, para evitar que la falta de luz limite la velocidad del proceso de foto-oxidación. De manera, que además de los parámetros convencionales de catálisis heterogénea, deben tenerse en cuenta propiedades tales como las propiedades ópticas de los fotocatalizadores empleados, para llegar a desarrollar modelos cinéticos completos, capaces de reproducir con exactitud las velocidades de fotodegradación obtenidas experimentalmente, y así llegar a diseñar con rigor el correspondiente fotorreactor catalítico. En la bibliografía científica es habitual encontrar expresiones cinéticas del tipo Langmuir-Hinshelwood [1] para modelar la fotodegradación de contaminantes modelo, como el fenol. Sin embargo, como consecuencia de la presencia de fotones en los fotorreactores catalíticos, los parámetros cinéticos obtenidos con este tipo de expresiones no son utilizables en fotorreactores con diferentes geometrías, dimensiones o con diferentes fuentes de iluminación [2]. Esto se debe a que en los procesos fotocatalíticos la eficiencia óptima del proceso depende fundamentalmente, de la forma e intensidad con la que incide la radiación sobre el reactor, por tanto sobre la partícula catalítica, y también de la longitud del camino óptico, es decir, la longitud de reactor a la que la radiación es capaz de penetrar [3]. En este contexto, el aprovechamiento óptimo de la radiación incidente va a estar influenciado de manera significativa por el tamaño de las partículas catalíticas en suspensión. De este modo, para obtener parámetros extrapolables a otros fotorreactores (parámetros intrínsecos) es necesario el desarrollo de modelos cinéticos que presenten una dependencia explícita de la radiación, la cual puede calcularse mediante la resolución de la ecuación de transferencia radiativa (RTE) [4].

Por todo ello, se ha desarrollado un modelo cinético intrínseco capaz de reproducir y simular los resultados experimentales obtenidos en la fotodegradación de fenol, contaminante modelo presente en los efluentes de numerosas industrias, cuyo vertido puede resultar muy peligroso y dañino para el medio ambiente [5]. Con este modelo se obtuvieron los correspondientes parámetros cinéticos intrínsecos para tres catalizadores comerciales de TiO<sub>2</sub>, con idénticas propiedades físico-químicas pero con diferentes tamaños de partícula hidrodinámicos en suspensión. Los catalizadores seleccionados permitieron evaluar la importancia del tamaño de partícula

hidrodinámico en las propiedades ópticas de una suspensión de  $TiO_2$ , lo cual determina la cantidad de radiación absorbida, y en la eficiencia fotocatalítica final.

Los tres fotocatalizadores comerciales de  $TiO_2$  estudiados en este capítulo fueron P25 Aeroxide®, P25/20 VP Aeroperl® y P90 Aeroxide®, de la casa comercial Evonik, que aunque presentan prácticamente las mismas propiedades físico-químicas, tienen valores muy diferentes de sus diámetros de partícula hidrodinámico ( $d_{PHD}$ ), medidos en suspensión acuosa mediante la técnica de difracción láser (DL). Debido a las fuerzas atractivas existentes entre las partículas de  $TiO_2$  cuando se encuentran en suspensión acuosa, se puede producir la formación de agregados que pueden afectar significativamente a la actividad fotocatalítica. Por lo tanto, el tamaño de partícula hidrodinámico da idea del tamaño aparente de la partícula hidratada en movimiento. En la Figura 3.1 se muestra la distribución de tamaños de partícula hidrodinámicos para los tres catalizadores de  $TiO_2$  estudiados que presentan una distribución monomodal, con valores de  $d_{PHD}$  medios próximos a 1,2, 2,6 y 11,3  $\mu m$  respectivamente para los catalizadores P25, P90 y P25/20.

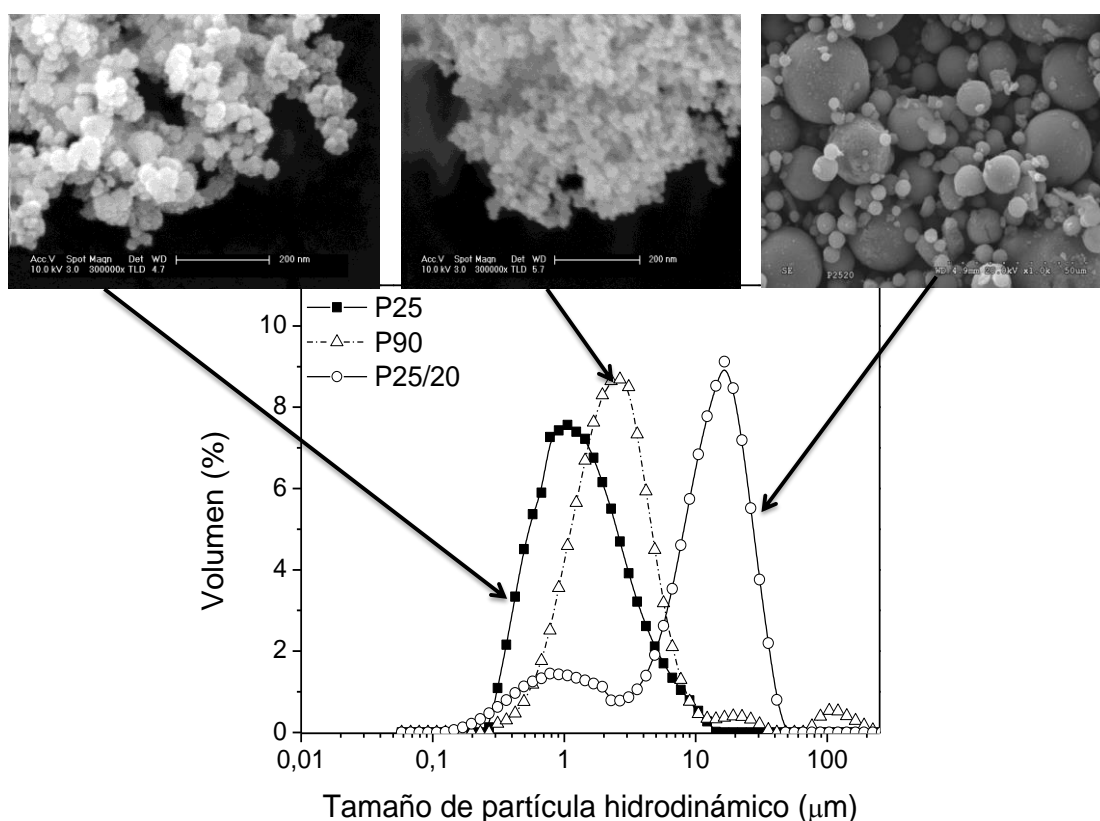


Figura 3.1. Distribución de tamaños de partícula hidrodinámico y micrografías SEM de los fotocatalizadores P25, P90 y P25/20.

Todas las reacciones fotocatalíticas se llevaron a cabo a temperatura ambiente en un fotorreactor cilíndrico, de Pyrex, de 1 L rodeado por 10 lámparas fluorescentes (6 lámparas Black Light Blue UV-A y 4 day-light). A partir de las medidas de actinometría realizadas con ferrioxalato potásico se determinó que la radiación incidente de UV-A en el fotorreactor estudiado fue de  $1,4 \cdot 10^{-8}$  Einstein $\cdot$ cm<sup>-2</sup> $\cdot$ s<sup>-1</sup>. La concentración inicial de fenol utilizada en reacción fue 50 mg $\cdot$ L<sup>-1</sup>.

Los parámetros cinéticos intrínsecos se obtuvieron siguiendo el esquema representado en la Figura 3.2. En primer lugar, se determinó el flujo de radiación incidente al reactor a cada longitud de onda. A partir de las intensidades incidentes y de las propiedades ópticas de cada fotocatalizador se determinó el campo de radiación dentro del fotorreactor mediante la resolución de la ecuación de transferencia radiativa (RTE, ecuación 1). Posteriormente, los valores de la velocidad volumétrica local de absorción de fotones (LVRPA) se calcularon para cada elemento diferencial del reactor y a partir de ellos, se calculó el valor de la velocidad volumétrica global de absorción de fotones (VRPA). Por último, a partir de todos los resultados anteriores se compararon los valores calculados de la concentración de fenol con los valores obtenidos experimentalmente para estimar los correspondientes parámetros cinéticos ( $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ ) mediante regresiones múltiples no lineales.

La determinación y estimación de las propiedades ópticas de las suspensiones de TiO<sub>2</sub>, que incluyen tanto los coeficientes volumétricos de extinción ( $\beta_\lambda$ ), como los de absorción ( $\kappa_\lambda$ ) y *scattering* ( $\sigma_\lambda$ ) se llevaron a cabo a partir de una serie de medidas experimentales mediante espectroscopía UV-Vis en el intervalo de longitudes de onda (345 - 405 nm) correspondientes a las lámparas utilizadas. Además, para determinar las propiedades ópticas fue necesario resolver un modelo unidimensional-unidireccional de la ecuación de transferencia radiativa (RTE), ecuación 1, mediante el método de la ordenada discreta (DOM).

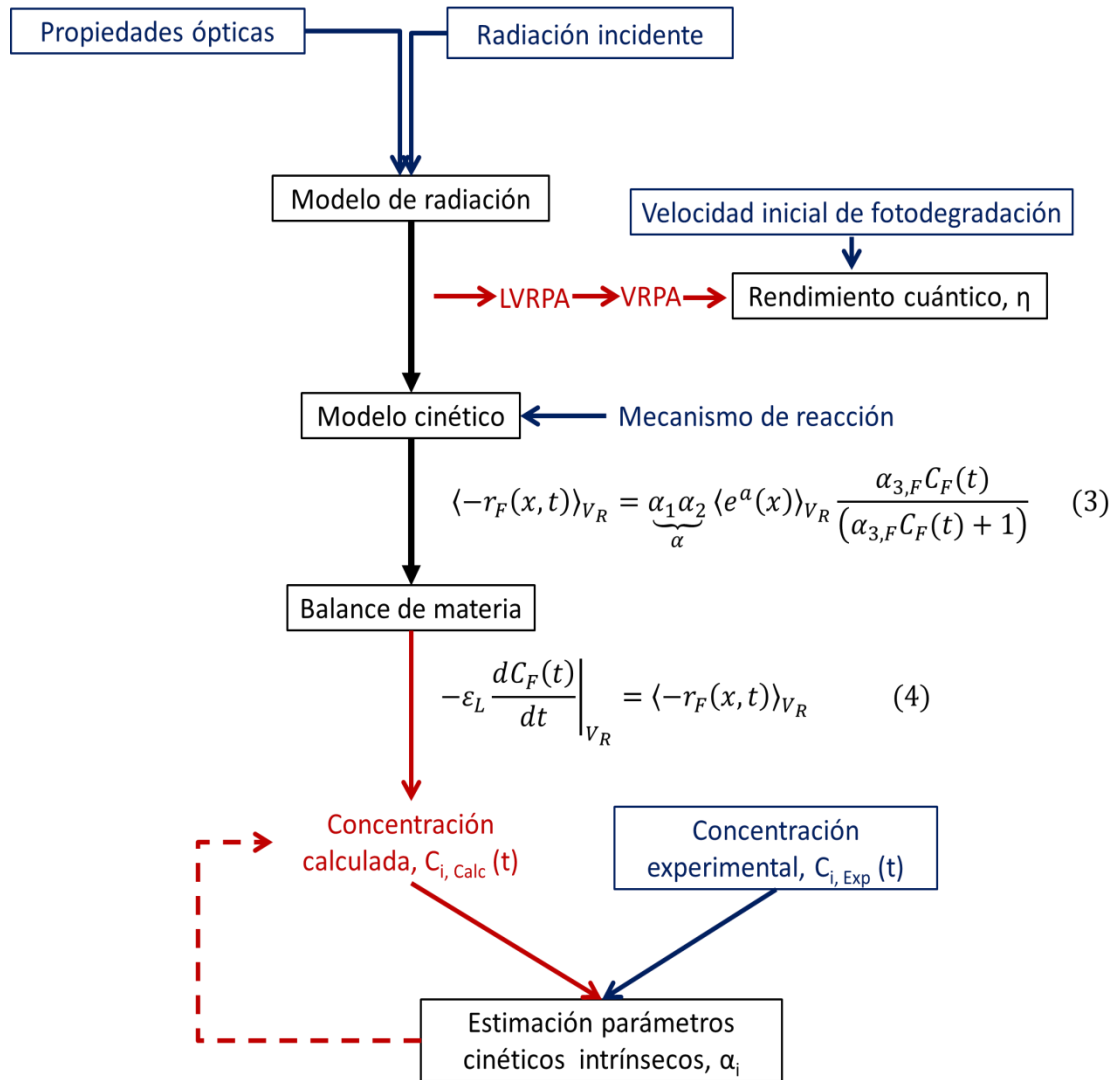


Figura 3.2. Esquema del procedimiento planteado para estimar los distintos parámetros cinéticos intrínsecos, relativos a la fotodegradación catalítica de fenol, para cada uno de los catalizadores de TiO<sub>2</sub> estudiados.

$$\underbrace{\mu \cdot \frac{dI_\lambda(x, \mu)}{dx}}_{\text{Variación sobre la dirección } x \text{ y ángulo } \mu} + \underbrace{\beta_\lambda \cdot I_\lambda(x, \mu)}_{\text{Pérdida por absorción y Out-scattering}} = \underbrace{\frac{\sigma_\lambda(x)}{2} \int_{\mu'=-1}^{\mu'=1} p(\mu, \mu') \cdot I_\lambda(x, \mu) \cdot d\mu'}_{\text{Ganancia por In-scattering}} \quad (1)$$

A partir de los resultados obtenidos en la Figura 3.3 se puede observar que las suspensiones de los fotocatalizadores P25 y P90, con menores valores de diámetro medio de partícula hidrodinámico (1,2 y 2,6 μm respectivamente), han presentado valores mucho más altos de sus coeficientes volumétricos de extinción (β<sub>λ</sub>), absorción (κ<sub>λ</sub>) y scattering (σ<sub>λ</sub>), que el catalizador P25/20, con un valor de diámetro medio de partícula hidrodinámico de 11,3 μm.

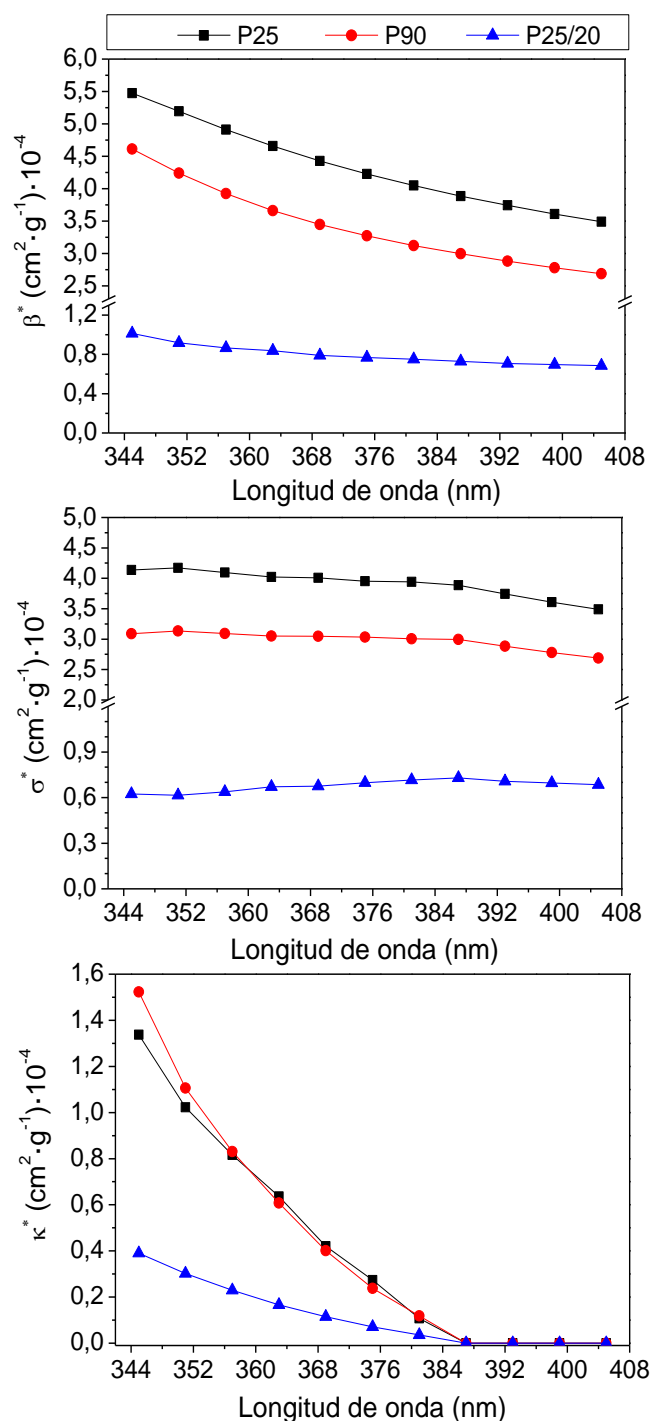


Figura 3.3. Propiedades ópticas específicas de los catalizadores. De arriba a abajo: Coeficiente de extinción ( $\beta_\lambda$ ), coeficiente de *scattering* ( $\sigma_\lambda$ ) y coeficiente de absorción ( $\kappa_\lambda$ ).

Al comparar los valores del albedo ( $\omega$ ), relación entre el coeficiente de *scattering* y el de extinción, se encontró que  $\omega$  aumentaba al disminuir el tamaño de partícula hidrodinámico del fotocatalizador. Por tanto, se puede establecer que menores valores de diámetro medio de partícula hidrodinámico ( $d_{PHD}$ ) pueden llegar a favorecer el

esparcimiento de las partículas catalíticas en suspensión, provocando una mayor dispersión de la radiación.

A continuación, en las mismas condiciones experimentales en las que se llevaron a cabo todas las reacciones fotocatalíticas, se realizaron medidas de actinometría y se utilizó la distribución espectral de energía de las lámparas empleadas para determinar el flujo de radiación incidente al reactor a cada longitud de onda, representado en la Figura 3.4.

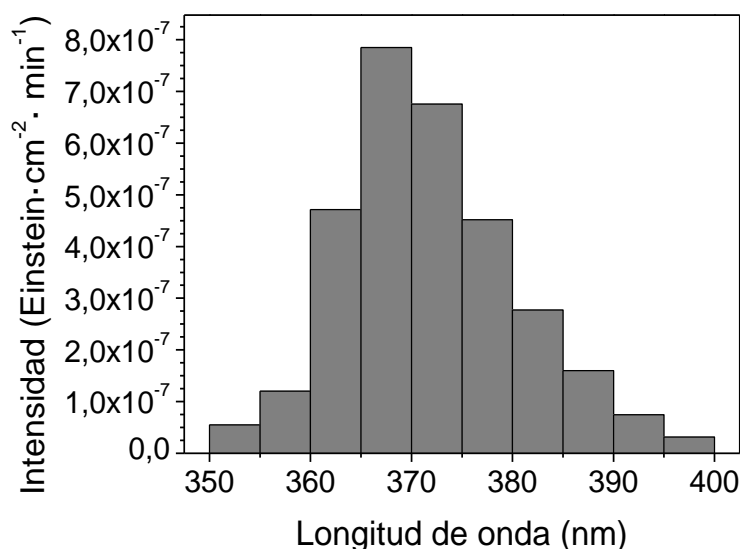


Figura 3.4. Intensidad incidente al reactor a cada longitud de onda.

Una vez obtenidas las propiedades ópticas de los tres fotocatalizadores estudiados y las intensidades que llegan al reactor, se determinó la velocidad volumétrica local de absorción de fotones (LVRPA). Como se puede observar en la Figura 3.5, al incrementar la concentración de catalizador se alcanzó una mayor atenuación en el centro del fotorreactor, a la vez que se observó una mayor absorción de la radiación en las proximidades de las paredes del fotorreactor catalítico. Al utilizar concentraciones bajas del catalizador P25/20 se obtuvieron perfiles de radiación más uniformes que los obtenidos con P25 y P90. Los catalizadores con menores valores de  $d_{\text{PHD}}$ , P25 y P90, fueron los que absorbieron mayor radiación con concentraciones bajas de catalizador ( $0-0,1 \text{ g}\cdot\text{L}^{-1}$ ) debido a que presentaban valores más altos de sus propiedades ópticas.

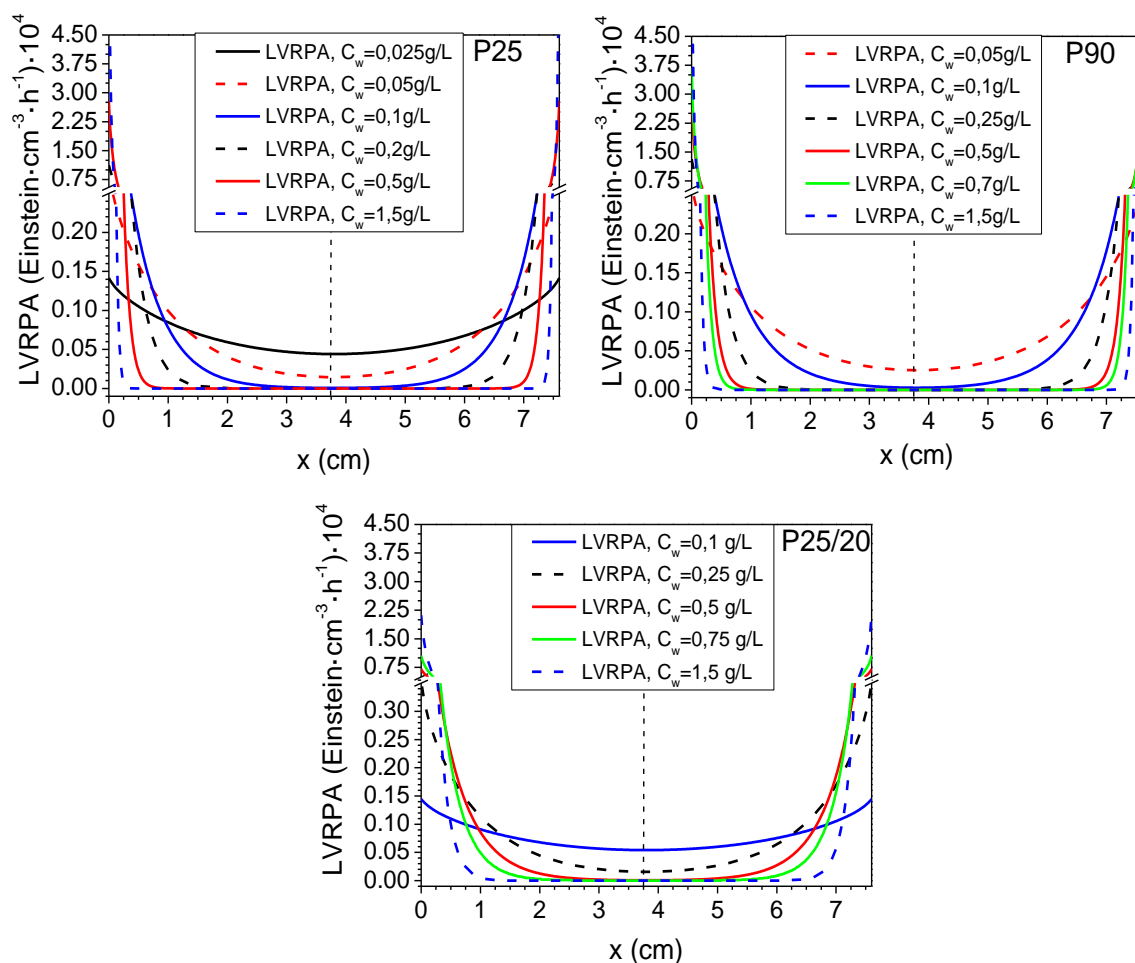


Figura 3.5. Velocidad volumétrica local de absorción de fotones (LVRPA) al usar diferentes concentraciones de P25, P90 y P25/20.

En la Tabla 3.1 se representan los valores de la eficiencia cuántica de los tres fotocatalizadores de  $TiO_2$  estudiados, en función de la concentración de catalizador empleada ( $0-1,5 \text{ g} \cdot \text{L}^{-1}$ ). A pesar de que el fotocatalizador P90 fue capaz de absorber más radiación ( $2,64 \cdot 10^{-4} \text{ Einstein} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$ ), se alcanzaron menores velocidades de fotodegradación ( $2,9 \cdot 10^{-3} \text{ mmol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$ ), indicando una menor eficiencia cuántica que en el caso del P25 (que absorbió  $2,43 \cdot 10^{-4} \text{ Einstein} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$ ). Las mayores velocidades iniciales de fotodegradación se obtuvieron para el fotocatalizador P25 ( $3,3 \cdot 10^{-3} \text{ mmol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$ ) aunque con elevadas concentraciones del catalizador P25/20 ( $1,5 \text{ g} \cdot \text{L}^{-1}$ ) se alcanzaron también altas velocidades.



Tabla 3.1. Influencia de la concentración de los fotocatalizadores P25, P90 y P25/20 en la eficiencia cuántica.

$\eta$ (mol·Einstein <sup>-1</sup> )					
$C_{P25}$ (mg·L <sup>-1</sup> )	$\eta_{P25} \cdot 10^2$	$C_{P90}$ (mg·L <sup>-1</sup> )	$\eta_{P90} \cdot 10^2$	$C_{P25/20}$ (mg·L <sup>-1</sup> )	$\eta_{P25/20} \cdot 10^2$
25	0.66				
50	0.82	50	0.56		
100	1.24	100	0.89	100	0.79
200	1.22	250	1.15	250	1.04
500	1.33	500	0.99	500	1.28
		700	1.12	750	1.34
1500	1.36	1500	1.08	1500	1.31

Se derivó la ecuación cinética a partir de un mecanismo propuesto, en el que se consideraron las siguientes etapas de reacción: (1) activación del catalizador de TiO<sub>2</sub> mediante radiación para formar los pares electrón-hueco (e<sup>-</sup>/h<sup>+</sup>), (2) adsorción de agua, del fenol y del radical hidroxilo en la superficie del catalizador, (3) recombinación de los pares electrón-hueco formados, (4) captación de huecos por la especies adsorbidas, (5) captación de electrones siendo el oxígeno el principal aceptor, y (6) el ataque de radicales hidroxilos (HO<sup>•</sup>). A partir del desarrollo del modelo cinético se obtiene la siguiente expresión de la velocidad de fotodegradación de fenol:

$$-r_F = S_{BET} C_{cat} \alpha_1 \frac{\alpha_{3,F} C_F}{(\alpha_{3,F} C_F + 1)} \left\{ -1 + \sqrt{1 + \frac{\alpha_2 e^a}{S_{BET} C_{cat}}} \right\} \quad (2)$$

Debido a que el intervalo de confianza de alguno de los parámetros cinéticos estimados para el modelo propuesto era muy elevado, se planteó una simplificación del modelo asumiendo que los experimentos fueron desarrollados en condiciones de baja irradiación,  $\frac{\alpha_2 e^a}{S_{BET} C_{cat}} \ll 1$  (ecuación 3 de la Figura 3.2). Esta simplificación implicó que el modelo dependía linealmente de la radiación absorbida. Los parámetros cinéticos intrínsecos estimados al utilizar el modelo simplificado y los valores obtenidos de la raíz del error cuadrático medio vienen resumidos en la Tabla 3.2. De manera que a partir de los resultados obtenidos se pudo observar que los resultados experimentales fueron simulados con gran exactitud a lo largo de toda la reacción, con valores de la raíz del error cuadrático medio inferiores al 5%.

Tabla 3.2. Parámetros cinéticos calculados a partir del modelo cinético propuesto asumiendo bajos flujos de irradiación.

Catalyst	$\alpha$ (mmol·Einstein <sup>-1</sup> )		$\alpha_3$ (L·mmol <sup>-1</sup> )		Error (%)
	Valor	Int. Confianza	Valor	Int. Confianza	
<b>P25</b>	160,60	±35,06	23,81	±6,82	4,24
<b>P90</b>	129,96	±20,86	25,91	±3,72	4,80
<b>P25/20</b>	191,48	±35,20	17,21	±7,71	4,12

En conclusión, el modelo cinético intrínseco desarrollado permite simular la fotodegradación de fenol en fotorreactores con diferentes configuraciones utilizando catalizadores comerciales de TiO<sub>2</sub>. Fotocatalizadores de TiO<sub>2</sub> con menor tamaño de partícula hidrodinámico absorben mayor radiación a bajas concentraciones, lo que implica mayores velocidades de reacción.

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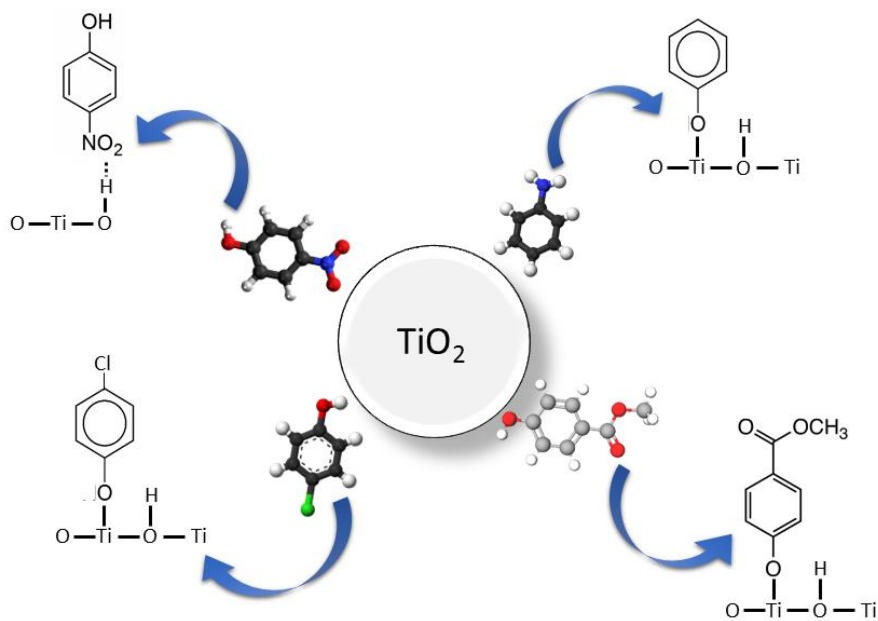
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# Capítulo 4:

## Efecto del tipo de sustituyente en la adsorción y fotodegradación de compuestos fenólicos con catalizadores de $\text{TiO}_2$

*"Defining the role of substituents on adsorption and photocatalytic degradation of phenolic compounds". Journal of Environmental Chemical Engineering 5 (2017) 4612-4620.*

El segundo objetivo planteado en esta Tesis Doctoral ha sido analizar la influencia de la naturaleza química de diferentes grupos funcionales sustituyentes en la posición *para*- del fenol, siendo este el contaminante elegido como modelo. Se ha estudiado la adsorción y fotodegradación catalítica de estos compuestos con catalizadores comerciales de  $\text{TiO}_2$ .



Hoy en día el dióxido de titanio es uno de los fotocatalizadores más empleados y estudiados en procesos fotocatalíticos, tales como la fotodegradación de contaminantes orgánicos en aguas residuales [1]. En líneas generales, la eficiencia fotocatalítica puede estar estrechamente ligada con las propiedades específicas de cada catalizador (propiedades intrínsecas), entre otras, su cristalinidad o textura, sus propiedades ópticas, su naturaleza química superficial, etc. Sin embargo, en la literatura científica ya se ha demostrado que una única característica no puede razonablemente justificar el comportamiento fotocatalítico de un determinado catalizador [2]. También es necesario tener en cuenta su interacción con el medio donde se produce la reacción, es decir, las condiciones de operación en las que se lleva a cabo el proceso fotocatalítico, siendo relevantes muchas características del sistema, entre otras, pH, tipo de contaminante, etc.[3]. En este contexto, las potenciales interacciones que pueden llegar a tener lugar en la superficie del TiO<sub>2</sub>, según sean las condiciones del medio de reacción, pueden provocar cambios significativos en su estado de agregación, llegando, incluso, a formar diferentes tamaños de partículas catalíticas en reacción. En este sentido, diferentes tamaños de agregados pueden incluso llegar a modificar su actividad fotocatalítica final, como consecuencia del efecto que el tamaño medio hidrodinámico puede tener en la radiación absorbida por el fotocatalizador, al influir en sus propiedades ópticas.

Teniendo en cuenta las condiciones de operación en las que se lleva a cabo el proceso fotocatalítico, es importante también considerar la naturaleza química del sustrato a degradar y los grupos funcionales que presente, dado que la adsorción y la fotodegradación dependen también, en gran medida, de la interacción sustrato-fotocatalizador [4]. Por ejemplo, la adsorción es determinante en la fotodegradación de ácidos de cadena corta, tales como ácido oxálico o succínico [5, 6].

Por tanto, en la evaluación final de la actividad catalítica de procesos basados en fotocatalisis heterogénea para su aplicación al tratamiento de aguas residuales, hay que tener en cuenta numerosos factores que incluyen desde las propiedades intrínsecas de cada fotocatalizador, las condiciones de operación y del medio de reacción, hasta las potenciales interacciones sustrato-fotocatalizador [4]. De este modo, propiedades tales como la textura o la acidez superficial pueden llegar a ser decisivas en el comportamiento final de un determinado fotocatalizador.

En este capítulo, para abordar el efecto del tipo de sustituyente en la adsorción y fotodegradación de compuestos fenólicos con catalizadores de TiO<sub>2</sub> se han estudiado, además del fenol, tres compuestos fenólicos con diferentes grupos funcionales en

posición *para*: 4-clorofenol, 4-nitrofenol y metil 4-hidroxibenzoato. Se seleccionaron cinco catalizadores comerciales con diferentes propiedades fisicoquímicas, que están resumidas en la Tabla 4.1.

Tabla 4.1 Propiedades fisicoquímicas de los fotocatalizadores de TiO<sub>2</sub> estudiados.

Catalizador	A	R	d <sub>A</sub>	d <sub>R</sub>	S <sub>BET</sub>	V <sub>meso</sub>	V <sub>macro</sub>	IEP	Acidez
	(%)	(%)	(nm)	(nm)	(m <sup>2</sup> ·g <sup>-1</sup> )	(cm <sup>3</sup> ·g <sup>-1</sup> )	(cm <sup>3</sup> ·g <sup>-1</sup> )		(mmol H <sup>+</sup> ·m <sup>-2</sup> )
P25	84	16	21	33	54	0,00	0,65	6,8	0.006
P90	87	13	17	32	81	0,00	0,26	6,7	0.008
P25/20	88	12	21	33	54	0,00	0,55	5,4	0.005
PC105	100	0	19	-	79	0,00	0,30	4,8	0.006
HBK	100	0	8	-	356	0,32	0,54	6,3	0.003

A: Anatasa; R: Rutilo; IEP: Punto Isoeléctrico o Punto de Carga Cero

En primer lugar, se analizó la influencia que la superficie específica (S<sub>BET</sub>) de cada fotocatalizador ejercía en la capacidad de adsorción de cada uno de los compuestos aromáticos estudiados. Aunque en general los valores de adsorción fueron siempre muy bajos, del orden de 0,08 mmol<sub>contaminante</sub>·g<sub>catalizador</sub><sup>-1</sup>, se observó que la cantidad de contaminante adsorbida estaba relacionada con la acidez superficial de cada catalizador; a pesar de que estos valores, obtenidos a partir de isothermas de adsorción de amoníaco, no permitieron una discriminación muy detallada. Por tanto, la cantidad adsorbida dependía más de las propiedades superficiales del fotocatalizador que de la propia naturaleza química del contaminante y su sustituyente, como se puede observar en la Figura 4.1. Al calcular la cantidad adsorbida (q<sub>e</sub>) por unidad de superficie de catalizador se obtuvo la siguiente secuencia: q<sub>e</sub><sup>P25</sup> > q<sub>e</sub><sup>P25/20</sup> > q<sub>e</sub><sup>PC105</sup> > q<sub>e</sub><sup>P90</sup> > q<sub>e</sub><sup>HBK</sup>. De manera que a partir de estos resultados se detectó que los catalizadores con superficies específicas más altas, Hombikat (HBK) y P90 con 356 y 81 m<sup>2</sup>·g<sup>-1</sup> respectivamente, fueron los que adsorbieron menor cantidad de contaminante por unidad de superficie de fotocatalizador.

Las isothermas obtenidas se ajustaron a los modelos de Langmuir y Freundlich, y sus correspondientes parámetros se calcularon mediante regresiones no lineales, alcanzando valores del mismo orden de magnitud que los reportados en la bibliografía para fotocatalizadores de TiO<sub>2</sub> [4, 5]. Cabe destacar que el modelo que mejor se ajusta a los resultados obtenidos depende del fotocatalizador y del contaminante orgánico seleccionado.

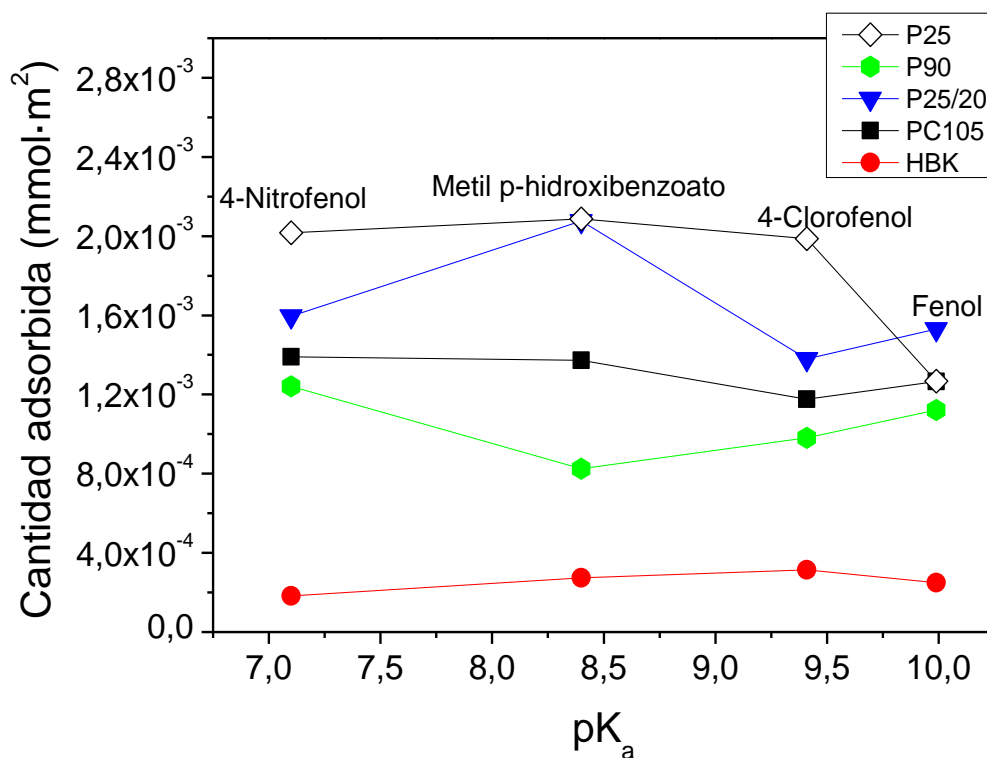


Figura 4.1. Relación entre la cantidad adsorbida, a una concentración de equilibrio de  $200 \text{ mg}\cdot\text{L}^{-1}$  de compuesto fenólico, con el  $\text{pK}_a$  de los respectivos compuestos fenólicos, para todos los fotocatalizadores de  $\text{TiO}_2$  estudiados.

Se realizaron medidas de espectroscopía infrarroja de reflectancia difusa (DRIFTS) con el objetivo de profundizar en el estudio de adsorción e intentar determinar la principal vía por la cual los diferentes compuestos fenólicos se adsorbían sobre la superficie del catalizador. Todos estos espectros DRIFTS están representados en la Figura 4.2 junto a la descripción de las distintas interacciones entre los fotocatalizadores y los respectivos contaminantes. A partir de estos resultados, se apreció que la mayoría de estos contaminantes aromáticos (fenol, 4-clorofenol y metil-4-hidroxibenzoato) se adsorbían principalmente debido a las interacciones entre los grupos  $-\text{OH}$  de los respectivos compuestos fenólicos y la superficie del  $\text{TiO}_2$ , dando lugar a Ti-fenolatos. Sin embargo, tras analizar el del 4-nitrofenol se observó que su adsorción probablemente se debía a la aparición de puentes de hidrógeno entre grupos  $\text{Ti-OH}$  de la superficie del catalizador y el grupo nitro.

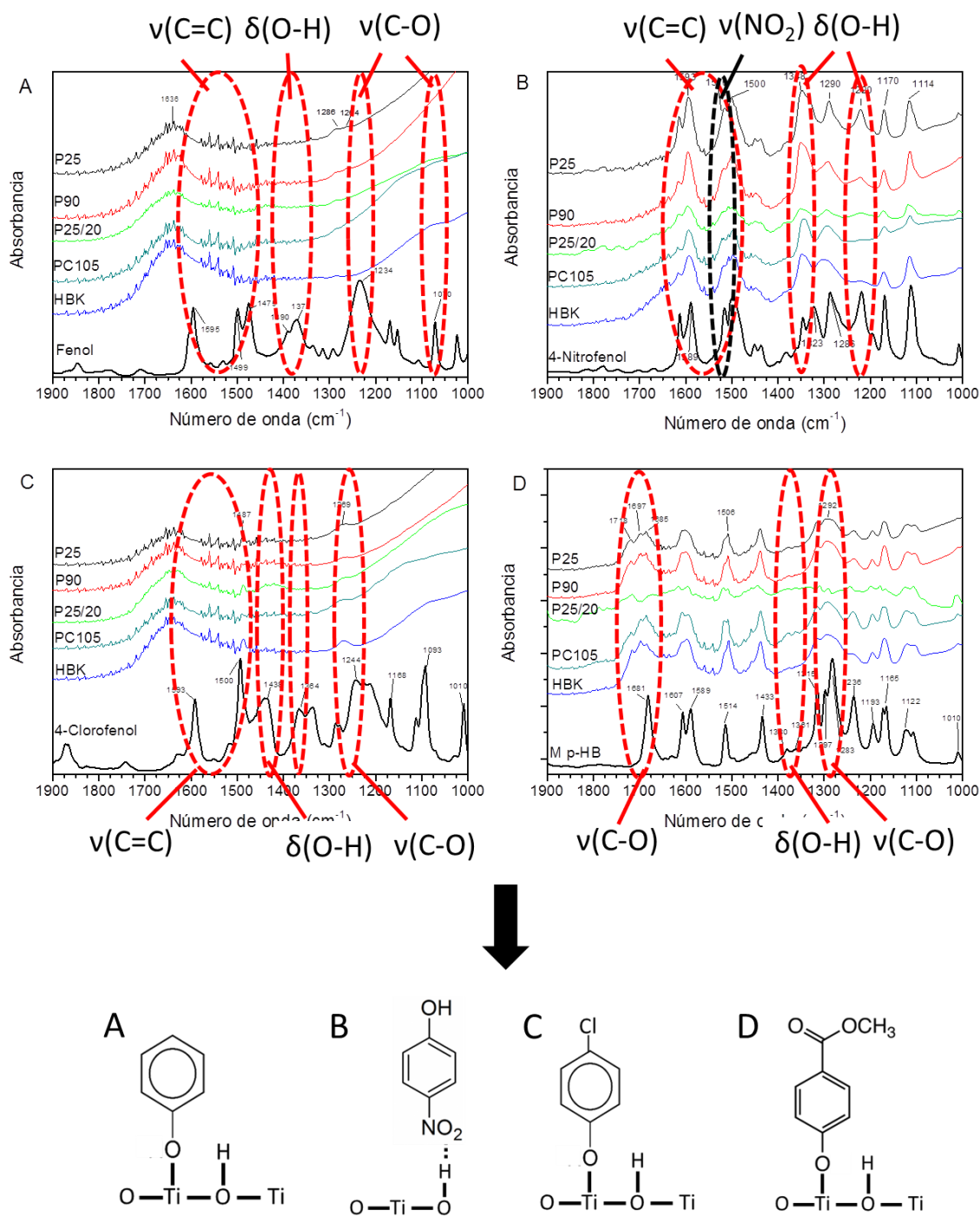


Figura 4.2. Espectros DRIFTs y representación esquemática de la interacción entre los compuestos orgánicos adsorbidos y el  $TiO_2$ : (A) fenol, (B) 4-nitrofenol, (C) 4-clorofenol y (D) metil 4-hidroxibenzoato.

Al comparar la actividad fotocatalítica de todos los contaminantes orgánicos estudiados, se obtuvo que la velocidad inicial de fotodegradación, independientemente del compuesto fenólico a degradar, seguía la siguiente secuencia: P25 > P90 > P25/20 > PC105 > HBK. La mayor velocidad inicial de fotodegradación se alcanzó en fotocatalizadores con estructuras cristalinas con mezcla de fases (anatasa y rutilo) y

menores tamaños de partícula hidrodinámico en suspensión. Esta misma secuencia se observó en el estudio de la generación de radicales hidroxilo, a través de los experimentos de formación del ácido 2-hidroxitereftálico (ATOH), como se observa en la Figura 4.3. Estos resultados indican que, para estos contaminantes, la superficie específica del catalizador no tiene una gran influencia en la foto-oxidación catalítica. Probablemente se debe al hecho de que su adsorción fue tan baja que la fotodegradación de estos compuestos fenólicos se dio preferentemente por reacción con los radicales hidroxilo, generados cuando la molécula de agua capta los huecos y se oxida para dar radicales  $\text{HO}^\bullet$ .

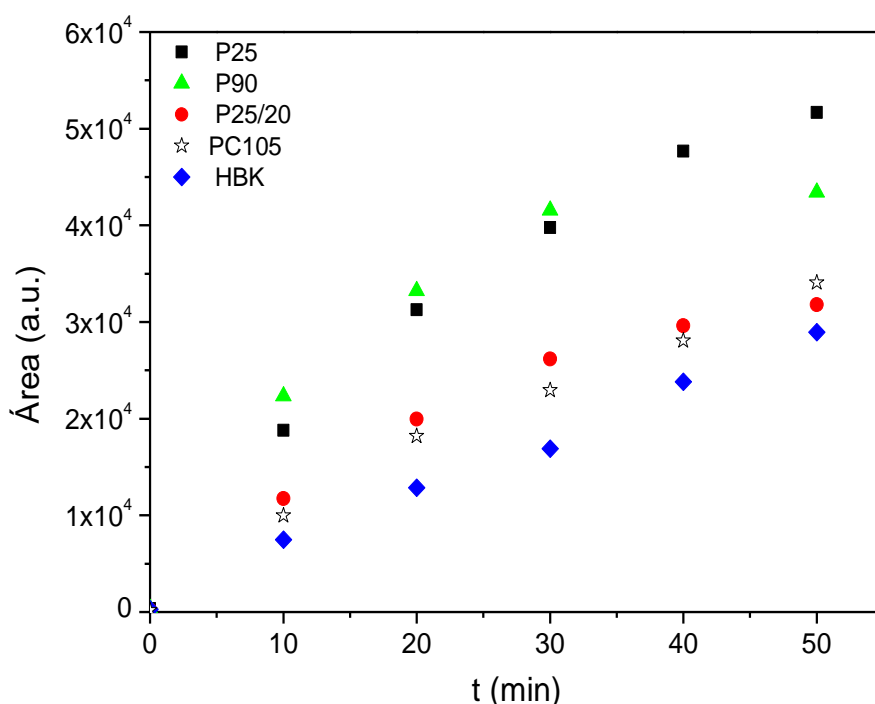


Figura 4.3. Evolución del área integrada del pico correspondiente al ácido 2-hidroxitereftálico para los diferentes fotocatalizadores de  $\text{TiO}_2$ .

Por último, considerando al fenol como sistema de referencia, se puede establecer una clara relación entre la velocidad inicial de fotodegradación de estos contaminantes con las constantes de Hammett ( $\sigma$ ) de los sustituyentes, para todos los fotocatalizadores estudiados, como puede verse en la Figura 4.4. Las constantes de Hammett ( $\sigma$ ) representan el efecto que los sustituyentes tienen en el carácter electrónico de un sistema aromático dado, en este caso fenol. De este modo, se obtiene que cuanto mayor es la constante de Hammett, y por tanto, menor es el carácter electrodonador del sustituyente, menor es la velocidad de fotodegradación catalítica.



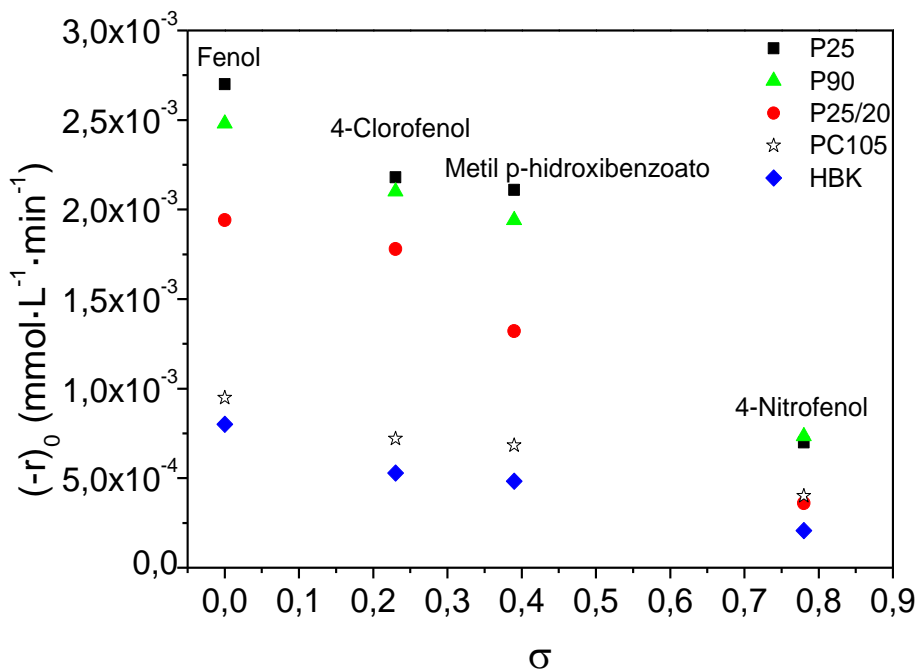


Figura 4.4. Influencia de la constante de Hammett en la velocidad inicial de fotodegradación de los compuestos fenólicos.

A partir de los resultados obtenidos se puede concluir que la naturaleza del sustituyente presenta una baja influencia en la cantidad adsorbida de los compuestos fenólicos estudiados. Además, la adsorción sobre el fotocatalizador no juega un papel crucial en las velocidades iniciales de fotodegradación alcanzadas. Sin embargo, la fotoactividad sí que depende de la naturaleza del sustituyente, siendo la velocidad inicial de eliminación menor para sustituyentes con carácter más electrofílico.

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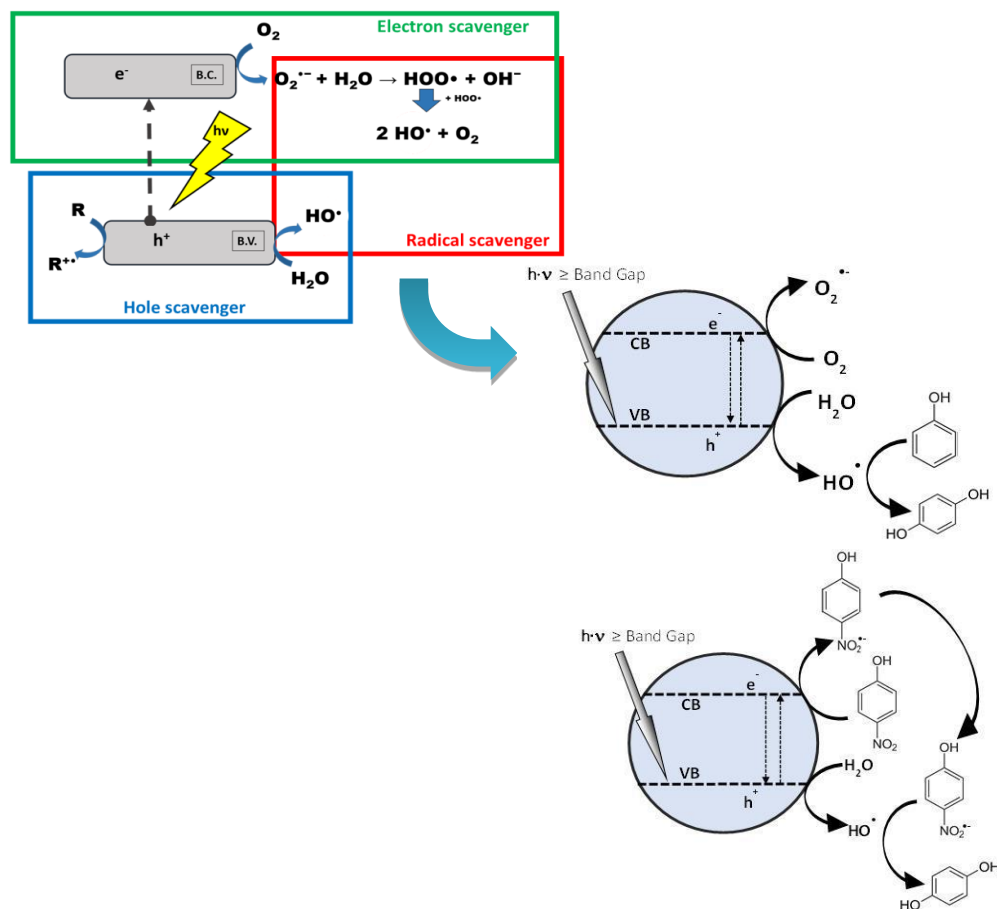
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# Capítulo 5:

## Elucidación del mecanismo de fotodegradación de contaminantes fenólicos con catalizadores de $\text{TiO}_2$

*"Elucidation of the photocatalytic-mechanism of phenolic compounds". Journal of Environmental Chemical Engineering 6 (2018) 5712-5719.*

La fotodegradación catalítica de contaminantes orgánicos en fase acuosa puede ser iniciada mediante diferentes mecanismos. De manera que el tercer objetivo ha consistido en establecer el mecanismo más relevante en la foto-oxidación catalítica de compuestos fenólicos con catalizadores comerciales de  $\text{TiO}_2$ . Previamente, se determinó la radiación absorbida por los fotocatalizadores estudiados en presencia de los diferentes compuestos orgánicos, y se calculó la eficiencia cuántica del proceso en la fotodegradación.



Todavía hoy en día, siguen existiendo dudas sobre cómo tiene lugar el proceso de la foto-oxidación catalítica de contaminantes orgánicos en fase acuosa. No obstante, en la bibliografía científica se han descrito tres vías principales a partir de las cuales se produce la fotodegradación catalítica [1-3]: (i) vía la transferencia directa de electrones, entre el contaminante orgánico a degradar y los huecos fotogenerados en el fotocatalizador (oxidación directa), (ii) mediante especies reactivas de oxígeno (Reactive Oxygen Species, ROS), formadas por interacción con los electrones de la banda de conducción del fotocatalizador, (iii) o a partir de radicales hidroxilo ( $\text{HO}^\bullet$ ) producidos por la interacción del  $\text{H}_2\text{O}$  con los huecos de la banda de valencia. Además, también hay que tener en cuenta la relevancia que puede llegar a tener la adsorción de contaminantes, sobre la superficie del fotocatalizador [4, 5]. La determinación del mecanismo es esencial para entender la eficiencia del fotocatalizador y las condiciones óptimas de operación, ya que se ha observado en la bibliografía que la foto-oxidación directa mediante transferencia directa de electrones a la banda de valencia es siempre más eficiente [5]. Sin embargo, a pesar de que el mecanismo depende en gran medida del tipo de contaminante, se ha asumido que la mayoría de los compuestos son fotodegradados por el ataque de radicales  $\text{HO}^\bullet$  [5].

Después de estudiar en el capítulo anterior la influencia de la naturaleza química del tipo de sustituyente en la adsorción y fotodegradación de distintos compuestos fenólicos sustituidos en la posición para (fenol, 4-clorofenol, 4-nitrofenol y metil 4-hidroxibenzoato), se concluyó que la naturaleza química del sustituyente tenía poco efecto sobre la adsorción. Sin embargo, sí se apreciaron diferencias significativas en el tipo de enlace y la forma en la que estos compuestos se adsorbían sobre la superficie del  $\text{TiO}_2$ . Como consecuencia, en este capítulo se ha tratado de elucidar y especificar el tipo de mecanismo de fotodegradación que gobierna la fotodegradación de estos cuatro compuestos orgánicos, utilizando para ello tres tipos diferentes de *scavengers*. El tipo de mecanismo que gobierna la fotodegradación se relacionó con la forma en que cada contaminante se adsorbe. Como se concluyó en el capítulo 3, es muy importante determinar la radiación absorbida por cada fotocatalizador. Por ello, se calcularon los perfiles de la radiación absorbida dentro del reactor para analizar la eficiencia con la que los fotocatalizadores aprovechaban los fotones.

En este estudio se emplearon dos catalizadores comerciales de  $\text{TiO}_2$ , Hombikat UV-100 (HBK) y Aeroxide® P25 (P25), con diferentes propiedades físico-químicas. La fotoactividad catalítica se determinó en el mismo sistema de reacción que se ha

utilizado en los dos capítulos anteriores. La concentración de fotocatalizador y de contaminante orgánico utilizada fueron 250 y 50 mg·L<sup>-1</sup>, respectivamente.

Independientemente del contaminante considerado, el fotocatalizador P25 dio siempre lugar a los mejores resultados de fotodegradación, con velocidades iniciales de fotooxidación entre tres y cuatro veces más elevadas que las conseguidas con el HBK, como se observa en la Figura 5.1, donde se compara la evolución de la fotodegradación de todos los contaminantes estudiados. En todos los casos se obtuvieron conversiones de carbono orgánico total (COT) superiores al 90% (excepto para el 4-nitrofenol) tras 5 horas de reacción con el catalizador P25, aunque en el mismo intervalo de tiempo solo se alcanzaron valores inferiores al 40% con el fotocatalizador HBK.

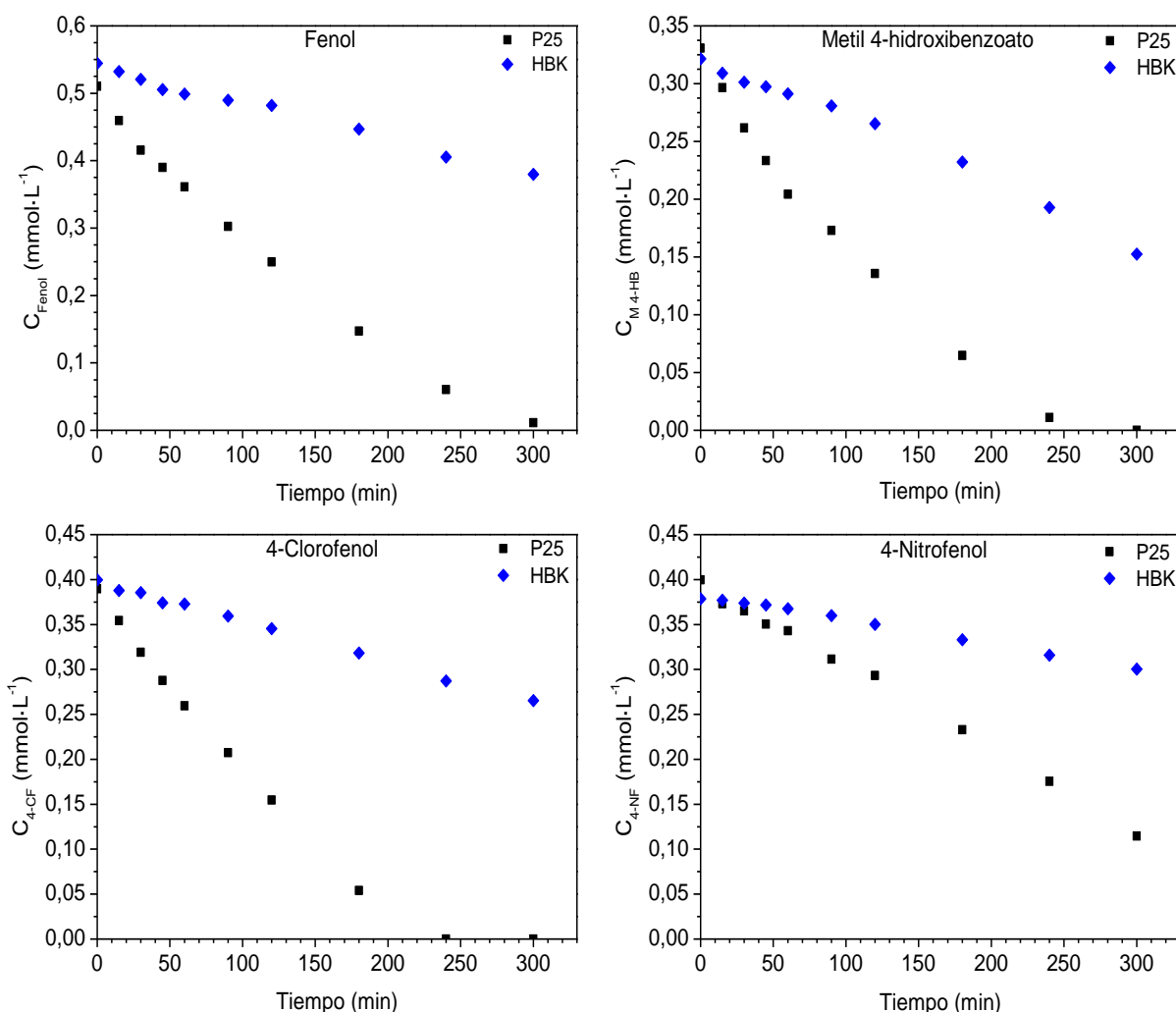


Figura 5.1. Comparación de la fotodegradación de fenol, metil 4-hidroxi benzoato (M p-HB), 4-clorofenol (4-CF) y 4-nitrofenol (4-NF) con P25 y Hombikat (HBK).

Por otro lado, se estimaron los valores de la velocidad volumétrica local de absorción de fotones (LVRPA), que están representados en la Figura 5.2 para los dos catalizadores de  $\text{TiO}_2$  estudiados, asumiendo un modelo de radiación unidimensional-unidireccional y utilizando el método de Monte Carlo [6] para resolverlo. Este método se basa en la generación de números aleatorios, entre 0 y 1, para determinar las trayectorias de los fotones y su interacción con el medio. Cuando se utilizó el catalizador P25 toda la radiación se absorbió en aproximadamente 0,5 cm, siendo nula en el centro del reactor. Sin embargo, en el caso del fotocatalizador HBK, la atenuación de la radiación fue menor, observándose absorción de la radiación incluso a 2,5 cm de las paredes del reactor. Estos resultados pudieron explicarse a partir de la teoría de Mie [7], ya que al ser menor el tamaño de partícula hidrodinámico del catalizador P25 (comparado con el del HBK) y comparable con la longitud de onda de la radiación incidente, la luz se absorbe y se dispersa más eficientemente, permitiendo alcanzar mayores eficiencias cuánticas. Sin embargo, en presencia de 4-nitrofenol la radiación absorbida por los dos catalizadores fue menor, debido a la propia absorción del 4-nitrofenol en el rango de emisión de las lámparas UV-A utilizadas en el fotorreactor. No obstante, se alcanzaron siempre eficiencias cuánticas inferiores al 0,2% en la fotodegradación de los diferentes compuestos orgánicos estudiados, como queda reflejado en la Figura 5.3 donde se comparan las eficiencias cuánticas de los dos catalizadores para todos los contaminantes estudiados. En líneas generales, al comparar las eficiencias cuánticas de ambos catalizadores, independientemente del contaminante, se obtienen valores 3 o 4 veces superiores con el P25, lo cual indica una mayor eficiencia del aprovechamiento de los fotones absorbidos para degradar los compuestos orgánicos. Solo en el caso del 4-nitrofenol la eficiencia cuántica obtenida por el Hombikat superaba la correspondiente al fotocatalizador P25. Esto se debe a que el Hombikat alcanzó velocidades de fotodegradación de 4-nitrofenol significativas, a pesar de presentar valores de la radiación absorbida 4 veces menores a los de P25.

Para determinar la relevancia de los huecos fotogenerados ( $h^+$ ), de los radicales hidroxilo ( $\text{HO}^\bullet$ ) y de los electrones de la banda de conducción ( $e^-$ ) en el mecanismo que gobierna la fotodegradación de los compuestos orgánicos analizados, se llevaron a cabo también reacciones en presencia de tres *scavengers*: ácido fórmico para atrapar los  $h^+$ , metanol para atrapar los radicales  $\text{HO}^\bullet$  y nitrato de cobre (II) para capturar los electrones de la banda de conducción.

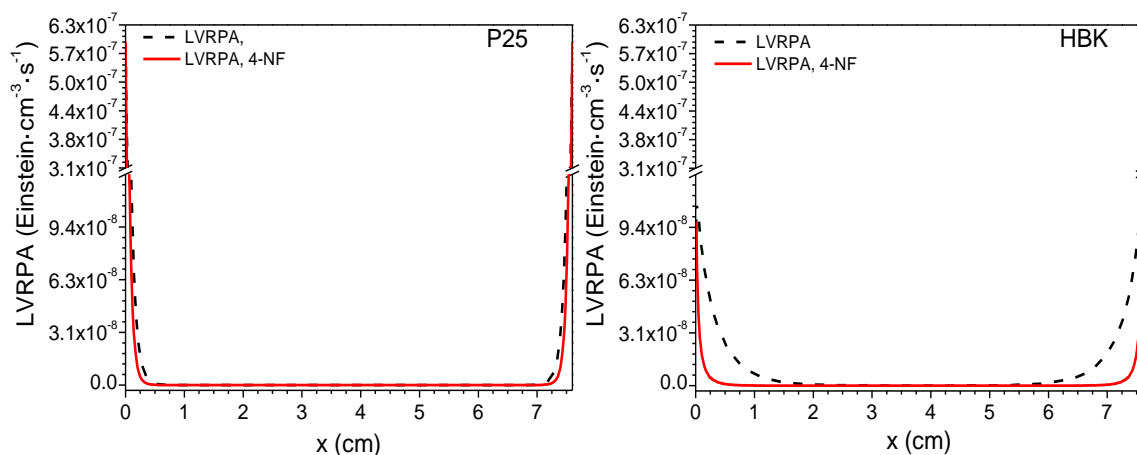


Figura 5.2. Perfiles de la radiación absorbida por P25 y Hombikat en presencia de fenol, metil 4-hidroxibenzoato, 4-clorofenol ( - - ) y 4-nitrofenol ( — ).

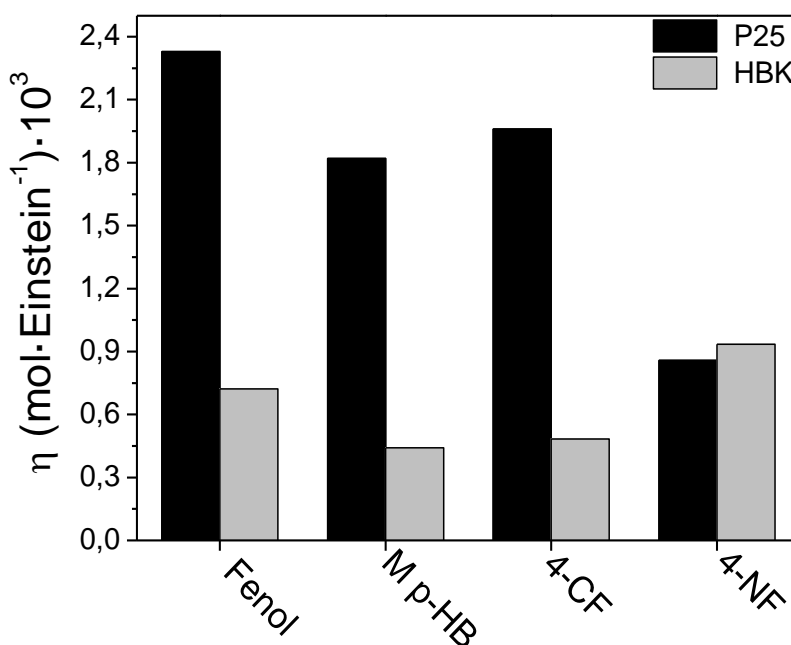


Figura 5.3. Comparación de las eficiencias cuánticas ( $\eta$ ) calculadas para los diferentes catalizadores y contaminantes.

La evaluación de la importancia de estos mecanismos en la fotodegradación de los diferentes compuestos fenólicos estudiados se realizó cualitativamente a través de las siguientes tres relaciones, calculadas a partir de las correspondientes constantes cinéticas aparentes de primer orden estimadas para las reacciones en presencia de  $CH_3OH$ ,  $HCOOH$  y  $Cu(NO_3)_2$  ( $k_{CH_3OH}$ ,  $k_{HCOOH}$  y  $k_{Cu(NO_3)_2}$ , respectivamente):

$$k_1 = (k - k_{HCOOH} - k_{CH_3OH})/k$$

$$k_2 = k_{CH_3OH}/k$$

$$k_3 = k_{HCOOH}/k$$

Donde  $k$  es la constante cinética aparente de primer orden estimada para el proceso más rápido.  $k_1$ ,  $k_2$  y  $k_3$  son las relaciones que representan la relevancia que tienen en la fotodegradación los radicales HO<sup>•</sup>, los huecos y los electrones fotogenerados, respectivamente. Como se puede observar en la Figura 5.4 A, los radicales hidroxilo (HO<sup>•</sup>), formados a partir de los huecos fotogenerados, son los principales responsables de la fotodegradación de todos los contaminantes estudiados, excepto en el caso del 4-nitrofenol (ver, Figura 5.4 B). Como resultado se identificó la presencia de varios intermedios hidroxilados, como hidroquinona, catecol o 4-clorocatecol, durante la fotodegradación de fenol, metil 4-hidroxibenzoato y 4-clorofenol.

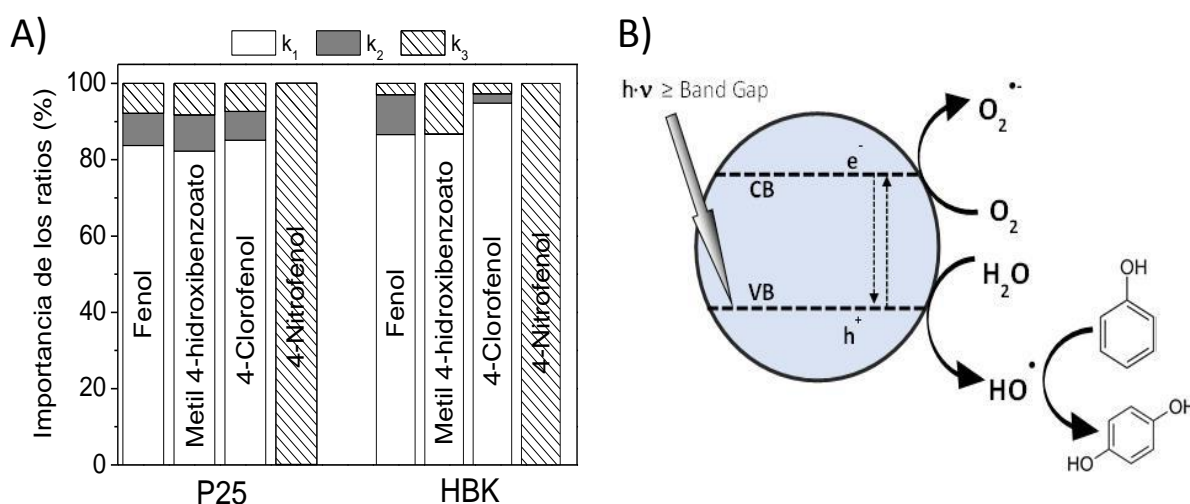


Figura 5.4. (A) Relevancia de las distintas relaciones cinéticas definidas para los diferentes compuestos aromáticos con los dos catalizadores de TiO<sub>2</sub> estudiados. (B) Esquema del mecanismo por el cual se fotodegrada el fenol, metil 4-hidroxibenzoato y 4-clorofenol.

En el caso del 4-nitrofenol, un mecanismo iniciado a partir de los electrones fotoinducidos de la banda de conducción del fotocatalizador parece ser el responsable de su fotodegradación, independientemente del fotocatalizador utilizado, como se representa en la Figura 5.5 A. Se comprobó que la velocidad de fotodegradación del 4-nitrofenol puede incrementarse al llevar a cabo su oxidación en presencia de un *scavenger* de huecos fotogenerados ( $h^+$ ), como ácido fórmico u oxálico, como puede verse en la Figura 5.5 B, que favorecen la disminución del proceso de recombinación. Como consecuencia, una mayor cantidad de electrones podrán ser transferidos al 4-nitrofenol para iniciar así su fotodegradación. Esta diferencia entre los mecanismos de fotodegradación se debe fundamentalmente a la capacidad del 4-nitrofenol para adsorberse sobre la superficie del TiO<sub>2</sub> formando un complejo debido a la interacción



entre el  $Ti-OH$  y el grupo  $NO_2$  del 4-nitrofenol, como se dedujo en el capítulo anterior en la Figura 4.2.

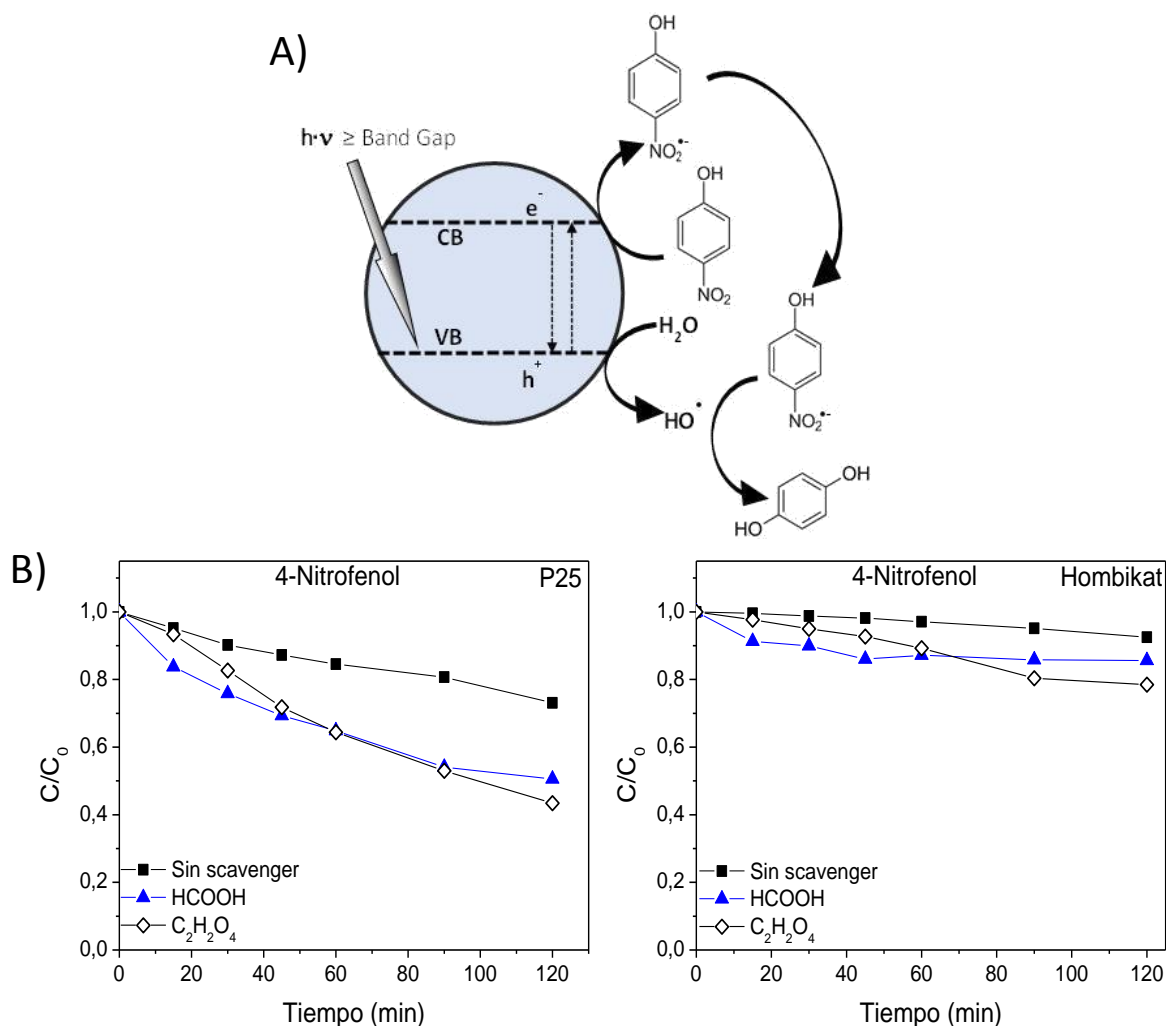


Figura 5.5. (A) Esquema del mecanismo por el cual se fotodegrada el 4-nitrofenol; (B) Mejora en la evolución de la fotodegradación de 4-nitrofenol al introducir ácido fórmico u oxálico como atrapador de los huecos fotogenerados.

En definitiva se puede concluir que el fotocatalizador P25 es capaz de absorber mayor radiación y de alcanzar mayores eficiencias cuánticas. En cuanto al mecanismo de fotodegradación, fenol, 4-clorofenol y metil 4-hidroxibenzoato fueron principalmente fotodegradados por radicales  $HO^\bullet$ . Sin embargo, un mecanismo iniciado por los electrones de la banda de conducción parece ser más importante en la fotodegradación de 4-nitrofenol.

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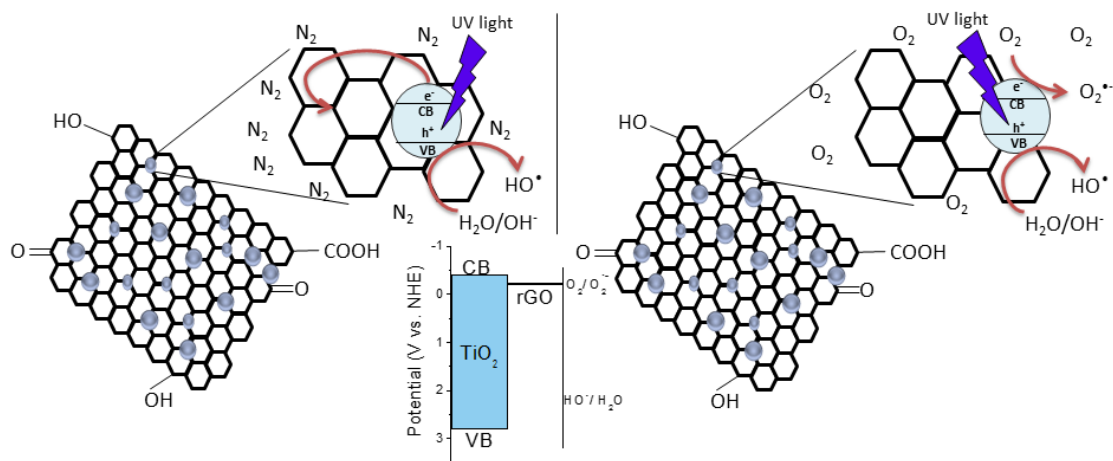
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# Capítulo 6:

## Naturaleza y fotoactividad catalítica de nanocomposites de $\text{TiO}_2$ -rGO en suspensiones acuosas con radiación UV-A

*"Nature and photoreactivity of  $\text{TiO}_2$ -rGO nanocomposites in aqueous suspensions under UV-A irradiation". Applied Catalysis B: Environmental 241 (2019) 375-384.*

El cuarto objetivo planteado en esta Tesis Doctoral ha sido la síntesis de nanocomposites de  $\text{TiO}_2$ -rGO, con distintas relaciones máxicas de GO: $\text{TiO}_2$ , mediante una metodología hidrotérmal. Los resultados obtenidos en la caracterización se han utilizado para evaluar la separación y recombinación de los pares electrón-hueco, así como para justificar los resultados de la fotodegradación de ácido oxálico en disolución acuosa.



La eficiencia final de la reacción fotocatalítica depende de diversos factores [1, 2], uno de los más críticos es la alta probabilidad de recombinación de los pares electrón-hueco en el semiconductor, debido a que no hay una separación física entre los sitios de las reacciones anódicas (oxidación por huecos) y catódica (reducción por electrones). Además, se tiene que tener en cuenta que el TiO<sub>2</sub> es solo capaz de absorber radiación electromagnética por debajo de 390 nm, debido a su elevado valor de band-gap [3]. Como consecuencia, la energía del espectro solar aprovechable por el TiO<sub>2</sub> en fotocatalisis solar alcanza, en términos cuantitativos, alrededor del 5% [4]. Por ello, en las últimas décadas se han dedicado muchos esfuerzos a extender la respuesta espectral a la zona del visible, mediante modificaciones de la estructura del TiO<sub>2</sub> [5, 6]. Entre las alternativas más implantadas destacan, desde el dopaje del TiO<sub>2</sub> con otros metales [3, 7], hasta su combinación con otros materiales para obtener materiales híbridos o composites con mayor fotoeficiencias en el rango UV-visible del espectro solar [8].

Recientemente se ha considerado al grafeno [9] como uno de los materiales más interesantes como consecuencia de sus excelentes propiedades. La unión del grafeno con partículas sólidas de un semiconductor como el TiO<sub>2</sub> introduce mejoras importantes en la separación de cargas, reduce considerablemente la recombinación del par electrón-hueco fotogenerado, aumenta el área superficial del catalizador y genera una mayor cantidad y calidad de centros de adsorción [10, 11]. En este contexto, distintos tipos de materiales híbridos de grafeno-TiO<sub>2</sub> han sido desarrollados y estudiados en la bibliografía para su aplicación en procesos fotocatalíticos, como una simple mezcla física [12], la síntesis de composites a través de procesos sol-gel [13] o métodos de preparación basados en síntesis hidrotermal o solvotermal de nanopartículas de TiO<sub>2</sub> y grafeno [14-16]. La posibilidad de obtener óxido de grafeno (GO) u óxido de grafeno reducido (rGO) empleando métodos químicos sencillos, facilita su aplicación en la síntesis de composites o catalizadores híbridos con semiconductores como el TiO<sub>2</sub>, con costes de producción razonables y posibilidad de escalado [17]. Por tanto, el gran potencial que actualmente presenta el grafeno podría suponer un importante avance en la mejora de la fotoeficiencia final de los procesos fotocatalíticos, a través del desarrollo de composites o sistemas híbridos basados en grafeno y nanopartículas cristalinas de dióxido de titanio.

A pesar de que se han publicado numerosos trabajos relacionados con la síntesis y actividad de este tipo de fotocatalizadores, las conclusiones obtenidas pueden llegar a resultar contradictorias. Por ejemplo, mientras que algunos estudios detectaron un

gran incremento de la velocidad de fotodegradación de un contaminante modelo como el fenol [18], en otros se observó un descenso de la actividad al modificarse el TiO<sub>2</sub> con rGO [15]. Esto podría estar relacionado con variaciones en las posiciones de las bandas de valencia y conducción que pueden llegar a variar según el grado de reducción del óxido de grafeno [11]. Del mismo modo, algunos autores postulan que esta mejora en la eficiencia de la transferencia de carga, originada por la presencia del óxido de grafeno, podría reducir el proceso de recombinación, incrementando considerablemente la actividad fotocatalítica del TiO<sub>2</sub> en nanocomposites GO-TiO<sub>2</sub> [19]. Sin embargo, otros autores apuntan al rol del GO como fotosensibilizador, donde los electrones podrían ser directamente transferidos desde el óxido de grafeno hasta la banda de conducción del TiO<sub>2</sub> [20, 21]. Por lo tanto, resulta crucial conocer el papel que juega el rGO en este tipo de fotocatalizadores, ya que dependiendo de la longitud de onda de la radiación absorbida y del grado de reducción del GO, el proceso fotocatalítico puede tener lugar a partir de diferentes mecanismos de fotodegradación. Además, la función del rGO en el foto-mecanismo también va a depender de la adsorción del contaminante que se va a degradar, ya que el tipo de adsorción puede llegar a afectar a la transferencia de electrones entre el nanocomposite y el propio sustrato [15].

En este capítulo se ha estudiado y analizado el efecto que la incorporación de óxido de grafeno reducido (rGO) presenta en la actividad fotocatalítica de nanocomposites de TiO<sub>2</sub>-rGO. A partir del catalizador comercial Aeroxide® P25, que fue con el que se alcanzaron los mejores resultados de fotoactividad y eficiencia en los estudios anteriores, se han sintetizado distintos fotocatalizadores híbridos de P25-rGO mediante síntesis hidrotermal. Para analizar las ventajas que aporta la modificación del TiO<sub>2</sub> con rGO, se llevó a cabo una caracterización químico-física completa mediante medidas electroquímicas, espectroscopía UV-vis por reflectancia difusa, DRX, TEM, etc. Por último, se evaluó el efecto del rGO en la actividad de estos fotocatalizadores híbridos mediante experimentos de fotodegradación de ácido oxálico, cuyos resultados se han relacionado con estudios de Espectroscopía de Resonancia Paramagnética Electrónica (EPR) y Espectroscopía de Absorción Transitoria (TAS).

Los fotocatalizadores de TiO<sub>2</sub>-rGO se sintetizaron mediante un procedimiento hidrotermal a 120°C y 18 h. Se sintetizaron nanocomposites con diferentes relaciones máxicas de GO:TiO<sub>2</sub>, denominados P25-rGO 0%, P25-rGO 0,1%, P25-rGO 0,5% y P25-rGO 1%, y se caracterizaron mediante diferentes técnicas.

A partir de los resultados de espectroscopía Raman, representados en la Figura 6.1 A, se detectó la presencia de las bandas D y G correspondientes al óxido de grafeno parcialmente reducido (rGO). A partir del cálculo de las relaciones entre las áreas de estos dos picos, se detectó un aumento de la relación  $A_D/A_G$  en todos los nanocomposites como consecuencia de la interacción entre el  $\text{TiO}_2$  y el rGO.

Por otro lado, la introducción de rGO en los fotocatalizadores híbridos de  $\text{TiO}_2$ -rGO no alteró el valor del band-gap (3,1 eV) del fotocatalizador, calculado a partir de medidas de espectroscopía UV-vis por reflectancia difusa.

Tras analizar los difractogramas de rayos-X, representados en la Figura 6.1 B, no se detectó la presencia de ningún pico asociado al GO en ninguno de los nanocomposites estudiados, lo cual podría estar relacionado con la reducción del GO durante la síntesis hidrotérmal, o con su relativa baja cantidad. Se observa en todos los casos, una estructura cristalina caracterizada por la presencia de mezcla de fases de anatasa y rutilo, análoga a la estructura cristalina del fotocatalizador sin rGO (P25-rGO 0%).

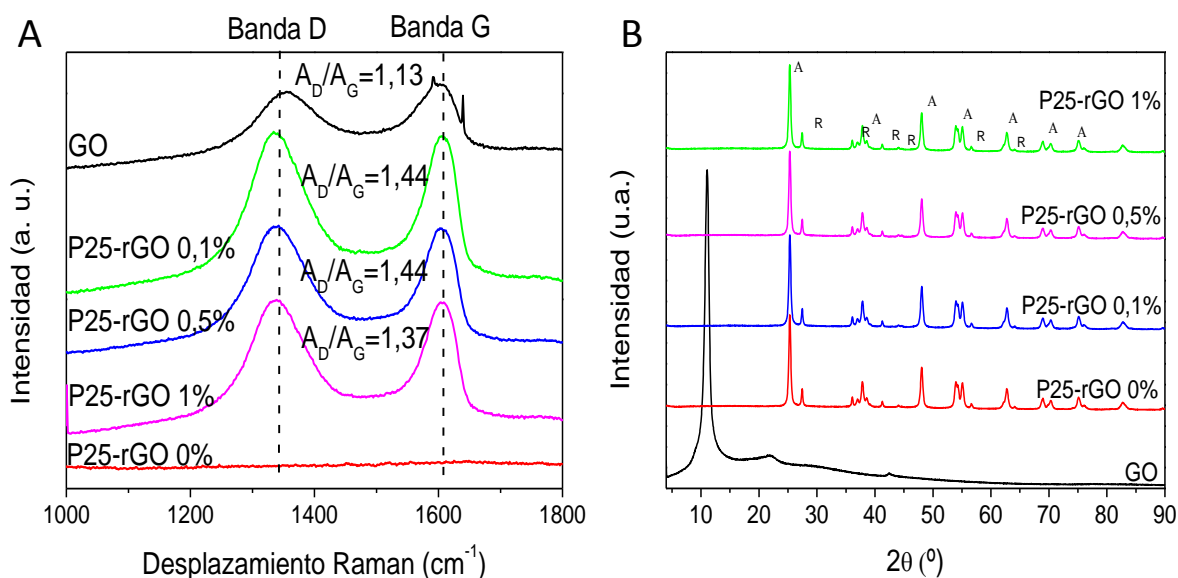


Figura 6.1. Espectros Raman (A) y difractogramas de rayos X (B) de GO, P25-rGO 0%, P25-rGO 0,1%, P25-rGO 0,5% y P25-rGO 1%.

El tamaño y morfología de las partículas del  $\text{TiO}_2$  en los nanocomposites de  $\text{TiO}_2$ -rGO se analizaron de forma cualitativa llevando a cabo análisis mediante Microscopía Electrónica de Transmisión (TEM) y Microscopía de Barrido (SEM). Un análisis detallado, a partir de estas técnicas, requiere observar varias partículas en distintas regiones de la muestra. En las Figuras 6.2 A y 6.2 B, se muestran como ejemplo, dos micrografías, una TEM y otra SEM, representativas del fotocatalizador híbrido P25-rGO



0,5% que permitieron establecer que el tamaño de las partículas primarias de  $\text{TiO}_2$ , en el nanocomposite, era del orden de 15-40 nm. El hecho de que las partículas de dióxido de titanio estuviesen cubiertas por óxido de grafeno reducido (rGO) demuestra una íntima interacción entre ambos.

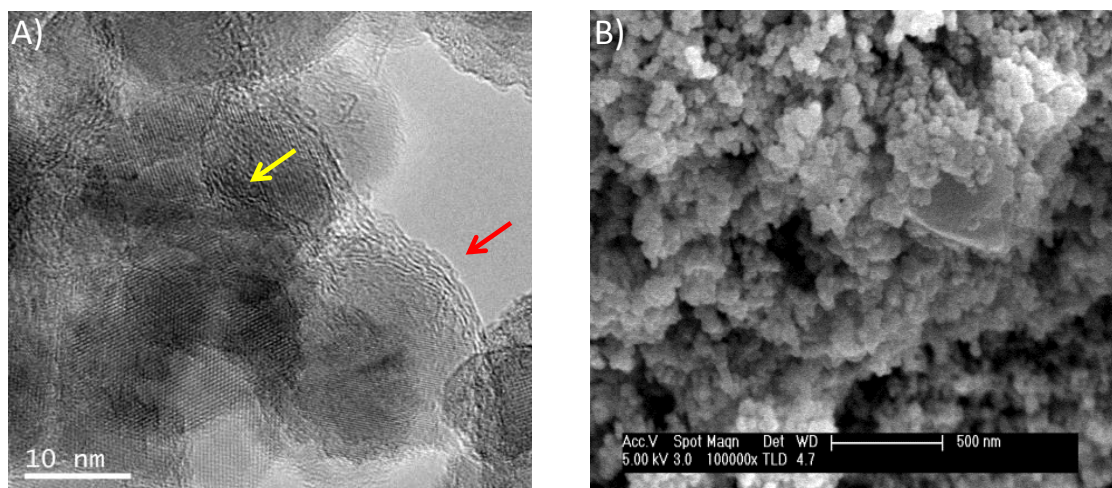


Figura 6.2. Imagen HRTEM (C) e imagen SEM del fotocatalizador P25-rGO 0,5%.

Se determinó el valor del potencial de las bandas de conducción y valencia para así evaluar si la modificación del  $\text{TiO}_2$  con rGO provocaba un desplazamiento de las mismas. Para ello, se llevaron a cabo medidas de Espectroscopia de Impedancia Electroquímica (EIS) y se ajustaron los espectros correspondientes a los diferentes potenciales al circuito Randles. Los valores obtenidos de los potenciales de las bandas de conducción y valencia fueron muy similares (-0,38 y 2,75 V vs. RHE, respectivamente) para todos los fotocatalizadores híbridos estudiados, lo cual es indicativo de que la modificación del  $\text{TiO}_2$  con rGO no alteraba ni el nivel de Fermi, ni las posiciones de las bandas de conducción ni de valencia.

La eficiencia en la separación de cargas, en todos los nanocomposites estudiados, se analizó mediante medidas de EIS y análisis de la fotocorriente inducida, cuyos resultados vienen representados en las Figuras 6.3 A y 6.3 B, respectivamente. A través de las medidas de EIS se observa que la presencia de rGO en el nanocomposite redujo la resistencia a la transferencia de carga a través de la interfase semiconductor-electrolito. Además, los valores de fotocorriente obtenidos para los fotocatalizadores P25-rGO 1% y P25-rGO 0,5% ( $6,5$  y  $3,75 \mu\text{A}\cdot\text{cm}^{-2}$ , respectivamente) fueron 10 y 6 veces mayores que el obtenido para el caso del fotocatalizador sin rGO (P25-rGO 0%). Estos resultados implican que la modificación del  $\text{TiO}_2$  con rGO da lugar, en todos los casos, a una mayor eficiencia en la separación de los pares  $e^-/h^+$ , lo

que introducirá mejoras en su fotoactividad catalítica. También se realizaron voltamperometrías de barrido lineales para medir las corrientes de reducción de oxígeno, ya que en la mayoría de las aplicaciones fotocatalíticas el oxígeno es el principal aceptor de electrones disponible. Por tanto, es crucial estudiar el proceso mediante el cual el oxígeno es reducido por los electrones foto-generados y la capacidad de los fotocatalizadores para llevar a cabo dicha reducción. Los valores de la corriente de reducción aumentaban al incrementar la cantidad de rGO presente en el nanocomposite, como se puede apreciar en la Figura 6.3 C, como consecuencia del descenso de la resistencia a la transferencia de carga.

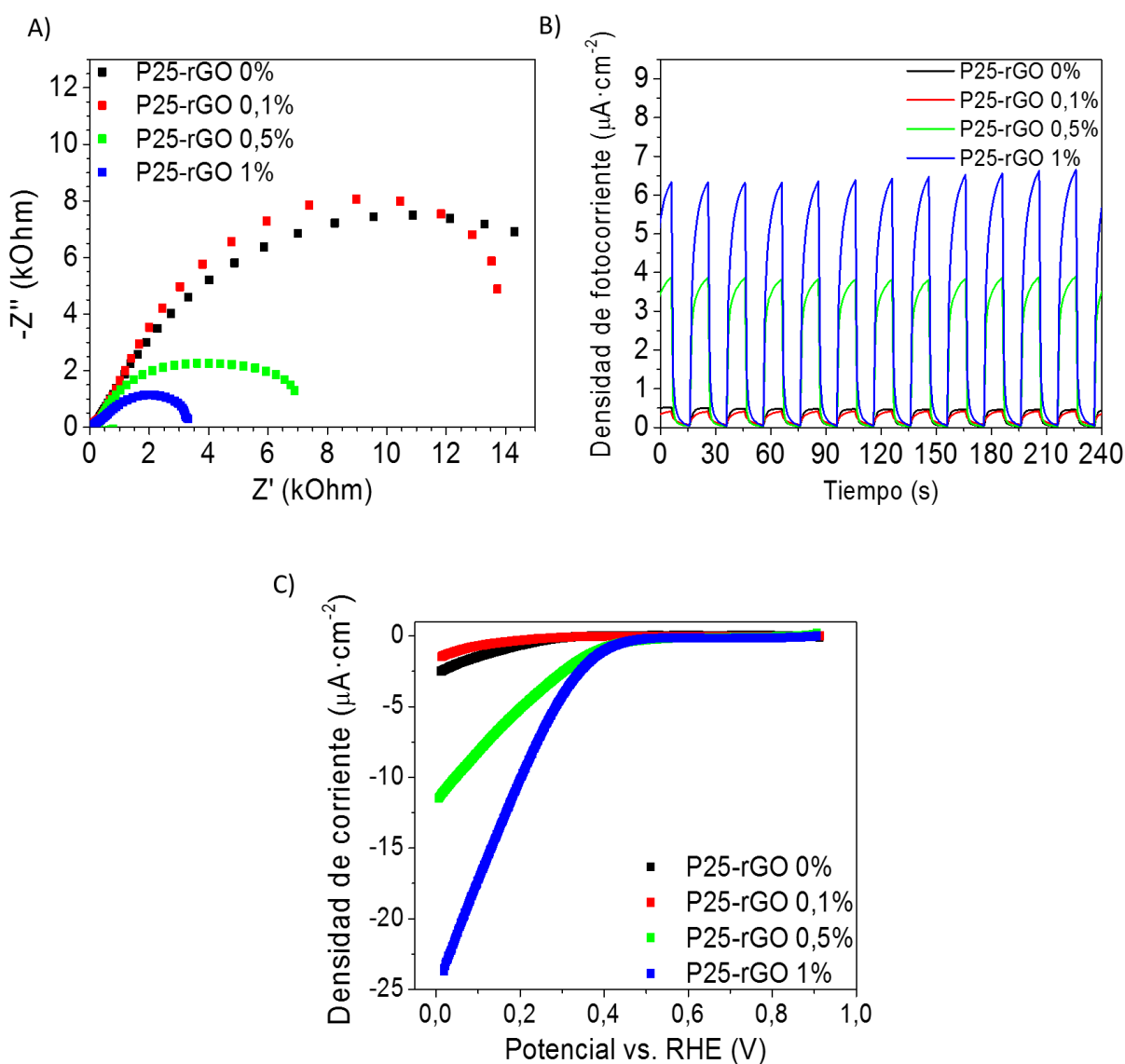


Figura 6.3. Representación de Nyquist (A), donde  $Z'$  y  $Z''$  son las componentes real e imaginaria de la impedancia total,  $Z$ ; (B) curvas de densidad de fotocorriente frente al tiempo, al ser los fotocatalizadores irradiados con luz UV-vis; (C) corrientes de reducción de  $\text{O}_2$  frente al potencial aplicado para los diferentes fotocatalizadores de  $\text{TiO}_2$ -rGO estudiados.



La actividad fotocatalítica se evaluó mediante reacciones de fotodegradación de ácido oxálico (1mM) utilizando radiación UV-A ( $I=1,0 \text{ mW}\cdot\text{cm}^{-2}$ ). El seguimiento de la reacción superficial se realizó mediante espectroscopía de infrarrojo por transformada de Fourier, con un accesorio de reflexión total atenuada (ATR-FTIR). Se detectó una mayor cantidad de ácido oxálico adsorbido en oscuridad en los nanocomposites con mayor proporción de rGO, lo cual podría estar relacionado con la mayor afinidad del rGO. Se siguió la evolución de los picos correspondientes al ácido oxálico adsorbido durante dos horas de irradiación y se calcularon las correspondientes constantes cinéticas aparentes de primer orden, obteniendo los siguientes valores:  $5,2\cdot 10^{-3}$ ,  $5,5\cdot 10^{-3}$ ,  $5,7\cdot 10^{-3}$  y  $6,8\cdot 10^{-3} \text{ min}^{-1}$  para P25-rGO 0%, P25-rGO 0,1%, P25-rGO 0,5% y P25-rGO 1%, respectivamente. El ligero aumento detectado en el valor de la constante cinética aparente al aumentar el contenido de rGO en el nanocomposite puede deberse a una reducción más eficiente del oxígeno.

También se realizaron estudios de actividad fotocatalítica de los fotocatalizadores híbridos estudiados en suspensión. Los fotocatalizadores se dispersaron en disoluciones de ácido oxálico 1 mM y se iluminó el sistema de reacción con 4 lámparas fluorescentes UV-A (con una intensidad de  $1,0 \text{ mW}\cdot\text{cm}^{-2}$ ). Sin embargo, aunque el fotocatalizador P25-rGO 0,5% fue el que dio lugar a los mejores resultados de fotodegradación, las diferencias encontradas en la evolución de la foto-oxidación del ácido oxálico entre los diferentes fotocatalizadores fueron muy pequeñas, como se puede observar en la Figura 6.4 A.

La influencia de la cantidad de rGO presente en el nanocomposite, en la generación de radicales  $\text{HO}^\bullet$  y de radicales superóxido ( $\text{O}_2^{\bullet-}$ ), se evaluó a partir de medidas de Espectroscopía de Resonancia Paramagnética Electrónica (EPR). Para ello se utilizó 5,5-dimetil-1-pirrolina N-óxido (DMPO) como atrapador de espín. En la Figura 6.4 B vienen representadas comparativamente la integración de las áreas de los espectros de  $\text{DMPO-HO}^\bullet$  y  $\text{DMPO-O}_2^{\bullet-}$ . Cuando los fotocatalizadores híbridos fueron suspendidos en disoluciones acuosas saturadas en  $\text{O}_2$ , las áreas correspondientes a  $\text{DMPO-HO}^\bullet$  y  $\text{DMPO-O}_2^{\bullet-}$  fueron muy similares en todos los casos, siendo el P25-rGO 0,5% el que alcanzó la mayor área integrada de ambos radicales,  $\text{HO}^\bullet$  y  $\text{O}_2^{\bullet-}$ . Este ligero aumento se atribuyó a una separación más eficiente de las cargas fotogeneradas y a su mayor capacidad para reducir el  $\text{O}_2$ . Sin embargo, en disoluciones acuosas saturadas en  $\text{N}_2$ , los valores del área integrada del espectro del  $\text{DMPO-HO}^\bullet$  obtenidos con el P25-rGO 0,1%, P25-rGO 0,5% y P25-rGO 1% triplicaron el área obtenida con el P25-rGO 0%. Estos resultados indican que en disoluciones con

muy bajas concentraciones de  $O_2$  los nanocomposites son capaces de generar mayor cantidad de radicales  $HO^\bullet$ .

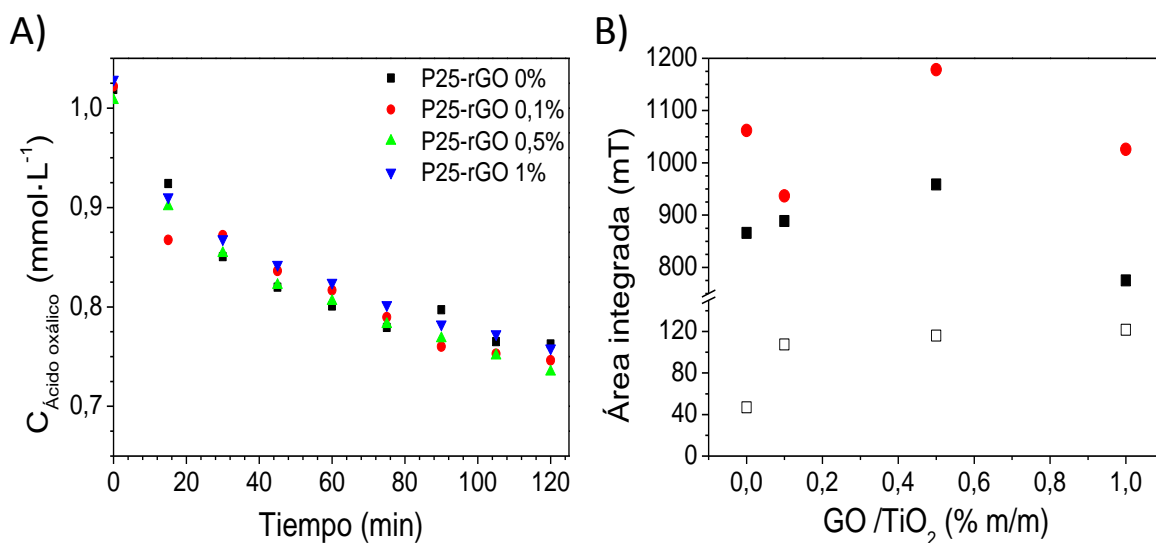


Figura 6.4. (A) Evolución de la concentración de ácido oxálico al utilizar los fotocatalizadores en suspensión y radiación UV-A; (B) área integrada de la señal medida mediante EPR correspondiente a los aductos  $^{\bullet}DMPO-OH$  en  $O_2$  (■),  $^{\bullet}DMPO-O_2^-$  en  $O_2$  (●) y  $^{\bullet}DMPO-OH$  en  $N_2$  (□) en función de la cantidad de GO añadida en la síntesis de los nanocomposites P25-rGO.

Dada la importancia de los procesos de atrapamiento y relajación, recombinación y transferencia de las especies fotogeneradas en el proceso fotocatalítico, se realizaron medidas de Espectroscopía de Absorción Transitoria (TAS) en la escala de microsegundos, cuyos resultados se pueden ver en la Figura 6.5. Las medidas del fotocatalizador en polvo en atmósferas de  $N_2$  y  $O_2$  se llevaron a cabo para relacionar y comparar estos resultados con los obtenidos en EPR. Tras ajustar los resultados al modelo propuesto por Sieland y colaboradores [22], se comprobó que el rGO actuaba como aceptor de electrones, produciéndose la transferencia de  $e^-$  del  $TiO_2$  al rGO en la escala de picosegundos. Esta transferencia facilita la separación de cargas en presencia de  $N_2$ , lo que explica el aumento del área del espectro del  $DMPO-HO^\bullet$  obtenido incluso con el fotocatalizador P25-rGO 0,1%, como se representa esquemáticamente en la Figura 6.6 A. Sin embargo, en presencia de  $O_2$ , que también actúa como aceptor de electrones, se dificulta la transferencia de electrones desde el  $TiO_2$  al rGO (representado esquemáticamente en la Figura 6.6 B), disminuyendo, por tanto, la velocidad de recombinación de los pares  $e^-/h^+$ . De manera que puede concluirse que, en presencia de  $O_2$ , la diferencia entre la generación de  $O_2^{\bullet-}$  y  $HO^\bullet$  alcanzada por el P25-rGO 0% y el resto de los nanocomposites de P25-rGO no es tan relevante.

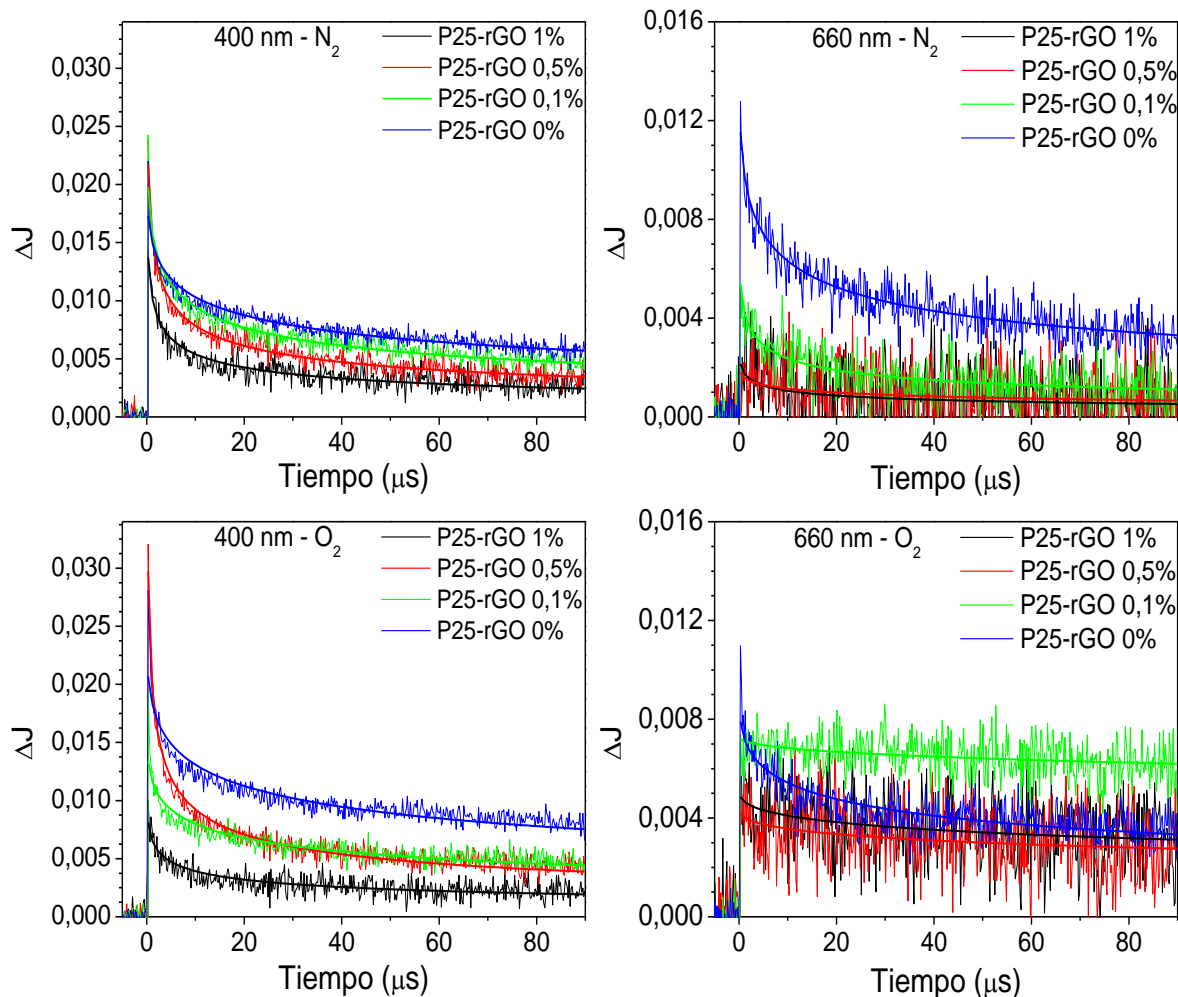


Figura 6.5. Evolución de la absorción transitoria, medida en atmósferas de  $N_2$  y  $O_2$  a 400 nm y 660 nm, de P25-rGO 0%, P25-rGO 0,1%, P25-rGO 0,5% and P25-rGO 1%.

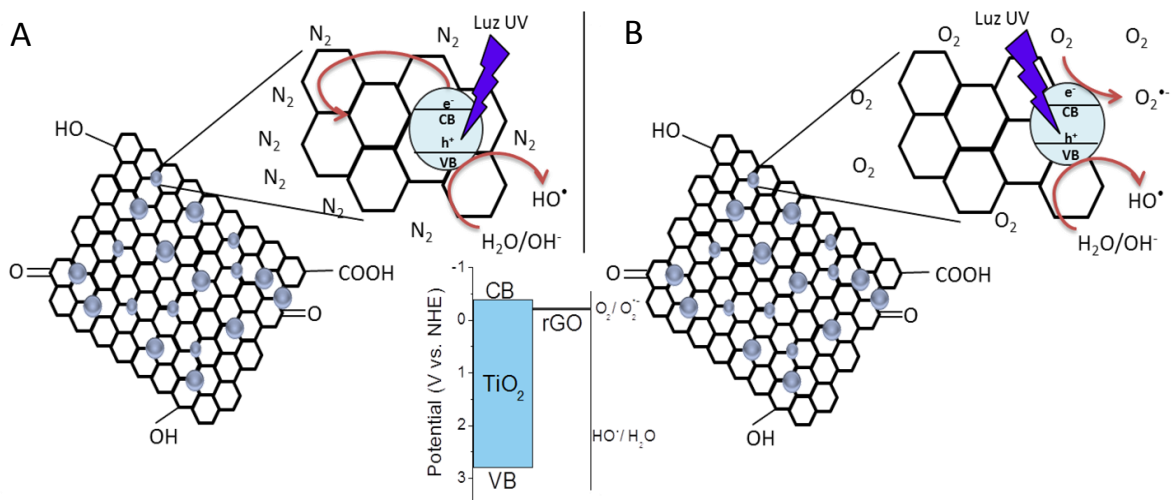


Figura 6.6. Esquema de la transferencia de cargas fotogeneradas en el fotocatalizador P25-rGO en una suspensión saturada de  $N_2$  y  $O_2$ .

A partir de los resultados obtenidos se concluye que la presencia de rGO permite alcanzar mayores eficiencias en la separación de las cargas fotogeneradas y un descenso de la resistencia de la transferencia de carga en la interfase electrodo-electrolito. Sin embargo, esas mejoras no contribuyen a alcanzar una mayor fotoactividad en la fotodegradación de ácido oxálico.

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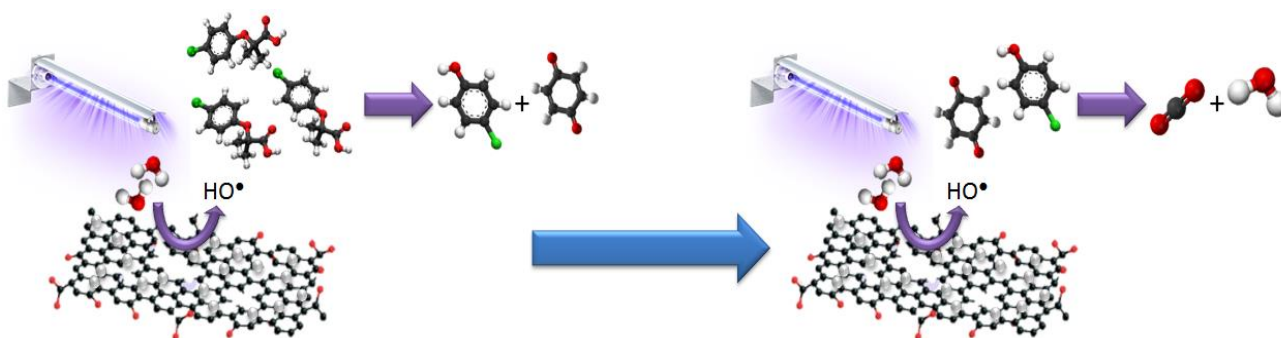
# Capítulo 7:

## Influencia de las propiedades ópticas de nanocomposites de TiO<sub>2</sub>-rGO en la actividad fotocatalítica y su eficiencia para fotodegradar un contaminante emergente: Modelado cinético

*"Influence of TiO<sub>2</sub>-rGO optical properties in the photocatalytic activity and efficiency to photodegrade an emerging pollutant". Applied Catalysis B: Environmental 246: 1-11.*

*"TiO<sub>2</sub>-rGO photocatalytic degradation of an emerging pollutant: kinetic modelling and determination of intrinsic kinetic parameters". Enviado para su publicación al Applied Catalysis B: Environmental.*

Los dos últimos objetivos desarrollados en esta Tesis Doctoral consisten en analizar la eficiencia cuántica obtenida por diferentes fotocatalizadores de TiO<sub>2</sub>-rGO en la fotodegradación de ácido clofíbrico, así como desarrollar un modelo cinético intrínseco con el que simular la evolución de ácido clofíbrico y sus principales intermedios. Para alcanzarlos se han estimado las propiedades ópticas de una serie de fotocatalizadores de TiO<sub>2</sub>-rGO con el objetivo de evaluar el efecto de la unión del rGO en la radiación absorbida. En último lugar, se han obtenido los correspondientes parámetros cinéticos intrínsecos con los que modelar la fotorreacción estudiada.





Como se ha mencionado en los capítulos anteriores, el uso del TiO<sub>2</sub> como fotocatalizador presenta ciertas limitaciones en aplicaciones fotocatalíticas, como por ejemplo, su capacidad de absorber fotones en un intervalo pequeño de longitudes de onda o sus bajas eficiencia cuánticas [1]. Por esa razón, a lo largo de estos capítulos se ha modificado al TiO<sub>2</sub> con óxido de grafeno reducido (rGO) y se ha analizado la influencia del rGO en la velocidad de recombinación y en la generación de las especies oxidantes en el proceso fotocatalítico estudiado.

Por otra parte, para llegar a alcanzar una aplicación comercial de los procesos fotocatalíticos para el tratamiento de aguas residuales, es necesario el desarrollo de modelos cinéticos precisos con los que diseñar y escalar correctamente los reactores fotocatalíticos [2, 3]. Como consecuencia, es imprescindible desarrollar modelos cinéticos intrínsecos, basados en un mecanismo de reacción fotocatalítico, con una dependencia explícita de la radiación absorbida en cada punto del reactor para diseñar y escalar los procesos fotocatalíticos. Previamente, para poder calcular los perfiles de radiación, mediante la resolución de la ecuación de transferencia radiativa (RTE), es necesario obtener información relacionada con las propiedades ópticas de los fotocatalizadores [4]. Sin embargo, hasta ahora no hay estudios en los cuales se haya analizado la influencia de la cantidad de rGO presente en el nanocomposite de TiO<sub>2</sub>-rGO en sus propiedades ópticas o en su eficiencia cuántica.

En los últimos años, el desarrollo de nuevos métodos de análisis ha permitido alertar de la presencia de un tipo de contaminantes, potencialmente peligrosos, denominados globalmente como emergentes [5-7], los cuales no han sido regulados ni incluidos entre los parámetros de monitorización de la calidad de las aguas habituales, pero que han sido detectados en diversos efluentes en concentraciones del orden de micro a ng·L<sup>-1</sup>. Estos contaminantes emergentes se definen como contaminantes previamente desconocidos o no reconocidos como tales, cuya presencia en el medio ambiente no es necesariamente nueva pero si la preocupación por su posibles consecuencias. Por tanto, su estudio se encuentra entre las líneas de investigación prioritarias de los organismos dedicados a la protección de la salud pública y medioambiental, tales como la Organización Mundial de la Salud (OMS), la Agencia para la Protección del Medio Ambiente (EPA), o la Unión Europea. Este tipo de contaminantes pueden dañar a los ecosistemas acuáticos y afectar a la salud de los seres humanos, debido a que pueden alterar la estructura de distintos microbios y promover su resistencia a antibióticos [8, 9].



Por tanto, el objetivo de este capítulo ha sido estudiar la influencia que diferentes proporciones de TiO<sub>2</sub>:GO provocaba en las propiedades ópticas de fotocatalizadores de TiO<sub>2</sub>-rGO. Una vez estimadas y calculadas, fueron utilizadas para obtener los correspondientes perfiles de radiación absorbida por cada composite. Se analizó también, el efecto que la concentración de fotocatalizador y la relación de TiO<sub>2</sub>:GO en los composites estudiados ejercían en la fotodegradación catalítica de ácido clofíbrico (AC), un metabolito de un compuesto farmacéutico, y en las eficiencias cuánticas. En último lugar, se ha desarrollado un modelo cinético intrínseco, para obtener los parámetros cinéticos correspondientes al fotocatalizador más activo en la reacción fotocatalítica estudiada.

Los nanocomposites de TiO<sub>2</sub>-rGO estudiados se sintetizaron mediante un procedimiento hidrotérmal a partir del dióxido de titanio comercial P25 de Evonik, con diferentes relaciones másicas de GO:TiO<sub>2</sub>, denominados a lo largo de este capítulo como P25-rGO 0%, P25-rGO 0,1%, P25-rGO 0,5% y P25-rGO 1%. La síntesis de estos nanocomposites fue optimizada previamente para reducir su duración, siendo 120 °C y 3h las condiciones óptimas. Las principales propiedades de estos nanocomposites se obtuvieron a partir de diferentes estudios de caracterización químico-física. A partir de los difractogramas de rayos X, cuyos resultados se muestran en la Figura 7.1 A, se dedujo que la presencia de rGO en el nanocomposite no modificó la estructura cristalina detectada en el fotocatalizador sin rGO (P25-rGO 0 %), observándose en todos los casos una mezcla cristalina de fases anatasa y rutilo. Además, el pico asociado al GO ( $2\theta=11,1^\circ$ ) prácticamente desapareció después de la síntesis hidrotérmal, lo cual puede ser indicativo de su reducción. Al igual que en el capítulo anterior, al comparar los espectros Raman, representados en la Figura 7.1 B, no se observó ningún cambio en el espectro del rGO con respecto al del GO, indicando que incluso después de la reducción se mantuvo la estructura desordenada. A su vez, se detectó un aumento del área de la banda D con respecto a la de la banda G,  $A_D/A_G$ , debido a la interacción entre el TiO<sub>2</sub> y el rGO, como se observa en la Figura 7.1 B. La presencia de rGO en el fotocatalizador no implicó una reducción del valor del band-gap (3,1 eV), obtenido mediante medidas de espectroscopía UV-vis de reflectancia difusa, como queda reflejado en la Figura 7.1 C, ni modificó el valor del área BET del fotocatalizador sin óxido de grafeno reducido (P25-rGO 0 %) ( $57 \text{ m}^2\cdot\text{g}^{-1}$ ). Por último, se analizó la morfología y estructura de los nanocomposites estudiados mediante microscopía electrónica de barrido (SEM) y microscopía electrónica de transmisión (TEM). En la Figura 7.2 A y B se muestran como ejemplo, dos micrografías TEM, representativas del fotocatalizador híbrido P25-rGO 1%, donde se

observa que el tamaño de las partículas primarias de  $\text{TiO}_2$  se encontraba entre 20 y 45 nm, las cuales estaban recubiertas por óxido de grafeno reducido (rGO), lo que favorece un íntimo contacto entre el  $\text{TiO}_2$  y el óxido de grafeno reducido.

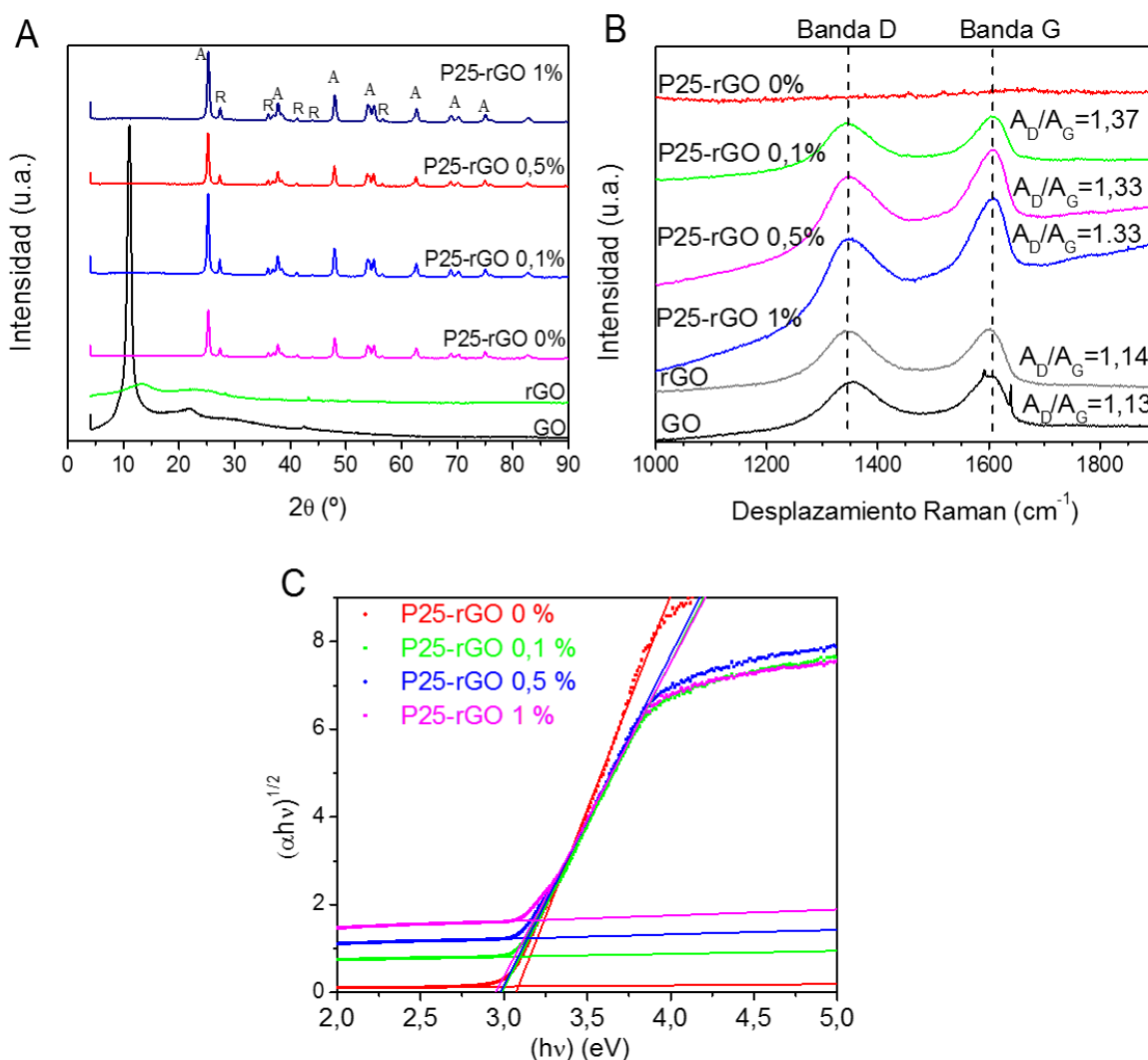


Figura 7.1. Difractogramas de rayos X (A) y espectros Raman (B) de GO, rGO, P25-rGO 0%, P25-rGO 0,1%, P25-rGO 0,5% y P25-rGO 1%. Representación de Tauc para obtener los valores de band-gap (C).

Las medidas de fotoactividad catalítica se llevaron a cabo en un sistema de reacción constituido por un fotorreactor, una bomba peristáltica, un baño termostatzado y un tanque de almacenamiento de 1 L, recubierto por una camisa por la que se pasaba agua en continuo para mantener una temperatura de 25 °C durante todo el experimento. El fotorreactor estaba recubierto interiormente de teflón, presentaba geometría cilíndrica y tenía en sus extremos dos ventanas de vidrio borosilicato. Cada una de las ventanas se irradiaba con un conjunto de 4 lámparas (TL 4W/08 Black Light UV-A de Philips), las cuales presentaban un espectro de emisión en el intervalo de

longitudes de onda de 310-420 nm, con un máximo alrededor de 355 nm. Todos los experimentos de fotodegradación catalítica de ácido clofibrico se realizaron en condiciones ambientales de presión y temperatura, con una concentración inicial de contaminante de  $20 \text{ mg}\cdot\text{L}^{-1}$ .

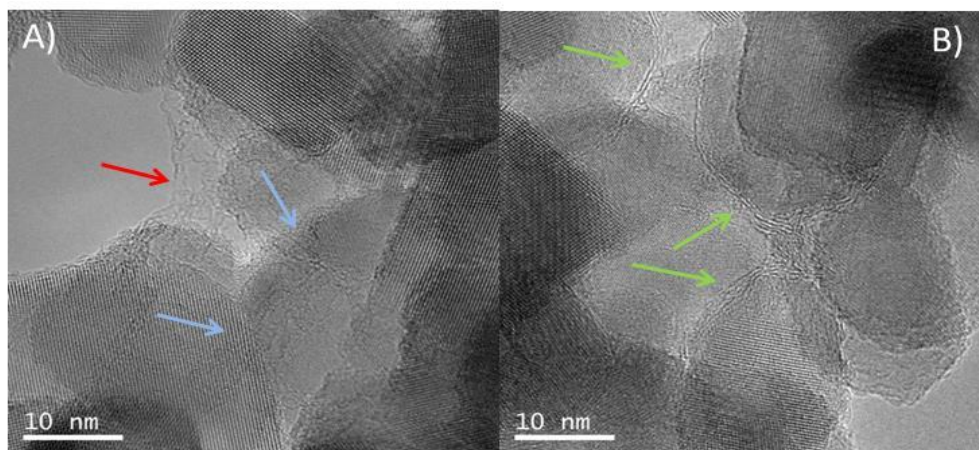


Figura 7.2. Imagen HRTEM del fotocatalizador P25-rGO 1% (A y B).

Se determinaron los flujos de radiación incidente al reactor a cada longitud de onda, en las mismas condiciones experimentales en las que se llevaron a cabo todas las reacciones de fotodegradación catalítica, realizando medidas de actinometría y utilizando el espectro de emisión de las lámparas usadas. Estos flujos de radiación incidente al fotorreactor se muestran en la Figura 7.3.

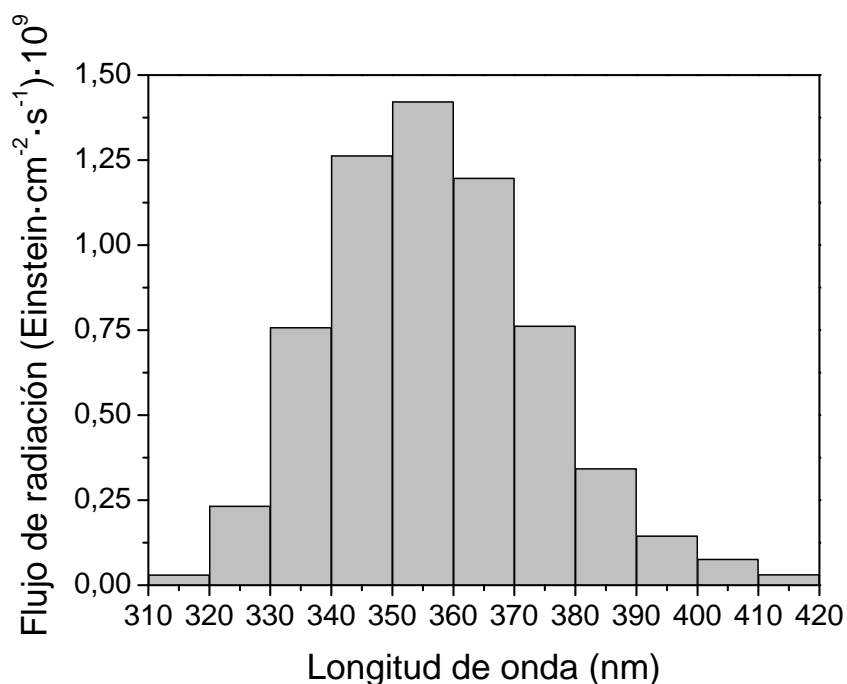


Figura 7.3. Intensidad incidente al reactor a cada longitud de onda.

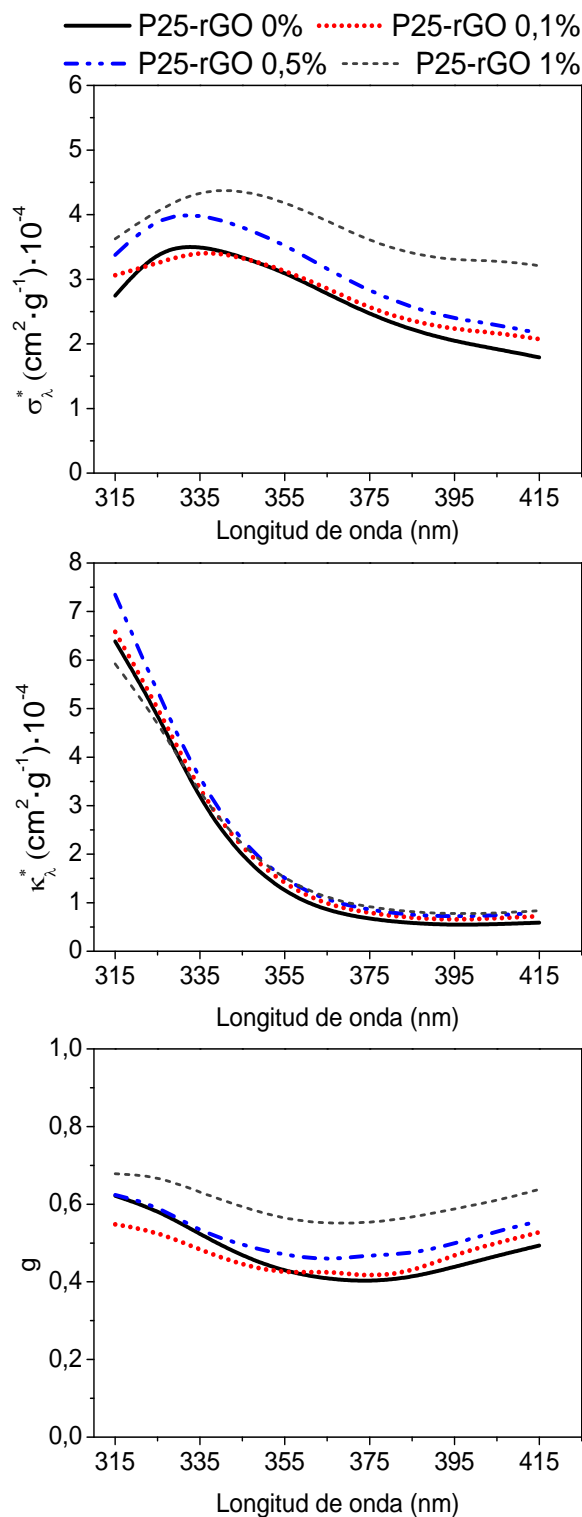


Figura 7.4. Propiedades ópticas específicas de todos los nanocomposites  $\text{TiO}_2$ -rGO estudiados. De arriba a abajo: Coeficiente de *scattering* ( $\sigma_{\lambda}$ ), coeficiente de *absorción* ( $\kappa_{\lambda}$ ) y factor de asimetría ( $g$ ).

Por otro lado, se estimaron las propiedades ópticas de las suspensiones de  $\text{TiO}_2$  y  $\text{TiO}_2$ -rGO, que incluyen el factor de asimetría ( $g$ ) y los coeficientes volumétricos de extinción ( $\beta_{\lambda}$ ), absorción ( $\kappa_{\lambda}$ ) y *scattering* ( $\sigma_{\lambda}$ ), cuyos valores han sido representados

en la Figura 7.4. Para ello se realizaron una serie de medidas experimentales mediante espectroscopía UV-vis en el intervalo de 315 a 415 nm. Además, fue necesario resolver un modelo unidimensional-unidireccional de la ecuación de transferencia radiativa (RTE) [4] mediante el método de Monte Carlo (MC) [10]. Se observó un aumento de los coeficientes de extinción y *scattering*, por debajo de 325 nm, al aumentar la cantidad añadida de GO en la síntesis de los fotocatalizadores de TiO<sub>2</sub>-rGO. De hecho, la presencia de rGO pareció afectar más al coeficiente de *scattering* que al coeficiente de absorción. Una mayor relación de rGO:TiO<sub>2</sub> en el nanocomposite favoreció la dispersión de la radiación en el mismo sentido en que se propaga, como se aprecia por los mayores valores del factor de simetría (valores de  $g$  de 0,4-0,63 para P25-rGO 0% a 0,55-0,68 para P25-rGO 1%).

Respecto a los resultados de fotodegradación catalítica de ácido clofibrico, tras 6 horas de reacción solo se detectaron trazas del ácido clofibrico y de sus correspondientes intermedios, 4-clorofenol y p-benzoquinona, al usar concentraciones suficientemente altas de catalizador. A partir del cálculo de las constantes cinéticas aparentes de primer orden se observó que la actividad de los fotocatalizadores seguía la siguiente secuencia: P25-rGO 0,5% > P25-rGO 0,1%  $\approx$  P25-rGO 0% > P25-rGO 1%. De manera que puede establecerse que un exceso de rGO en el nanocomposite conllevó un descenso en la velocidad de fotodegradación.

Una vez conocidos los flujos de radiación incidentes y las correspondientes propiedades ópticas de los fotocatalizadores estudiados, se determinaron los perfiles de radiación dentro del fotorreactor, mediante la resolución de la RTE. A continuación, se calcularon los valores de la radiación absorbida en cada punto del reactor (LVRPA), a partir de los cuales se calculó el valor de la velocidad volumétrica global de absorción de fotones (VRPA). En líneas generales, los valores de VRPA de los diferentes fotocatalizadores fueron siempre muy similares e incrementaron al aumentar la concentración de fotocatalizador. Para analizar la influencia de la presencia de óxido de grafeno reducido en la eficiencia cuántica, se compararon los resultados obtenidos con el catalizador más fotoactivo, P25-rGO 0,5%, con el fotocatalizador sin rGO, P25-rGO 0%, y estos valores están recogidos en la Tabla 7.1. La mayor eficiencia cuántica se obtuvo al utilizar 100 mg·L<sup>-1</sup> de P25-rGO 0,5%, cuyo valor incrementó un 11% con respecto al obtenido con el P25-rGO 0%. Este aumento de la eficiencia cuántica se ha asociado a una reducción de la recombinación de las cargas fotogeneradas debido a la capacidad del rGO de actuar como aceptor de electrones.

Tabla 7.1. Influencia de la concentración de P25-rGO 0% y P25-rGO 0,5% en la velocidad inicial de fotodegradación de AC  $\langle -r_{AC}(x, t_0) \rangle_{V_R}$ , VRPA y eficiencia cuántica ( $\eta$ ).

$C_{Cat}$ (mg·L <sup>-1</sup> )	$\langle -r_{AC}(x, t_0) \rangle_{V_R}$ (mol·s <sup>-1</sup> ·cm <sup>-3</sup> ) · 10 <sup>11</sup>		VRPA (Einstein·s <sup>-1</sup> ·cm <sup>-3</sup> ) · 10 <sup>9</sup>		$\eta$ (mol·Einstein <sup>-1</sup> ) · 10 <sup>2</sup>	
	P25-rGO 0%	P25-rGO 0,5%	P25-rGO 0%	P25-rGO 0,5%	P25-rGO 0%	P25-rGO 0,5%
	25	7,81	8,22	4,51	4,62	1,73
50	9,66	9,68	4,91	4,94	1,97	1,96
100	10,84	12,03	4,97	4,96	2,18	2,42

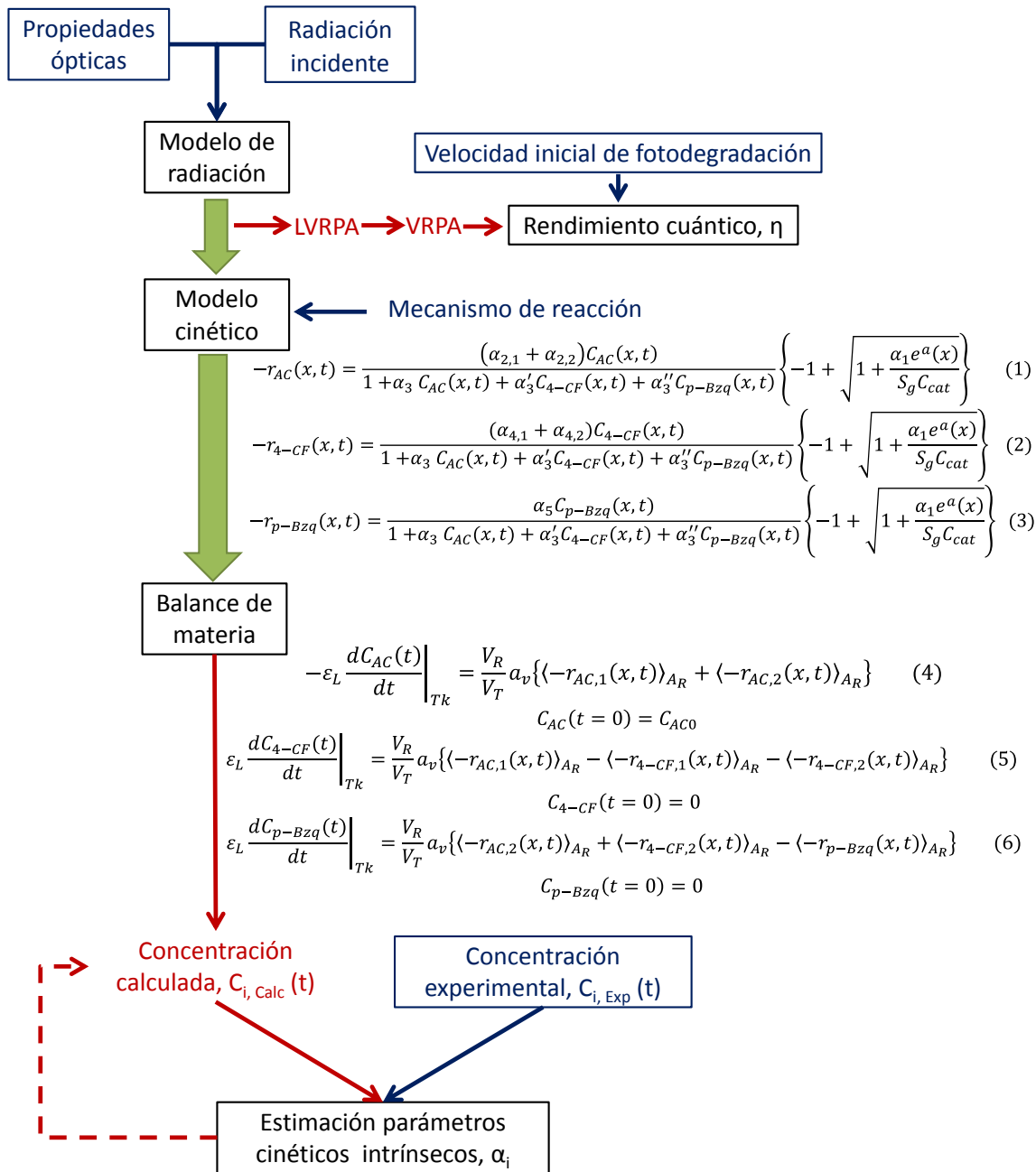


Figura 7.5. Esquema del procedimiento seguido para estimar los parámetros cinéticos intrínsecos relativos a la fotodegradación catalítica de ácido clofibrico.

El modelo cinético intrínseco utilizado para simular la evolución del ácido clofíbrico usando el fotocatalizador híbrido más activo, P25-rGO 0,5%, se desarrolló a partir del esquema resumido en la Figura 7.5. Para su resolución se recurrió a las propiedades ópticas estimadas previamente y a los valores de los flujos de radiación incidentes, para así calcular los valores de la radiación absorbida en cada punto del fotorreactor (LVRPA). Para simular este proceso de fotodegradación y obtener la concentración teórica de cada contaminante a los respectivos tiempos de reacción, es necesario, además de conocer los valores de LVRPA, proponer los correspondientes balances de materia y derivar las ecuaciones cinéticas de fotodegradación del ácido clofíbrico, 4-clorofenol y p-benzoquinona. Las ecuaciones cinéticas se derivaron a partir de un mecanismo de reacción, en el que se consideró que los principales responsables de la fotodegradación fueron los radicales hidroxilo generados a partir de la oxidación del agua. Por último, a partir de los resultados anteriores se compararon los valores teóricos de concentración del ácido clofíbrico, 4-clorofenol y p-benzoquinona con los correspondientes valores experimentales para estimar los parámetros cinéticos ( $\alpha_1$ ,  $\alpha_{2,1}$ ,  $\alpha_{2,2}$ ,  $\alpha_{4,1}$ ,  $\alpha_{4,2}$ ,  $\alpha_5$ ) mediante regresiones múltiples no lineales.

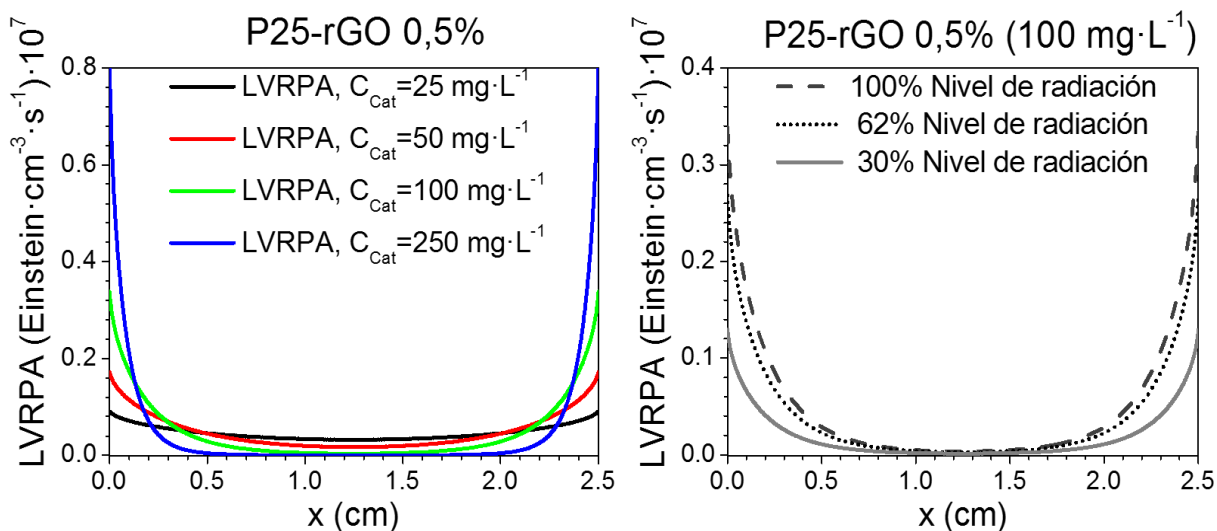


Figura 7.6. Velocidad volumétrica local de absorción de fotones (LVRPA) al usar diferentes concentraciones de P25-rGO 0,5% y diferente niveles de radiación.

Los perfiles de la velocidad volumétrica local de absorción de fotones (LVRPA) para las diferentes condiciones de operación en las que se llevaron a cabo los estudios de fotoactividad vienen representados en la Figura 7.6. Se observó que incluso cuando se utilizaron bajas concentraciones de nanocomposite, la mayor parte de la radiación era absorbida cerca de las paredes del reactor. Además, se estimaron los valores de LVRPA con diferentes niveles de irradiación (100%, 62% y 30%), los cuales se



consiguieron mediante la utilización de filtros, y 100 mg·L<sup>-1</sup> de P25-rGO 0,5%, que fue la concentración de nanocomposite con la que se alcanzó la mayor velocidad de fotodegradación y eficiencia cuántica. Como era de esperar, menores niveles de radiación implicaron un mayor volumen del reactor donde no se produjo absorción de la luz. De manera que utilizando solo el 30% de la radiación total, la conversión de ácido clofíbrico después de 2 h de irradiación fue próxima al 41%, mientras que se alcanzó una conversión del 73% al emplear el 100% de la radiación.

Tabla 7.2. Parámetros cinéticos estimados para el nanocomposite P25-rGO 0,5 %.

	Parámetro	Valor	Unidades
Modelo con 6 parámetros	$\alpha_1$	$5.77 \cdot 10^{11}$	$\text{s cm}^2 \text{ Einstein}^{-1}$
	$\alpha_{2,1}$	$1.72 \cdot 10^{-6}$	$\text{cm s}^{-1}$
	$\alpha_{2,2}$	$2.62 \cdot 10^{-6}$	$\text{cm s}^{-1}$
	$\alpha_{4,1}$	$3.78 \cdot 10^{-6}$	$\text{cm s}^{-1}$
	$\alpha_{4,2}$	$1.67 \cdot 10^{-7}$	$\text{cm s}^{-1}$
	$\alpha_5$	$3.91 \cdot 10^{-5}$	$\text{cm s}^{-1}$
	RMSE	10.8	%
Modelo con 5 parámetros	$\alpha_{2,1}$	1.03	$\text{cm}^2 \text{ s}^{-1/2} \text{ Einstein}^{-1/2}$
	$\alpha_{2,2}$	1.61	$\text{cm}^2 \text{ s}^{-1/2} \text{ Einstein}^{-1/2}$
	$\alpha_{4,1}$	2.56	$\text{cm}^2 \text{ s}^{-1/2} \text{ Einstein}^{-1/2}$
	$\alpha_{4,2}$	0.02	$\text{cm}^2 \text{ s}^{-1/2} \text{ Einstein}^{-1/2}$
	$\alpha_5$	22.52	$\text{cm}^2 \text{ s}^{-1/2} \text{ Einstein}^{-1/2}$
	RMSE	16.3	%

Se desarrollaron las ecuaciones cinéticas de la fotodegradación de ácido clofíbrico, 4-clorofenol y p-benzoquinona. Para ello se partió de un mecanismo en el que la fotodegradación de los compuestos orgánicos tenía lugar principalmente por el ataque de radicales hidroxilo ( $\text{HO}^\bullet$ ). En la Figura 7.5 vienen dadas las ecuaciones cinéticas para las reacciones de fotodegradación de ácido clofíbrico, 4-clorofenol y p-benzoquinona (ecuaciones 1, 2 y 3, respectivamente), obtenidas de acuerdo al esquema de reacción considerado en la Figura 7.7, donde  $(-r_{AC}) = (-r_{AC,1}) + (-r_{AC,2})$  y  $(-r_{4-CF}) = (-r_{4-CF,1}) + (-r_{4-CF,2})$ . Según este este esquema de reacción, el ácido clofíbrico se puede fotodegradar para producir 4-clorofenol ( $-r_{AC,1}$ ) o p-benzoquinona ( $-r_{AC,2}$ ). A continuación, el 4-clorofenol se puede seguir foto-oxidando y generar más p-benzoquinona ( $-r_{4-CF,1}$ ) u otros intermedios orgánicos ( $-r_{4-CF,2}$ ),  $X_i$ , que finalmente



producirán HCl,  $CO_2$  y  $H_2O$ . De la misma manera, la p-benzoquinona puede ser fotodegradada para formar más intermedios aromáticos ( $-r_{p-Bzq}$ ),  $X_j$ , que finalmente serán mineralizados. Posteriormente se propusieron los balances de materia para el ácido clorofénico y sus principales intermedios, 4-clorofenol y p-benzoquinona. Estos balances corresponden a las ecuaciones 4, 5 y 6 representadas en la Figura 7.5.

Los parámetros cinéticos se estimaron mediante regresiones múltiples no lineales, comparando los valores experimentales de concentración con aquellos proporcionados por el modelo. Los valores de los parámetros cinéticos estimados junto con el valor de la raíz del error cuadrático medio (RMSE) vienen recogidos en la Tabla 7.2.

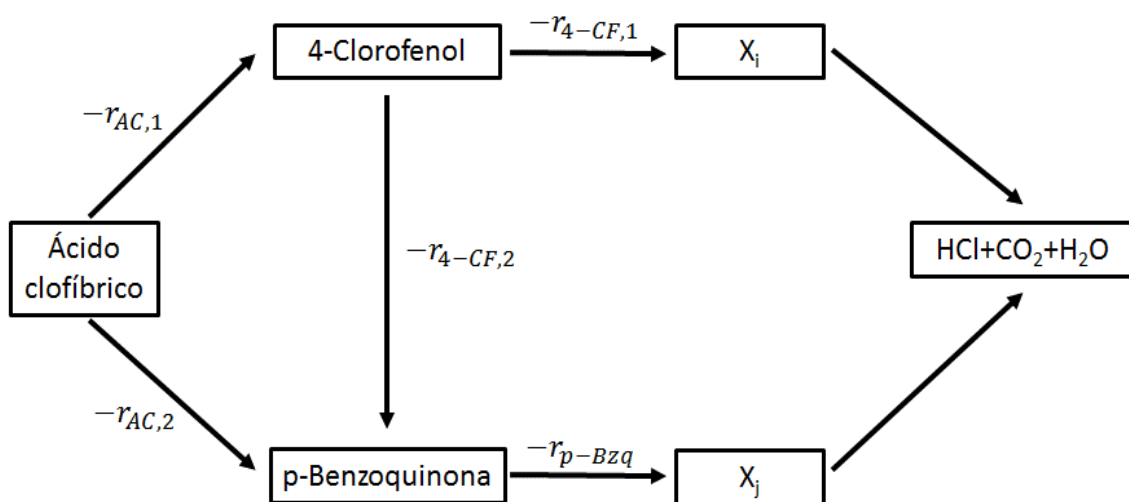


Figura 7.7. Esquema de fotodegradación del ácido clorofénico.

Se ha observado que los resultados experimentales obtenidos fueron simulados con gran exactitud a lo largo de toda la reacción, como se corrobora en la Figura 7.8, donde se representa la evolución de la concentración experimental y simulada de ácido clorofénico (AC) y la de sus principales intermedios, 4-clorofenol (4-CF) y p-benzoquinona (p-Bzq), para diferentes concentraciones de P25-rGO 0,5%. Los valores de la raíz del error cuadrático medio (RMSE) fueron inferiores al 11% considerando solo las concentraciones de ácido clorofénico.

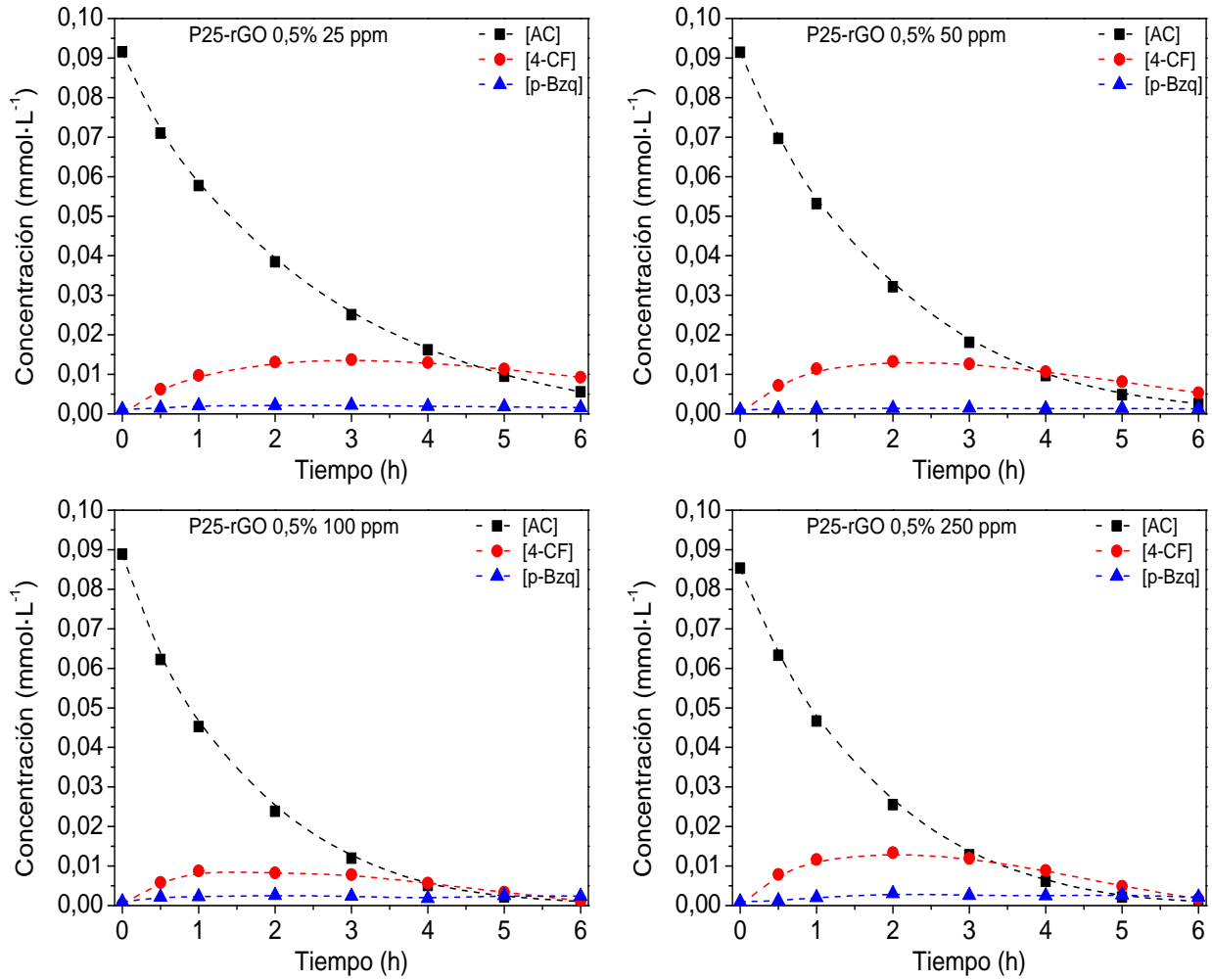


Figura 7.8. Evolución de la concentración de ácido clofibrico (AC) y de los principales intermedios, 4-clorofenol (4-CF) y p-benzoquinona (p-Bzq), para diferentes concentraciones de P25-rGO 0,5%.

Dado que el valor de  $\alpha_1$  fue tan elevado, se asumió que  $\alpha_1 e^a(x) \gg 1$ , lo que permitió simplificar las ecuaciones cinéticas para obtener un modelo cinético con 5 parámetros.

El modelo incluía las siguientes expresiones:

$$-r_{AC}(x, t) = (\alpha'_{2,1} + \alpha'_{2,2}) C_{AC}(x, t) \sqrt{\frac{e^a(x)}{S_g C_{cat}}} \quad (7)$$

$$-r_{4-CF}(x, t) = (\alpha'_{4,1} + \alpha'_{4,2}) C_{4-CF}(x, t) \sqrt{\frac{e^a(x)}{S_g C_{cat}}} \quad (8)$$

$$-r_{p-Bzq}(x, t) = \alpha'_5 C_{p-Bzq}(x, t) \sqrt{\frac{e^a(x)}{S_g C_{cat}}} \quad (9)$$

Los valores estimados de estos 5 parámetros cinéticos junto al correspondiente RMSE vienen también resumidos en la Tabla 7.2. Se puede apreciar que la simplificación del modelo implicó un aumento del error en la estimación de los valores simulados. Por tanto, aunque un modelo con menor número de parámetros cinéticos siempre es deseable, el modelo con 6 parámetros fue el elegido para simular las concentraciones de los contaminantes.

Tras analizar los resultados obtenidos se puede concluir que el fotocatalizador P25-rGO 0,5% proporciona la mayor velocidad inicial de fotodegradación de ácido clofíbrico y eficiencia cuántica (un 11% superior a la obtenida por el fotocatalizador sin rGO). Además, el modelo cinético desarrollado, con una dependencia explícita de la radiación absorbida, es capaz de predecir la evolución de la concentración del ácido clofíbrico y sus principales intermedios.

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# Capítulo 8:

Conclusiones / Conclusions

Los resultados presentados en esta Tesis Doctoral han dado lugar a las siguientes conclusiones:

- a) Respecto al estudio en el que se desarrolló un modelo cinético intrínseco para simular la fotodegradación de fenol con catalizadores de TiO<sub>2</sub> comerciales:
1. Un aumento del diámetro de partícula hidrodinámico en suspensión acuosa implica menores valores del coeficiente de *scattering*, y por lo tanto del coeficiente de extinción. Como consecuencia, partículas de TiO<sub>2</sub> con menor tamaño en suspensión, tales como los fotocatalizadores P25 y P90, presentan mayores velocidades de absorción de fotones.
  2. El fotocatalizador P25 presenta la mayor eficiencia cuántica en todas las condiciones estudiadas, al alcanzar elevadas velocidades iniciales de reacción absorbiendo menor radiación.
  3. El modelo cinético obtenido, con una dependencia explícita de la radiación, para simular la fotodegradación de fenol es el siguiente:

$$\langle -r_F(x, t) \rangle_{V_R} = -\varepsilon_L \frac{dC_F(t)}{dt} \Big|_{V_R} = \alpha \langle e^a(x) \rangle_{V_R} \frac{\alpha_{3,F} C_F(t)}{(\alpha_{3,F} C_F(t) + 1)}$$

Este modelo es capaz de describir con exactitud la evolución de fenol obtenida al utilizar fotocatalizadores de TiO<sub>2</sub>.

- b) De los resultados alcanzados en los estudios relacionados con el efecto del tipo de sustituyente en la adsorción y fotodegradación de compuestos fenólicos (fenol, 4-clorofenol, 4-nitrofenol y metil 4-hidroxibenzoato) con fotocatalizadores comerciales de TiO<sub>2</sub>:
4. La adsorción de los compuestos fenólicos se favorece sobre fotocatalizadores con mayor acidez superficial. La naturaleza química del sustituyente no parece afectar a la cantidad adsorbida.
  5. Todos los compuestos fenólicos estudiados, excepto el 4-nitrofenol, se adsorben mediante interacciones entre los grupos –OH de los compuestos aromáticos y el TiO<sub>2</sub>, dando lugar a Ti-fenolatos, conforme indican los resultados de espectroscopía infrarroja de reflectancia difusa (DRIFTS).

6. Fotocatalizadores constituidos por una mezcla de anatasa y rutilo (P25, P90 y P25/20) alcanzan mayores velocidades iniciales de fotodegradación que los que presentan una sola fase (PC105 y Hombikat).
  7. Cuanto mayor es el valor de la constante de Hammett del correspondiente sustituyente en el compuesto fenólico, menor es la velocidad inicial de foto-oxidación.
- c) Del análisis y elucidación del tipo de fotomecanismo más relevante en la foto-oxidación catalítica de los compuestos fenólicos estudiados, con catalizadores comerciales de  $\text{TiO}_2$ :
8. El catalizador P25 alcanza mayores eficiencias cuánticas en la fotodegradación de todos los compuestos fenólicos estudiados debido a una mejor utilización de los fotones absorbidos, salvo en el caso del 4-nitrofenol, cuya adsorción no se debe a la formación de fenolatos.
  9. Los radicales hidroxilo ( $\text{HO}^\bullet$ ) generados a partir de los huecos fotogenerados ( $\text{h}^+$ ) son los principales responsables de la fotodegradación de fenol, 4-clorofenol y metil 4-hidroxibenzoato. Sin embargo, la fotodegradación del 4-nitrofenol se inicia vía los electrones foto-inducidos en la banda de conducción.
- d) Del estudio relacionado con la actividad de fotocatalizadores de  $\text{TiO}_2$  modificados con rGO, mediante un tratamiento hidrotermal:
10. La unión del  $\text{TiO}_2$  con el rGO evita la recombinación inefectiva de las cargas. Los resultados obtenidos en la caracterización electroquímica indican una mayor velocidad de transferencia al medio de reacción.
  11. Aunque los fotocatalizadores P25-rGO presentan diferentes proporciones de rGO: $\text{TiO}_2$ , su actividad catalítica en la foto-oxidación de ácido oxálico no mejora porque existen efectos contrapuestos entre la mayor disposición de electrones y su transferencia al  $\text{O}_2$  del medio.
  12. La presencia de rGO en los fotocatalizadores P25-rGO favorece una alta eficiencia inicial en la descomposición inicial de  $\text{H}_2\text{O}$  en radicales  $\text{HO}^\bullet$  al transferirse los electrones al rGO. Sin embargo, este efecto deja de observarse cuando el rGO se satura en electrones al no poder cederlos a mayor velocidad al  $\text{O}_2$ .

e) Del estudio relacionado con el análisis de la fotodegradación de ácido clofíbrico con fotocatalizadores de TiO<sub>2</sub>-rGO y con el desarrollo de un modelo cinético para su simulación:

13. La presencia de rGO en el composite de TiO<sub>2</sub>-rGO aumenta los valores del coeficiente de *scattering* en todo el intervalo del UV-A y del factor de asimetría.

14. El catalizador P25-rGO 0,5% presenta la mayor velocidad inicial de fotodegradación del ácido clofíbrico y permite aumentar ligeramente (11%) la eficiencia cuántica del proceso en comparación con el TiO<sub>2</sub> (P25-rGO 0%).

15. El modelo cinético intrínseco desarrollado es capaz de simular con exactitud la evolución del ácido clofíbrico y de sus principales intermedios, al utilizar P25-rGO 0,5% como fotocatalizador. Las ecuaciones que constituyen este modelo son las siguientes:

$$\varepsilon_L \frac{dC_{AC}(t)}{dt} \Big|_{Tk} = -\frac{V_R}{V_T} a_v \langle (\alpha_{2,1} + \alpha_{2,2}) C_{AC}(x, t) \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a(x)}{S_g C_{cat}}} \right\} \rangle_{AR}$$

$$C_{AC}(t = 0) = C_{AC0}$$

$$\varepsilon_L \frac{dC_{4-CF}(t)}{dt} \Big|_{Tk} = \frac{V_R}{V_T} a_v \langle (\alpha_{2,1} C_{AC}(x, t) - (\alpha_{4,1} + \alpha_{4,2}) C_{4-CF}(x, t)) \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a(x)}{S_g C_{cat}}} \right\} \rangle_{AR}$$

$$C_{4-CF}(t = 0) = 0$$

$$\varepsilon_L \frac{dC_{p-BQ}(t)}{dt} \Big|_{Tk} =$$

$$= \frac{V_R}{V_T} a_v \langle (\alpha_{2,2} C_{AC}(x, t) + \alpha_{4,2} C_{4-CF}(x, t) - \alpha_5 C_{p-Bzq}(x, t)) \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a(x)}{S_g C_{cat}}} \right\} \rangle_{AR}$$

$$C_{p-BQ}(t = 0) = 0$$



The results presented in this Doctoral Thesis support the following conclusions:

a) Regarding the study where an intrinsic kinetic model was developed to simulate phenol photodegradation with commercial TiO<sub>2</sub> catalysts:

1. Scattering coefficient values, and therefore extinction coefficients, drop on increasing TiO<sub>2</sub> hydrodynamic particle sizes. Hence, photocatalysts with lower hydrodynamic particle size, such as P25 and P90, reach higher volumetric rates of photon absorption (VRPA).
2. Higher quantum efficiencies are observed when P25 is used at the operating conditions studied here, since it is able to reach high initial photodegradation rates absorbing moderate values of VRPA.
3. To simulate phenol photodegradation, the following kinetic model with an explicit dependence on absorbed radiation is obtained:

$$\langle -r_{Ph}(x, t) \rangle_{VR} = -\varepsilon_L \frac{dC_{Ph}(t)}{dt} \Big|_{VR} = \alpha \langle e^{\alpha(x)} \rangle_{VR} \frac{\alpha_{3,Ph} C_{Ph}(t)}{(\alpha_{3,Ph} C_{Ph}(t) + 1)}$$

This model is able to accurately predict the experimental evolution of phenol when TiO<sub>2</sub> photocatalysts are used.

b) From the results obtained in the studies relating to the role of *para*-positioned substituents on adsorption and photodegradation of phenolic compounds (phenol, 4-chlorophenol, 4-nitrophenol and methyl 4-hydroxybenzoate), with commercial TiO<sub>2</sub> photocatalysts:

4. The amount of adsorbed organic compound is higher in photocatalysts with higher surface acidity. The chemical nature of the substituent seems to have little influence on the phenolic compound uptake.
5. All the studied phenolic compounds, except 4-nitrophenol, are adsorbed via interactions between the phenolic –OH group and TiO<sub>2</sub> surface, leading to the formation of Ti–phenolates, as it was observed from diffuse reflectance infrared spectroscopy (DRIFTS) measurements.
6. Photocatalysts made up of a mixture of anatase and rutile crystalline phases (P25, P90 y P25/20) yield faster initial photodegradation rates than those photocatalysts composed only of anatase crystals (PC105 and Hombikat).

7. A clear relation between photodegradation rates and the Hammett constant values, relating to the nature of the substituent, was obtained. According to this relation, the greater the Hammett's constant of the substituent on the phenolic compound, the lower the photo-oxidation rate.
- c) From the analysis and elucidation of the most relevant photocatalytic-mechanism in the photocatalytic oxidation of phenolic compounds, with commercial TiO<sub>2</sub> photocatalysts:
8. P25 yields higher values of the quantum efficiency in the photocatalytic degradation of all the phenolic compounds because of a better use of adsorbed photons, except in the case of 4-nitrophenol, whose adsorption does not occur through generation of 4-nitrophenolate.
  9. Regardless of the photocatalyst, phenol, methyl 4-hydroxybenzoate and 4-chlorophenol are mostly degraded by HO<sup>•</sup> radicals generated from photogenerated h<sup>+</sup>. However, a conduction band electron mediated mechanism is the most relevant for 4-nitrophenol photodegradation.
- d) From the work concerning the photoactivity of TiO<sub>2</sub> modified with rGO, synthesized by a hydrothermal method:
10. The modification of TiO<sub>2</sub> with rGO prevents inefficient recombination of the charge carriers. The results obtained from electrochemical characterization indicate higher transfer rates to the reaction medium.
  11. Even though several P25-rGO nanocomposites were synthesized with different GO:TiO<sub>2</sub> ratios, no improvement in their photocatalytic degradation of oxalic acid is observed. This is due to the fact that the greater amount of electrons available in rGO opposes the electron transfer to O<sub>2</sub> in the reaction medium.
  12. It was proven that rGO in P25-rGO photocatalysts favor higher initial efficiencies in the HO<sup>•</sup> radical generation from H<sub>2</sub>O decomposition because of the electron transfer to rGO. However, this effect is no longer noted when rGO becomes saturated with electrons since it is not able to transfer electrons at a faster rate.
- e) From the study related to the analysis of clofibrac acid photodegradation using TiO<sub>2</sub>-rGO nanocomposites and the development of a kinetic model to simulate the process:

13. The presence of rGO leads to a rise of the scattering coefficient and asymmetry factor in the whole UV-A range.
14. P25-rGO 0.5% reaches the fastest clofibric acid photodegradation rate and achieves a slight increase (11%) of the quantum efficiency of the process compared to the value obtained for bare TiO<sub>2</sub> (P25-rGO 0%).
15. The developed intrinsic kinetic model is able to simulate with great accuracy the evolution of the concentration of clofibric acid and its main intermediates, using P25-rGO 0.5% as photocatalyst. The kinetic equations that describe the reaction rates of clofibric acid, 4-chlorophenol and p-benzoquinone are:

$$\varepsilon_L \frac{dC_{CA}(t)}{dt} \Big|_{Tk} = -\frac{V_R}{V_T} a_v \langle (\alpha_{2,1} + \alpha_{2,2}) C_{CA}(x, t) \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a(x)}{S_g C_{cat}}} \right\} \rangle_{AR}$$

$$C_{CA}(t = 0) = C_{CA0}$$

$$\varepsilon_L \frac{dC_{4-CP}(t)}{dt} \Big|_{Tk} = \frac{V_R}{V_T} a_v \langle (\alpha_{2,1} C_{CA}(x, t) - (\alpha_{4,1} + \alpha_{4,2}) C_{4-CP}(x, t)) \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a(x)}{S_g C_{cat}}} \right\} \rangle_{AR}$$

$$C_{4-CP}(t = 0) = 0$$

$$\begin{aligned} \varepsilon_L \frac{dC_{p-BQ}(t)}{dt} \Big|_{Tk} &= \\ &= \frac{V_R}{V_T} a_v \langle (\alpha_{2,2} C_{CA}(x, t) + \alpha_{4,2} C_{4-CP}(x, t) - \alpha_5 C_{p-Bzq}(x, t)) \left\{ -1 \right. \\ &\quad \left. + \sqrt{1 + \frac{\alpha_1 e^a(x)}{S_g C_{cat}}} \right\} \rangle_{AR} \end{aligned}$$

$$C_{p-BQ}(t = 0) = 0$$

# Capítulo 9:

Anexos

# Anexo I:

Influence of  $\text{TiO}_2$  optical parameters in a slurry photocatalytic reactor: Kinetic modelling



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# Influence of TiO<sub>2</sub> optical parameters in a slurry photocatalytic reactor: Kinetic modelling

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## ABSTRACT

A kinetic model, based on a proposed reaction photo-mechanism and explicitly dependent on the volumetric rate of photon absorption (VRPA), has been performed and analyzed for the photocatalytic degradation of phenol in aqueous suspensions. UVA–vis simulated solar radiation and three commercial TiO<sub>2</sub> powder photocatalysts, with identical chemical structure but with different morphology and hydrodynamic particle size (P25 Aeroxide<sup>®</sup>, P25/20 VP Aeroperl<sup>®</sup> and P90 Aeroxide<sup>®</sup> provided by Evonik) have been used. The effect of TiO<sub>2</sub> hydrodynamic particle size on the optical coefficients has revealed that this property is playing an important role on the absorbed radiation evaluation. Radiation profiles inside the photoreactor were determined by solving the radiative transfer equation (RTE), and the corresponding kinetic parameters were obtained.

A comparative study of TiO<sub>2</sub> loading effect on calculated quantum efficiency ( $\eta$ ) revealed P25 was the most photo-efficient catalyst, whereas P25/20 reached similar efficiencies only when higher TiO<sub>2</sub> concentrations were used. On the contrary, P90 presented the lowest photo-efficiency with lower photodegradation rates despite absorbing more radiation.

The obtained kinetic model has been successfully validated by experimental data, being able to reproduce the evolution of phenol photodegradation at a wide range of catalyst concentrations for the three studied TiO<sub>2</sub>. In the experimental conditions of this work, low irradiation power conditions can be considered; after simplification, the model adopted a linear dependence on the volumetric rate of photon absorption; showing good agreement between predicted and experimental values, with root-square-mean errors below 5%.

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## 1. Introduction

The heterogeneous photocatalytic process is based on the excitation of a catalytic solid, usually a broad bandgap semiconductor as TiO<sub>2</sub>, through the absorption of photons whose energy is equal or greater than their *band-gap* energy. Photo-generated electrons (e<sup>-</sup>) and holes (h<sup>+</sup>) will react with adsorbed molecules located at catalyst surface, leading to the oxidization of the organic matter by direct hole (h<sup>+</sup>) transfer or by indirect hydroxyl radical–oxidation (HO<sup>•</sup>) [1]. In this context, solar photocatalytic processes contemplate the use of a natural light source such as the sun, environmental friendly, wherein the nanostructured TiO<sub>2</sub> catalysts can improve their final photoefficiency [2]. It is known that photocatalytic

processes are affected by different parameters which govern photo-oxidation rates, such as spectral distribution and intensity of the incident radiation, concentration and type of oxidizing agent, mass of catalyst, pH, etc. [1,3]. Therefore, to discriminate the overall performance of a photocatalyst is essential to know its intrinsic kinetic parameters to design new and improved photo-reactors. Then, a crucial requirement to develop novel photoreactors would be to build a kinetic model able to successfully reproduce the experimental rates obtained during photo-catalytic reaction [4]. Analysis of liquid-phase kinetics for titania powder suspensions have relied largely on Langmuir-Hinshelwood (LH) rate forms, which assumes equilibrated adsorption of reactants and implies the existence of a subsequent slow, rate-controlling surface step [5,6]. This kinetic model has demonstrated to well fit the concentration evolution of many organic pollutants in the photocatalytic literature [6]. However to carry out valuable comparison studies of the kinetic parameters among different labs, reactors and research works, it

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**Nomenclature**

%A	Anatase crystalline phase percentage
%R	Rutile crystalline phase percentage
ABS	Value of a absorbance spectrophotometric measurement
$a_V$	Interfacial area per unit suspension volume, $m^{-1}$
BG	Band-gap, eV
$C_{cat}$	Mass catalyst concentration, $g\ cm^{-3}$
$C_{Ph}$	Molar phenol concentration, $mmol\ L^{-1}$
$d_A$	Anatase mean diameter, nm
$d_{PHD}$	Hydrodynamic particle diameter, $\mu m$
$d_R$	Rutile mean diameter, nm
$e^a$	Volumetric rate of photon absorption, Einstein $cm^{-3}\ s^{-1}$
f	Spectral energy distribution of the lamp
I	Specific radiation intensity, Einstein $cm^{-2}\ s^{-1}$
k	Kinetic constant, its units depend on the step considered
K	Equilibrium constant
LVRPA	Local volumetric rate of photon absorption, Einstein $cm^{-3}\ s^{-1}$
p	Function phase, dimensionless
q	Radiation flux, Einstein $cm^{-2}\ s^{-1}$
R	Value of a reflectance spectrophotometric reflectance
$r_g$	Surface rate of electron-hole generation, $mol\ cm^{-2}\ s^{-1}$
$(-r_{Ph})$	Phenol photodegradation rate, $mmol\ L^{-1}\ min^{-1}$
$r_{Fe(II)}$	Fe(II) production rate, $mol\ L^{-1}\ min^{-1}$
S	Relative to a subproduct species
$S_{BET}$	Catalyst surface area (BET), $m^2\ g^{-1}$
$S_{irr}$	Area of the inlet radiation window, $cm^2$
t	Time, min
$V_R$	Reactor volume, l
VRPA	Volumetric rate of photon absorption, Einstein $cm^{-3}\ s^{-1}$

**Greek letters**

$\alpha_1$	Kinetic parameter, $mmol\ cm\ L^{-1}\ min^{-1}$
$\alpha_2$	Kinetic parameter, $cm^2\ s\ Einstein^{-1}$
$\alpha_3$	Kinetic parameter, $L\ mmol^{-1}$
$\beta$	Extinction coefficient, $cm^{-1}$
$\eta$	Quantum efficiency, $mol\ Einstein^{-1}$
$\phi$	Quantum yield, $mol\ Einstein^{-1}$
$\bar{\phi}$	Mean quantum yield, $mol\ Einstein^{-1}$
$\kappa$	Absorption coefficient, $cm^{-1}$
$\lambda$	Wavelength, nm
$\mu$	Director cosine, $\mu = \cos\theta$
$\theta$	Spherical coordinate, rad
$\Omega$	Direction of radiation propagation
$\omega$	Spectral albedo

**Subscripts**

0	Initial value
$\lambda$	Indicates a dependence on wavelength
Cat	Relative to catalyst
Exp	Experimental value
max	Maximum value
min	Minimum value
Mod	Simulated value
Ph	Relative to phenol
S	Relative to a subproduct
T	Total
$V_R$	Relative to reactor volume

**Superscripts**

*	Specific properties
$\pm$	Direction in which $\mu > 0$
-	Direction in which $\mu < 0$
0	Value at $x = 0$
s	Relative to catalytic area

**Special symbols**

$\langle \rangle$	Average value over a defined space
[ ]	Relative to concentration

will be needed to pay attention to intensity of absorbed radiation in any single photoreactor, given that different parameters such as light intensity are grouped in LH model kinetic rate constants.

Therefore, to get a kinetic expression which can be employed within a great range of operating conditions and allow to scaling up the process, the model must have an explicit dependence on the absorbed radiation. Hence, volumetric rate of photon absorption (VRPA) inside photoreactor must be evaluated, since it is involved in the photocatalytic reaction by means of activation step [7]. In this context, the Radiative Transfer Equation (RTE) must be solved to determine the radiation field [8,9]. The RTE describes the radiation intensity at any position along a ray pathway through medium. Besides, it can be also applied to evaluate the radiation field in a heterogeneous system constituted by  $TiO_2$  particles suspended in aqueous suspensions.

Consequently, the aim of this work has consisted on developing an intrinsic kinetic model, where the explicit radiation absorption has been included to reproduce the experimental results obtained with three  $TiO_2$  powder catalysts in the photodegradation of phenol in aqueous suspensions using a slurry photoreactor with external surrounding radiation.  $TiO_2$  catalysts (P25 Aeroxide®, P25/20 VP Aeroxide® and P90 Aeroxide®) with identical chemical structure, but with different morphologic and hydrodynamic particle size were deliberately chosen to study the influence of catalyst loading on phenol photodegradation without any other collateral effect.

The main optical properties (extinction, absorption and scattering coefficients) which affect the overall photocatalytic behavior, have been determined, and its dependence on the hydrodynamic particle size in aqueous suspensions has been settled.

Finally, a comparison study of calculated quantum efficiency for different  $TiO_2$  loading was also analyzed to establish the most photo-efficient catalyst under the studied conditions.

**2. Experimental section****2.1. Photocatalysts**

Photocatalytic experiments were performed using three  $TiO_2$  commercial catalysts: P25 Aeroxide®, P90 Aeroxide® and P25/20 VP Aeroxide®, all of them provided by Evonik Company.

Analytical grade phenol was purchased from Panreac. All reagents used for chromatographic analyses: (Milli-Q water, Ortho-phosphoric acid, methanol) were HPLC grade.

**2.2. Photocatalysts characterization**

Catalysts structural characterization were performed with a X polycrystal PANalytical X'Pert PRO using nickel-filtered  $Cu\ K\alpha$  ( $1.541874\ \text{\AA}$ ) radiation operating at 40 kV and 40 mA, with a  $0.02^\circ$  step size and accumulating a total of 50 s per point, crystal size was estimated by employing the Scherrer equation [10].

Nitrogen adsorption-desorption isotherms measurements were obtained at 77 K in a Micromeritics Tristar automatic apparatus,

samples were previously outgassed overnight at 413 K to a vacuum of  $<10^{-4}$  Pa to ensure a dry and clean surface free from any loosely adsorbed species and, specific surface areas were determined by the BET method [11].

UV–vis diffuse reflectance spectra of the photocatalytic powders were using Agilent Cary 5000 spectrophotometer equipped with an integrating sphere. Band-gap was determined by the equation  $\alpha \times h \times \nu = A \times (h\nu - E_g)^{n/2}$  [12].

Laser Diffraction (LD) measurements were performed to characterize the hydrodynamic particle size distribution of TiO<sub>2</sub> aggregates in aqueous suspensions using Mastersizer S by Malvern Instruments.

Finally, the optical properties of the catalyst suspensions were determined with a Agilent Cary 5000 UV–vis spectrophotometer following the methodology proposed by Cassano et al. [13–15]. Extinction measurements were carried out in transmission mode, placing a narrow slit before detector to reduce the collection of out-scattered rays. The sample cell, made of quartz (optical length, 2 mm) was located as far as possible from detector slit (Milli-Q water was used as baseline). The experimental setup for absorbance and reflectance measurements was constituted by the quartz sample cell fixed to a magnetic stirrer placed in the inlet and outlet of the integrating sphere, respectively (Milli-Q water and PTFE-Spectralon® were used as reference, respectively). Measurements were performed on freshly prepared and non-sonicated suspensions at different catalyst loadings. Under all the studied conditions, the suspensions were rather stable and fairly reproducible during the three consecutive measurements carried out.

### 2.3. Photocatalytic activity

Photodegradation runs were carried out in a stirred 1 L Pyrex semi-continuous slurry photoreactor [16] set in a Multirays apparatus (Helios Italquartz) at atmospheric pressure and room temperature (details about the reactor are shown in Supporting Information Table 1). The cylindrical reactor (76 mm i.d.) was enclosed by 10 fluorescent lamps of 15 W each (6 Black Light Blue UVA lamps and 4 day-light lamps) surrounded by an aluminum reflecting surface. This set of lamps was used to work with a total radiant flux in the UV-A range closed to the typical average solar UV flux values, found to be  $30 W_{UVA} m^{-2}$  [17] Total irradiance,  $38 W m^{-2}$ , was measured by a Kipp & Zonen model CUV-4 broadband UV radiometer in UV-A range (306–383 nm). Furthermore, radiation flow entering to the reactor and provided by the 6 Black Light Blue UVA lamps was determined by carrying out a potassium ferrioxalate actinometry [18].

Phenol photo-oxidation runs were carried out at the following operating conditions: atmospheric pressure, initial concentration of  $50 mg L^{-1}$  phenol at natural pH 6, with a continuous oxygen flow of  $75 Ncm^3 min^{-1}$ . Different TiO<sub>2</sub> catalysts loadings ( $25$ – $150 mg L^{-1}$ ) were also studied at the same operating conditions. First, the reactant mixture with the corresponding catalyst loading were premixed in dark conditions during 30 min to guarantee homogeneous mixing in the photoreactor, to take into account the adsorption equilibrium stage. After that, photocatalytic runs started by turning on all lamps, and small portions of the solutions were extracted at selected times to follow the reaction.

Phenol and aromatic intermediates were identified and quantified by means of High Performance Liquid Chromatography HPLC (Varian 920 LC) with photo-diode array detector. A Nucleosil C18  $5 \mu m$  column (15 cm long, 4.6 mm diameter) was used as stationary phase at  $40^\circ C$ . Mobile phase flow was  $0.8 mL min^{-1}$  and 20/80% v/v methanol/acidic water (0.1% phosphoric acid) mixture were used as solvent.

## 3. Results and discussion

### 3.1. Catalyst properties

In Table 1 are summarized the main physico-chemical properties of these three studied TiO<sub>2</sub> catalysts. From XRD measurements, all of them present similar crystallinity, with two titania crystal phases, approximately 88–85% anatase and 12–15% rutile respectively. Although P90 presented slightly lower anatase and rutile crystal sizes than P25 and P25/20 catalysts, the crystal structure do not seem to affect their band-gap values. Their specific surface areas ( $S_{BET}$ ) revealed that both P25 and P25/20 catalyst presented the same area ( $54 m^2 g^{-1}$ ), whereas P90 shows a higher surface area ( $81 m^2 g^{-1}$ ).

These Evonik commercial titania materials are characterized by unique macroporosity as correspond to non-porous type II isotherm [19], which must be only related to agglomerates, aggregates, small particles, or inter-particle spaces, given that their surface areas exactly agrees with their external surface areas (as it can be seen in Table 1), where total pore volume only corresponds to inter-particle spaces.

It is essential to understand TiO<sub>2</sub> particle interactions over a broad range of physicochemical conditions, given that aggregation of titania particles in the aqueous suspensions could have an important effect on final photocatalytic activity. In this context, the hydrodynamic particle size measured by Laser Diffraction (LD) will be indicative of the apparent size of the dynamic hydrated/solvated particle; hence the terminology, *hydrodynamic diameter* [20,21]. Considering that photocatalytic particles should favor efficient absorption of incident photons to avoid reduction of photodegradation rate due to lack of light [22], identifying the hydrodynamic particle size of TiO<sub>2</sub> particles in aqueous media must be crucial to understand photocatalyst phenomena.

The hydrodynamic particle size values determined by Laser Diffraction measurements are shown in Table 1. P25/20 sample has presented a significantly larger sizes than P25 and P90, being its hydrodynamic mean diameter value about 10 times higher. However, although P90 and P25 presented particle sizes of the same order of magnitude, P90 hydrodynamic particle size was more than double than TiO<sub>2</sub> P25. These important differences found in titania particles behavior in aqueous suspensions could well lead to a very different photocatalytic performance, in spite of the similarity found among the rest of their physico-chemical properties.

Therefore, these studied TiO<sub>2</sub> catalysts present a set of common structural and surface properties which will allow evaluating how photocatalytic activity could be independently affected by their hydrodynamic particle sizes.

### 3.2. Optical properties

The optical properties of these studied TiO<sub>2</sub> catalysts were carried out in the range of used lamps, from 345 to 405 nm, following the methodology proposed by Cabrera et al. [14], and Satuf et al. [15]. Extinction coefficients were calculated from conventional spectrophotometric measurements of corresponding TiO<sub>2</sub> suspensions. Thus, for each wavelength ( $\lambda$ ) and each path cell ( $L$ ), the extinction coefficient is:

$$\beta_{\lambda} = \frac{2.303 Abs_{\lambda}}{L} \quad [cm^{-1}] \quad (1)$$

Subsequently, the specific extinction coefficients ( $\beta_{\lambda}^*$ ) for each catalyst were obtained by means of linear regressions of  $\beta_{\lambda}$  data vs  $C_{cat}$ .

It was also necessary to carry out transmittance or reflectance spectrophotometric measurements by means of an integrating sphere which allowed collect not only the non-absorbed radia-



**Table 1**  
Physico-chemical properties of TiO<sub>2</sub> catalysts.

Catalyst	% A	% R	d <sub>A</sub> (nm)	d <sub>R</sub> (nm)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	A <sub>external</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>Pore</sub> (cm <sup>3</sup> g <sup>-1</sup> )	d <sub>HDP</sub> (μm)	BG (eV)
P25	85	15	21.5	33.0	54	54	0.65	1.2	3.2
P90	87	13	17.3	31.5	81	81	0.50	2.6	3.2
P25/20	88	12	21.0	33.0	54	54	0.26	11.3	3.2

A: Anatase; R: Rutile; HDP: Hydrodynamic particle size.

tion, but also the forward-scattered radiation to determine the absorption coefficient ( $\kappa_\lambda$ ). Nevertheless, these measures had to be corrected considering the scattered radiation in other directions. Then, the absorption coefficient was calculated by solving the Radiative Transfer Equation (RTE) (Eq. (2)) in the sample cell, where TiO<sub>2</sub> aqueous suspensions are contained.

$$\begin{aligned} \frac{dI_\lambda(s, \underline{\Omega})}{ds} &+ \underbrace{\kappa_\lambda I_\lambda(s, \underline{\Omega})}_{\text{Absorption}} + \underbrace{\sigma_\lambda I_\lambda(s, \underline{\Omega})}_{\text{Out-scattering}} \\ &= \underbrace{\frac{\sigma_\lambda}{4\pi} \int_{\Omega'=4\pi} p(\underline{\Omega}' \rightarrow \underline{\Omega}) I_\lambda(s, \underline{\Omega}') d\Omega'}_{\text{In-scattering source term}} \end{aligned} \quad (2)$$

In the case of the studied set-up (a sample cell irradiated by a collimated-unidirectional beam) a one-dimensional-one-directional radiation transport model can be applied to attain scattering of the system (mathematical derivation of a 1-dimensional, 1-directional radiation model can be found in the Supporting information). Theoretical values of the absorption coefficients can be determined from the proposed model [14,15]. The RTE model takes the following form:

$$\begin{aligned} \mu \cdot \frac{dI_\lambda(x, \mu)}{dx} + \beta_\lambda \cdot I_\lambda(x, \mu) \\ = \frac{\beta_\lambda - \kappa_\lambda}{2} \int_{\mu'=-1}^{\mu'=1} p(\mu, \mu') \cdot I_\lambda(x, \mu') \cdot d\mu' \end{aligned} \quad (3)$$

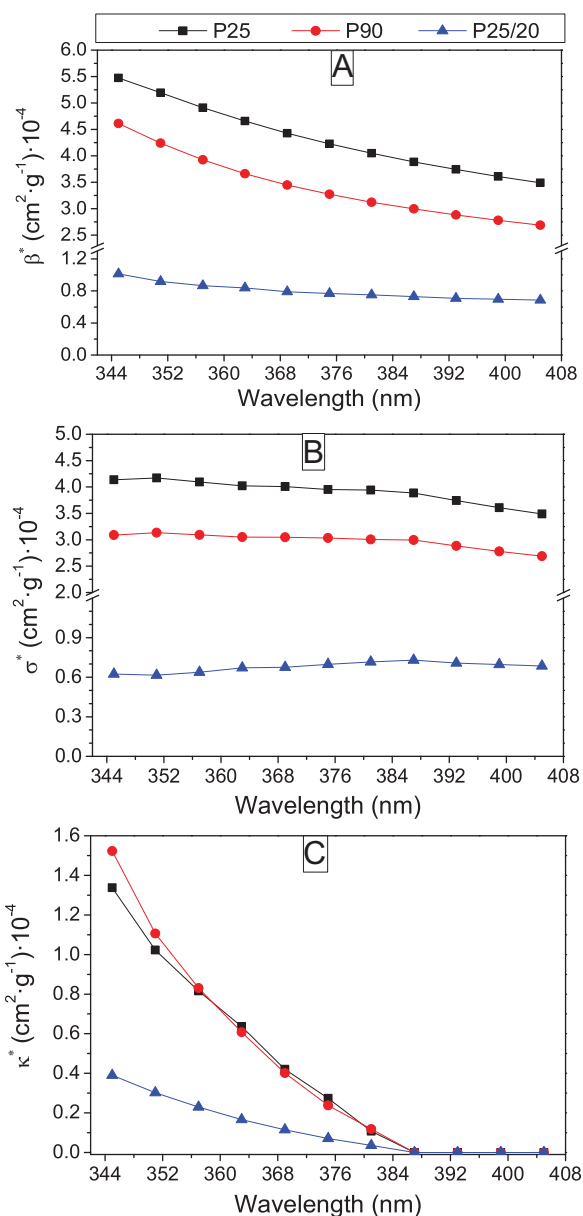
where  $\mu = \cos \theta$ . An isotropic phase function has been assumed in this work, as one of the most adequate to describe the scattering properties of a semiconductor catalysts such as titania [9,23,24] where  $p(\mu, \mu') = 1$ . The two boundaries conditions at  $x=0$  and at  $x=L$ , required for this model, depend on the kind of spectrophotometric measures carried out [8,13,14].

A discretization mathematical algorithm, known as Discrete Ordinate Method (DOM), has been applied to obtain the numerical solution of the RTE. This method consists on the transformation of the integral-differential RTE into a system of algebraic equations, which describes transport of photons in such way that they can be solved following the direction of propagation, starting from the values provided by the boundary conditions [8,9].

Absorption coefficient and its specific absorption coefficient ( $\kappa_\lambda^*$ ) were obtained [14,15] by comparison of experimental information with model predictions, and minimizing errors. Finally, the specific scattering coefficient can be determined as,

$$\sigma_\lambda^* = \beta_\lambda^* - \kappa_\lambda^* \quad (4)$$

Results of the specific extinction, specific absorption and specific scattering coefficients for each TiO<sub>2</sub> catalyst are shown in Fig. 1. It can be noticed that values obtained for P25 and P90 samples are far higher than those obtained for P25/20 catalyst, despite all of them present similar responses over all investigated wavelength range. From Fig. 1C, the absorption coefficients undergo an important decrease along wavelength values until becoming null above



**Fig. 1.** Optical properties of TiO<sub>2</sub> catalysts (P25, P90 and P25/20). (A) Extinction Coefficient; (B) Scattering Coefficient; (C) Absorption Coefficient.

390 nm, which exactly corresponds to the bandgap of TiO<sub>2</sub> semiconductors.

On the other side, P25 has showed the highest scattering coefficients whereas P25/20 has presented the lowest values. This could be well related to the hydrodynamic particle size given that P25 and P25/20 with identical structural and surface properties, presented the wider and smaller hydrodynamic particle diameters, respectively. To go deepening into the understanding of hydrodynamic particle size effect on scattering, the ratio of the scattering to the extinction coefficients, usually called albedo ( $\omega$ ), has been com-

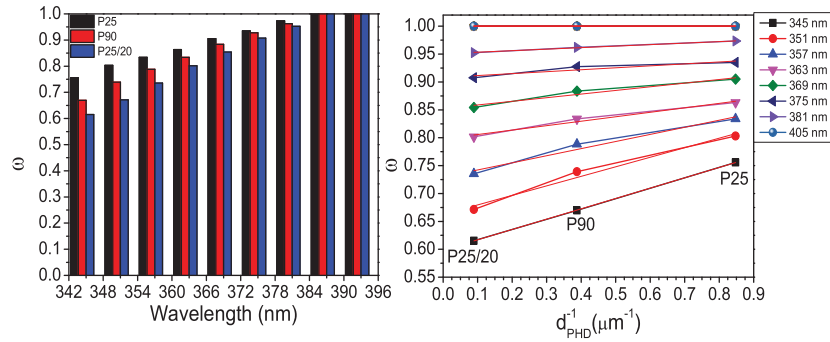


Fig. 2. Influence of wavelength (A) and hydrodynamic particle size (B) on the albedo coefficient ( $\omega$ ).

**Table 2**  
Scheme of the proposed phenol photodegradation mechanism over  $\text{TiO}_2$  catalysts.

Activation	$\text{TiO}_2 \xrightarrow{h\nu} \text{TiO}_2 + e^- + h^+$	[1]
Adsorption	$\text{O}_2^- + \text{Ti}^{\text{IV}} + \text{H}_2\text{O} \leftrightarrow \text{O}_2\text{H}^- + \text{Ti}^{\text{IV}} - \text{OH}^-$	[2a]
	$\text{Ti}^{\text{IV}} + \text{H}_2\text{O} \leftrightarrow \text{Ti}^{\text{IV}} - \text{H}_2\text{O}$	[2b]
	$\text{Site} + \text{Ph} \leftrightarrow \text{Ti}^{\text{IV}} \text{Ph}$	[3]
	$\text{HO} + \text{Ti}^{\text{IV}} \leftrightarrow \text{Ti}^{\text{IV}} \text{HO}$	[4]
Recombination	$e^- + h^+ \rightarrow \text{heat}$	[5]
Holes trapping	$\text{Ti}^{\text{IV}} - \text{OH}^- + h^+ \rightarrow \text{Ti}^{\text{IV}} \text{HO}$	[6a]
	$\text{Ti}^{\text{IV}} - \text{H}_2\text{O} + h^+ \rightarrow \text{H}^+ + \text{Ti}^{\text{IV}} \text{HO}$	[6b]
	$\text{Ti}^{\text{IV}} \text{Ph} + h^+ \leftrightarrow \text{Ti}^{\text{IV}} \text{Ph}^+$	[7]
Electron trapping	$e^- + \text{Ti}^{\text{IV}} \leftrightarrow \text{Ti}^{\text{III}}$	[8a]
	$\text{O}_2 + \text{Ti}^{\text{III}} \leftrightarrow \text{Ti}^{\text{IV}} - \text{O}_2^-$	[8b]
Hydroxyl attack	$\text{Ti}^{\text{IV}} \text{HO} + \text{Ti}^{\text{IV}} \text{Ph} \rightarrow \text{Ti}^{\text{IV}} + \text{Ti}^{\text{IV}} \text{S}$	[9]
	$\text{HO} + \text{Ti}^{\text{IV}} \text{Ph} \rightarrow \text{Ti}^{\text{IV}} \text{S}$	[10]
	$\text{Ti}^{\text{IV}} \text{HO} + \text{Ph} \rightarrow \text{Ti}^{\text{IV}} + \text{S}$	[11]
	$\text{HO} + \text{Ph} \rightarrow \text{S}$	[12]

pared in Fig. 2; where a linear dependence with the inverse of the hydrodynamic particle size was always observed for these three  $\text{TiO}_2$  catalysts. Lower hydrodynamic particle diameters provoke high particle dispersions which would lead to high albedo coefficient values. Therefore, could be concluded that P25 presented a major proportion of scattering coefficient than the other two studied  $\text{TiO}_2$  catalysts.

### 3.3. Kinetic model

The phenol photocatalytic mineralization mechanism used in this work is based on that proposed by Turchis and Ollis [25], and Alfano et al. [26] (see Table 2); where the following steps are considered: activation by photons absorption to form the electron-hole pair (1), adsorption of water, the organic compound, and hydroxyl radical on the catalyst surface (2), recombination of electron and holes formed (3), hole trapping (4), electron trapping (5), and hydroxyl attack ( $\text{HO}^\bullet$ ), where adsorbed and non-adsorbed hydroxyl radicals can react not only with the adsorbed organic compound on the catalyst surface, but also with the organic compounds in aqueous solution (Eqs. (9)–(12)).

Thus, the following kinetic expression was obtained from the above reaction pathway assuming the kinetic steady state for the  $\text{HO}^\bullet$  and holes generation (see Appendix A):

$$(-r_{\text{Ph}})_{V_R} = S_{\text{BET}} C_{\text{cat}} \alpha_1 \frac{\alpha_{3,\text{Ph}} C_{\text{Ph}}}{(\alpha_{3,\text{Ph}} C_{\text{Ph}} + 1)} \left\{ -1 + \sqrt{1 + \frac{\alpha_2 e^a(x)}{S_{\text{BET}} C_{\text{cat}}}} \right\} \quad (5)$$

To determine all kinetic parameters: first, incident radiation flux for each wavelength was calculated; secondly, the radiative transfer equation (RTE) was solved by using DOM with the corresponding boundaries conditions. Following, once the radiation intensities were determined, the volumetric rate of photon absorption (VRPA) could be calculated [9].

### 3.4. Volumetric rate of photon absorption (VRPA) and quantum efficiencies for phenol degradation

Ferrioxalate actinometry runs were carried out to estimate inlet radiation fluxes into the photoreactor used in this work [18], which were calculated by applying reactor mass balance [27]. Then, total inlet radiation flux was determined as,

$$q_T^0 = (r_{\text{Fe(II)},0}(x,t))_{V_R} \cdot \frac{V_R}{\phi_\lambda \cdot S_{\text{IRR}}} \quad (6)$$

where  $\phi_\lambda = 1.2$ , for all studied wavelength range. As  $q_T^0$  is the total flux, a discretization must be performed to calculate the intensities entering the reactor for each wavelength [27,28]:

$$I_\lambda^0 = \frac{q_T^0 \cdot f_\lambda}{\pi} = \frac{q_\lambda^0}{\pi} \quad (7)$$

where  $f_\lambda$  is the spectral energy distribution of the lamp obtained from the relative intensities of the lamp emission spectrum and the following normalization condition:  $q_T^0 = \int_\lambda q_\lambda^0 d\lambda$  [27].

Once inlet spectral intensities were known, and the RTE was solved by using DOM, the radiation field could be evaluated [8]. One-dimensional-one-directional radiation transport model was applied (Eq. (8)) because azimuthal symmetry was assumed as a considerable percentage of diffuse radiation was entering into the reactor due to the surrounding reflective surface [29]. A schematic representation of the radiation field inside the photoreactor is depicted in Fig. 1 of Supporting Information.

$$\begin{aligned} \mu \cdot \frac{dI_\lambda(x,\mu)}{dx} + (\kappa_\lambda + \sigma_\lambda) \cdot I_\lambda(x,\mu) \\ = \frac{\sigma_\lambda}{2} \int_{\mu'=-1}^{\mu'=1} p(\mu,\mu') \cdot I_\lambda(x,\mu') \cdot d\mu' \end{aligned} \quad (8)$$

where  $\kappa_\lambda + \sigma_\lambda = \beta_\lambda$ . An isotropic phase function has been taken again [9,14]. In this case the boundaries conditions needed to solve the RTE are:

$$\begin{aligned} I_\lambda(x=0,\mu) &= I_\lambda^0 \quad \mu > 0 \\ I_\lambda(x=L,\mu) &= I_\lambda^0 \quad \mu < 0 \end{aligned} \quad (9)$$

After calculating the radiation intensities, the local volumetric rate of photon absorption (LVRPA,  $e^a(x)$ ) in each point of the photoreactor, could be determined by the following equation:

$$e^a(x) = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \kappa_\lambda 2\pi \int_{\mu=-1}^{\mu=1} I_\lambda(x,\mu) d\mu d\lambda \frac{\text{Einstein}}{\text{cm}^3 \cdot \text{s}} \quad (10)$$

Before obtaining the volumetric rate of photon absorption (VRPA,  $e^a$ ), the average volumetric photon rate over the suspension

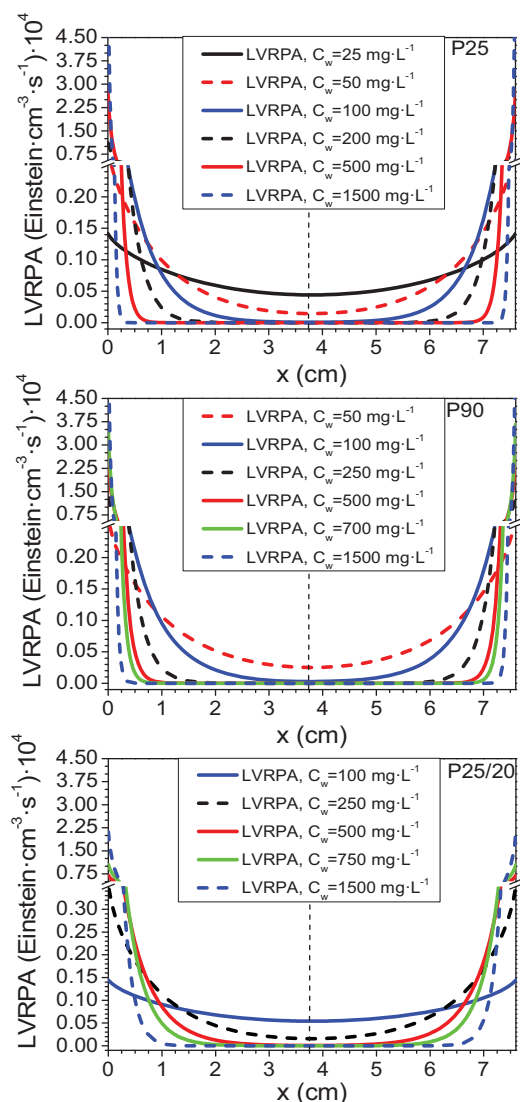


Fig. 3. Local Volumetric Rates of Photon Absorption (LVRPA) at different catalysts concentrations, for P25, P90 and P25/20.

bulk must be calculated by integrating the LVRPA values obtained for each point.

In Fig. 3 LVRPA profiles inside the reactor thickness ( $x$ ) are depicted for each catalyst, analyzing the effect of  $\text{TiO}_2$  catalyst loading.

On increasing  $\text{TiO}_2$  catalyst loading in this studied photoreactor two effects can be observed: higher attenuation in the center of photoreactor joined to increased absorption of radiation near the walls. Attenuation values were significantly higher when P25 and P90 were employed as a consequence of their significantly higher absorption and scattering coefficients compared to those found for P25/20 catalyst (see Fig. 1). Finally, in the center of photoreactor almost null absorbed radiation could be observed when  $0.1 \text{ g L}^{-1}$  of P25 or P90 catalysts were used, whereas higher P25/20 concentrations ( $0.5 \text{ g L}^{-1}$ ) were necessary to reach the same conditions.

A comparison study of the average VRPA evolution as a function of the catalyst concentration for the studied catalysts is showed in Fig. 4. Important increases of VRPA with rising catalyst loading were observed in all cases until  $0.2 \text{ g L}^{-1}$  of  $\text{TiO}_2$  concentration. Whereas almost any difference was found for both P25 and P90 ( $0.15\text{--}0.2 \text{ g L}^{-1}$ ), higher catalyst loading ( $0.6 \text{ g L}^{-1}$ ) was required to get similar VRPA values in the case of P25/20.

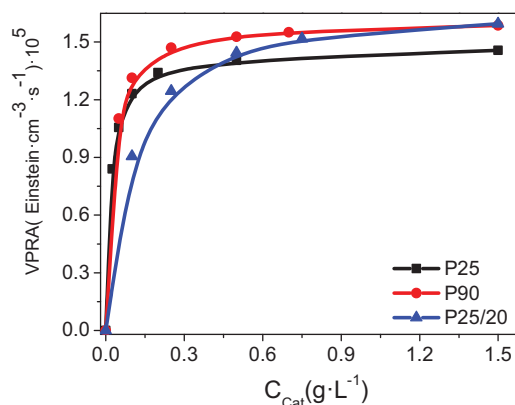


Fig. 4. Effect of different  $\text{TiO}_2$  catalyst loading on mean Volumetric Rate of Photon Absorption inside the photoreactor.

Table 3 presents the effect of catalyst concentration ( $C_{\text{Cat}}$ ) and VRPA on the initial phenol photo-oxidation rate ( $-r_{\text{Ph},0}$ ), for each  $\text{TiO}_2$ , in this studied photoreactor. The highest initial phenol photo-oxidation rate ( $3.6 \times 10^{-3} \text{ mmol L}^{-1} \text{ min}^{-1}$ ) was obtained at high concentrations of P25/20 catalyst, as a consequence of its low extinction and scattering coefficients that allowed the use of higher catalyst loadings at the same time that higher VRPA values were reached. Meanwhile, at lower catalyst concentrations, whatever the VRPA value was, higher reaction rates were always arisen for both P25 and P90 catalyst. However, it can be noted the maximum initial photodegradation rate reached by P90 ( $2.9 \times 10^{-3} \text{ mmol L}^{-1} \text{ min}^{-1}$ ) was lower than that reached by P25 ( $3.3 \times 10^{-3} \text{ mmol L}^{-1} \text{ min}^{-1}$ ), in spite of P25 absorbed lower radiation than P90. Therefore, for the reactor employed in this study it can be considered as optimal catalyst concentration,  $0.3$ ,  $0.2$  and  $0.6 \text{ g L}^{-1}$  for P25, P90 and P25/20, respectively, for the photoreactor used in this work.

In the case of P90 catalyst, initial reaction rate barely depends on catalyst concentration. Besides, the total amount of absorbed photons resulted invariable for P90 concentrations over  $0.1 \text{ g L}^{-1}$ , despite most of the radiation was absorbed close to the walls (see Figs. 3 and 4), that could be explained because photons absorbed near the walls are able to generate so many effective carriers as when they are absorbed in the bulk, given that at lower irradiation power conditions, photodegradation rate linearly depends on VRPA.

Comparison of different  $\text{TiO}_2$  intrinsic activity and their corresponding efficiency in the use of photons, were carried out considering the known parameter quantum efficiency ( $\eta$ ), that was calculated for each catalyst from relation between initial reaction rate of phenol photodegradation ( $-r_{\text{Ph},0}$ ) and the average volumetric rate of absorbed photons ( $e^a$ ) [27].

Considering the initial phenol reaction rate is:

$$(-r_{\text{Ph},0}) = \lim_{t \rightarrow 0} - \frac{\Delta C}{\Delta t} \quad (11)$$

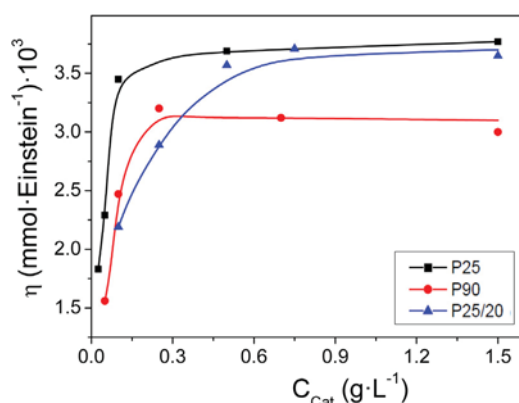
Quantum efficiency can be calculated as,

$$\eta = \frac{(-r_{\text{Ph},0})}{e^a} \quad (12)$$

The effect of catalyst loading on the calculated quantum efficiency is shown in Fig. 5, where the highest photo-efficiency was achieved when a great amount of P25/20 ( $0.6 \text{ g L}^{-1}$ ), or low P25 catalyst concentration, was used ( $0.1 \text{ g L}^{-1}$ ). However, P90 presented the lowest catalytic photoefficiency providing lower photo-oxidation rates in spite of absorbing more photons; what points to a higher likelihood of suffering recombination of the

**Table 3**  
Influence of catalyst concentration on initial rate of phenol photodegradation and VRPA, for P25, P90 and P25/20.

P25			P90			P25/20		
$C_{\text{Cat}}$ ( $\text{mg L}^{-1}$ )	$-\Gamma_{\text{Ph},0} \times 10^3$ ( $\text{mmol L}^{-1} \text{min}^{-1}$ )	$\text{VRPA} \times 10^5$ ( $\text{Einstein cm}^{-3} \text{s}^{-1}$ )	$C_{\text{Cat}}$ ( $\text{mg L}^{-1}$ )	$-\Gamma_{\text{Ph},0} \times 10^3$ ( $\text{mmol L}^{-1} \text{min}^{-1}$ )	$\text{VRPA} \times 10^5$ ( $\text{Einstein cm}^{-3} \text{s}^{-1}$ )	$C_{\text{Cat}}$ ( $\text{mg L}^{-1}$ )	$-\Gamma_{\text{Ph},0} \times 10^3$ ( $\text{mmol L}^{-1} \text{min}^{-1}$ )	$\text{VRPA} \times 10^5$ ( $\text{Einstein cm}^{-3} \text{s}^{-1}$ )
25	0.92	0.84	50	1.03	1.10	100	1.19	0.91
50	1.45	1.06	100	1.95	1.31	250	2.16	1.24
100	2.55	1.23	250	2.82	1.47	500	3.09	1.44
200	2.73	1.34	500	2.52	1.53	750	3.38	1.52
500	3.11	1.40	700	2.90	1.55	1500	3.49	1.59
1500	3.30	1.46	1500	2.86	1.59			



**Fig. 5.** Calculated quantum efficiency for different  $\text{TiO}_2$  catalyst concentration.

formed electron-holes pairs, which can be detrimental for the overall photocatalytic efficiency.

### 3.5. Kinetic parameters

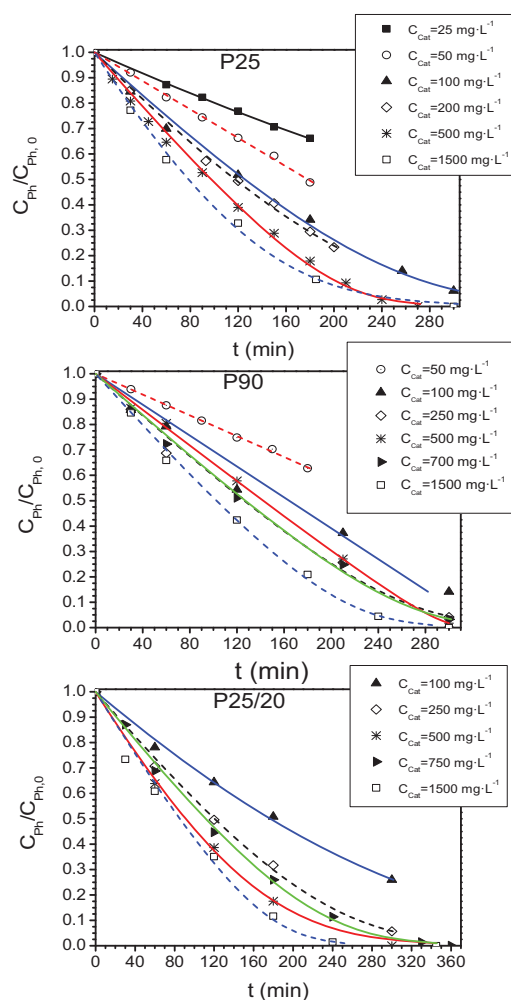
Experimental results of phenol photodegradation were compared with the average reaction rates in whole reactor volume to estimate or predict the kinetic parameters for the proposed model (Eq. (5)), applying non-linear regressions based on Levenberg-Marquardt algorithm.

Total root-square-mean errors (RSME) were calculated [29] to evaluate the mathematical goodness of fit. Very good correlations between predicted and experimental values can be seen in Fig. 6, where phenol evolution as a function of catalysts loading is followed for the three studied titania catalysts. Moreover, estimated values of kinetic parameters for each  $\text{TiO}_2$  catalyst with their 95% confidence intervals and their corresponding errors are shown in Table 4.

Concluding, the proposed kinetic model is able to simulate with very good accuracy the obtained experimental results of phenol photodegradation using these  $\text{TiO}_2$  catalysts.

However, for some parameters ( $\alpha_3$ ) the values of confidence intervals are close to the corresponding parameter itself. This could be due to possible interactions among the high number of parameters acting in the kinetic model proposed, what means there is at least a parameter to spare. Thus, the model was simplified assuming that the experiments were carried out under low irradiation conditions.

When the reactor operates at low values of irradiation power, originates low rate of photon absorption, consequently, the term containing VRPA becomes lower,  $\frac{\alpha_2 e^a}{S_{\text{BET}} C_{\text{cat}}} \ll 1$ , and the square root can be simplified by the first term of the Taylor series expansion



**Fig. 6.** Evolution of phenol photodegradation on P25, P90 and P25/20, at different catalysts concentrations (Lines correspond to fittings from experimental data).

$(\sqrt{1+x} = 1 + x/2)$ , where the model takes the following form, which shows a linear dependence on the average of the VRPA [30]:

$$\langle -r_{\text{Ph}} \rangle_{\text{VR}} = \underbrace{a_1 a_2}_{a} (e^a(x)) \frac{a_{3,\text{Ph}} C_{\text{Ph}}}{(a_{3,\text{Ph}} C_{\text{Ph}} + 1)} \quad (13)$$

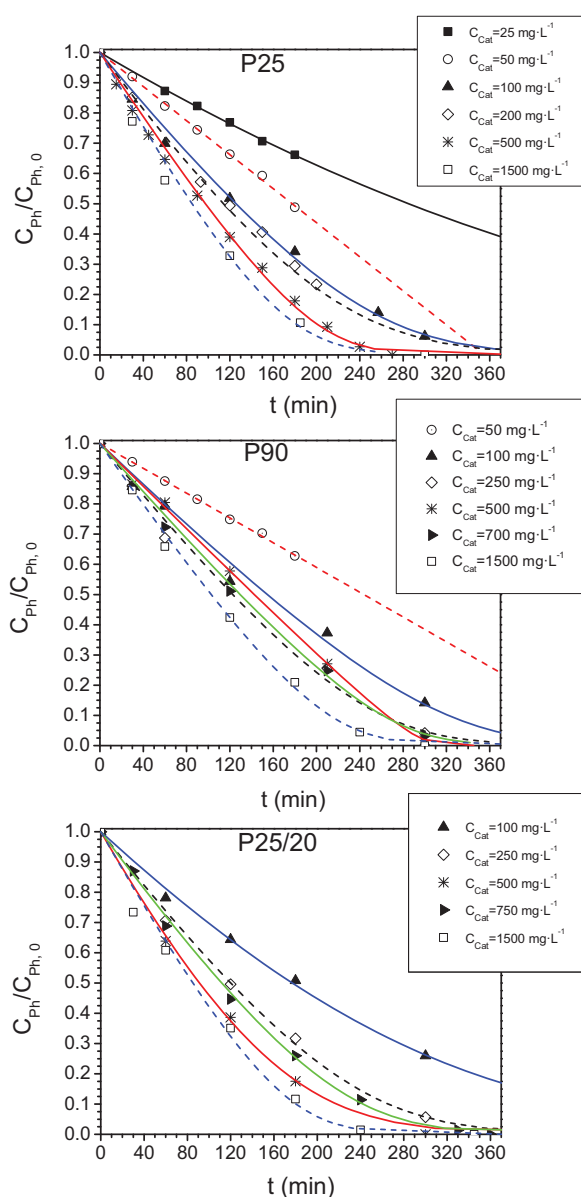
The kinetic parameters estimated for this simplified model (Table 5) presented smaller associated errors, what permits to accept the simplification of the model is adequate to reproduce the obtained experimental values accurately. This conclusion is supported by Fig. 7 under low radiation power conditions, where the good correlation between the prediction of the model and the experimental data can be seen, especially taking into account that there is no explicit dependence on catalyst concentration.

**Table 4**  
Kinetic parameters calculated by means of nonlinear multiple regressions.

Catalyst	$\alpha 1$ (mmol cm <sup>-1</sup> min <sup>-1</sup> )		$\alpha 2$ (cm <sup>2</sup> s Einstein <sup>-1</sup> )		$\alpha 3$ (L mmol <sup>-1</sup> )		RSME (%)
	Value	Confidence Int.	Value	Confidence Int.	Value	Confidence Int.	
P25	8.79	±2.22	18.49	±2.73	5.45	±2.39	4.37
P90	1.24	±1.03	39.44	±7.97	13.33	±9.58	4.68
P25/20	4.64	±1.33	30.96	±4.65	6.23	±2.55	4.63

**Table 5**  
Kinetic parameters calculated by means of nonlinear multiple regressions for the proposed kinetic in which a low irradiant power is considered.

Catalyst	$\alpha$ (mmol Einstein <sup>-1</sup> )		$\alpha 3$ (L mmol <sup>-1</sup> )		RSME (%)
	Value	Confidence Int.	Value	Confidence Int.	
P25	160.60	±35.06	23.81	±6.82	4.24
P90	129.96	±20.86	25.91	±3.72	4.80
P25/20	191.48	±35.20	17.21	±7.71	4.12



**Fig. 7.** Evolution of phenol photodegradation on P25, P90 and P25/20, at different catalysts concentrations (Lines correspond to fittings from experimental data).

It is noteworthy that when low power irradiation is assumed the proposed kinetic model satisfactorily reproduces the experimental results.

#### 4. Conclusions

An intrinsic kinetic model, able to simulate the behavior of three commercial TiO<sub>2</sub> catalysts with identical chemical structure but with different morphology and hydrodynamic particle size (P25 Aeroxide®, P25/20 VP Aeroxide® and P90 Aeroxide®) has been developed for phenol photocatalytic oxidation process in aqueous suspensions.

The proposed kinetic model takes into account not only the physico-chemical reaction parameters, but also the key parameters related to radiation interaction with these TiO<sub>2</sub> catalysts during the photocatalytic process. As far as the optical coefficients were concerned, lower scattering coefficients were arisen for larger TiO<sub>2</sub> hydrodynamic particle sizes, and consequently lower extinction coefficients were found. Therefore, the effect of TiO<sub>2</sub> hydrodynamic particle size on the optical coefficients has revealed the important role played by this property on the absorbed radiation evaluation.

The performed kinetic model, based on a proposed reaction photo-mechanism, has an explicit dependence on the volumetric rate of photon absorption (VRPA). P25 and P90 catalysts reached their highest VRPA at low catalyst concentrations (0.2 g L<sup>-1</sup>), whereas P25/20 was able to go on absorbing more radiation even when more than 1.0 g L<sup>-1</sup> catalyst concentration was employed. The obtained kinetic model has been successfully validated by experimental data, being able to reproduce the evolution of phenol photodegradation at a wide range of catalyst concentrations for these three studied TiO<sub>2</sub>.

From comparison study of calculated quantum efficiency ( $\eta$ ) as a function of TiO<sub>2</sub> loading, P25 was the most photo-efficient catalyst, whereas P25/20 reached similar efficiencies only when higher TiO<sub>2</sub> concentrations were employed. On the contrary, P90 presented the lowest photo-efficiency with lower photodegradation rates despite absorbing more radiation.

Finally, low irradiation power conditions show a good agreement between predicted and experimental values, with root-square-mean errors below 5%, regardless catalyst concentration or studied TiO<sub>2</sub>.

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### Appendix A. Derivation of the kinetic model

The derivation of the kinetic model is shown below:

By applying the kinetic steady state approximation, we can obtain HO<sup>•</sup> concentration:

$$r_{\cdot OH} = k_{6a+}[Ti^{IV}(OH)][h^+] + k_{6b+}[Ti^{IV}(H_2O)][h^+] - k_9[Ti^{IV}|HO][Ph_{ads}] - k_{10}[HO][Ph_{ads}] - k_{11}[Ti^{IV}|HO][Ph] - k_{12}[HO][Ph] - \sum_{S=1}^n k_{S,I}[Ti^{IV}|HO][S_{ads}] + k_{S,II}[HO][S_{ads}] + k_{S,III}[Ti^{IV}|HO][S] + k_{S,IV}[HO][S] \cong 0 \quad (1)$$

Furthermore, taken into account:

$$k_{6+} = k_{6a+}[Ti^{IV}(OH)] + k_{6b+}[Ti^{IV}(H_2O)] \quad (2)$$

$$[Ph_{ads}] = K_{3,Ph}[site][Ph] \quad (3)$$

$$[Ti^{IV}|HO] = K_4[HO][Ti^{IV}] \quad (4)$$

Introducing Eqs. (2)–(4) into Eq. (1), it leads to:

$$[HO] = k_{6+}[h^+] / \{ (k_9K_4[Ti^{IV}]K_{3,i}[site] + k_{10}K_{3,Ph}[site] + k_{11}K_4[Ti^{IV}] + k_{12})[Ph] + \sum_{S=1}^n (k_{S,I}K_4[Ti^{IV}]K_{3,Ph}[site] + k_{S,II}K_{3,I}[site] + k_{S,III}K_4[Ti^{IV}] + k_{S,IV})[S] \} \quad (5)$$

Defining:

$$\alpha'_{3,Ph} = k_9K_4[Ti^{IV}]K_{3,Ph}[site] + k_{10}K_{3,Ph}[site] - k_{11}K_4[Ti^{IV}] - k_{12} \quad (6)$$

$$\alpha'_{3,S} = k_{S,I}K_4[Ti^{IV}]K_{3,Ph}[site] + k_{S,II}K_{3,I}[site] + k_{S,III}K_4[Ti^{IV}] + k_{S,IV} \quad (7)$$

Phenol photo-degradation proceeds through a complex scheme of reaction giving rise to intermediate compounds before mineralization is finally reached [16]. Hydroquinone, *p*-benzoquinone (in traces), resorcinol and catechol were detected as first hydroxylation products of phenol with all these TiO<sub>2</sub> catalysts, which undergo further oxidation to yield short organic acids, such as maleic, oxalic, acetic and formic among others. Therefore, taking into account the maximum detected aromatic by-products (hydroquinone, catechol and resorcinol) along photocatalytic reaction was not more than 5.5 ppm, a constant aromatic intermediates concentration was assumed in the kinetic analysis:

$$[HO] = \frac{k_{6+}[h^+]}{\alpha'_{3,Ph}[Ph] + \sum_{S=1}^n \alpha'_{3,S}[S]} = \frac{k_{6+}[h^+]}{I(\alpha_{3,Ph}[Ph] + 1)} \quad (8)$$

where:

$$I = \sum_{S=1}^n \alpha'_{3,S}[S] \text{ y } \alpha_{3,Ph} = \alpha'_{3,Ph} / \sum_{S=1}^n \alpha'_{3,S}[S]$$

By applying the steady state approximation again in order to obtain hole concentration:

$$r_{(h^+)} = r_g - k_5[h^+][e^-] - k_{(6+)}[h^+] \cong \sim 0 \quad (9)$$

where  $r_g$  is the surface rate of electron-hole generation [28].

Since photo-generation rates of electrons and holes are equal and the semiconductor intrinsic carriers density is comparable low,

we can also make the approximation that  $[h^+] = [e^-]$ . From Eq. (8) we can extract  $[h^+]$  and substitute into Eq. (9) to obtain  $[HO]$ :

$$[HO] = \frac{(k_{6+})^2}{2k_5I(\alpha_{3,Ph}[Ph] + 1)} \left\{ -1 + \sqrt{1 + \frac{4k_5}{(k_{6+})^2} r_g} \right\} \quad (10)$$

Phenol photodegradation rate per unit catalytic area is expressed by:

$$-r_{Ph}^S = k_9[Ti^{IV}|HO][Ph_{ads}] + k_{10}[HO][Ph_{ads}] + k_{11}[Ti^{IV}|HO][Ph] + k_{12}[HO][Ph] \quad (11)$$

Substituting Eqs. (3), (4) and (10) into Eq. (11) and rearranging:

$$-r_{Ph}^S = (k_9K_4[Ti^{IV}]K_{3,Ph}[site] + k_{10}K_{3,Ph}[site] + k_{11}K_4[Ti^{IV}] + k_{12})[Ph][HO] = \frac{(k_{6+})^2}{2k_5I} \frac{\alpha_{3,Ph}[Ph]}{(\alpha_{3,Ph}[Ph] + 1)} \left\{ -1 + \sqrt{1 + \frac{4k_5}{(k_{6+})^2} r_g} \right\} \quad (12)$$

By knowing that the surface rate of electron-hole generation take the form:

$$r_g = \frac{\bar{\phi}e^a}{(S_{BET}C_{cat})} \quad (13)$$

where  $e^a$  correspond to volumetric rate of photon absorption (VRPA) and  $\bar{\phi}$  is the primary quantum yield averaged overall wavelengths. Reaction rate per unit catalytic area is affected by TiO<sub>2</sub> interfacial area per unit suspension volume,  $a_v$ . Then, the reaction rate per unit suspension volume takes the form:

$$-r_p = a_v \frac{(k_{6+})^2}{2k_5I} \frac{\alpha_{3,Ph}[Ph]}{(\alpha_{3,Ph}[Ph] + 1)} \left\{ -1 + \sqrt{1 + \frac{4k_5}{(k_{6+})^2} \frac{\bar{\phi}e^a}{S_{BET}C_{cat}}} \right\} = S_{BET}C_{cat} \alpha_1 \frac{\alpha_{3,Ph}[Ph]}{(\alpha_{3,Ph}[Ph] + 1)} \left\{ -1 + \sqrt{1 + \frac{\alpha_2 e^a}{S_{BET}C_{cat}}} \right\} \quad (14)$$

where  $S_{BET}C_{cat}$  are the TiO<sub>2</sub> specific Surface and the catalyst concentration respectively. Then, in Eq. (14) we have defined:

$$\alpha_1 = \frac{(k_{6+})^2}{2k_5I} \text{ y } \alpha_2 = \frac{4k_5\bar{\phi}}{(k_{6+})^2}$$

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.06.063>.

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# INFLUENCE OF TiO<sub>2</sub> OPTICAL PARAMETERS IN A SLURRY PHOTOCATALYTIC REACTOR: KINETIC MODELLING

## SUPPORTING INFORMATION

Table 1.- Detailed description of the photoreaction system

<b>Photo-reactor</b>	
Material	Pyrex
Height	30 cm
Inner diameter	7.6 cm
Thickness	0.2 cm
Total Volume	1360 cm <sup>3</sup>
Used Volume	1000 cm <sup>3</sup>
<b>Lamps</b>	
Model	Narva LT 15W/073 Black Light Blue
Power	15 W
Number	6
Emission Wavelength	350-410 nm
Model	Narva LT 15 W/865 COLOURLUX plus cool daylight
Power	15 W
Number	4
Emission Wavelength	400-725 nm
Irradiance	38 W·m <sup>-2</sup> (306-383 nm)
<b>Reflective surface</b>	
Material	Aluminum sheets
Length	50 cm



## Mathematical derivation of a one-dimensional-one-directional radiation transport model.

From the multidimensional RTE equation:

$$\frac{dI_\lambda(\underline{s}, \underline{\Omega})}{ds} + \kappa_\lambda I_\lambda(\underline{s}, \underline{\Omega}) + \sigma_\lambda I_\lambda(\underline{s}, \underline{\Omega}) = \frac{\sigma_\lambda}{4\pi} \int_{\Omega' = 4\pi} p(\underline{\Omega}' \rightarrow \underline{\Omega}) I_\lambda(\underline{s}, \underline{\Omega}') d\Omega' \quad (1)$$

Assuming azimuthal symmetry, the radiation field inside the reactor is calculated for one direction (x coordinate) and one dimension ( $\theta$  angular coordinate):

$$\frac{d}{ds} = \frac{\partial}{\partial x} \frac{dx}{ds} = \mu \frac{\partial}{\partial x} \quad (2)$$

where  $\mu = \cos \theta$ ,

$$\mu \frac{dI_\lambda(x, \underline{\mu})}{dx} + \kappa_\lambda I_\lambda(x, \underline{\mu}) + \sigma_\lambda I_\lambda(x, \underline{\mu}) = \frac{\sigma_\lambda}{4\pi} \int_{\mu' = -1}^1 I_\lambda(x, \underline{\mu}') \int_{\phi' = -1}^{2\pi} p(\mu_0) d\phi' d\mu' \quad (3)$$

Expanding the phase function using the Legendre Polynomials of order n ( $P_n(\mu_0)$ ) whose argument is  $\mu_0$  and the expansion coefficients  $a_n$ :

$$p(\mu_0) = \sum_{n=0}^N a_n P_n(\mu_0), \quad a_n = 1 \quad (4)$$

In the case azimuthal symmetry is considered:

$$\int_{\phi' = -1}^{2\pi} p(\mu_0) d\phi' = 2\pi \sum_{n=0}^N a_n P_n(\mu) P_n(\mu') = 2\pi p(\underline{\mu}, \underline{\mu}') \quad (5)$$

Introducing equation 3 into equation 5 yields:

$$\mu \cdot \frac{dI_\lambda(x, \mu)}{dx} + (\kappa_\lambda + \sigma_\lambda) \cdot I_\lambda(x, \mu) = \frac{\sigma_\lambda}{2} \int_{\mu' = -1}^{\mu' = 1} p(\mu, \mu') \cdot I_\lambda(x, \mu) \cdot d\mu' \quad (6)$$

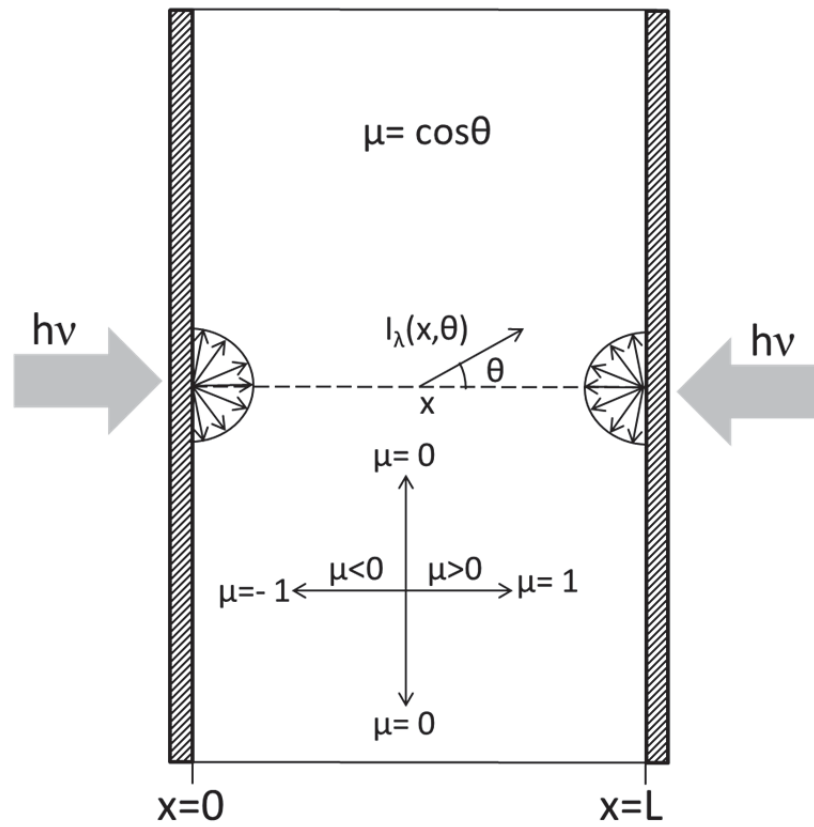


Figure 1.- Schematic representation of the radiation field inside the photoreactor [26].

# Anexo II:

Defining the role of substituents on adsorption and photocatalytic degradation of phenolic compounds



## Research Paper

## Defining the role of substituents on adsorption and photocatalytic degradation of phenolic compounds

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## ABSTRACT

The influence of adsorption behavior and the chemical nature of different *para*-positioned substituents was analyzed in the photocatalytic decomposition of phenol and other phenolic compounds (4-chlorophenol, 4-nitrophenol and methyl-*p*-hydroxybenzoate). Five commercial TiO<sub>2</sub> photocatalysts, with differences in their physico-chemical properties, were selected for comparative purpose: P25 Aeroxide<sup>®</sup>, P25/20 VP Aeroperl<sup>®</sup> and P90 Aeroxide<sup>®</sup>, provided by Evonik Company, and UV 100 from Hombikak and PC 105 from Crystal Global. On the basis of adsorption isotherms it can be concluded that the maximum uptake of the different organic compounds are directly related to the specific surface area and surface acidity of the titania. Infrared spectroscopy in diffuse reflectance mode (DRIFTS) shows that the phenolic compounds are mainly adsorbed via interactions between the phenolic –OH group and TiO<sub>2</sub> surface leading to formation of Ti-phenolates and Ti–OH. The photocatalytic removal of the phenolic compounds for the different titania samples does not follow a ranking based on the extent of adsorption whereas the initial photodegradation rate was strongly dependent on the chemical nature of the substituent, and could be correlated with the corresponding Hammett constant.

## 1. Introduction

Phenol and phenolic compounds have been deemed as a matter of environmental significance due to their high toxicities [1,2]. Unfortunately, more and more pharmaceuticals and personal care products (PPCPs) have been detected in river waters and effluents from waste treatment plants [3,4]. Among them, parabens, widely used in the cosmetics and food industry are suspected of being linked to breast cancer [5]. Photocatalytic degradation of the original compounds can lead to formation of highly toxic intermediates. Therefore, it is essential to develop advanced treatment technologies to achieve a complete elimination of these types of compounds before their release into natural waters.

In this sense heterogeneous photocatalysis has been reported to be an efficient oxidation process with a potential to achieve complete elimination of organic compounds, including PPCPs [6–8]. Among the various photocatalysts, TiO<sub>2</sub> is considered as one of the most active and appropriate because it is non-toxic, inexpensive, and relatively stable both chemically and biologically [9].

In photocatalytic processes several aspects have to be taken into account. Among them the presence of appropriate active centers for

degradation of contaminants as this is thought to play a key role in the mechanism through which organic compounds are removed. Adsorption of short chain acids such as oxalic acid, succinic acid, dichloroacetic acid and other diacids are essential in the photocatalytic process [10,11]. However, as degradation is dependent on the molecule-photocatalyst interaction, determined by the functional group, prediction of photocatalytic and adsorption behavior of pollutants with similar functional groups can be difficult [12].

The aim of this study involved performing an analysis on the adsorption of phenolic compounds with different substituents (phenol, 4-chlorophenol, methyl *p*-hydroxybenzoate and 4-nitrophenol) on the surface of different commercial TiO<sub>2</sub> photocatalysts that possess different physico-chemical properties. The compounds were selected due to their detection in the aquatic environment as they can be used as intermediates in several industries and be formed as byproducts in the photocatalytic degradation of some pesticides and contaminants. For example, phenol has been reported as a possible intermediate of methyl *p*-hydroxybenzoate photodegradation [6]. Diffuse reflectance infrared spectroscopy (DRIFTS) was used to determine the nature of the interaction between the organic compound and the TiO<sub>2</sub> surface. Photocatalytic activity measurements were performed to assess the

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degradability of the different phenolic compounds and evaluate the influence of adsorption and relationship with the adsorptive characteristics of a wide number of different titanias.

## 2. Material and methods

### 2.1. Catalysts and chemicals

Analytical grade phenol (Panreac), 4-chlorophenol (4-CP), methyl *p*-hydroxybenzoate (M *p*-HB) and 4-nitrophenol (4-NP) (Sigma-Aldrich, SA) were employed as received without further purification. Solutions were prepared with milli-Q water. Five commercial TiO<sub>2</sub> catalysts were selected, including Evonik P25 (abbreviated as P25 throughout the text), Evonik P25/20 (P25/20), Evonik P90 (P90), Hombikat UV100 (HBK), and CristalACTIV PC105 (PC105), all employed as received. All reagents used for chromatographic analyses, Milli-Q water, *ortho*-phosphoric acid, methanol, sulphuric acid and sodium carbonate, were HPLC grade.

### 2.2. Photocatalyst characterization

The specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method [13] based on N<sub>2</sub> isotherm data measured at 77 K in a Micromeritics ASAP 2420 apparatus on samples previously outgassed overnight at 413 K to a vacuum of < 10<sup>-4</sup> Pa in order to ensure a dry, clean surface free from any weakly held adsorbed species. The micropore volume and external surface area were calculated from the corresponding t-plots from the adsorption data, and the mesopore volumes were determined from the amount adsorbed at a relative pressure of 0.96 on the desorption branch of the isotherm (equivalent to the filling of all pores below 50 nm, minus any microporosity previously determined from the corresponding t-plot). The porosity studies were completed by mercury intrusion porosimetry (MIP) using CE Instruments Pascal 140/240 and applying the Washburn equation. Total pore volume was evaluated by combining both techniques.

Catalyst surface acidity was determined by titration with ammonia at room temperature, using an ASAP-2010C instrument (Micromeritics). The TiO<sub>2</sub> catalysts were first outgassed at 623 K for 2 h, and then cooled to 303 K before determining the relative quantities of ammonia physisorption plus chemisorption. After outgassing the samples at 303 K for 4 h to remove the physisorbed ammonia, a second adsorption isotherm was obtained to determine the chemisorbed amount by difference between the two isotherms.

Diffuse reflectance spectra were recorded with a UV–visible Agilent–Varian, Cary 5000, equipped with an integrating sphere. Analyses of the band gap transitions of the samples were made using the equation  $\alpha \cdot h \cdot \nu = A \cdot (h\nu - E_g)^{n/2}$  [14]. Catalysts structural characterization were performed with a X-ray polycrystal PANalytical X'Pert PRO using nickel-filtered Cu K $\alpha$  (1.541874 Å) radiation operating at 40 kV and 40 mA, with a 0.02° step size and accumulating a total of 50 s per point. Crystallite sizes was estimated by employing the Scherrer equation [15] and the crystalline phases were identified by comparison with ICDD PDF database [16]. The quantification of each previously selected crystalline phase was automatically calculated by X'Pert Highscore Plus software by RIR (Reference Intensity Ratio) method. Laser Diffraction (LD) measurements were performed to characterize the hydrodynamic particle size distribution of TiO<sub>2</sub> aggregates in aqueous suspensions using Mastersizer S by Malvern Instruments equipped with a He-Ne laser ( $\lambda = 632.8$  nm).

### 2.3. Adsorption isotherms

Adsorption isotherms were carried out at constant temperature of 25 ± 0.1 °C and natural pH of the corresponding suspensions in Milli-Q water in a bath-cum-shaker for 24 h. Isotherms were conducted using

0.5 g L<sup>-1</sup> as photocatalyst concentrations. The TiO<sub>2</sub> concentration was added and mixed in darkness in a series of capped 100 mL Pyrex bottles containing 25 mL of the component solution with concentrations ranging from 5 to 200 mg L<sup>-1</sup>. After 24 h, the suspensions were centrifuged, filtered with 0.45 μm syringe filter (Millipore) and then analyzed to obtain the equilibrium concentrations of the corresponding compound using a UV–visible spectrophotometer (Lambda 25, PerkinElmer). Concentrations were calculated from linear calibration curves carried out in triplicate with a mean slope of 3.94, 2.55, 3.94 and 0.33 and a standard deviation of 0.03, 0.01, 0.05 and 0.02 for phenol, 4-nitrophenol, 4-chlorophenol and methyl 4-hydroxybenzoate, respectively.

The maximum uptake per unit mass of the material was calculated from the following expression:

$$q_e = \frac{V \cdot (C_i - C_e)}{m_{\text{cat}}} \quad (1)$$

where  $q_e$  is the amount adsorbed at equilibrium (mmol g<sup>-1</sup>),  $C_i$  is the initial concentration (mmol L<sup>-1</sup>),  $C_e$  is the equilibrium concentration (mmol L<sup>-1</sup>),  $V$  is the volume of the liquid phase (L) and  $m$  is the mass of photocatalyst used.

### 2.4. Diffuse reflectance FTIR (DRIFTS) experiments

DRIFT spectra were measured using a Shimadzu IRTracer-100 infrared spectrophotometer equipped with an MCT cryogenic detector. Spectra were recorded in the 4000–1000 cm<sup>-1</sup> region, employing a resolution of 4 cm<sup>-1</sup>, averaging of 80 interferograms. The analyzed samples were obtained by shaking 25 mL solution with 100 mg L<sup>-1</sup> of the organic pollutant and 0.5 g L<sup>-1</sup> of TiO<sub>2</sub> for 24 h at 25 °C. Afterwards, suspensions were left to dry at room temperature. Spectra of reference phenolic compounds were obtained after dilution in KBr.

### 2.5. Photocatalytic activity

The photocatalytic degradation measurements were carried out using a 1 L semi-continuous cylindrical reactor made of Pyrex and placed in a Multirays apparatus (Helios Italquartz) where it was surrounded by 6 Black Light Blue UVA Lamps and 4 day-light lamps of 15 W each. The distance between the lamps and the wall of the reactor was around 10 cm. This set of lamps was used to obtain a UV-A radiant flux approximating the usual average solar UV flux values [17]. The system included a fan as cooling system to perform photocatalytic reactions at room temperature (25–30 °C) and atmospheric pressure. The mass of photocatalyst and pollutant were held constant at 250 mg L<sup>-1</sup> and 50 mg L<sup>-1</sup>, respectively. The mixture was continually agitated while bubbling air (75 NmL min<sup>-1</sup>). Prior to reaction, the mixture was premixed for 30 min in darkness to allow adsorption equilibrium to be reached. Samples were taken out at certain times to follow the reaction. A more detailed description is given in [18].

High Performance Liquid Chromatography, HPLC, was used to identify and quantify phenolic compounds and aromatic intermediates in a Varian 920 LC with photo-diode array detector. A Nucleosil C18 5 μm column (15 cm length, 4.6 mm diameter) was used at 30 °C. A simple flow gradient was adopted: 0.6 mL min<sup>-1</sup>, 40/60% v/v methanol/acidic water (0.1% phosphoric acid) mixture were used as solvent in the range 0–8 min and 1 mL min<sup>-1</sup>, 20/80% v/v methanol/acidic water in the range 8–18 min.

Nitrate and nitrite ions and short-chain organic acids were measured by Ion Chromatography with chemical suppression (Metrohm 883 IC) and a conductivity sensor using a Metrosep A supp 7-250 column (250 mm length, 4 mm diameter) as stationary phase. When Ammonium ions and other cations were detected, the stationary phase was a Metrosep C 6-250 column (250 mm length, 4 mm diameter).

**Table 1**  
Physico-chemical properties of TiO<sub>2</sub> catalysts.

Catalyst	A (%)	R (%)	d <sub>A</sub> (nm)	d <sub>R</sub> (nm)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	A <sub>int</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>micro</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>meso</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>macro</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>Total</sub> (cm <sup>3</sup> g <sup>-1</sup> )	IEP	Acidity (mmol H <sup>+</sup> g <sup>-1</sup> )	Acidity (mmol H <sup>+</sup> g <sup>-1</sup> m <sup>-2</sup> )	BG (eV)
P25	84	16	21	33	54	0	0.00	0.00	0.65	0.65	6.8	0.30	0.006	3.26
P90	87	13	17	32	81	0	0.00	0.00	0.26	0.26	6.7	0.68	0.008	3.28
P25/20	88	12	21	33	54	0	0.00	0.00	0.55	0.55	5.4	0.29	0.005	3.26
PC105	100	0	19	–	79	2	0.00	0.00	0.30	0.30	4.8	0.46	0.006	3.27
HBK	100	0	8	–	356	81	0.03	0.32	0.54	0.89	6.3	1.24	0.003	3.26

A: Anatase; R: Rutile; HDP: Hydrodynamic particle size; IEP: Isoelectric Point or Point of Zero Charge.

## 2.6. Hydroxyl radicals analysis

A study of hydroxyl radical generation (HO·) was performed using the same described reactor and radiation. For the detection of HO·, terephthalic acid (TA) in alkaline solution was used as the probe molecule [19,20]. 0.25 g L<sup>-1</sup> of TiO<sub>2</sub> and 0.5 mM of TA were mixed in a suspension in which NaOH 2 mM was dissolved and the mixture was stirred and irradiated. Fluorescence emission of the product, 2-hydroxyterephthalic acid (TAOH) was measured at an emission wavelength of 425 nm and an excitation wavelength of 315 nm using a Perkin Elmer Luminescence spectrometer LS 50B.

## 3. Results and discussion

### 3.1. Catalysts properties

In Table 1 the main physico-chemical properties of the studied TiO<sub>2</sub> photocatalysts are summarized. From XRD measurements, P25, P90 and P25/20 presented two crystalline phases, 82 ± 5% anatase and 17 ± 5% rutile, PC105 and HBK only presented the anatase phase.

P25, P25/20, P90 and PC105 powder nanoparticles are characterized by unique macroporosity as corresponding to non-porous type II isotherm [21], which is related to agglomerates or inter-particle spaces. The TiO<sub>2</sub> catalysts showed a wide range of specific surface areas. The higher surface area found in P90 and PC105 catalysts would appear to be related to its slightly smaller anatase crystallite sizes (17 and 29 nm, respectively), whereas HBK presented a complete micro, meso and macropore size distribution and the highest BET surface area (356 m<sup>2</sup> g<sup>-1</sup>) (Table 1).

The Isoelectric Point (IEP) may give a good indication about the surface oxygen complexes and the electronic surface charges of these samples. Pure titania materials generally present isoelectric point values in the pH range of 6.0–6.5 [22], which are characteristic of materials with slightly acidic or almost neutral character, such as P25 [23], P90 and HBK. The low values found for P25/20 and especially PC105, indicate a certain acidic character in their surfaces. Shifts in the isoelectric points can occur in response to changes in cation coordination, crystallinity, hydration state, surface composition and structural charge or ion exchange capacity, amongst others [24].

The surfaces of the TiO<sub>2</sub> materials do not present significant levels of acidity. The ammonia uptake values are in general very low (Table 1). When normalized per unit surface area, HBK seems to have the lowest acidity whereas P25 and P25/20 showed similar levels.

In terms of their electronic properties, no significant differences were found in UV–vis spectra, with values between 3.26 and 3.28 eV (Table 1) for the estimated band gap (BG).

### 3.2. Adsorption studies

Equilibrium adsorption studies were conducted in order to determine the uptake capacity of the adsorbent and to derive a better understanding of the surface properties and adsorbent-adsorbate affinity. From the data obtained, Langmuir and Freundlich model

isotherms were employed as these two models are the most frequently used to establish the adsorption equilibrium. Eq. (2) represents the Langmuir isotherm:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where  $q_e$  is the uptake at equilibrium,  $C_e$  is the equilibrium concentration,  $K_L$  is the Langmuir constant and  $q_m$  is the maximum adsorption capacity. Eq. (3) expresses the Freundlich model:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where  $q_e$  is the amount of organic compound adsorbed,  $C_e$  is the equilibrium concentration,  $K_F$  is the Freundlich constant which indicates adsorption affinity between adsorbate and adsorbent [25] and  $1/n$  is correlated with the averaged energies of adsorption [12].

The adsorption isotherms for phenol, 4-CP, M *p*-HB and 4-NP for each photocatalyst (P25, P25/20, P90, HBK and PC105) showed more uniform behavior for phenol across the series than for the other phenolic compounds that exhibited more heterogeneity and uptake depending on photocatalyst (Fig. 1). All isotherms exhibit an L-Shape which is the most common type observed for adsorption from solution. This trend results more remarkable in the case of 4-nitrophenol and 4-chlorophenol as an indicator of adsorbate-photocatalyst surface affinity [26]. The data were fitted by using nonlinear regressions to obtain the Freundlich and Langmuir parameters (shown in Supplementary information Table 1). As far as the parameters related to the uptake capacity are concerned ( $q_m$ ,  $K_F$ ), both models show the same response for the amount adsorbed by each photocatalyst. These parameters are of the same order of magnitude as those reported in the literature for similar photocatalytic systems [10,12]. The relationship between uptake and BET surface area and phenol acidity were attempted for an initial concentration of 200 mg L<sup>-1</sup> (Fig. 2). No correlation was found between uptake and phenol acidity (pKa). When uptake is normalized per unit surface area, it would appear that, in general speaking, P25 adsorbs most of every organic compound (with the exception of phenol itself). This may be related to the acidity density (Table 1) although the limited differences between acidity levels measured using ammonia adsorption does not allow detailed discrimination.

In terms of Freundlich and Langmuir parameters related to adsorption affinity, again both models show the same trend for each adsorbent for the different adsorbates (SI, Table 1). All Freundlich  $n$ -values are higher than unity, consistent with the expectation for a chemisorption process [27] and are indicative of the average adsorption energy, with higher solid-adsorbate affinity giving higher  $n_F$  values [12].

It is noteworthy that the model that best fit each isotherm changes for each photocatalyst and organic pollutant. The dependence of adsorption on the two different isotherms types may be explained by considering that the oxide surfaces have different types of surface sites with different affinities. Therefore, the amount adsorbed is the summation of adsorption on all sites, with the stronger binding sites being occupied initially and following the Langmuir model while the



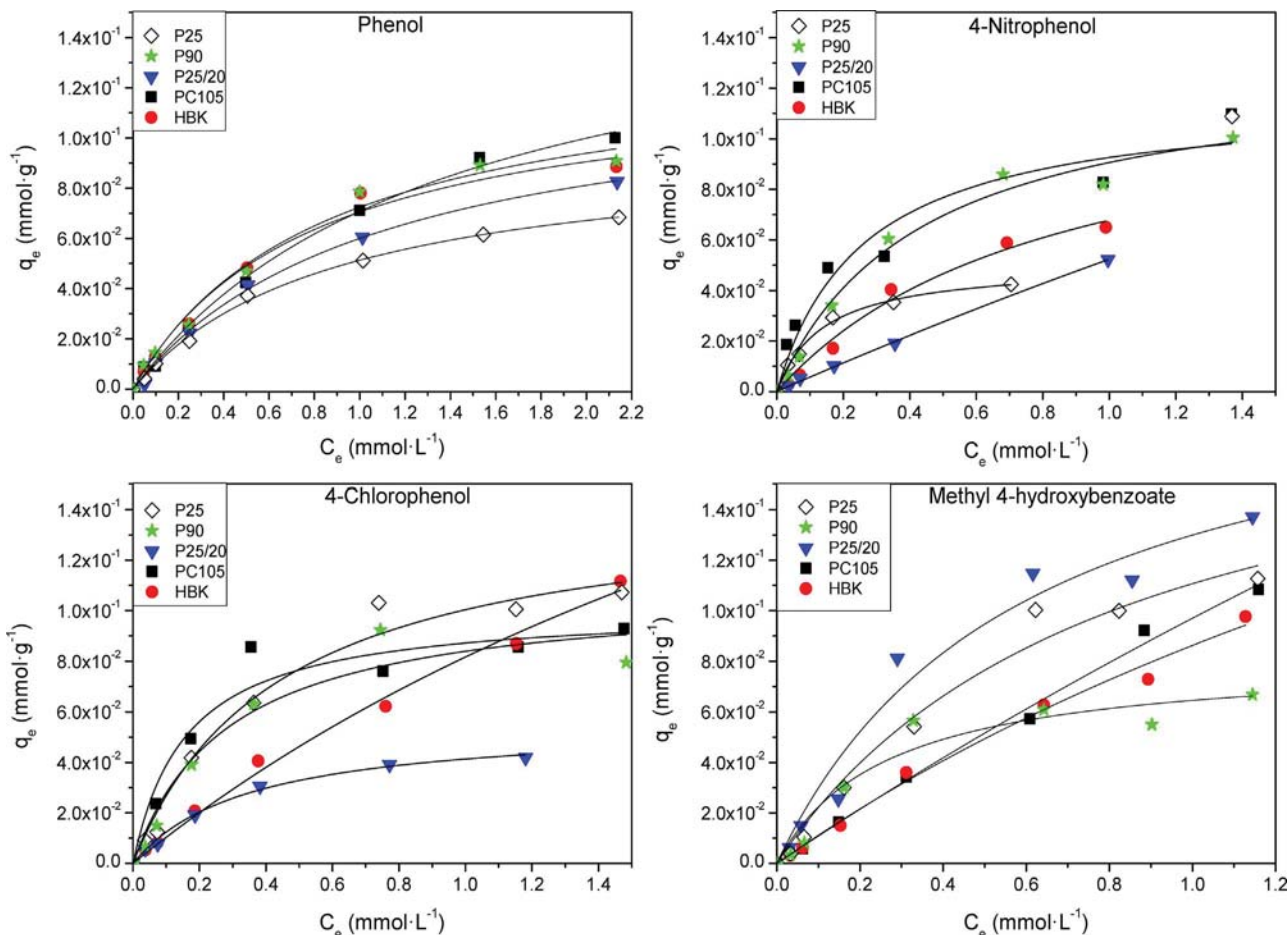


Fig. 1. Adsorption isotherms of the phenolic compounds obtained as non-linear representation of Langmuir model.

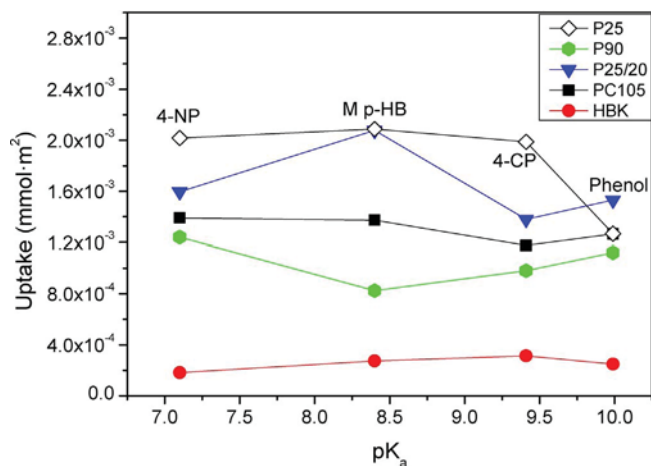


Fig. 2. Amount adsorbed by each photocatalyst at an equilibrium concentration of 200 mg L<sup>-1</sup> of phenolic compound and relationship with acidity of the different phenols.

Table 2

Partition octanol-water coefficient (log K<sub>OW</sub>), Hammett constants (σ) and pK<sub>a</sub>'s of the studied phenolic compounds.

Pollutant	log k <sub>ow</sub>	σ	pK <sub>a</sub>
Phenol	1.47	0.00	10.0
4-CP	2.41	0.23	9.4
M p-HB	2.00	0.39	8.4
4-NP	1.92	0.78	7.1

Freundlich model indicates a multisite adsorption process involving strong and weak binding sites [27]. This multisite process will also depend on the hydrophobicity and field effects of the organic molecule and the manner in which it was adsorbed. That is the reason why a relationship between the uptake of each organic pollutant and the hydrophobicity and field effects was attempted. To do this, the octanol-water partition coefficient (log K<sub>OW</sub>) was used as an indicator of water solubility (the higher the log K<sub>OW</sub>, the lower the solubility in water) of the different phenols [28,29] (Table 2). Additionally, the Hammett constants (σ) were employed as a measure of the total electronic influence (resonance and field effects) of a substituent on the base aromatic system, phenol [30]. A positive value of the constant indicates an electron-withdrawing group and a negative value an electron-donating group. The similarity observed (Fig. 2) between the uptakes of the different adsorbates by a specific photocatalyst suggests minimal effect of hydrophobicity such that it does not greatly affect the amount adsorbed. Similarly, the influence of the effect of substituents on the electronic character of phenol plays only a limited role. The uptake for the catalysts, normalized per unit surface area, followed the sequence:

$$q_e^{P25} > q_e^{P25/20} > q_e^{PC105} > q_e^{P90} > q_e^{HBK}$$

### 3.3. DRIFTS studies

Adsorption phenomena has been reported to be of significant importance in the degradation of some organic compounds, such as dichloroacetic acid [31]. To obtain a better description of the way in which the phenols were adsorbed, DRIFTS studies were performed. A first overview of the spectra showed that both zones 4000–1000 cm<sup>-1</sup>

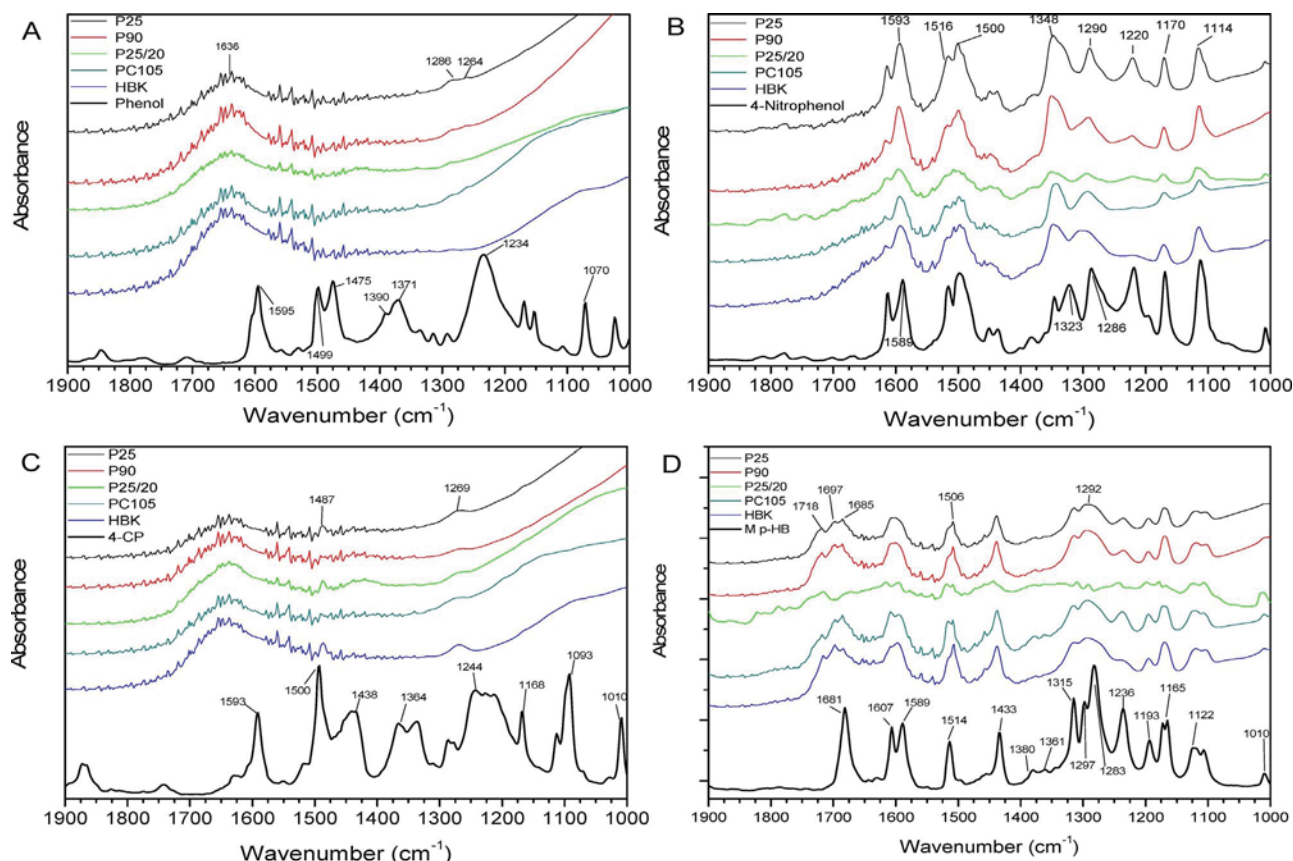


Fig. 3. DRIFT spectra of the adsorbed organic compounds on different  $\text{TiO}_2$  and of the reference phenols spectra: (A) phenol, (B) 4-nitrophenol, (C) 4-chlorophenol, (D) methyl 4-hydroxybenzoate.

(SI Fig. 1) and in detail, the region  $1900\text{--}1000\text{ cm}^{-1}$  (Fig. 3) present the characteristic spectra of pure 4-nitrophenol, phenol, 4-chlorophenol and methyl 4-hydroxybenzoate and in their adsorbed forms in the presence of the series of titania photocatalysts. However the spectra in the adsorbed forms were extremely attenuated in the case of phenol and 4-chlorophenol as adsorbates with the only apparent features appearing between  $1300$  and  $1200\text{ cm}^{-1}$ . An overview of the band assignments of each phenolic compound are given in Table 3.

In the case of phenol (Fig. 3(A)), the most important spectral changes originating from exposure to titania are the disappearance of bands due to the O–H bending modes ( $1390$  and  $1371\text{ cm}^{-1}$ ), a sharp reduction of the intensities and shift of the  $\nu\text{C–O}$  ( $1234$  and  $1070\text{ cm}^{-1}$ ) and a strong decrease of bands attributed to the aromatic ring stretching modes between  $1600$  and  $1450\text{ cm}^{-1}$ . The loss in intensity of this feature may be caused by the formation of phenolate or by adsorption of the phenol in a flat lying orientation on  $\text{TiO}_2$  [10].

The  $\nu\text{CO}$  mode of the phenol in the region  $1260\text{--}1200\text{ cm}^{-1}$  was replaced by a doublet at  $1264$  and  $1286\text{ cm}^{-1}$  in the adsorbed state. The formation of monodentate phenolates located on different faces of  $\text{TiO}_2$  could be responsible of the generation of this doublet [32–34]. This might be interpreted as acidic phenol molecules being dissociatively adsorbed on the  $-(\text{Ti–O–})$  acid-base pairs to form  $-\text{OH}$  groups and Ti-phenolates. The shift of the C–O stretching mode is due to a strong interaction with the surface Ti cations, associated with local oxygen vacancies [33].

The maxima at  $3800\text{--}3000\text{ cm}^{-1}$  (SI Fig. 1) was attributed to the stretching mode of hydroxyl groups  $\nu(\text{OH})$  with the band at  $3698\text{ cm}^{-1}$  observed in sample P25, P90, P25/20 and PC105 indicative of isolated hydroxyl groups characteristic of defects or oxygen vacancies on the photocatalyst surface. The hydroxyl group band at lower wavenumber ( $3616\text{ cm}^{-1}$ ) may have been due to the formation of  $-\text{OH}$  groups

following the dissociative adsorption of phenol and causing the rupture Ti–O–Ti bonds [33,35]. The broad absorption in the region  $3600\text{--}3000\text{ cm}^{-1}$  was caused mainly by hydrogen bonding between water molecules forming a multilayer, and between water molecules and dissociated phenol. The bending mode of water  $1636\text{ cm}^{-1}$  is consistent with the presence of multilayers of water.

The aromatic nitro compounds (Fig. 3(B)) have a strong absorption due to the stretching mode of vibrations of the  $\text{NO}_2$  group [36]. The peak assigned to the aromatic ring stretching vibrations of *p*-nitrophenol is shown at  $1589$  and  $1500\text{ cm}^{-1}$  [37]. Only a small shift in the position of the band is observed ( $1593\text{ cm}^{-1}$ ) following exposure to  $\text{TiO}_2$  surface suggesting that electrodonation to the aromatic ring is not altered after interaction [12]. This could indicate that the predominant adsorption mode is between the nitro and OH groups as considered at acidic pH by Vargas et al. [38]. To support this, the peak at  $1516\text{ cm}^{-1}$ , ascribed to anti-symmetric  $\text{NO}_2$  stretching vibrations [36], remained at the same position in the adsorbed state but with lower intensity since hydrogen bonding has a minimal effect on the anti-symmetric  $\text{NO}_2$  stretching mode. Peaks at  $1323$  and  $1286\text{ cm}^{-1}$  seen in the *p*-nitrophenol spectra [37] are attributed to symmetric  $\text{NO}_2$  stretching vibrations plus C–O stretching vibrations [39]. In the adsorbed state, these bands shift to  $1335$  and  $1290\text{ cm}^{-1}$ , respectively. The peaks at  $1348$  and  $1220\text{ cm}^{-1}$  are described by the OH bending modes [36]. The small variation in frequencies of these bands suggests that interaction does not mainly occur through generation of 4-nitrophenolate monodentate. Strong absorption bands at  $1170$  and  $1114\text{ cm}^{-1}$  are assigned to C–H in-plane and out-of-plane bending vibrations, respectively.

In the case of the free 4-chlorophenol (Fig. 3(C)), several bands can be distinguished in the region  $1600\text{--}1000\text{ cm}^{-1}$  in the infrared spectrum. Bands at  $1593$  and  $1500\text{ cm}^{-1}$  can be ascribed to the aromatic ring modes of vibration [40]. The band at  $1438\text{ cm}^{-1}$  can be attributed





to a combination of C=C stretching plus O–H bending modes while the peak at 1364 is attributed to O–H bending plus C–H in-plane bending vibrations [40,41]. C–H in-plane bending vibrations also give rise to the bands at 1010  $\text{cm}^{-1}$ , 1168  $\text{cm}^{-1}$  and coupled to C–O stretching mode describes the peak at 1244  $\text{cm}^{-1}$ . The band at 1093  $\text{cm}^{-1}$  is characteristic of *p*-chlorophenol and can be assigned to the C=C stretching coupled with C–Cl stretching vibrations [40,41]. However, in the adsorbed state, analogously to phenol, a strong decrease of the bands attributed to the bands due to ring stretching modes (between 1600 and 1450  $\text{cm}^{-1}$ ) are noted which could be due to the formation of chlorophenolate anion. This is also supported by a reduction in intensity of the O–H bending bands (two bands at 1438 and 1364  $\text{cm}^{-1}$ ) and a shift of the band due to the  $\nu\text{C}=\text{C}$  suggesting an electrodonation reduction to the ring. Additionally, the band due to the C–O stretching mode can be seen although it was shifted from 1244 to 1269  $\text{cm}^{-1}$ .

In the case of methyl 4-hydroxybenzoate (Fig. 3(D)), the O–H stretching mode in the 3800–2500  $\text{cm}^{-1}$  region, manifests as a band at 3321 which points out the importance of hydrogen bonding in the adsorption of methyl *p*-hydroxybenzoate species [42]. The peaks at 3080 and 3033  $\text{cm}^{-1}$  arise from the aromatic C–H modes [43]. The  $\text{CH}_3$  stretching mode gives rise to one peak at 2964; also peaks at 1380 and 1361  $\text{cm}^{-1}$  are attributed to the  $\text{CH}_3$  deformations. Bands at 1918 and 1681  $\text{cm}^{-1}$  are assigned to overtone or combination of the C–H stretching mode, and C=O stretching mode, respectively. The aromatic ring skeletal stretching vibration are indicated by the peaks between 1615 and 1500  $\text{cm}^{-1}$ , plus a peak at 1433  $\text{cm}^{-1}$  [42,43]. Bands due to C–H in-plane bending vibrations are identified at 1315, 1236, 1193 and 1010  $\text{cm}^{-1}$ , with the peak at 1236  $\text{cm}^{-1}$  coupled with the C–O stretching band which is also assigned to the peaks at 1297 and 1165  $\text{cm}^{-1}$  [43]. When methyl 4-hydroxybenzoate is considered in the adsorbed state a disappearance of O–H bending band between 1350 and 1370  $\text{cm}^{-1}$  can be clearly observed and an increase of the band intensity at 1292  $\text{cm}^{-1}$ , corresponding to the C–O stretching mode, which would indicate that it is adsorbed forming Ti-methyl *p*-hydroxybenzoate anion. Additionally, the band due to the  $\nu(\text{C}=\text{O})$  mode is shifted from 1681  $\text{cm}^{-1}$  and resolved to give 3 features at 1718, 1697 and 1685  $\text{cm}^{-1}$ . The shift towards higher wavenumbers could be related to the interaction between OH groups of methyl *p*-hydroxybenzoate and the Ti atoms, as observed in the presence of alcohols, which leads to an increase of electron density of the phenyl-carbonyl system [44].

By considering the above analysis it can be concluded that the organic compounds studied are adsorbed forming a Ti-phenolate anion and a Ti–OH because of the interaction of the OH group of the organic molecule with the  $\text{TiO}_2$  surface. Furthermore, in the case of *p*-nitrophenol, adsorption could possibly take place via a hydrogen bond interaction between the Ti–OH and the nitro group of 4-NP.

### 3.4. Photodegradation of substituted phenols

The different activities of the  $\text{TiO}_2$  samples in the degradation of the four organic compounds were compared by performing photocatalytic degradation runs of each phenolic compound. The results are shown in Supplementary information Fig. 2. The efficiency of photocatalysts

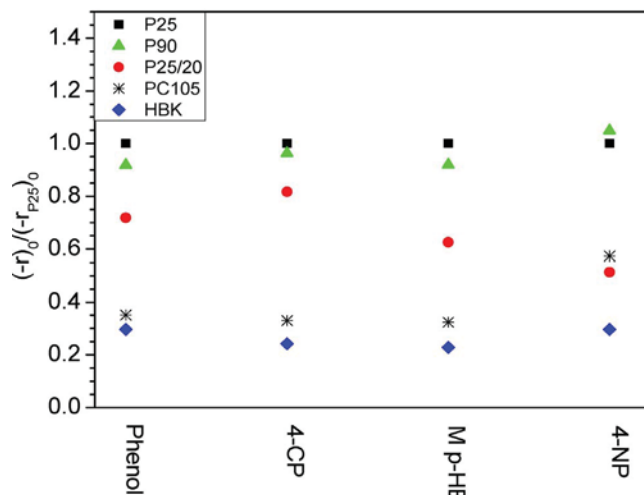


Fig. 4. Ratio of the initial photodegradation rate for each photocatalyst to the initial photodegradation rate obtained using P25, for the different phenolic compounds.

followed the order: P25 > P90 > P25/20 > PC105 > HBK (Table 4). The three catalysts from Evonik (P25, P90 and P25/20) turned out to be the most active even though their BET surface areas were much lower than that of HBK (356  $\text{m}^2 \text{g}^{-1}$ ). This behavior has been related to the existence of a mixture of crystalline phases in which rutile is dispersed into anatase phase, resulting in an improvement of the electronic interactions between the anatase and rutile phases [45,46]. The reason why photocatalysts with higher area, such as HBK, present lower photoactivity is supported by the fact that the extent of adsorption of any of the organic compounds studied was relatively low (SI Table 1) and is very similar for all the photocatalysts. No changes in the manner in which they were adsorbed have been observed. The difference in the photocatalytic performance could be influenced by differences in hydrodynamic particle sizes and optical properties (absorption, scattering and extinction coefficient) among the different photocatalysts [18,47]. The sequence related to the activity of the photocatalysts mentioned above was maintained for all of the organic compounds studied (Fig. 4), in which the ratio of the initial photodegradation rate for a given photocatalyst to the initial photodegradation rate obtained using P25 for the different phenolic compounds is plotted. The fact that the ratio does not change for the different organic compounds supports that adsorption is not a key factor in determining the relative rate of photodegradation. The formation of  $\text{HO}\cdot$  upon UV irradiation was also measured given that it is an indicator of the photocatalytic efficiency. Hydroxyl radical generation was analyzed by integration of the fluorescence intensity of 2-hydroxyterephthalic acid (TAOH) formed by the reaction between  $\text{HO}\cdot$  and terephthalic acid (TA). Under these conditions, the hydroxylation of TAOH was due only to oxidation by  $\text{HO}\cdot$  [20]. In Fig. 5 the results show an increase of the fluorescence intensity over irradiation time. It can be seen that the formation rate followed the same sequence as that for the photodecomposition of the organic compounds, with P25 and HBK being the photocatalysts that showed the highest and the lowest  $\text{HO}\cdot$

Table 4

Initial degradation rate of 4-CP and 4-NP, and initial formation rate of  $\text{NO}_2^-$  and  $\text{Cl}^-$ . The ratio of the initial formation rate of  $\text{NO}_2^-$  and  $\text{Cl}^-$  to the initial rate of 4-NP and 4-CP removal is given.

Catalyst	$(-r_{0,4\text{-CP}}) \cdot 10^3$ ( $\text{mmol min}^{-1} \text{L}^{-1}$ )	$(-r_{0,4\text{-NP}}) \cdot 10^3$ ( $\text{mmol min}^{-1} \text{L}^{-1}$ )	$(r_{0,\text{NO}_2^-}) \cdot 10^3$ ( $\text{mmol min}^{-1} \text{L}^{-1}$ )	$(r_{0,\text{Cl}^-}) \cdot 10^3$ ( $\text{mmol min}^{-1} \text{L}^{-1}$ )	$(r_{0,\text{NO}_2^-}) / (-r_{0,4\text{-NP}})$	$(r_{0,\text{Cl}^-}) / (-r_{0,4\text{-CP}})$
P25	2.18	0.70	0.58	1.65	0.834	0.757
P90	2.10	0.73	0.50	1.83	0.679	0.871
P25/20	1.78	0.36	0.31	1.31	0.859	0.736
PC105	0.72	0.40	0.26	0.42	0.650	0.578
HBK	0.53	0.21	0.16	0.45	0.772	0.857

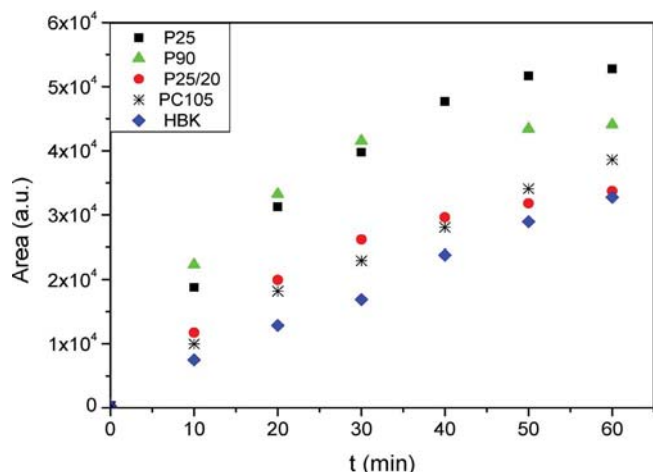


Fig. 5. Integrated area of 425 nm fluorescence peak for the different TiO<sub>2</sub> photocatalysts.

formation rate, respectively. This result could indicate that degradation reactions mainly took place in the solution of the surroundings of photocatalyst surface, mediated by the HO· that are formed on the semiconductor but diffuse from TiO<sub>2</sub> surface and therefore diminish/eliminate any significance of adsorption.

The TiO<sub>2</sub> catalysts also exhibited different performance in the substitution of the –Cl and –NO<sub>2</sub> groups in 4-chlorophenol and 4-nitrophenol, respectively. To analyze the ease with which –Cl and –NO<sub>2</sub> groups are released in terms of the initial rate of formation of Cl<sup>–</sup>, NO<sub>2</sub><sup>–</sup> and the ratio of the initial rate of chloride and nitrite formation to the initial rate of 4-CP and 4-NP removal were calculated and summarized in Table 4. 4-nitrophenol over P25 and P25/20 were able to achieve (r<sub>0,NO<sub>2</sub><sup>–</sup>)/(–r<sub>0,4-NP</sub>) ratios of over 83% what means that disappearance of 4-NP would correspond to –NO<sub>2</sub> abstraction. In terms of 4-chlorophenol, the highest (r<sub>0,Cl<sup>–</sup>)/(–r<sub>0,4-CP</sub>) ratios were obtained for P90 and HBK reaching over 85%. These results indicate that disappearance of 4-CP would correspond to –Cl abstraction. Both the abstraction of –Cl and the complete conversion of TOC are desirable to avoid the presence of chlorinated organic compounds and intermediates that could be more toxic than the original compound, and to convert non-biodegradable organic substances into biodegradable forms [7].</sub></sub>

The influence of substituents on the photodecomposition of the phenolic compounds was analyzed by comparing the initial degradation rates of the different studied organic compounds with phenol as a reference. The results of the initial degradation rates are reported in Table 5. It can be noted that if the influence of the substituent is considered, the initial reaction rates followed the order: (–r<sub>0,Phenol</sub>) > (–r<sub>0,4-CP</sub>) > (–r<sub>0,Mp-HB</sub>) > (–r<sub>0,4-NP</sub>), for all the studied commercial TiO<sub>2</sub>. When 4-nitrophenol was considered, the initial reaction rate was reduced nearly four times compared to that obtained for phenol. An explanation to this fact is discussed below.

The Hammett constant (Table 1) was considered as a means of assessing the role played by the nature of the substituent. By depicting the initial degradation rate of each phenolic compound against the Hammett constant (Fig. 6), a correlation is attained that indicates the

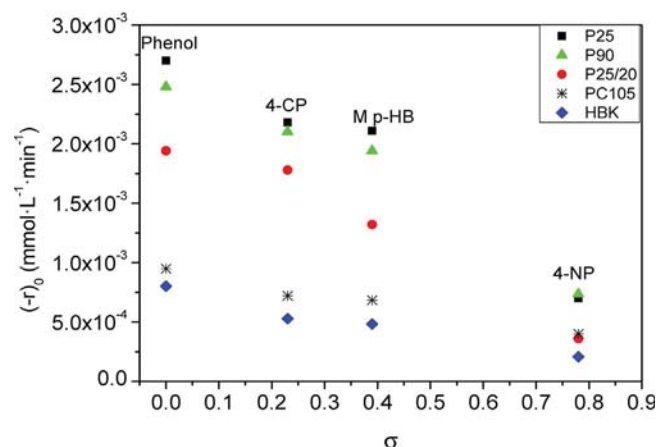


Fig. 6. Influence of the Hammett constant on the initial rate of degradation of the phenolic compounds, for the different photocatalysts.

electrophilic nature of the photocatalytic reaction. This relationship indicates a decrease in the removal rate of the phenolic compound as the Hammett constant is increased. The stronger the electron-withdrawing substituent is, the higher the deactivating ability, which means a lower likelihood of reaction in unsubstituted positions [7]. Hammett constant appears to have no influence on the amount of pollutant adsorbed (Fig. 2/Table 2). However, it does have a great effect on the photocatalytic reaction rate, meaning that adsorption is not crucial in this case, supporting the earlier statement that the reaction takes place in the solution rather than the adsorbed state.

#### 4. Conclusions

Analysis on the adsorption of different phenolic compounds was carried out by adsorption isotherms and DRIFTS. The photocatalyst with the lowest acidity per surface area, HBK, showed the lowest uptake whilst for other catalyst with far less area, such as P25 or P25/20, the uptake was higher. In spite of the differences in hydrophobicity and electrical character, the nature of the substituent appears to have no influence on the amount of the organic compound adsorbed.

It can be concluded on the basis of DRIFTS experiments that the phenols are adsorbed leading to Ti-phenolate anions and Ti–OH groups formation. Furthermore, in the case of *p*-nitrophenol, adsorption could possibly take place via a hydrogen bond interaction between the Ti–OH and the nitro group of 4-NP.

The fastest initial degradation rates were obtained for P25 followed by P90 and P25/20, all of which contain a mixture of anatase and rutile crystalline phases. The sequence related to the activity of the photocatalysts was maintained for all the organic compounds. The same sequence was found for the formation rate of TAOH indicating that degradation occurred primarily by HO· in the solution of the surroundings of the photocatalyst surface and adsorption is not crucial in this case. This hypothesis is supported by the fact that even though it was found no influence of the Hammett constants on the adsorption, they did show a clear effect on the initial photodecomposition rate of the phenolic compounds. This relationship indicates that

Table 5  
Initial degradation rates of phenol, 4-CP, M *p*-HB and 4-NP.

Catalyst	(–r <sub>Phenol</sub> )·10 <sup>3</sup> (mmol min <sup>–1</sup> L <sup>–1</sup> )	(–r <sub>4-CP</sub> )·10 <sup>3</sup> (mmol min <sup>–1</sup> L <sup>–1</sup> )	(–r <sub>Mp-HB</sub> )·10 <sup>3</sup> (mmol min <sup>–1</sup> L <sup>–1</sup> )	(–r <sub>4-NP</sub> )·10 <sup>3</sup> (mmol min <sup>–1</sup> L <sup>–1</sup> )
P25	2.70	2.18	2.11	0.70
P25/20	1.94	1.78	1.32	0.36
P90	2.48	2.10	1.94	0.73
PC105	0.95	0.72	0.68	0.40
HBK	0.80	0.53	0.48	0.21

photodegradation depends on the nature of the substituent; the stronger the electron-withdrawing substituent (higher Hammett constant), the slower the photodegradation rate.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jece.2017.08.053>.

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Table 1. Langmuir and Freundlich parameters obtained by nonlinear fittings and the corresponding coefficient of determination ( $R^2$ ).

Langmuir parameters								
Photocatalysts	$q_m$ (mmol·m <sup>-2</sup> ) · 10 <sup>3</sup>				$K_L$ (L·mmol <sup>-1</sup> )			
	Phenol	4-NP	4-CP	M p-HB	Phenol	4-NP	4-CP	M p-HB
P25	1.80	18.88	2.67	3.70	1.12	0.08	2.28	1.24
P90	1.65	1.60	1.34	1.01	1.18	2.31	3.47	3.78
P25/20	2.32	10.00	1.03	3.10	0.91	0.00	2.87	3.31
PC105	2.15	1.48	1.28	6.30	0.71	3.85	6.23	0.25
HBK	0.36	0.36	0.98	0.96	1.26	1.19	0.30	0.34
Freundlich parameters								
Photocatalyst	$K_F$ (mmol·m <sup>-2</sup> ) · 10 <sup>3</sup>				$n_F$			
	Phenol	4-NP	4-CP	M p-HB	Phenol	4-NP	4-CP	M p-HB
P25	0.87	1.47	1.79	2.07	1.79	1.26	1.99	1.52
P90	0.82	1.10	1.00	0.82	1.85	1.93	2.35	2.14
P25/20	1.02	1.02	0.77	2.45	1.67	0.77	2.04	1.98
PC105	0.84	1.15	1.08	1.24	1.58	2.37	3.34	1.11
HBK	0.18	0.20	0.23	0.24	1.87	1.43	1.24	1.18
Photocatalyst	Phenol		4-NP		4-CP		M p-HB	
	$R^2_{Langmuir}$	$R^2_{Freundlich}$	$R^2_{Langmuir}$	$R^2_{Freundlich}$	$R^2_{Langmuir}$	$R^2_{Freundlich}$	$R^2_{Langmuir}$	$R^2_{Freundlich}$
P25	1.00	0.98	0.90	0.92	0.98	0.93	0.98	0.96
P90	0.99	0.96	0.98	0.95	0.94	0.84	0.94	0.87
P25/20	1.00	0.97	0.96	0.98	0.99	0.96	0.97	0.93
PC105	1.00	0.98	0.94	0.98	0.94	0.88	1.00	1.00
HBK	0.99	0.94	0.98	0.96	0.99	1.00	0.99	0.99

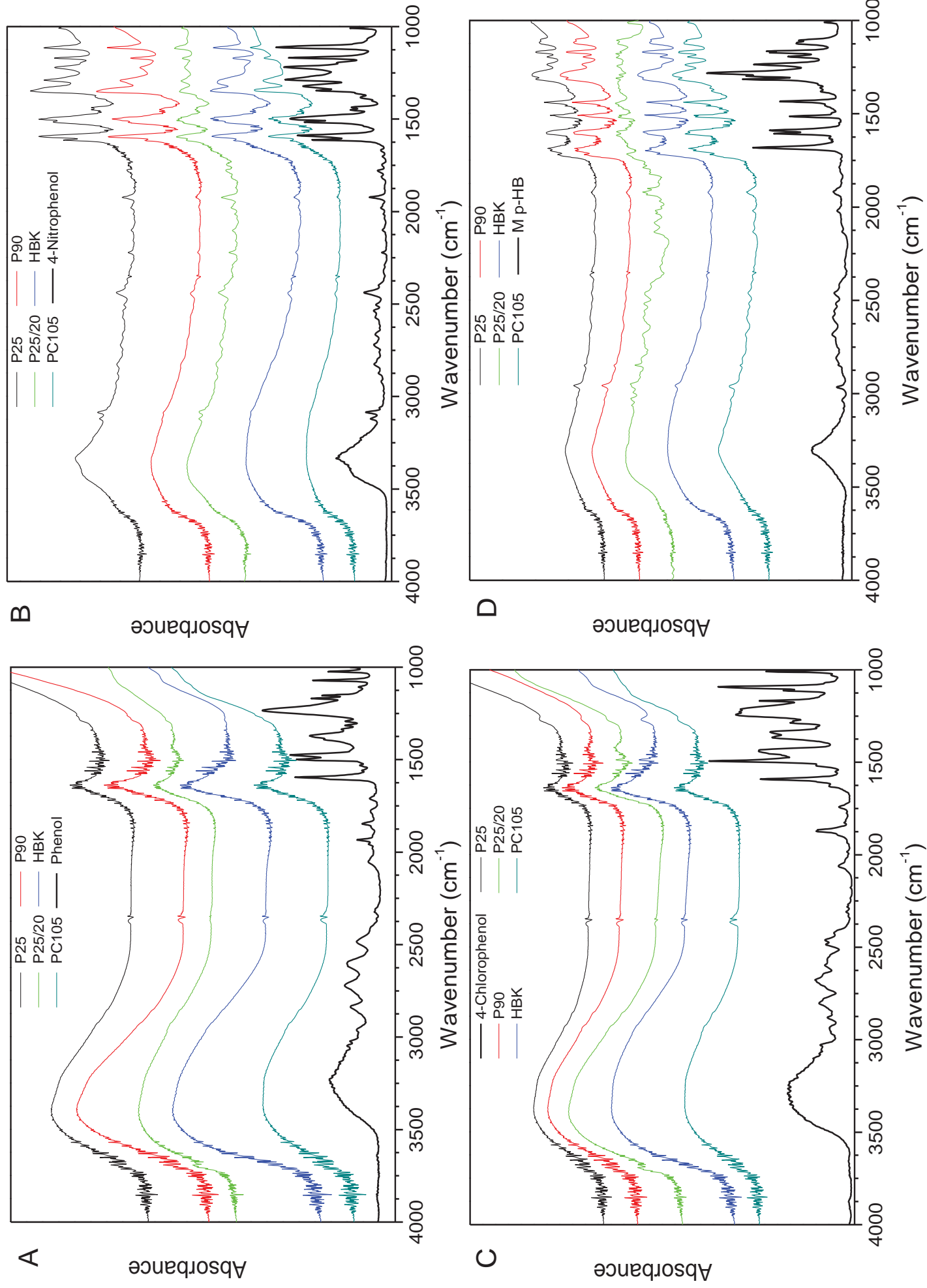


Figure 1. DRIFT spectra of the adsorbed organic compounds on TiO<sub>2</sub>: (A) phenol, (B) 4-nitrophenol, (C) 4-chlorophenol, (D) methyl 4-hydroxybenzoate. Reference spectra are also shown.

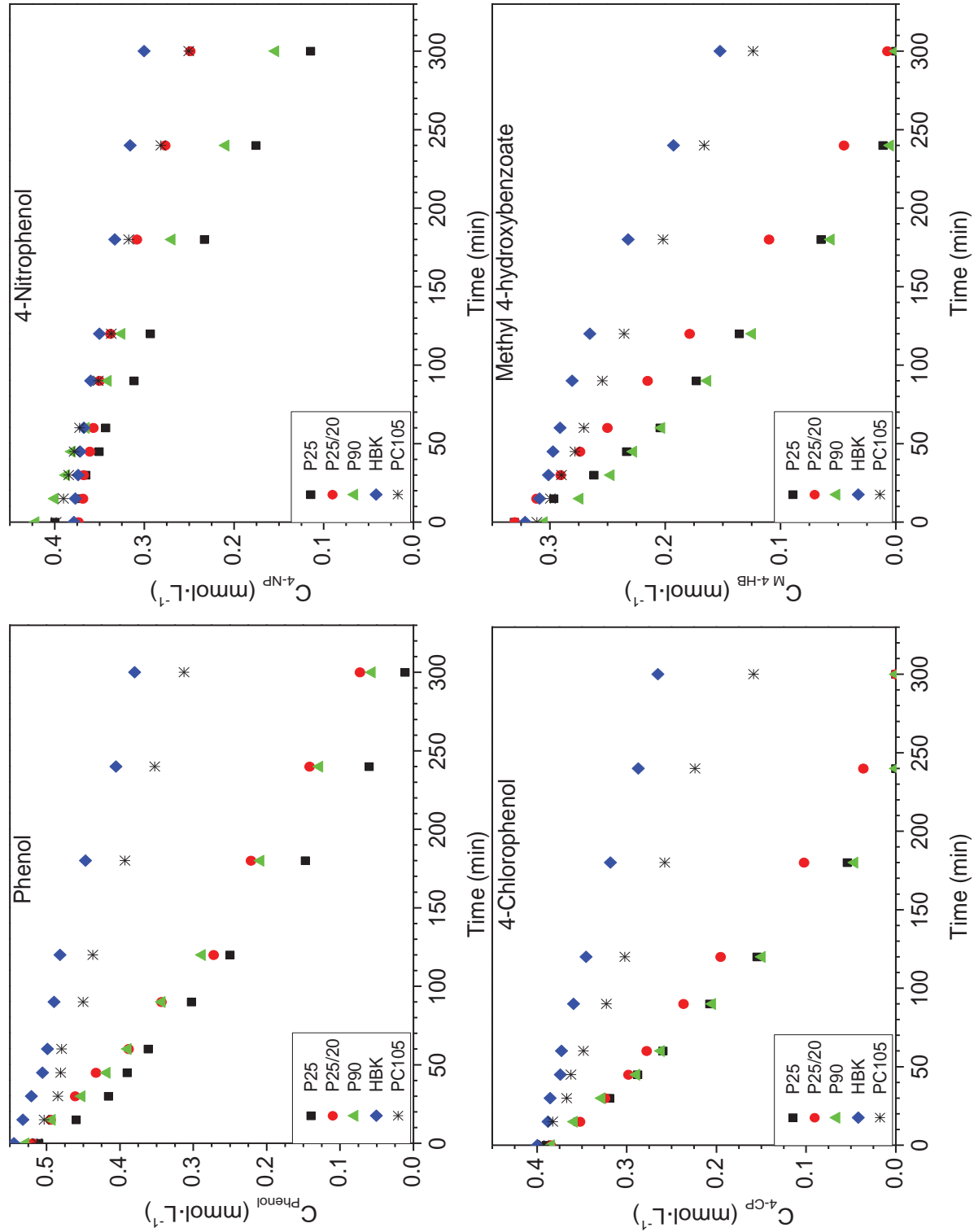


Figure 2. Photocatalytic removal of substituted phenols with the different  $\text{TiO}_2$  catalysts.



# Anexo III:

Elucidation of the photocatalytic-mechanism of phenolic compounds





## Elucidation of the photocatalytic-mechanism of phenolic compounds

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Photocatalyst  
Phenolic compounds  
Photo-Mechanism  
Scavenger  
Quantum efficiency

### ABSTRACT

In the present work, phenol and other phenolic compounds (4-chlorophenol, 4-nitrophenol and methyl-p-hydroxybenzoate) as typical aromatic pollutants were selected to investigate and elucidate their photocatalytic-mechanism over two commercial TiO<sub>2</sub> catalysts: Hombikat UV-100 and Aeroxide® P25, with different physico-chemical properties. To try to clarify which pathway is more relevant in the corresponding photodegradation mechanism, the following scavengers were employed: formic acid (scavenger of photogenerated holes), methanol (strong hydroxyl radical scavenger) and copper (II) nitrate (scavenger of electrons from conduction band). Higher photodegradation rates were always reached with P25, regardless of the studied parent compound.

The radiation absorbed by these TiO<sub>2</sub> catalysts were calculated by means of Monte Carlo simulations, and volumetric rate of photon absorption (VRPA) values were always higher for P25 because of its greater scattering and absorption coefficients. At the same time, higher values of the quantum efficiency were found in the photocatalytic degradation of phenol, methyl 4-hydroxybenzoate and 4-chlorophenol with P25, whereas in the case of 4-nitrophenol Hombikat catalyst was more photo-efficient despite the drop of the VRPA caused by the 4-nitrophenol light absorption.

Regardless of the used photocatalyst, phenol, methyl 4-hydroxybenzoate and 4-chlorophenol were mostly degraded by HO• radicals generated from photo-generated holes, whereas an electron mediated mechanism was the most relevant in the case of 4-nitrophenol. Finally, it was demonstrated that the photodegradation rate of this parent compound could be appreciably increased by adding a hole acceptor, such as formic or oxalic acid, which promotes electrons from titania valence band (VB) to the conduction band (CB).

### 1. Introduction

Nowadays, a key idea for the new water management approach is beginning to be assumed, considering the problem as a whole that is nominated “integral water cycle”. Therefore, the development of technologies that allows wastewater treatments for decontamination and/or reuse, as a key to achieve sustainable water use, is essential. In this context, heterogeneous photocatalytic process appears as a promising Advanced Oxidation Catalytic Technology [1–3], that operating at atmospheric pressure and temperature conditions, reaches a remarkable efficiency in the treatment of poorly biodegradable substances, being a clear example of the successful use of solid catalysts.

Since the photocatalytic activity measured by different research groups is usually difficult to compare because of the use of reactors with different geometry, lamps with different spectral emission or lamps which provides different inlet intensities, the light absorbed by the suspension must be estimated. The radiation absorbed is normally

calculated by solving the Radiative Transfer Equation (RTE) [4–7]. Numerical methods are frequently used to find the solution to the RTE; for example, the Discrete Ordinate Method (DOM) or the Monte Carlo method (MC). Monte Carlo method is usually employed to estimate the distribution of the absorbed radiation when the geometry of the reactor is complicated [4]. Once the radiation absorbed is known efficiency parameters, such as the quantum efficiency (it relates the initial reaction rate with the radiation absorbed), can be determined to compare results obtained in different works [4,8,9]. In this context, the analysis of the mechanism of photocatalytic degradation is a crucial point to understand catalyst performance in real wastewater and to try to determine the optimal operating conditions. Although the role of different photoactive species has been intensively study in depth, it is still an active polemic [10], and it is usually strongly dependent on the type of pollutant to be photo-oxidized [11]. It is still unknown if photo-oxidation process take place via direct electron transfer between organic substrate and positive holes, via Reactive Oxygen species (ROS)

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generated from Conduction Band (CB) electrons or via an HO• radical mediated pathway [12–16]. For all of that, scavengers are used such as alcohols for hydroxyl radicals [13,14], formic acid for photogenerated holes [11,13,17], and, Cu(NO<sub>3</sub>)<sub>2</sub> [13,17,18] to quench the electrons of conduction band (CB).

Nevertheless, it has been assumed that most of organic substrates have been photo-oxidized by HO•, as was already confirmed by detection of hydroxylated products, and ESR detection from the spin trapping [19]. However, direct hole oxidation has also been able to play an important role [20], as is the case of short-organic acids, where it seems they are mainly photo-oxidized via a photo-kolbe process [21]. Adsorption could have a pivotal influence on the pathway by which substrates are oxidized [22].

In this context, the goal of this work was to elucidate the photocatalytic-mechanism of phenol photodegradation, and other phenolic compounds (4-chlorophenol, 4-nitrophenol and methyl-p-hydroxybenzoate), over two commercial TiO<sub>2</sub> catalysts with different physico-chemical properties: Hombikat UV-100 and Aeroxide® P25. Quenching runs with three known molecules: formic acid (scavenger of photogenerated holes), methanol (a strong hydroxyl radical scavenger) and copper (II) nitrate (scavenger of conduction band electrons) were carried out to try to clarify the corresponding photo-mechanisms. The radiation absorbed (VRPA) by these photocatalysts was estimated by means of Monte Carlo simulations. At the same time quantum efficiency values were calculated for both catalysts to analyze the efficiency with which radiation is used to photodegrade the parent compounds.

## 2. Experimental

### 2.1. Photocatalysts and chemicals

The four different substrates studied in this work, phenol (Panreac), 4-chlorophenol (4-CP), methyl p-hydroxybenzoate (M p-HB) and 4-nitrophenol (4-NP) (Sigma-Aldrich, SA), were analytical grade and used as purchased. Ultrapure water were used to prepare solutions and all reagents employed in analytical measurements were HPLC grade. Two commercial TiO<sub>2</sub> catalysts were selected, P25 Aeroxide® titanium dioxide (P25), and Hombikat UV100 (HBK) both employed as received, and provided by Evonik and Sachtleben Chemie GmbH respectively. Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (> 99.99%) and HCOOH (> 98%) were purchased from Sigma-Aldrich and Fluka respectively.

### 2.2. Photocatalyst characterization

A Micromeritics ASAP 2420 was used for nitrogen adsorption-desorption isotherms at -196 °C. Prior to the measurements the samples were outgassed overnight at 140 °C. The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) procedure [23].

A UV-vis Agilent-Varian, Cary 5000, featured with an integrating sphere was employed to measure diffuse reflectance spectra. The Tauc Plot method [24] was employed to estimate the band gap. To analyze the difference of the spectra of both TiO<sub>2</sub> photocatalysts after being in contact with the studied four organic substrates, the TiO<sub>2</sub> suspensions (10 g·L<sup>-1</sup>) in contact with 100 mg·L<sup>-1</sup> of the organic compound were shaking for 24 h at 25 °C. Then, the liquid of the samples was evaporated at room temperature and the photocatalysts were collected to measure their spectra. The spectra of both TiO<sub>2</sub> photocatalysts in the presence of Cu<sup>2+</sup> ions after the 4-nitrophenol photodegradation experiment in the presence of Cu(NO<sub>3</sub>)<sub>3</sub> was measured. In this case the TiO<sub>2</sub> photocatalysts were recovered by filtering the suspension.

The measures performed to obtain the optical properties of the catalyst suspensions were carried out in an Agilent Cary 5000 UV-vis spectrophotometer, according to the procedure reported by Cassano et al. [5,25,26]. The samples were measured in a quartz cuvette with an optical length of 2 mm and using Milli-Q water as baseline. The sample were not sonicated and freshly prepared. The extinction coefficient

were calculated from measurements in transmission mode, placing the sample as distant as possible from the detector. In order to obtain the absorption coefficient, measurements in transmission mode were performed with the integrating sphere equipped in the spectrophotometer.

### 2.3. Photocatalytic activity

Photocatalytic activity of the TiO<sub>2</sub> photocatalysts in the photo-degradation of the different pollutants was measured using a cylindrical reactor located in a Multirays apparatus (Helios Italquartz). Inside the apparatus the Pyrex reactor, whose surface was 525 cm<sup>2</sup>, was enclosed by 10 fluorescent lamps of 15 W each: 6 Black Light Blue UVA Lamps and 4 day-light lamps. A potassium ferrioxalate actinometry was carried out to experimentally obtain the total inlet radiation at the reactor wall [27]. The total number of photons of wavelength below 410 nm (provided by the 6 Black Light Blue UVA lamps) entering the reactor was estimated to be 1.4 10<sup>-8</sup> Einstein cm<sup>-2</sup> s<sup>-1</sup>.

Reactions were carried out at atmospheric pressure and room temperature thanks to a fan included in the apparatus. In order to keep a high concentration of dissolved oxygen, air was continually flown into the suspension (75 N mL min<sup>-1</sup>). All the reactions were performed with an organic compound and photocatalyst loading of 250 mg L<sup>-1</sup> and 50 mg L<sup>-1</sup>. To avoid sedimentation of the photocatalyst the suspension was constantly stirred. The photocatalyst and the organic compound were mixed in the dark for 30 min before the lamps were turned on to ensure adsorption equilibrium. The used photoreaction system is described in deep detail in [28,29].

Concentration of aromatic compounds was measured by using a Varian 920 LC HPLC equipped with a photo-diode array detector, with a Nucleosil C18 5 μm column (15 cm length, 4.6 mm diameter at 30 °C,) as stationary phase and 0.6 mL·min<sup>-1</sup> of 40:60 methanol:acidic water (0.1% phosphoric acid) in the range 0–8 min and 1 mL·min<sup>-1</sup>, 20:80 methanol/acidic water in the range 8–18 min, mixtures were employed as mobile phases.

A Metrohm 883 Ion Chromatograph equipped with a conductivity sensor was employed to identify ions and short-chain organic acids. As stationary phase two different columns were used: a Metrosep A supp 7–250 column (250 mm length, 4 mm diameter) and a Metrosep C 6–250 column (250 mm length, 4 mm diameter) to measure anions and cations respectively.

## 3. Results and discussion

### 3.1. Comparison study of photocatalytic degradation of phenolic compounds

The photocatalytic activity of the commercial TiO<sub>2</sub> catalysts P25 and Hombikat (HBK) on the degradation of four aromatic compounds (phenol, methyl 4-hydroxybenzoate, 4-chlorophenol and 4-nitrophenol) is depicted in Fig. 1. Moreover, the corresponding initial reaction rates of every aromatic compound were estimated by applying Eq. (1) for the first 45 min, and are reported in Table 1.

$$(-r_{AC,0}) = \lim_{\Delta t \rightarrow 0} \left( -\frac{\Delta C}{\Delta t} \right) \quad (1)$$

It could be seen that, regardless of the parent compound, the highest initial rates were always reached when P25 was used as a photocatalyst, with values three or four times higher than those obtained by Hombikat.

Since several by-products could be formed after complete mineralization is achieved, the total organic carbon in solution was evaluated. TOC and the conversions of the original compound after 300 min of irradiation are shown in Fig. 2.

In the case of P25, conversions of TOC were always higher than 90%, except in the case of 4-nitrophenol. Differences between TOC and the parent compound conversions were noted, which indicates the

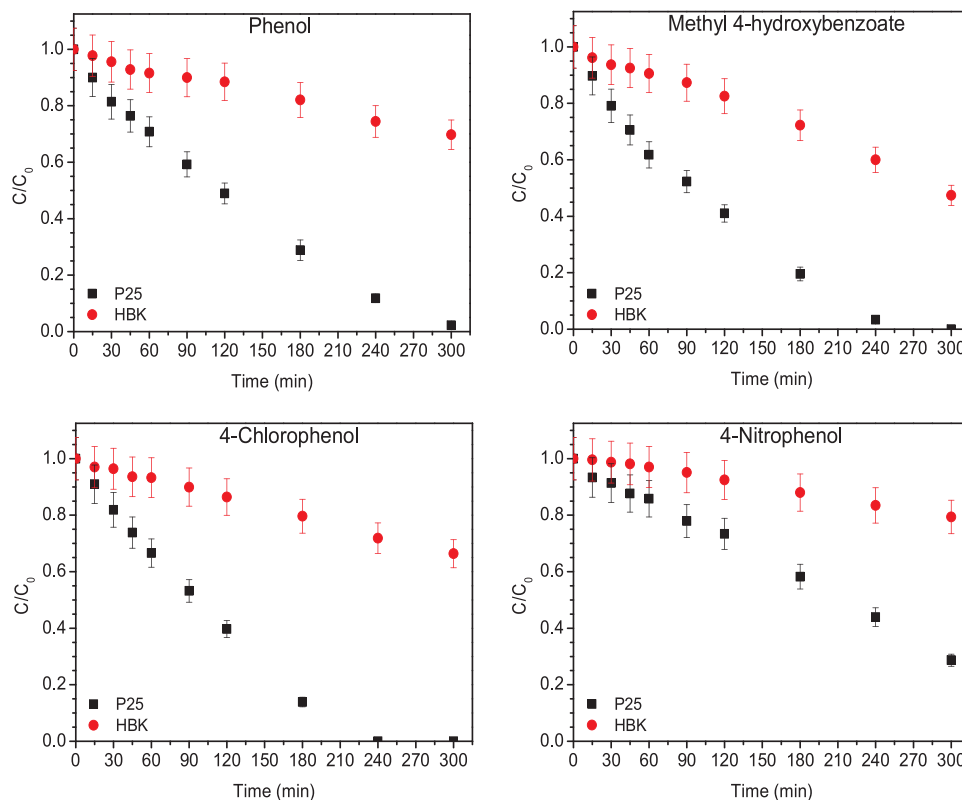


Fig. 1. Comparison study of photocatalytic degradation of phenol, methyl 4-hydroxybenzoate, 4-chlorophenol and 4-nitrophenol over P25 and Hombikat catalysts.

formation of byproducts, such as hydroquinone or some short chain acids, oxalic or formic acid, among others. In respect to the reactions carried out with Hombikat, conversions of TOC were always lower than ~40% and small differences between both TOC and the original compound conversions were observed too.

To take into account the effect of light absorption on photocatalytic performance Monte Carlo simulation were carried out to predict the local volumetric rate of photon absorption (LVRPA,  $e^a(x)$ ), whose values must be integrated over the reactor volume in order to determine the VRPA. This simulation method was used since it has been reported to be appropriate for complicated geometries [4,9,30,31]. In these simulations individual photons are traced, by using random numbers, from their creation until the photons are either absorbed or scattered from the system [4]. A detailed description of the steps followed to carry out the simulations can be found in Supplementary Information.

Assuming that a considerable amount of the inlet radiation was diffused a one-dimensional-one-directional radiation model was used. Furthermore, it could be considered that the extinction of the radiation mainly occurred along the radius of the reactor [9,30,32]. An isotropic phase function was chosen because it has been demonstrated that it provides good representation for the experimental LVRPA [4,31,33]. This model was already proved to be useful to simulate the radiation absorbed in our system [28]. The specific extinction, specific absorption and specific scattering coefficients for each TiO<sub>2</sub> catalyst were calculated as previously reported [25,28] and are shown in Supplementary Information Fig. 1. One million (10<sup>6</sup>) photon bundles for each wavelength were tracked in the simulations.

Phenol, methyl 4-hydroxybenzoate, 4-chlorophenol did not show any absorption in the range of wavelengths where the lamps emit and the photocatalysts are able to absorb radiation (between 350 and 390 nm). In order to obtain this information, spectra of the pollutants dissolved in ultrapure water were recorded by UV-vis spectroscopy (data only shown for 4-nitrophenol in Supplementary Information Fig. 2). However, in the case of 4-nitrophenol a new random number

had to be generated to take into account its absorption. The extinction coefficient of a 50 mg L<sup>-1</sup> solution of 4-nitrophenol was determined from the absorption spectrum (measured with a cell with 1 cm of path length (L)), shown in Supplementary Information Fig. 2, using Eq. (2).

$$\beta_{4-NP,\lambda} = \frac{2.303 Abs_{\lambda}}{L} [cm^{-1}] \quad (2)$$

In Fig. 3, LVRPA profiles along the reactor diameter (x) are plotted for each photocatalyst. The LVRPA calculated for the TiO<sub>2</sub> suspensions in 4-nitrophenol solution is also shown.

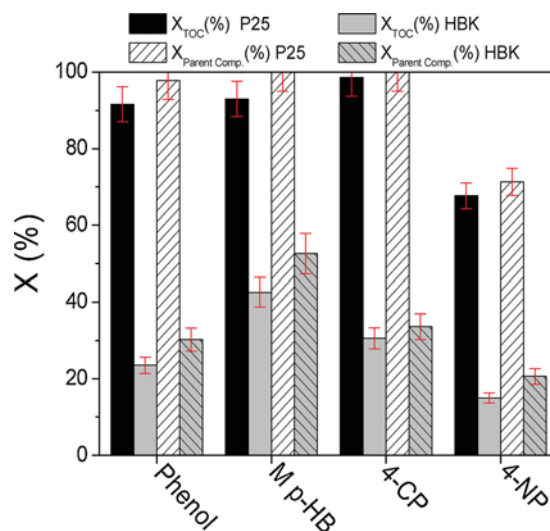
Regarding LVRPA obtained for P25 in those solutions where radiation was not absorbed by the aromatic compound, it is noteworthy that most of the radiation was absorbed within the closest 0.5 cm to the reactor wall and there was no radiation available to be absorbed in the center of the photoreactor. This absorption region was slightly reduced in the presence of 4-nitrophenol. However, in the case of Hombikat, values of LVRPA near the wall were five times lower and light could penetrate up to 2.5 cm inside the reactor, whereas in the presence of 4-nitrophenol, radiation was highly attenuated near the reactor walls.

These differences between both catalysts are due to their different hydrodynamic particle size distribution of the photocatalysts in suspension, plotted in Supporting Information Fig. 3. While P25 shows a mono-modal distribution with a mean hydrodynamic particle diameter near 2.8 μm, Hombikat exhibited a bimodal distribution ranging from 0.4 to more than 60 μm. As a consequence, larger hydrodynamic particle size led to smaller exposed surface of the suspended particles even though the external surface area of Hombikat (~275 m<sup>2</sup>) is almost five times higher than that of P25 (~55 m<sup>2</sup>). This could lead to a worse illumination and adsorption of the substrate on the TiO<sub>2</sub> particles. Furthermore, the smaller particle diameters of P25 will lead to greater values of the extinction, absorption and scattering coefficients [28,34], as observed in Supplementary Information Fig. 1, in which coefficients for P25 were between five and ten times greater than the same coefficients for Hombikat. These results could well be explained by the Mie theory [35,36]. When the size of the particle is comparable to the

**Table 1**  
Initial degradation rate of phenol, methyl 4-hydroxybenzoate (M p-HB), 4-chlorophenol (4-CP) and 4-nitrophenol (4-NP), and quantum efficiency in mol·Einstein<sup>-1</sup>. The volumetric rate of photon absorption (VRPA) in the absence and in the presence of 4-NP is also given.

Catalyst	$(-r_{0,Phenol}) \cdot 10^3$ (mmol·min <sup>-1</sup> , L <sup>-1</sup> )	$(-r_{0,M p-HB}) \cdot 10^3$ (mmol·min <sup>-1</sup> , L <sup>-1</sup> )	$(-r_{0,4-CP}) \cdot 10^3$ (mmol·min <sup>-1</sup> , L <sup>-1</sup> )	$(-r_{0,4-NP}) \cdot 10^3$ (mmol·min <sup>-1</sup> , L <sup>-1</sup> )	VRPA · 10 <sup>4</sup> (Einstein·min <sup>-1</sup> , L <sup>-1</sup> )	VRPA <sup>0</sup> · 10 <sup>4</sup> (Einstein·min <sup>-1</sup> , L <sup>-1</sup> )	$\eta_{Phenol} \cdot 10^3$	$\eta_{M p-HB} \cdot 10^3$	$\eta_{4-CP} \cdot 10^3$	$\eta_{4-NP} \cdot 10^3$
P25	2.70	2.11	2.27	0.70	11.6	8.2	2.33	1.28	1.96	0.86
HBK	0.79	0.48	0.53	0.21	11.0	2.2	0.72	0.44	0.48	0.93

<sup>a</sup> Volumetric rate of photon absorption (VRPA) calculated for TiO<sub>2</sub> suspensions in 4-nitrophenol solution (50 mg L<sup>-1</sup>).



**Fig. 2.** TOC and the parent compound conversions after 300 min of irradiation time with P25 or HBK photocatalysts.

wavelength of the radiation absorbed by the TiO<sub>2</sub>, the light will be effectively absorbed and scattered allowing to reach higher light utilization efficiencies.

In the presence of 4-nitrophenol, the VRPA value for P25 (included in Table 1) slightly decreased whereas a five-fold reduction of the value for Hombikat was estimated. This difference was attributed to the smaller values of the extinction coefficients of Hombikat which were similar to the calculated extinction coefficient of 4-nitrophenol in the studied range of wavelengths. A comparison of the radiation that arrives at the reactor with the volume integration of the VRPA indicates that only around 80% of the inlet radiation is absorbed when phenol, 4-chlorophenol or methyl 4-hydroxybenzoate was used. However, when 4-nitrophenol was dissolved in the reaction system this value dropped to 58 and 16% for P25 and Hombikat respectively.

Furthermore, in Table 1 the quantum efficiency for each organic compound degradation run is shown. This efficiency was calculated using Eq. (3) to analyze the efficiency with which photons absorbed are employed to degrade the aromatic compound [8,9].

$$\eta_{AC} = \frac{(-r_{AC,0})}{\langle e^a(x) \rangle_{V_R}} \quad (3)$$

Where  $\langle e^a(x) \rangle_{V_R}$  is the volumetric rate of photon absorption (VRPA) averaged over the reactor volume  $V_R$ .

The quantum efficiencies were nearly three-four times higher for P25 than for Hombikat when phenol, methyl 4-hydroxybenzoate and 4-chlorophenol are considered. However, in the case of 4-nitrophenol, the quantum efficiency obtained for Hombikat exceeded the value obtained by P25. This was ascribed to the relatively fast reaction rate achieved by Hombikat with the low absorbed radiation compared to P25. These results proved that photons absorbed by P25 are more efficiently employed to photodegrade the aromatic compounds, except for 4-nitrophenol.

To deepen into the understanding which degradation pathway is more relevant in the degradation mechanism [7–9], several scavengers have been used.

### 3.2. Effect of the presence of scavengers during photodegradation process

To investigate the role of holes ( $h^+$ ), hydroxyl radicals ( $HO\cdot$ ) and electrons ( $e^-$ ) in the photocatalytic degradation of these four aromatic compounds, different scavengers have been used.

Methanol is a strong scavenger of hydroxyl radicals in the liquid phase [13,14]. Formic acid was selected as a photogenerated hole

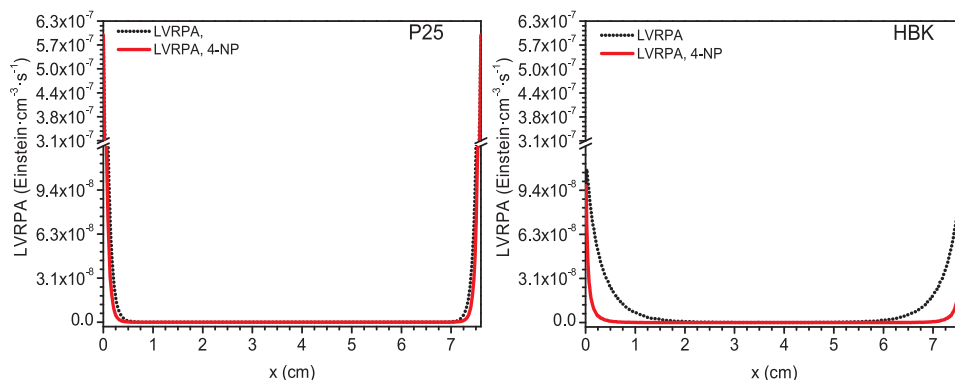


Fig. 3. Local Volumetric Rates of Photon Absorption (LVRPA) for P25 and Hombikat suspensions ( $250 \text{ mg L}^{-1}$ ) in: phenol, methyl 4-hydroxybenzoate or 4-chlorophenol solutions (.....) and 4-nitrophenol solution (—).

scavenger since recent studies have proved its excellent effectiveness [11,13,17]. Finally,  $\text{Cu}^{2+}$  was chosen as electron scavenger [13,17,18,37]. In addition,  $\text{Cu}(\text{NO}_3)_2$  was used because  $\text{NO}_3^-$  barely competes with the aromatic compounds for  $\text{HO}\cdot$  nor  $\text{h}^+$  [17]. After a previous study, the employed concentrations of methanol, formic acid and  $\text{Cu}(\text{NO}_3)_2$  were 125, 5 and 10 mM respectively. Ratios between scavenger concentration ( $\text{mmol}\cdot\text{L}^{-1}$ ) and pollutant concentration ( $\text{mmol}\cdot\text{L}^{-1}$ ) can be seen in Supplementary Information Table 1. The employed concentration of scavenger was always higher than 10 times the initial concentration of the pollutant.

The evolution of the normalized concentrations of the four organic compounds, in the absence and presence of each studied scavenger, with both studied catalysts, is shown in Figs. 4 and 5 respectively.

Almost negligible photodegradation of phenol, methyl 4-hydroxybenzoate, 4-chlorophenol and 4-nitrophenol was observed for both

catalysts when methanol was added to the reaction. This result makes sense as aromatic compounds have been reported to be mainly photo-degraded by  $\text{HO}\cdot$  radicals using UV light as irradiation source [13].

However,  $\text{HO}\cdot$  radicals generation can take place through two different pathways: (i) oxidation of water molecules on the surface by valence band holes that are able to reach the  $\text{TiO}_2$  surface and (ii) be produced from  $\text{H}_2\text{O}_2$  formed by coupling reaction of hydroperoxyl radicals ( $\text{HO}_2\cdot$ ) [11,15].

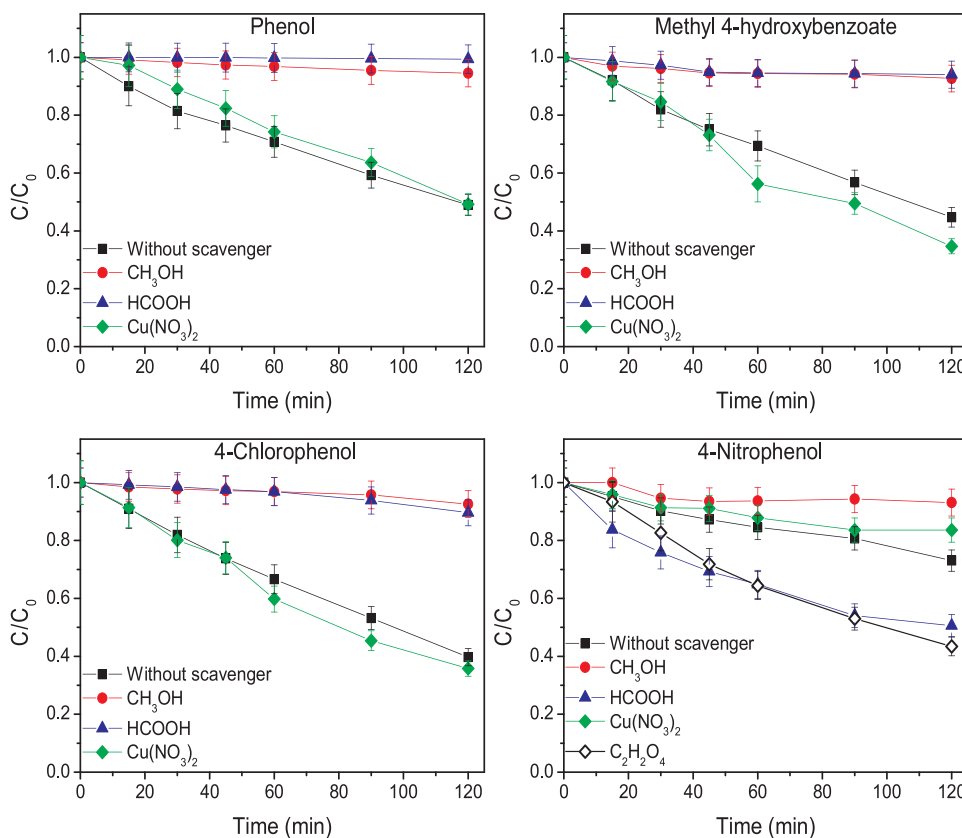


Fig. 4. Photocatalytic degradation of the phenolic aromatic compounds in absence and presence of  $\text{CH}_3\text{OH}$ ,  $\text{HCOOH}$  and  $\text{Cu}(\text{NO}_3)_2$  as  $\cdot\text{OH}$ ,  $\text{h}^+$  and  $\text{O}_2^{\cdot-}$  scavengers respectively, over  $\text{TiO}_2$  P25. 4-Nitrophenol removal in the presence of oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4$ ) is also shown.



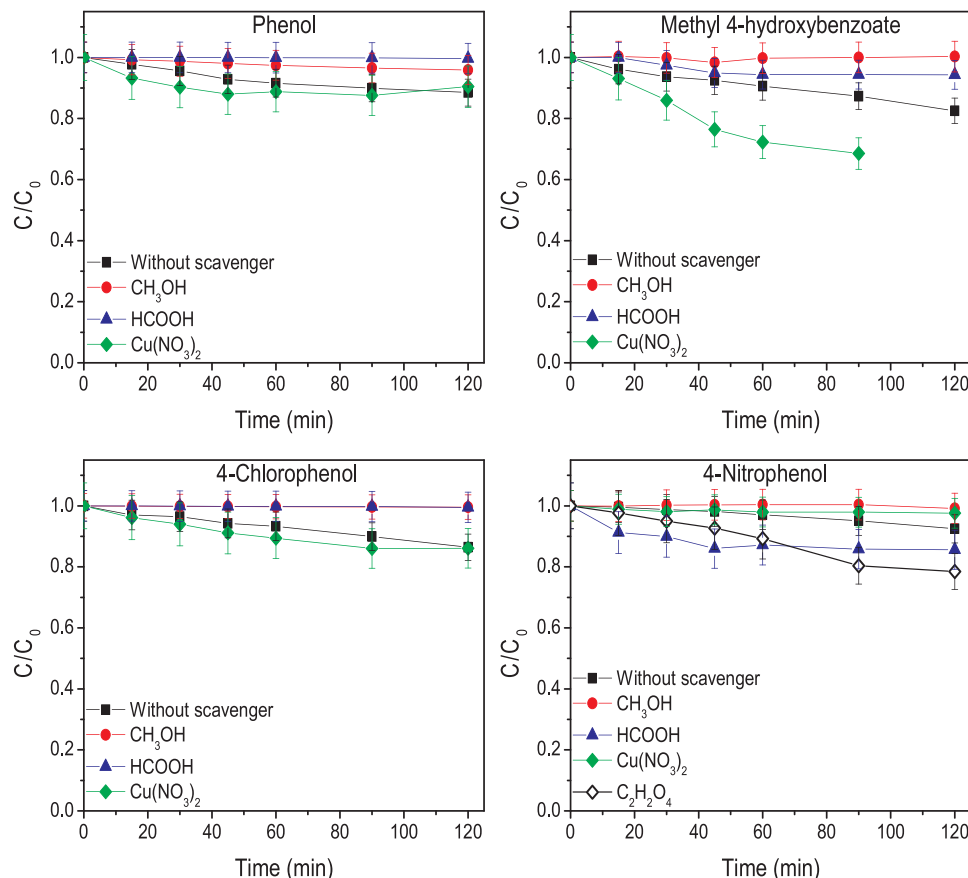


Fig. 5. Photocatalytic degradation of the phenolic aromatic compounds in absence and presence of  $\text{CH}_3\text{OH}$ ,  $\text{HCOOH}$  and  $\text{Cu}(\text{NO}_3)_2$  as  $\cdot\text{OH}$ ,  $\text{h}^+$  and  $\text{O}_2^{\cdot-}$  scavengers respectively, over  $\text{TiO}_2$  Hombikat. 4-Nitrophenol removal in the presence of oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4$ ) is also shown.



To study and establish the main pathway to form  $\text{HO}\cdot$  radicals formic acid was used as hole scavenger, which avoids  $\text{HO}\cdot$  radicals generation from water oxidation (Eq. (4)).

In these conditions two different trends in the photodegradation process were observed (see Figs. 4 and 5). In the case of phenol, methyl 4-hydroxybenzoate and 4-chlorophenol no conversions was obtained with neither of the two photocatalysts. When  $\text{CH}_3\text{OH}$  was used as scavenger, a similar behavior was obtained. These results were observed because hydroxyl radicals were not produced or available in the presence of these scavengers and therefore, these aromatic compounds could not be hydroxylated.

Only for 4-nitrophenol, important conversions were achieved in the presence of formic acid. This indicates that this compound is mainly oxidized following another pathway. This is probably related to its adsorption and transformation on the photocatalytic surface by the removal of the nitro group. The presence of  $\text{HCOOH}$  as hole scavenger enhances this process and consequently, 4-nitrophenol photodegradation. This behavior was similar for both of the studied  $\text{TiO}_2$ , P25 and Hombikat.

When no  $\text{HO}\cdot$  scavenger or when  $\text{Cu}(\text{NO}_3)_2$  (electron scavenger) was used, the hydroxyl radical generation is increased and, as a result, phenol, methyl 4-hydroxybenzoate and 4-chlorophenol oxidation was increased.  $\text{Cu}^{2+}$  presence showed a low contribution, which could be ascribed to the reduction of  $\text{Cu}^{2+}$  ions by conduction band electrons, which provoked a decrease of the recombination rate of photogenerated electron-hole pairs, leading to a slightly higher reaction rate.

The small effect of  $\text{Cu}^{2+}$  ions on the oxidation rates is probably because the formation of  $\text{H}_2\text{O}_2$  (Eq. (7)) is low and the production of

$\text{HO}\cdot$  by  $\text{H}_2\text{O}_2$  decomposition is also very low. Nevertheless,  $\text{HO}_2\cdot$  production seems to have a bigger contribution in the oxidation pathway of phenol since its disappearance rate is reduced by the presence of  $\text{Cu}^{2+}$  ions as electron scavengers.

### 3.3. Elucidation of mechanisms of photodegradation

In order to deepen into the understanding of the effect of the different studied scavengers and the importance of each mechanism on the photodegradation of these four aromatic compounds, the following ratios have been calculated [14]:

$$\bullet k_1 = (k - k_{\text{HCOOH}} - k_{\text{CH}_3\text{OH}})/k$$

represents the oxidation by  $\text{HO}\cdot$  radicals generated from photo-induced holes ( $\text{h}^+$ ).

$$\bullet k_2 = k_{\text{CH}_3\text{OH}}/k$$

represents direct photodegradation by holes ( $\text{h}^+$ ), because reactive radicals formed from photogenerated holes ( $\text{HO}\cdot$  radicals) or electrons ( $\text{O}_2^{\cdot-}$ ,  $\text{HO}_2\cdot$ ,  $\text{HO}\cdot$ ) were trapped.

$$\bullet k_3 = k_{\text{HCOOH}}/k$$

represents oxidation by reactive oxygen species generated from electrons ( $\text{O}_2^{\cdot-}$ ,  $\text{HO}_2\cdot$ ,  $\text{HO}\cdot$ ), as holes ( $\text{h}^+$ ) were quenched by  $\text{HCOOH}$  [13,38].

Where  $k_{\text{CH}_3\text{OH}}$ ,  $k_{\text{HCOOH}}$  and  $k_{\text{Cu}(\text{NO}_3)_2}$  are the pseudo-first order rate constants estimated for the reactions carried out in the presence of  $\text{CH}_3\text{OH}$ ,  $\text{HCOOH}$  and  $\text{Cu}(\text{NO}_3)_2$  respectively.

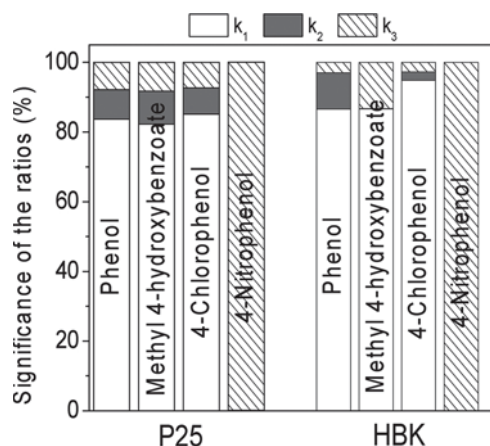


Fig. 6. Relative comparison significance of the defined kinetic ratios according to considered pathways in the simplified photodegradation mechanism of the four studied aromatic compounds using P25 and Hombikat photocatalysts.

- $k$  represents the total oxidation both by the mechanism mediated by the holes and the mechanism mediated by the electrons. Therefore,  $k$  is the constant obtained for the fastest process either in the presence or absence of scavenger. This constant will vary depending on the aromatic compound photodegraded. For example,  $k = k_{HCOOH}$  for 4-nitrophenol as it provides the fastest degradation rate, which indicates that fewer limitations were observed in those conditions.

It is important to note that all these calculated ratios should be considered as a simplification to easily compare the relevance of the different degradation pathways.

The contribution of the ratios related to the different mechanisms responsible for the photodegradation of each organic compound in ultrapure water, can be seen in Fig. 6.

High values of  $k_1$  (over 80%) were obtained for both catalysts and for all the aromatic compounds except for the case of 4-nitrophenol. That seems to indicate that  $HO^\bullet$  radicals formed from photogenerated holes (Eq. (4)) are playing a major role in their photocatalytic degradation. This result agrees with previous studies in which the photodegradation of phenol or other phenolic compounds followed an indirect transfer mechanism because of the weak interaction between the substrate and the  $TiO_2$  surface [11,17]. Nevertheless, the presence of the electron scavenger improved hydroxyl formation, highly important in the oxidation pathway of methyl 4-hydroxybenzoate and 4-chlorophenol. That is why hydroxylated products such as hydroquinone, 4-chlorocatechol or hydroxyhydroquinone have been detected in 4-chlorophenol photodegradation [39,40]. In the same way, phenol is primarily photodegraded to hydroquinone, resorcinol or catechol by hydroxyl radicals that will be further oxidized to form short chain organic acids [41,42]. Regarding methyl 4-hydroxybenzoate, 4-hydroxybenzoic acid is expected to be the primary hydroxylated intermediate in M p-HB photodegradation after  $HO^\bullet$  radicals attack at  $-CH_3$  and  $-H$  in the aromatic ring. Afterwards, this product is oxidized to generate phenol and dihydroxybenzene [43].

On the other hand, this effect changed when the disappearance of 4-nitrophenol is studied. In this case  $k_3$  values exceeded  $k_1$  and  $k_2$  values, so a mechanism mediated by photo-induced electrons is more important for both catalysts, P25 and Hombikat. The key role of electron scavengers and the different removal pathway of 4-nitrophenol is confirmed because, in the presence of  $Cu^{2+}$  ions, 4-nitrophenol removal rate is much lower than without scavenger. After the reaction in the presence of  $Cu^{2+}$  ions, the UV–vis spectrum of the filtered photocatalysts was measured, (see Supporting Information Fig. 4). It was noted that after reaction, P25 absorption extended over a wide range of the visible region. This was attributed to Cu reduced on the surface of

the  $TiO_2$  by CB electrons. However, for HBK no significant absorption beyond 400 nm was detected after the reaction, possibly because of its low photocatalytic activity.

Furthermore, when formic acid or oxalic acid were used as hole scavengers, 4-nitrophenol degradation rate became much faster, (see Figs. 4 and 5). This could be attributed to the role played as electron donors by these short chain organic acids, which helps promote electrons from the  $TiO_2$  valence band to the conduction band (CB). These CB electrons will later initiate 4-nitrophenol degradation, which acts as electron acceptor, leading to denitration and  $HO^\bullet$  substitution at para position to produce hydroquinone. It has also been reported that 4-Nitrophenol could also be photodegraded by one-electron reduction to produce 4-nitrocatechol [40,44]. However, hydroquinone was the main intermediate in the studied conditions and 4-nitrocatechol was not observed. Therefore, in contrast to other studies in which 4-nitrophenol removal is started by  $HO^\bullet$  radicals [40,44], it is important to point out that CB electrons are vital in these conditions as they initiate 4-nitrophenol degradation.

In order to understand this difference, the interaction between the phenolic compounds and the  $TiO_2$  photocatalysts was evaluated by diffuse reflectance UV–vis spectroscopy. The spectra of both photocatalysts fresh and after adsorption experiments of the dissolved organic compounds are shown in Supporting Information Fig. 4. As far as Hombikat is concerned, no shift towards higher wavelengths were noted after being the photocatalyst in contact with phenol, methyl 4-hydroxybenzoate and 4-chlorophenol, indicating that no surface complexes were formed [11]. Regarding P25, a slight shift could be seen that means that some molecules of those organic compounds are more strongly chemisorbed on the  $TiO_2$  surface. This could explain the higher values of  $k_2$  obtained for P25 compared to those for Hombikat. However, a clear red shift of the spectrum of both P25 and Hombikat in contact with 4-nitrophenol was observed which evinces the formation of a surface complex able to absorb in the visible region. In a previous study [29] DRIFTS studies were carried out to identify differences in the adsorption of these aromatic compounds on the  $TiO_2$  surface. It was found that adsorption of phenol, p-Chlorophenol and methyl p-hydroxybenzoate took place between the interaction of the OH group of the organic substrate with the  $TiO_2$  surface, generating a Ti-phenolate anion and a Ti–OH. In Supporting Information Fig. 5A, the pathway for phenol photo-oxidation is proposed. However, adsorption of p-nitrophenol occurred by an interaction between the Ti–OH and the nitro group of 4-NP. This difference in the way they are adsorbed could be the reason why 4-nitrophenol complex is more efficiently chemisorbed and 4-nitrophenol photocatalytic degradation is expected to proceed via one conduction-band electron reduction. So, that photodegradation pathway (see in Supporting Information Fig. 5B) evidences the relevance of mechanisms mediated by photo-induced electrons for these both photocatalysts.

#### 4. Conclusions

The photodegradation of four aromatic compounds (phenol, methyl 4-hydroxybenzoate, 4-chlorophenol and 4-nitrophenol) has been studied with two commercial titanium dioxides, P25 and Hombikat. Photodegradation rates obtained for P25 were always faster for each organic compound.

The radiation absorbed by the studied catalysts was calculated by carrying out Monte Carlo simulations and VRPA values were higher for P25 because of its greater scattering and absorption coefficients. Higher values of the absorbed radiation utilization efficiency, evaluated using the quantum efficiency, were found for P25 in the photocatalytic degradation of phenol, methyl 4-hydroxybenzoate and 4-chlorophenol. However, in the case of 4-nitrophenol Hombikat was more efficient despite the drop of the VRPA caused by the 4-nitrophenol light absorption.

To determine the primary mechanism in the photodegradation of

these substrates three different scavengers were used. Regardless of the photocatalyst employed, phenol, methyl 4-hydroxybenzoate and 4-chlorophenol were mostly degraded by HO<sup>•</sup> radicals generated from photogenerated holes. However, electron mediated mechanism was the most important for 4-nitrophenol. In this case, 4-nitrophenol accepts conduction band electrons and subsequently undergo denitrification and HO<sup>•</sup> substitution to produce hydroquinone. It was demonstrated that the photodegradation rate of this compound could be enhanced significantly by adding a hole acceptor, such as formic acid or oxalic acid, which promotes electrons from the TiO<sub>2</sub> valence band (VB) to the conduction band (CB).

### Acknowledgements

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### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jece.2018.08.068>.

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## SUPPORTING INFORMATION

### Monte Carlo simulations

To start the simulations, the inlet radiation flux into the photoreactor and the spectral energy distribution [1] of the lamp must be determined. The total number of photons was experimentally obtained by carrying out a ferrioxalate actinometry. Afterwards, the trajectories of the photon of each wavelength emitted by the lamp are built using numbers generated randomly ( $R_i$ ) according to the following steps [2-5]:

- 1) Firstly, it is necessary to know the trajectory of the photons emitted by the lamp. Since it was considered that the incoming radiation was diffuse all the directions had the same probability. Therefore, the zenith angle was determined by:

$$\sin \theta = 2R_1 - 1$$

- 2) The distance travelled by the photon inside the reactor medium without interaction is given by:

$$l = -\frac{1}{\beta_\lambda} \ln(1 - R_2)$$

where  $\beta_\lambda$  is the extinction coefficient for a specific wavelength of the reaction medium. It is important to highlight that in the presence of organic compounds that absorb in the UV region, such as 4-nitrophenol, this coefficient must include  $\beta_\lambda$  of the catalysts plus  $\beta_\lambda$  of the solution. After travelling a distance  $l$  the new position is determined by:

$$x_{new} = x_{old} + e_x l$$

where  $x_{old}$  represents the previous position and  $e_x$  is the direction cosine.

- 3) After travelling a distance  $l$  the photon can be either outside or inside the reactor. If the new position is within the reactor radius, the photon could be adsorbed by the organic compound in solution, such as in the case of 4-nitrophenol, or strike a catalyst particle. In order to determine if the photon is absorbed by the solution a random number ( $R_3$ ) must be higher than the transmittance calculated by:

$$T = e^{-\beta_{\lambda, NP} x}$$

where  $x$  is the distance travelled by the photon and  $\beta_{\lambda, NP}$  is the extinction coefficient of the 4-nitrophenol solution. The photon is not absorbed by the solution if:

$$T > R_3$$

In that case the photon strikes a  $TiO_2$  particle and it can be either absorbed or scattered. The likelihood that determines which event take place depends on the albedo coefficient ( $\omega_\lambda$ ):

$$\omega_{\lambda} = \frac{\sigma_{\lambda}}{\beta_{\lambda}}$$

where  $\sigma_{\lambda}$  is the spectral scattering coefficient. Therefore, the higher the  $\sigma_{\lambda}$ , the lower the probability that the photon is absorbed. So, if

$$1 - \omega_{\lambda} \geq R_4$$

the photon is absorbed and it is stored in the corresponding cell and a the trajectory of a new photon is tracked. In case the photon is scattered a new position is calculated using an isotropic phase function [4, 5].

$$\cos \theta = 2R_5 - 1$$

After establishing the new direction the new length of flight and position is calculated. This sequence will be repeated until the photon is absorbed or lost.

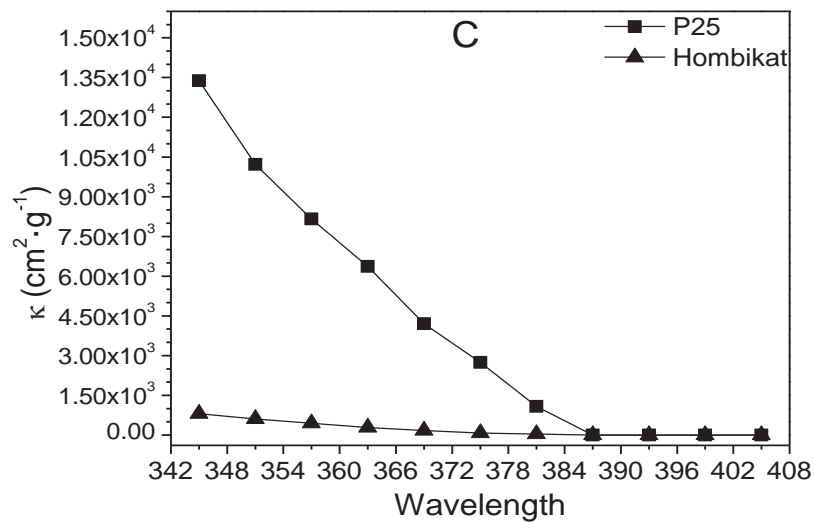
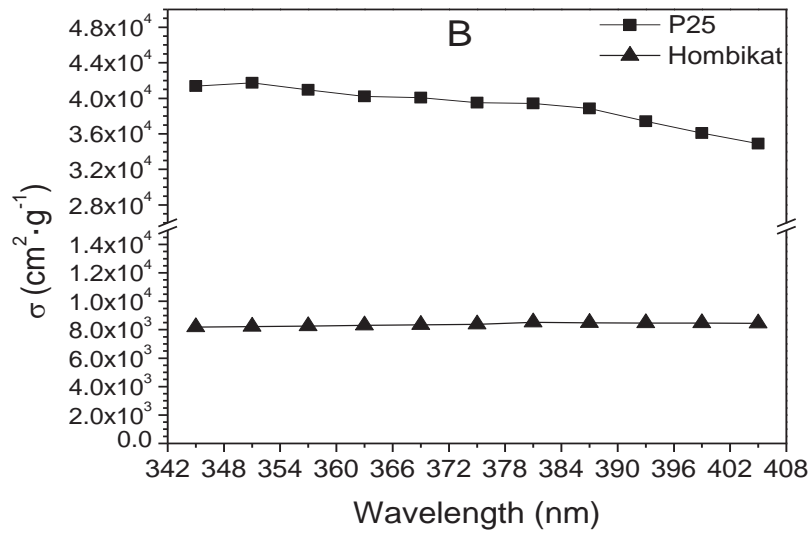
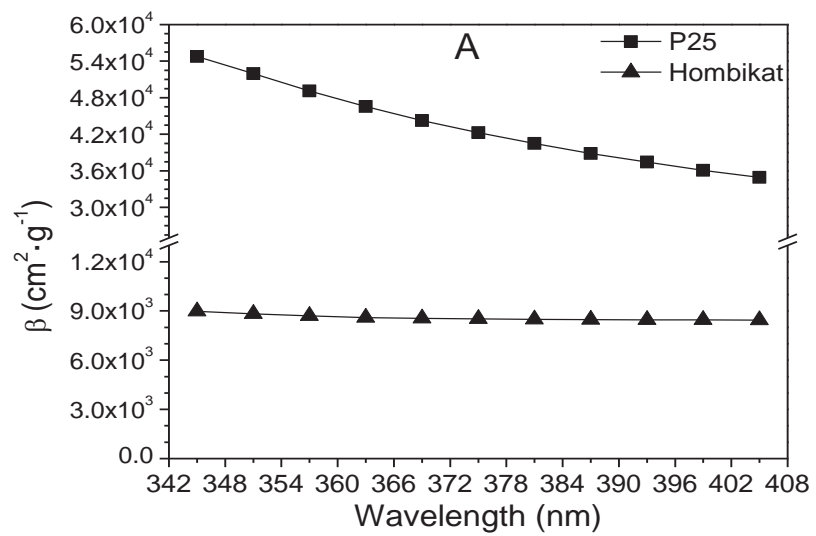
Finally the LVRPA in each cell is calculated by:

$$e^a(x) = \sum_{\lambda=350 \text{ nm}}^{\lambda=400 \text{ nm}} \frac{q_{w,\lambda} n_{ph,\lambda,abs}(x)}{n_{ph,T} \Delta x}$$

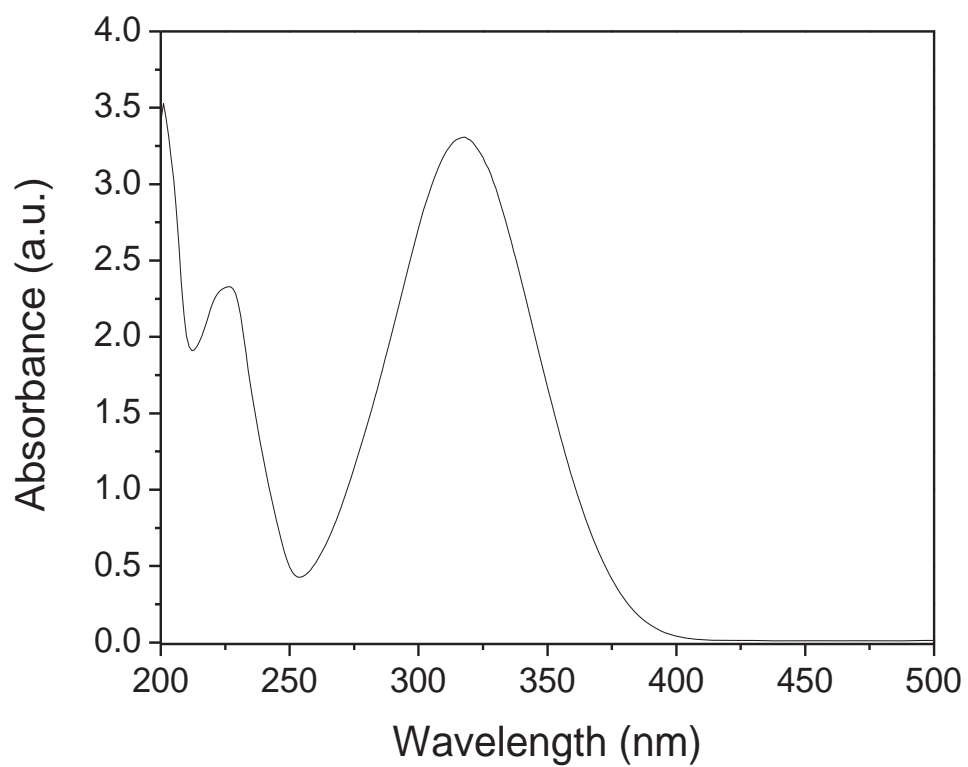
where  $q_{w,\lambda}$  is the inlet radiation flux of a wavelength  $\lambda$ ,  $n_{ph,\lambda,abs}(x)$  is the number of photons of a given wavelength absorbed in a cell,  $n_{ph,T}$  is the total number of photons considered in the simulation and  $\Delta x$  is the length of the cell.

**Table 1.** Ratio of scavenger to pollutant concentration used to study the degradation mechanism.

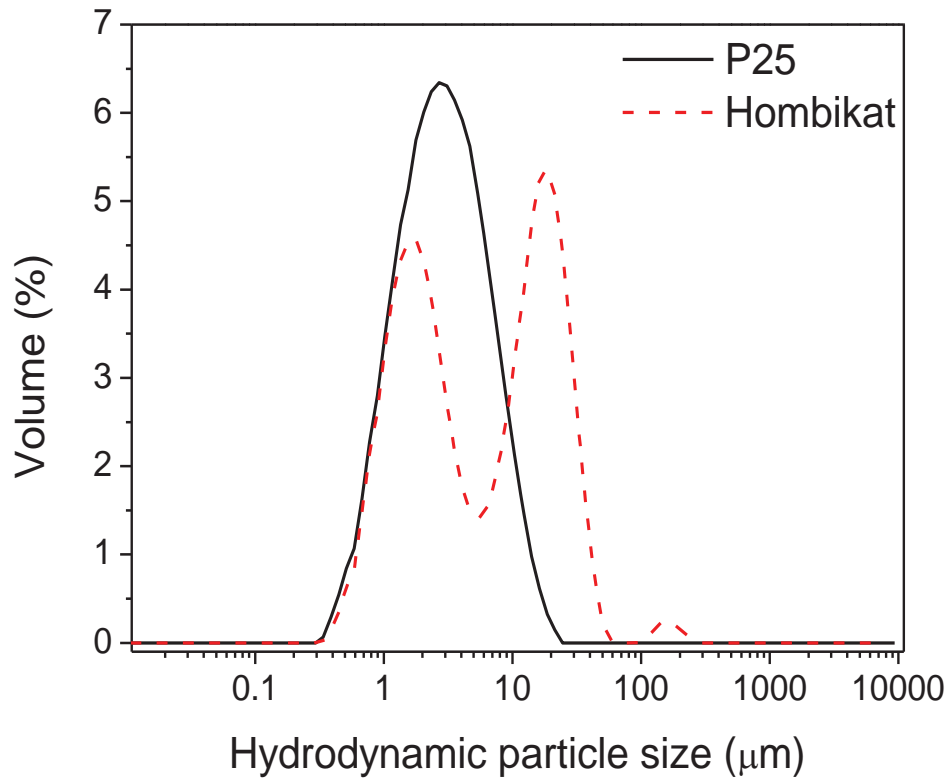
	Ratio scavenger/ pollutant (mmol/mmol)			
	Phenol	M-pHB	4-CP	4-NP
<b>CH<sub>3</sub>OH</b>	235.0	380.4	321.4	347.8
<b>HCOOH</b>	9.4	15.2	12.9	13.9
<b>Cu(NO<sub>3</sub>)<sub>2</sub></b>	18.8	30.4	25.7	27.8



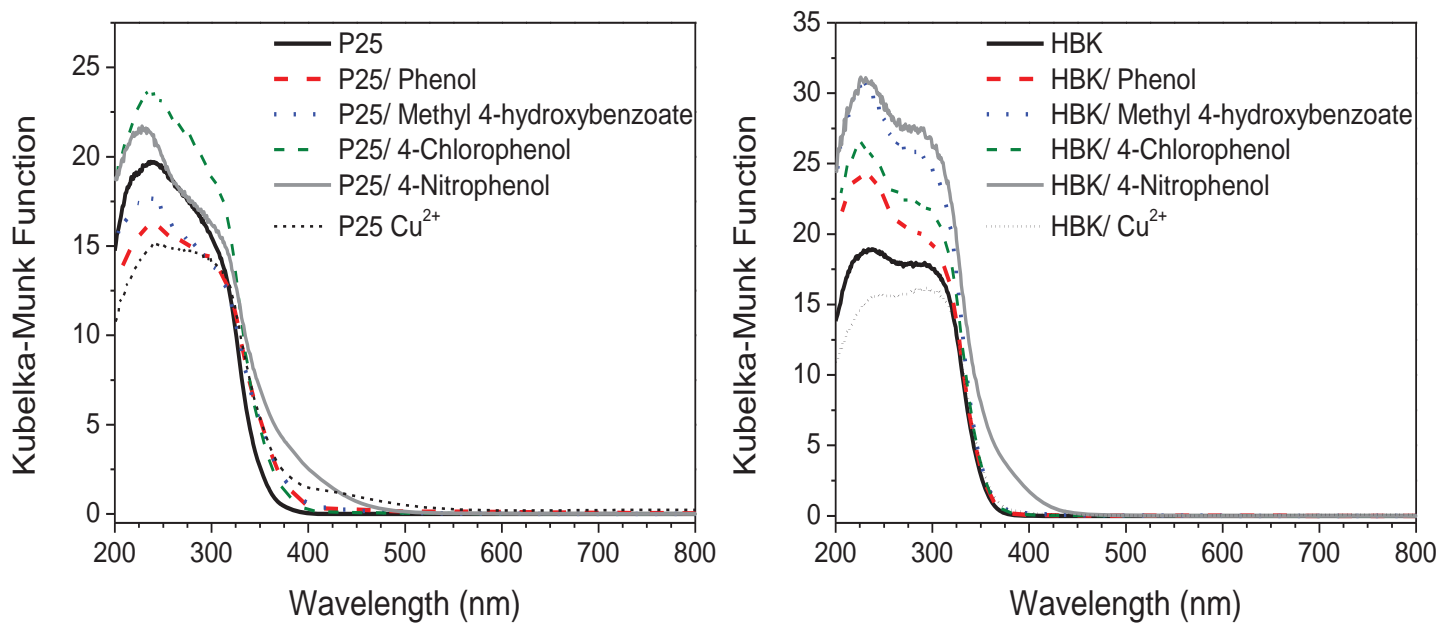
**Figures 1.-** Optical properties of TiO<sub>2</sub> catalysts. (A) Extinction Coefficient; (B) Scattering Coefficient; (C) Absorption Coefficient.



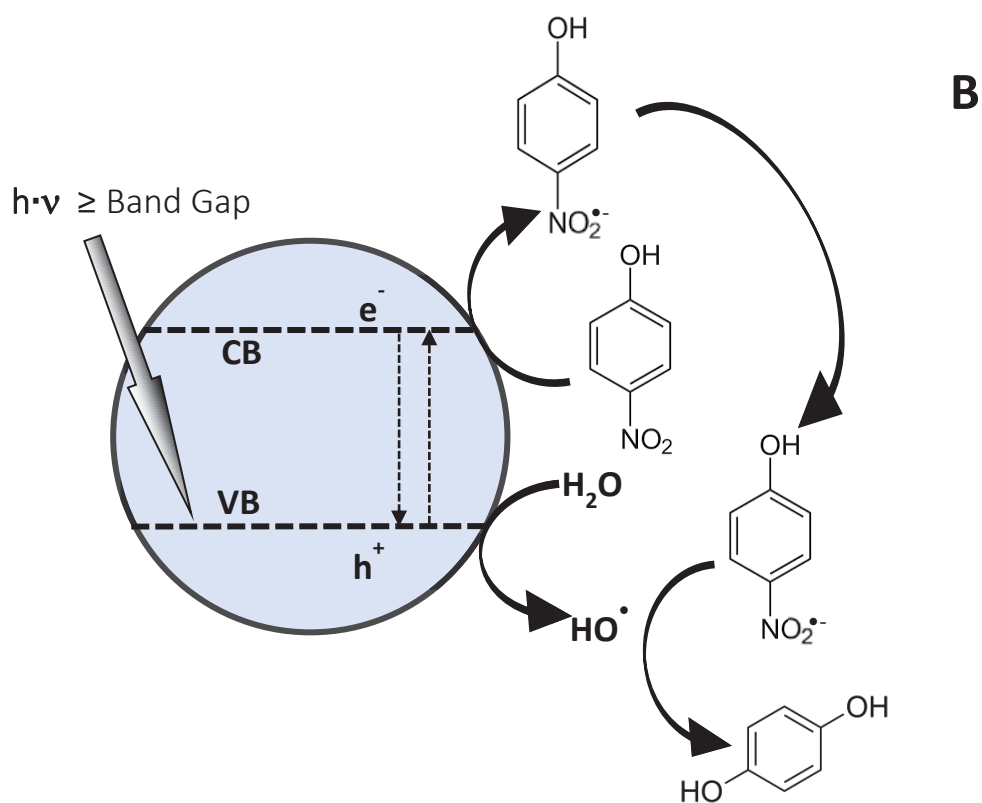
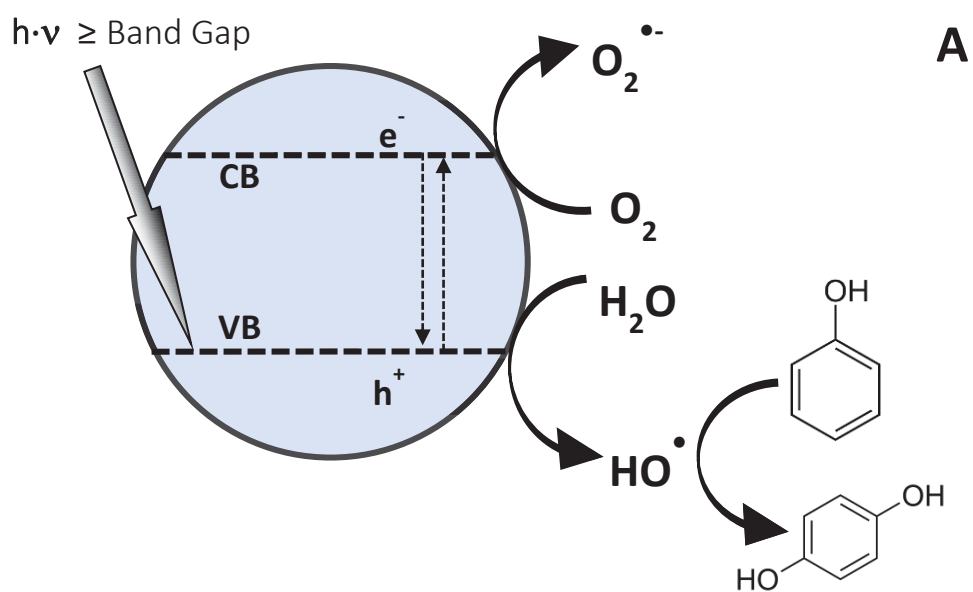
**Figure 2.-** Absorption spectrum of a 4-nitrophenol solution with a concentration of 50 mg·L<sup>-1</sup>.



**Figure 3.-** Distributions of hydrodynamic particle size distributions of TiO<sub>2</sub> photocatalysts in aqueous suspensions.



**Figures 4.-** Diffuse reflectance UV spectra of P25 and Hombikat photocatalysts previously adsorbed on the studied aromatic compounds. The spectra of the photocatalysts recovered after being used in the 4-nitrophenol photodegradation in presence of Cu<sup>2+</sup> ions are also shown.



**Figures 5.-** Proposed pathway for phenol photo-oxidation (A) and 4-nitrophenol (B).

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# Anexo IV:

Nature and photoreactivity of TiO<sub>2</sub>-rGO  
nanocomposites in aqueous suspensions under UV-A  
irradiation



## Nature and photoreactivity of TiO<sub>2</sub>-rGO nanocomposites in aqueous suspensions under UV-A irradiation



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Reduced graphene oxide  
Oxalic acid  
Mechanism  
ATR-FTIR

### ABSTRACT

Different studies to unravel the nature of the activity of TiO<sub>2</sub> photocatalysts modified with rGO were carried out. The band edge potentials and the band gap energy of the nanocomposites were determined by performing electrochemical impedance and UV–vis diffuse reflectance measurements, respectively. However, no changes were observed when TiO<sub>2</sub> is modified with rGO. Nevertheless, the presence of rGO in the hybrid composite led to a low charge transfer resistance across the electrode-electrolyte interface, observing even a tenfold increase in the photocurrent values in methanol photo-oxidation for P25-rGO 1%. Moreover, a higher oxygen reduction current was found when increasing the rGO concentration that could lead to a higher ROS formation. In order to analyze the beneficial properties of the hybrid materials, the influence of rGO doping ratio on oxalic acid photocatalytic degradation and on oxalic acid adsorption onto the nanocomposites surface was studied, both of them under UV-A light irradiation. In addition, the photoactivity of the conduction band electrons and the valence band holes was investigated by performing EPR and transient absorption spectroscopy measurements under UV-A illumination in O<sub>2</sub> or N<sub>2</sub> atmospheres. It was demonstrated that rGO behaved as an electron acceptor. Finally, TAS results under O<sub>2</sub> and N<sub>2</sub> atmospheres proved that the role played by rGO was not as crucial in excess of dissolved O<sub>2</sub> as in N<sub>2</sub> atmosphere. These findings agree with the observed photocatalytic activity and EPR measurements. Nevertheless, generation of HO<sup>•</sup> in N<sub>2</sub> saturated suspensions was highly increased with the addition of rGO.

### 1. Introduction

Photocatalytic Advanced Oxidation Process (AOP) based on semiconductors have emerged as a promising technology for water treatment [1]. The increasing interest is related to the ability of semiconductors to generate reactive electron-hole pairs when illuminated with light of energy greater than their band gap. These photogenerated charge carriers are able to form highly reactive chemical species, such as hydroxyl radicals HO<sup>•</sup>, which allow disinfecting water and/or degrading highly recalcitrant pollutants present in aqueous systems [2–4].

Because of the high band gap value and the low photonic efficiency exhibited by TiO<sub>2</sub>, a great deal of attention has been focused on the synthesis of new hybrid materials lacking these limitations [5–8]. Graphene- and graphene-derivative-based TiO<sub>2</sub> have been proposed as

highly photoactive nanocomposites due to their unique properties, such as large specific surface area and high electrical conductivity [9–14]. Furthermore, the photoactivity is enhanced on account on the fact that graphene oxide (GO) and reduced graphene oxide (rGO) absorb light in the UV–vis wavelength region, leading to the formation of reactive oxygen species [2,12,13].

Unfortunately, no consensus has been completely established so far about the role of rGO during the photocatalytic treatment of pollutants dissolved in water. Minella et al. [15] proposed a mechanism of underlying reactions in the presence of TiO<sub>2</sub>-rGO composites. The role played by rGO appears to depend on the adsorption and the light absorption properties of the substrate. Thus, only when the adsorption of the organic probe compound is significant, the electron transfer from the two phases can occur. This evinces the necessity to deepen into the

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understanding of the underlying mechanism. However, to evaluate the right development of the photocatalysts and the influence of their improved properties on the photocatalytic activity, the knowledge of the energetic position of the conduction and valence band edges and the reaction mechanism itself is crucial.

In this study, the nature of the activity of a TiO<sub>2</sub> photocatalyst modified with rGO synthesized by a hydrothermal method was investigated. Different rGO doping ratios were analyzed in the photodegradation of oxalic acid under UV-A light irradiation. In order to obtain a better knowledge about the origin and mechanism of the observed photoactivity, oxalic acid photodegradation runs were carried out. The actual position of the band edges and the band gap energy were determined by performing electrochemical impedance spectroscopy and UV–vis diffuse reflectance, respectively. Furthermore, electrochemical impedance spectroscopy and photocurrent response measurements were carried out to study the charge separation of the photo-generated charge carriers. Additionally, the reduction pathways of oxygen were investigated by measuring the oxygen reduction current at different potentials. Finally, EPR and transient absorption spectroscopy (TAS) experiments were performed to investigate the conduction band electrons and the valence band holes activity under UV-A illumination under O<sub>2</sub> or N<sub>2</sub> atmospheres. These results were related to the performance observed in the oxalic acid oxidation reactions.

## 2. Experimental section

### 2.1. Materials

Graphene oxide (GO) water dispersions (0.4 wt% Concentration) were purchased from Graphenea company. The GO used had a monolayer content over 95%, a particle size of 600 nm (DSL) and the following elemental analysis data was obtained: C = 49–56%, H = 0–1%, N = 0–1%, S = 2–4%, O = 41–50%. Titanium dioxide P25 Aeroxide® (80:20 anatase-rutile, BET specific surface area 54 m<sup>2</sup>/g, average anatase and rutile crystal size of 21 and 33 nm, respectively) was provided by Evonik Company. The spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), oxalic acid (OA) (≥ 99%), FTO (fluorine-doped tin oxide SnO<sub>2</sub>:F) glass and Dimethyl Sulfoxide (DMSO) were purchased from Sigma-Aldrich.

Deionized water (H<sub>2</sub>O) was supplied from a Millipore Milli-Q system with a resistivity equal to 18.2 MΩ cm. pH adjustments and measurements were performed using KOH provided by PanReac AppliChem. All the chemicals were used as received without further purification.

### 2.2. Synthesis of P25-rGO

P25-rGO composites were prepared by a hydrothermal method. To sum up, 2 g of P25 were suspended in 400 mL of deionized water and dispersed for 1 h using a 100 MHz tip (Misonix Microson 2000XL). Subsequently, the desired amount of GO was added to the suspension and sonicated for another hour to achieve a good dispersion of GO sheets in a homogenous medium. Subsequent to sonication, the mixture was transferred to a 600-mL Teflon-lined stainless steel autoclave reactor and subjected to hydrothermal treatment overnight at 120 °C. After that, the composite was collected by centrifugation and dried at 60 °C. The weight ratio P25: rGO was 0, 0.1, 0.5 and 1%, called along the paper as P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1%, respectively.

### 2.3. Photocatalyst characterization

Diffuse reflectance spectra were recorded with a UV–vis Varian, Cary 100 Bio UV–vis, equipped with an integrating sphere. Analyses of the band gap transitions of the samples were made using the Kubelka-Munk radiative transfer model and the Tauc plots [16]. An indirect allowed transition was considered to calculate the band gap energies

[17,18]. Raman spectrum was recorded on a Renishaw Micro Raman spectrometer (λ = 532 nm) equipped with a 20 mW He-Ne laser emitting at 532 nm. The spectra were recorded using 0.2 mW of incident power, 5 repetitions and 10 s of acquisition time.

Catalysts structural characterization were performed with a X-ray polycrystal PANalytical X'Pert PRO using nickel-filtered Cu Kα (1.541874 Å) radiation operating at 40 kV and 40 mA, with a 0.02° step size and accumulating a total of 50 s per point. Crystallite sizes was estimated by employing the Scherrer equation [19] and the crystalline phases were identified by comparison with ICDD PDF database [20]. The quantification of each previously selected crystalline phase was automatically calculated by X'Pert Highscore Plus software by the RIR (Reference Intensity Ratio) method.

Scanning electron microscopy (SEM) analyses were performed to determine morphology of the studied TiO<sub>2</sub> powders (Philips XL 30 S-FEG). Transmission Electron Microscope study of the composites was carried out in a field emission gun JEOL 2100 F microscope operating at 200KV. Specimens for Transmission electron microscopy were prepared by dry deposition of the composites in a lacey carbon copper grid.

Transient absorption spectroscopy (TAS), described previously in more detail [21], was carried out using an Applied Photophysics LKS 80 Laser Flash Photolysis Spectrometer. The proper diffuse reflectance accessory was used to measure in diffuse reflectance mode. The samples were excited by an Nd-YAG laser (Quantel; Brilliant B; 3rd harmonic, 355 nm) and light up by a pulsed xenon lamp (Osram XBO; 150 W) to analyze light absorption of the photogenerated transient species. Afterwards, the diffusely reflected light was led to the monochromator and detector (Hamamatsu PMT R928). For all the experiments excitations energy densities of 2.2 mJ cm<sup>-2</sup> per pulse were used, monitored by a Maestro energy meter (Gentec-EO). A 100 Ω value was always used as terminal resistance and the number of averages was 12 shots. All the samples were dry powder placed into a quartz flat cuvette and they were flushed with nitrogen or oxygen for more than 30 min before performing the measurements. To analyze the results obtained, the reflectance changes Δ*J* of the samples were obtained from the absorbance:

$$\Delta J = 1 - 10^{-Abs} = \frac{I_0 - I}{I_0} \quad (1)$$

Where Δ*J* can be correlated with the transient absorption of the photogenerated species and *I*<sub>0</sub> and *I* are the intensities of the reflected light before and after the laser pulse, respectively.

### 2.4. Electrochemical characterization

The photo-anodes of the synthesized photocatalysts were prepared by following the screen-printing method [22]. The detailed procedure is described in detail in the Supplementary Information: Procedure to prepare the photo-anodes by the screen-printing method.

The measurements were carried out with a three compartment cell consisting of a working (photo-) electrode (WE), a Pt wire counter electrode (CE) and an Ag/AgCl/KCl (3 M) reference electrode (RE). All potential values presented herein are pH-corrected and expressed vs. RHE (reversible hydrogen electrode). The photo-response of the prepared films was tested under chopped light irradiation at a constant potential 0.8 V vs. RHE by a Zennium potentiostat and a PECC-2 photoelectrochemical cell (Zahner-Elektrik GmbH & Co. KG). The illumination source, a 300 W Xe lamp with an AM 1.5-global filter providing an intensity of 680 W·m<sup>-2</sup> in the regime of 280–1000 nm (LOT-Quantum Design GmbH), was chopped on and off with a frequency of 300 mHz. Regarding the electrolyte, a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution with 10% v/v CH<sub>3</sub>OH was used.

For the rest of electrochemical experiments a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. The electrochemical impedance spectroscopies (EIS) of the as-prepared samples were carried out within a frequency range from 0.1 Hz to 30,000 Hz and the applied bias was

-0.0 V vs. RHE. The flat-band potentials ( $V_{fb}$ ) were determined from Mott–Schottky plots by Impedance spectra collected in the potential range of +1 to 0.2 V vs. RHE with a step width of -25 mV. Each spectrum was recorded at a fixed potential in the frequency range of 0.1 to 30,000 Hz with 10 steps per decade. A Randles circuit was used to fit the spectra to obtain the value of the space charge layer capacitance ( $C_{sc}$ ) at each potential. Rather than ordinary capacitance, constant phase elements (CPE) were used. In this work the flat-band potentials of the photo-anodes were calculated from the resulting Mott–Schottky plots ( $C^{-2}$  vs. applied potential). The extrapolation of the linear trend in the Mott–Schottky plot to the x-axis (potential) enables to calculate the  $V_{fb}$  for a given semiconductor oxide [8,16].

Oxygen reduction currents were obtained by performing linear sweep voltammetry both in nitrogen or oxygen-saturated electrolytic solutions in +0.8 V to -0.1 V potential range vs. RHE with a step width of 10 mV and a scan rate of 1 mV s<sup>-1</sup>. The difference between both scans constitutes the oxygen reduction current.

### 2.5. ATR-FTIR adsorption and photocatalytic experiments

The photocatalyst layer was performed following the procedure described in [23,24] and is summarized in the Supplementary Information: Deposition of the TiO<sub>2</sub>-rGO layer on the ATR crystal. Prior to starting, an infrared spectrum of the P25-rGO film was taken as a background. Two groups of blank reference spectra in the dark and under irradiation were obtained by adding 3 mL of Milli-Q water to the cell. Then, the sample was allowed to equilibrate with the water for 45 min in the dark and infrared spectra were recorded every 300 s. When the last spectrum was collected, the film was irradiated with UV-A light and a new set of spectra were collected every 300 s for 2 h. Right after both groups of blank spectra were recorded, the water was replaced by 3 mL of a 1 mM oxalic acid (OA) solution at pH 5 adjusted by adding KOH. Two new groups of spectra were monitored in the dark and under UV-A light irradiation. The final spectra were obtained by subtracting the corresponding blank. FTIR spectra were collected at room temperature using a FTIR spectrometer (IFS 66 BRUKER) equipped with an internal reflection element 45° ZnSe crystal and a deuterated triglycine sulphate (DTGS) detector. The interferometer and the infrared light path in the spectrometer were constantly purged with Argon to avoid H<sub>2</sub>O and CO<sub>2</sub> contamination. Spectra were recorded in the 1800–1200 cm<sup>-1</sup> region, employing a resolution of 4 cm<sup>-1</sup> and an averaging of 300 scans.

The samples were irradiated with UV-A light using a LED lamp (Model LED-Driver, THORLABS) emitting 365 nm UV light (FWHM = 7.5 nm). The lamp was placed at a distance of ca. 30 cm from the surface of the test solution to achieve an intensity of UV-A light of 1.0 mW cm<sup>-2</sup>, measured by an UV radiometer (Dr. Hönle GmbH, Martinsried, Germany).

### 2.6. Photocatalytic activity

The photocatalytic degradation measurements were carried out using a 0.25 L semi-continuous cylindrical reactor made of borosilicate glass and placed under four fluorescent lamps (PHILIPS CLEO 15 W, 365 nm, FWHM = 20 nm) used as an irradiation source. The distance to the lamps from the reactor was adjusted so that the average UV-A flux value was 1.08 mW cm<sup>-2</sup> measured by an UV-A radiometer (LT Lutron UVA Light Meter). The photoreactor was filled with 200 mL of a suspension with 0.20 g L<sup>-1</sup> of the hybrid photocatalysts and 1 mM of oxalic acid at pH 5 adjusted by adding KOH. The photocatalytic reactions were performed at room temperature (25–30 °C) and atmospheric pressure. The mixture was continually agitated while bubbling air using an air pump (Elite 801, 1000 cm<sup>3</sup> min<sup>-1</sup>). Prior to reaction, the mixture was premixed for 4 h in darkness to allow adsorption equilibrium to be reached. Samples were taken out every 15 min to follow the reaction and filtered using 0.2 μm-pore-size PTFE syringe filters.

High Performance Ionic Chromatography, HPIC, was used to identify and quantify oxalic acid concentration in a DIONEX ICS-1000 with a conductivity detector and an electro-regenerator-suppressor. An Ion Pac AS9-HC 2 × 250 mm and a guard column Ion Pac AG9-HC 2 × 50 mm from DIONEX was used. The eluent was an alkaline solution of 8·10<sup>-3</sup> mol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> and 1.5·10<sup>-3</sup> mol L<sup>-1</sup> NaHCO<sub>3</sub>. The temperature of the detector conductivity cell was kept constant at 35 °C.

### 2.7. EPR study

Generation of hydroxyl radical and superoxide radical anions upon UV light irradiation of the synthesized P25-rGO photocatalysts was examined by measuring the EPR signal of the DMPO–HO· and DMPO–O<sub>2</sub><sup>·-</sup> species, respectively. EPR spectra were recorded at room temperature on a MiniScope X-band EPR spectrometer (MS400 Magnetech GmbH, Germany) operating at 9.43 GHz field modulation. The acquisition parameters to detect DMPO–HO· / DMPO–O<sub>2</sub><sup>·-</sup> were as follows: center field: 339 m T, sweep width: 8/6 m T, sweep time: 25/15 s, number of scan: 1, modulation amplitude: 0.1 m T, power: 10 mW, gain: 5. The experimental EPR spectra acquisition and simulation were carried out using MiniScope and Winsim 2002 software. For the sample preparation, the photocatalyst (1 g L<sup>-1</sup>) was suspended in water or DMSO to detect DMPO–HO· or DMPO–O<sub>2</sub><sup>·-</sup>, respectively, and the suspension were subsequently dispersed by using an ultrasonic bath. Prior to the measurement, 1 mL of the suspension was introduced into the Eppendorf tube and then 200 μL of 40 mM of DMPO were immediately added. The tube was shaken by hand to homogenize the sample. The suspensions were transferred immediately to 50 μL borosilicate capillaries (Hirschmann ringcaps). The samples were irradiated directly in the EPR spectrometer microwave cavity by a spot UV-light (LC8, Hamamatsu, 200 W super-quiet mercury-xenon lamp) through the quartz window of the cell.

## 3. Results and discussion

### 3.1. Characterization of P25-rGO composites

In order to confirm the TiO<sub>2</sub> modification with rGO and to characterize the crystal structure of the carbon materials Raman spectroscopy was applied. Fig. 1 shows the Raman spectra of GO and of P25-rGO nanohybrid materials with different rGO mass doping ratio. All the TiO<sub>2</sub> based samples exhibited four different peaks corresponding to the vibration modes of anatase located at 145 cm<sup>-1</sup> (E<sub>g</sub>), 396 cm<sup>-1</sup> (B<sub>1g</sub>), 517 cm<sup>-1</sup> (B<sub>1g</sub> + A<sub>1g</sub>), and 638 cm<sup>-1</sup> (E<sub>g</sub>) [6,25]. As for GO, two

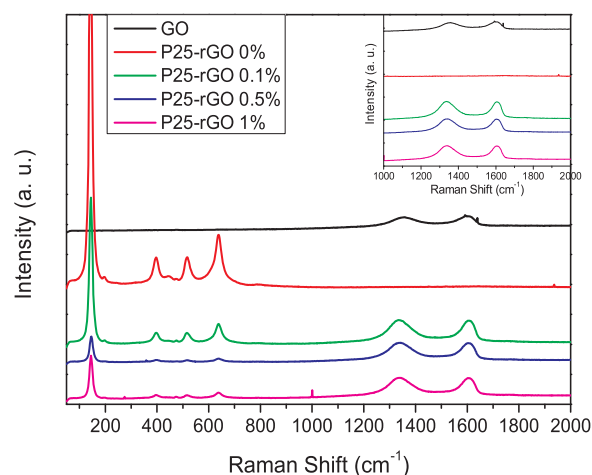


Fig. 1. Raman spectra of GO, P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5%, and P25-rGO 1%; and the magnified spectra ranging from 1000 cm<sup>-1</sup> to 2000 cm<sup>-1</sup> (upper right).



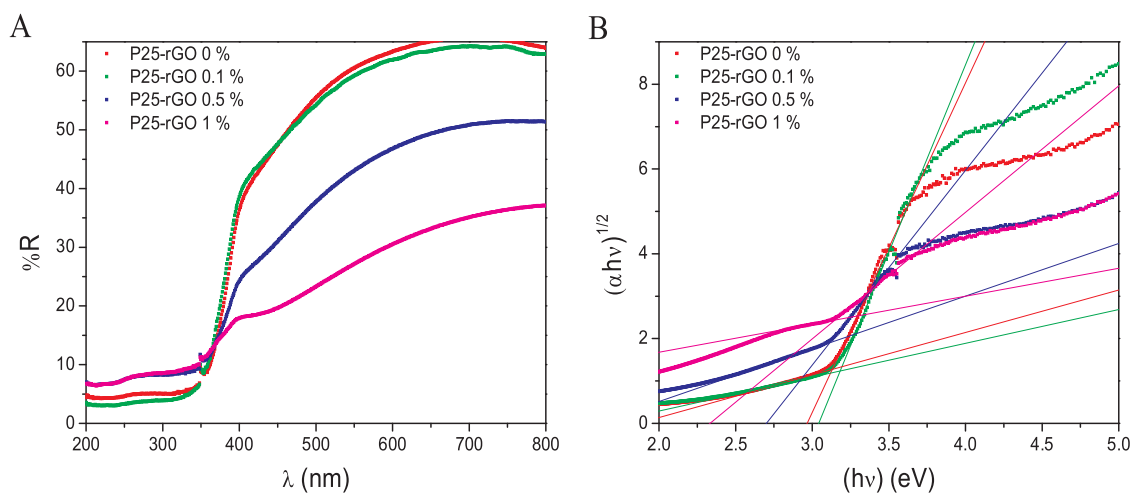


Fig. 2. Diffuse reflectance UV–vis spectra of P25-rGO composites (A) and Tauc plots (B) used to estimate the band gap values.  $\alpha$  represents the absorption coefficient.

different peaks ascribed to the D band and to the G band were observed at 1340 and 1605  $\text{cm}^{-1}$ , respectively. These two bands were also present in the Raman spectrum of the composites, proving the presence of rGO. Whereas the D peak is attributed to internal structural defects, edge defects or dangling defects caused by the existence of different oxygen-containing functional groups in the case of GO, the G peak is ascribed to C–C and C=C bonds [2,26]. Hence, a narrow G peak indicates a low amount of functional groups. The area under both peaks was calculated and the ratio  $A_D/A_G$  was compared. While GO yielded an  $A_D/A_G$  value close to 1.13, indicating a disordered structure [6,27], values of 1.44, 1.44 and 1.37 were estimated for P25-rGO 0.1%, P25-rGO 0.5%, and P25-rGO 1%, respectively. The ratio between the areas of both peaks increases as a consequence of the strong interaction between  $\text{TiO}_2$  and rGO sheets, giving rise to a higher disorder degree and suggesting the reduction of GO and the contribution of remaining oxygenated functional groups [6,7,25,28].

To further study the interaction between  $\text{TiO}_2$  and rGO and their effect on the light absorption, diffuse reflectance UV–vis spectroscopy measurements were conducted. Fig. 2A and B show the diffuse reflectance spectra of the different P25-rGO films and the Tauc plots, respectively. When the absorption spectra of the samples are evaluated, it could be noted that the higher the rGO content, the higher the absorption in the visible light range. The optical band gap energy of the samples was determined through the Tauc plots. Optical band gap values of 3.1 eV were found for pure  $\text{TiO}_2$ , P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1%, respectively, which indicates that the band gap energy remained unchanged by the introduction of rGO. So, as a result the variation is negligible and modification of  $\text{TiO}_2$  with rGO does not show a reduction of the band gap energy [15,25].

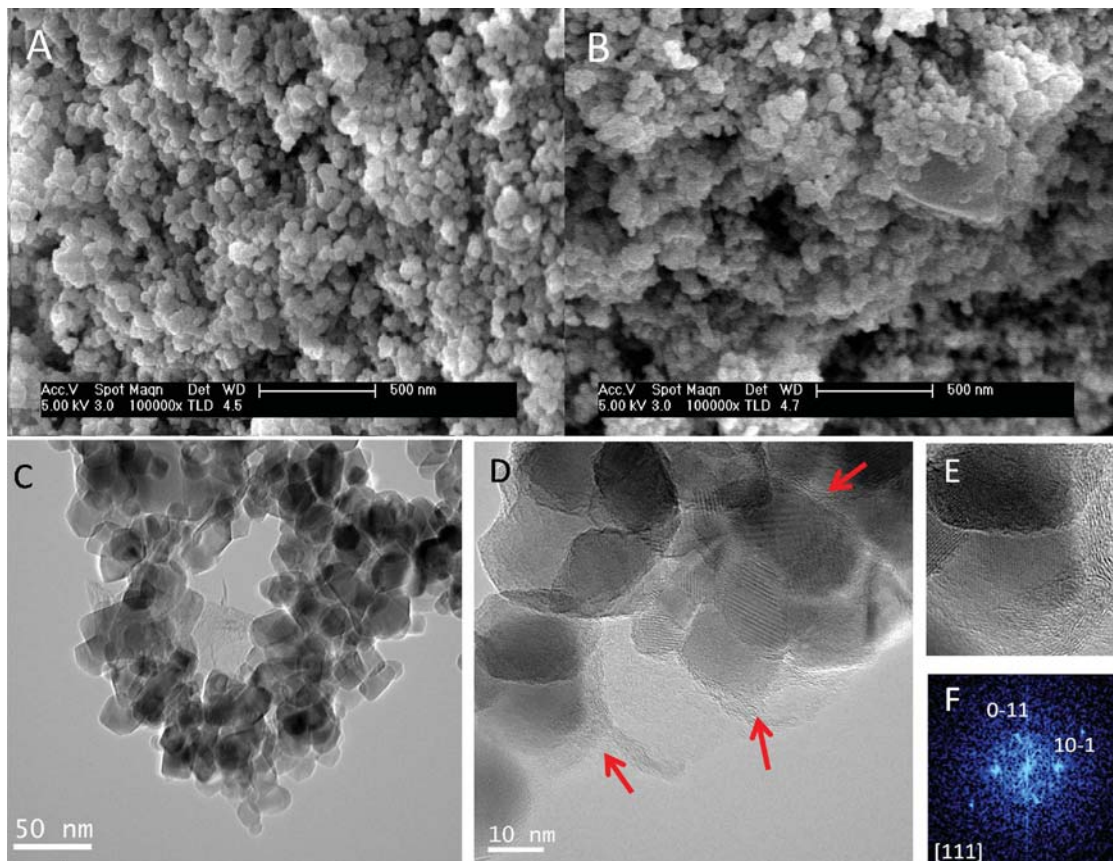
The XRD patterns of pure GO and P25-rGO composites are shown in Fig. S1. Although of GO exhibited a strong diffraction peak at  $11^\circ$ , this peak was not observed for any of the P25-rGO nanocomposites, which consisted of the characteristic peaks of anatase and rutile crystalline phases. This could be explained because of the reduction of GO to rGO and the relatively low amount and intensity of rGO/GO compared to the peaks of  $\text{TiO}_2$  [7,14,29].

To analyze the morphology and structure of the photocatalysts SEM and TEM were used. Some images of P25-rGO 0%, P25-rGO 0.5% and P25-rGO 1% can be seen in Fig. 3. From Fig. 3A and B it can be noted that primary particles have uniform shape and size for both samples. These primary particles were observed to be densely agglomerated. In Fig. 3B an rGO sheet loaded with  $\text{TiO}_2$  particles could be detected. A detailed insight into the microstructure of the P25-rGO 1% agglomerates is shown in the TEM micrograph of Fig. 3C. The picture exhibits  $\text{TiO}_2$  particles with a size ranging between 15 and 40 nm. The presence of graphene oxide is also evident in some areas. Through HRTEM we

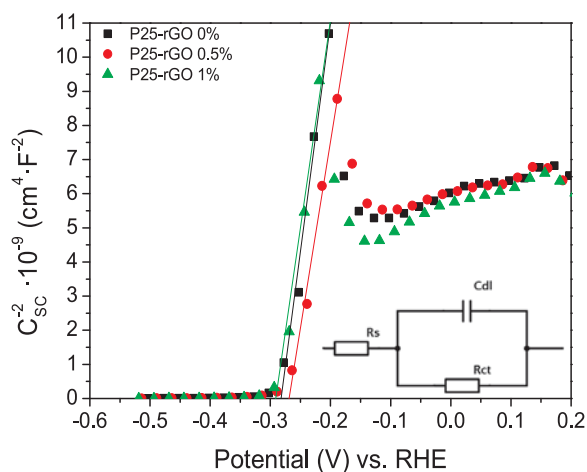
have located regions where the  $\text{TiO}_2$  particles appear surrounded by some sheets of graphene oxide as can be seen in Fig. 3D. The picture displays at least two or three particles surrounded by a wrinkled graphene sheet (Marked with red arrows). Fig. 3E displays one of these particles at higher magnifications. As can be deduced from its FFT (Fast Fourier Transform, Fig. 3F) the particle is oriented along the [111] zone axis of the anatase phase. Although the partially reduced graphene oxide is recovering part of the particles, it also seems to interconnect them proving an intimate contact between  $\text{TiO}_2$  and rGO that should improve electron transfer from the photo-excited  $\text{TiO}_2$  to rGO.

One of the most significant properties of semiconductors is the absolute position of the conduction and valence band edges as the possibility of an electron transfer to take place depends on the band potentials. In order to know whether the coexistence of  $\text{TiO}_2$  and rGO may shift the band position, electrochemical impedance spectroscopy experiments were carried out at different potentials. Values of the space charge layer capacitance ( $C_{SC}$ ) were derived by fitting the impedance spectra at each potential to a Randles circuit. The value of exponential parameter of the CPE was found to be between 0.9 and 1.0. Afterwards, Mott-Schottky plots were constructed by depicting the inverse square of the  $C_{SC}$  per unit of area against the respective applied potential (Fig. 4). Mott-Schottky plots showed a linear regimen which could be extrapolated to the x axis to obtain the flat-band potential ( $E_{FB}$ ) [8,16]. By the slope of the plots it was determined that the studied photocatalysts are n-type semiconductors [16]. The flat-band potentials of P25-rGO 0%, P25-rGO 0.5% and P25-rGO 1% were -0.28, -0.27, and -0.29 V vs. RHE respectively. Therefore, as expected, no shift of the  $E_{FB}$  was observed when  $\text{TiO}_2$  was modified with rGO. It is generally known that the conduction band edge ( $E_{CB}$ ) of an n-type semiconductor is around 0–0.2 V more negative than the  $E_{FB}$  [30–32]. In this study a value of 0.1 V was chosen and the estimated conduction band potentials for P25-rGO 0%, P25-rGO 0.5%, and P25-rGO 1% were -0.38, -0.37, and -0.39 V vs. RHE, respectively. Taking into account the value of the band gap energies obtained from optical spectroscopy, the values of the valence band potentials were also estimated (2.76 V, 2.75 V, and 2.75 V vs. RHE for P25-rGO 0%, P25-rGO 0.5%, and P25-rGO 1%, respectively).

To understand the difference in the electronic properties of pure  $\text{TiO}_2$  and rGO modified titania, the photocurrent response was measured as it provides useful information about the generation and separation of the photogenerated electron-hole pairs under irradiation [7,33]. Fig. 5 illustrates the photocurrent response of the films at 0.8 V bias potential vs. RHE in a 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution containing 10% v/v  $\text{CH}_3\text{OH}$  under chopped UV–vis irradiation (A) and visible irradiation ( $\lambda > 450$  nm) (B). In both figures, it can be noted that the photocurrent responses promptly decrease when the light is switched off and comes back to the maximum value when the light is turned on



**Fig. 3.** SEM images of P25-rGO 0% (A) and P25-rGO 0.5% (B). TEM and HRTEM images of P25-rGO 1% (C and D); High magnification of P25-rGO 1% showing the presence of rGO layers (E). Fast Fourier Transform (FFT) of the photocatalyst.



**Fig. 4.** Mott-Schottky plots of P25-rGO 0%, P25-rGO 0.5% and P25-rGO 1% electrodes. The intercept of the linear regime with the x-axis determines the flat-band potential. The equivalent Randles circuit is inseted.

again, showing a good reproducibility of the different cycles. When the samples were irradiated with UV–vis irradiation (Fig. 5A) the photocurrent values obtained for P25-rGO 1% and P25-rGO 0.5% were around  $6.5$  and  $3.75 \mu\text{A cm}^{-2}$  respectively, being 10 and 6 times higher than those values obtained for P25-rGO 0%. This effect in the photocurrent cycles could be attributed to the rGO /TiO<sub>2</sub> coupling which allows a faster transfer of the photogenerated electrons from the conduction band of TiO<sub>2</sub> to rGO and further transfer to the electrode. When the films were irradiated with visible light (Fig. 5B) the photocurrent response followed the same sequence. However, photocurrent values

less than 1% were reached when irradiating with wavelength higher than 450 nm. In both figures, a slow photocurrent response of P25-rGO 0% could be ascribed to the electrons trapped in trapping sites such as Ti<sup>3+</sup>. The photogenerated electrons are first trapped in surface or shallow bulk trap sites and further migrate to deeper states, becoming less mobile [5,34]. Therefore, while the “trap filling” process is taking place, only part of the photogenerated electrons can be transferred to the FTO leading to the slow increase of the photocurrent response [35]. The slow photocurrent fall when the light was turned off could be the result of stored electrons in rGO being released gradually [7]. To sum up, the photocurrents results reveal that more effective charge separations of the photogenerated electron-hole pairs were attained with rGO modified TiO<sub>2</sub>. This is mainly due to the higher conductance values when rGO was present, which enables a faster charge carrier transfer between the film and the electrode [26,33].

Electrochemical impedance spectroscopy (EIS) was carried out to obtain the respective Nyquist plots (Fig. 6). From these graphs, information about the electron-transfer process across the semiconductor-electrolyte interface can be obtained. It can be noted that the greater the amount of rGO mass concentration, the smaller the semicircle radius, which indicates a more efficient charge separation and lower interfacial charge transfer resistance [7,25,36]. A more detailed explanation related to this conclusion is included in the Supplementary Information: Nyquist plot explanation.

In most photocatalytic applications the only electron acceptor available is oxygen. Therefore, the reduction process of oxygen by the photogenerated electrons is crucial. The formation of superoxide anion radicals (O<sub>2</sub><sup>•-</sup>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) by oxygen reduction by one or more electrons is especially important when the photocatalysts are irradiated by visible light, as previously reported in water disinfection [10,37]. The different oxygen reduction reactions depending on

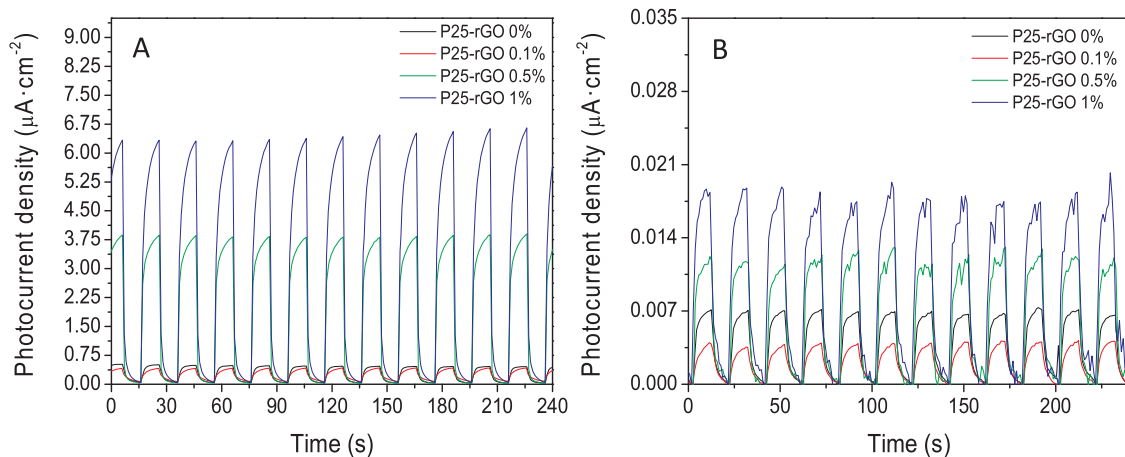


Fig. 5. Photocurrent density versus time curves for the hybrid materials with different rGO mass doping ratio under (A) chopped UV-vis light and (B) chopped visible light ( $\lambda > 450$  nm).

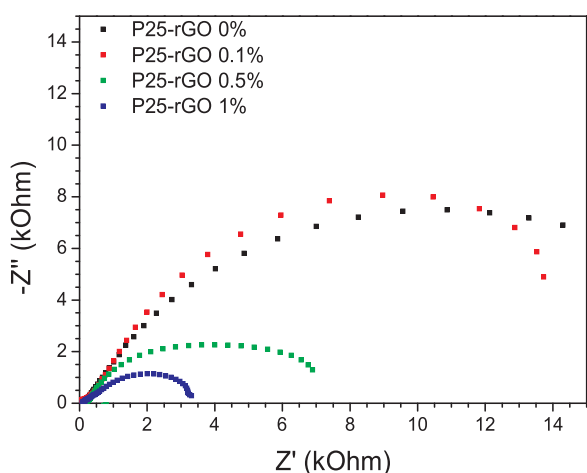
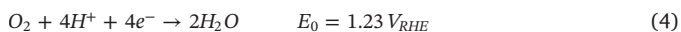
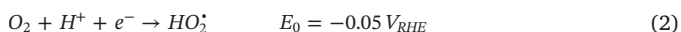


Fig. 6. Nyquist plots measured in 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution under 0 V bias vs. RHE. The employed frequency range was from 0.1 Hz to 30 kHz.

the number of electrons involved and their respective reduction potentials are shown below [8,38]:



Linear sweep voltammetry experiments were performed to measure the oxygen reduction currents and thus analyze the effect of rGO coupling with  $\text{TiO}_2$  on the reduction mechanism of oxygen (Fig. 7).

The unmodified  $\text{TiO}_2$  exhibited a negligible oxygen reduction current at potentials above 0 V vs. RHE ( $< 3 \mu\text{A cm}^{-2}$ ), pointing out that a slow reduction process occurred. On the other hand, when titanium dioxide was modified by rGO, a significant rise of the oxygen reduction current was detected up to 0.4 V vs. RHE. The reduction current values obtained at 0 V vs. RHE for P25-rGO 1% ( $> 23 \mu\text{A cm}^{-2}$ ) and P25-rGO 0.5% ( $< 12 \mu\text{A cm}^{-2}$ ) were nearly 10 and 5 times higher than the value reached by P25-rGO 0% ( $2.4 \mu\text{A cm}^{-2}$ ). In conclusion, the higher the amount of rGO in the nanocomposite, the larger the increase of the reduction current, probably because of the lower charge transfer resistance of these photocatalysts.

### 3.2. Photocatalytic activity of P25-rGO composites

To investigate the photocatalytic activity of P25-rGO 0% and P25

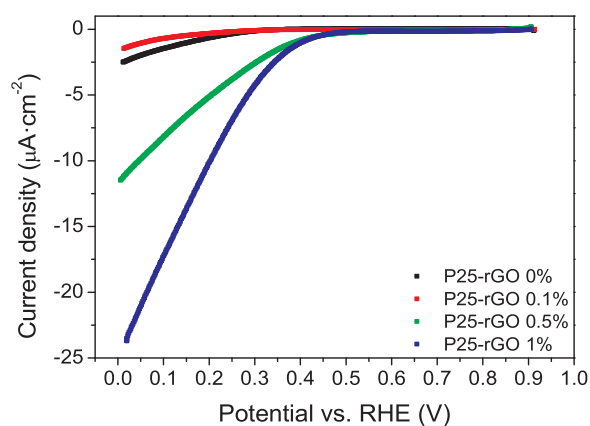


Fig. 7. Oxygen reduction current vs. applied potential for the different modified  $\text{TiO}_2$ .

modified with rGO, the degradation of 1 mM oxalic acid aqueous solution under UV-A irradiation was followed using ATR-FTIR. In situ ATR-FTIR is a useful technique to characterize the adsorbed species on the photocatalyst surface and monitoring the photodegradation of the surface complexes and intermediates adsorbed [23,39–41]. Oxalic acid was chosen since it is a model compound which is usually generated as an intermediate during the degradation of more complex pollutants, e.g. phenolic compounds, and because of its simple oxidation pathway [23,39]. Oxalic acid is transformed into  $\text{CO}_2$  and the process can be monitored in an easy way since few intermediates (formic acid or carbonates) are formed [39,41].

Firstly, measurements were carried out to follow the adsorption process for 45 min. Fig. S2 shows the time evolution of the recorded spectra of adsorbed oxalic acid in the dark (the time interval between every spectra was 5 min). Several studies have previously shown the main features of FTIR spectrum of oxalic acid adsorbed on  $\text{TiO}_2$  [39,40]. In brief, the band between  $1800$  and  $1600 \text{ cm}^{-1}$  and the shoulder at  $1590 \text{ cm}^{-1}$  were assigned to  $\text{C}=\text{O}$  symmetric stretching mode and  $\text{O}-\text{C}=\text{O}$  asymmetric stretching mode. In the region between  $1500$  and  $1200 \text{ cm}^{-1}$  two bands could easily be differentiated at around  $1420$  and  $1300 \text{ cm}^{-1}$ . The first band could be ascribed to the symmetric stretching mode of  $\text{C}-\text{O}$ ,  $\text{C}-\text{C}$ , and  $\text{O}-\text{C}=\text{O}$  bonds, whereas the second peak rise as a consequence of symmetric stretching mode of  $\text{C}-\text{O}$  bonds overlapping with the bending mode of the  $\text{O}-\text{C}=\text{O}$  bonds. A shoulder close to the peak observed at  $1300 \text{ cm}^{-1}$  has also been related to outer sphere complexes in the case of rutile [40]. By looking at the time evolution of the recorded spectra it could be noticed that the



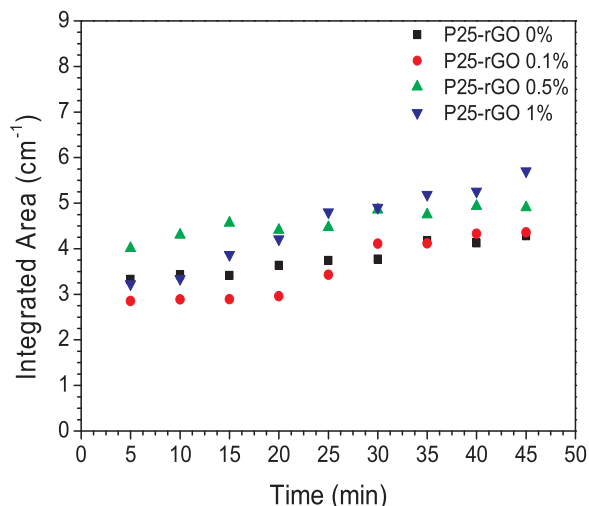


Fig. 8. Time evolution of the integrated IR spectral signals between 1200 and 1800  $\text{cm}^{-1}$  of the films in contact with 3 mL of oxalic acid solution in the dark.

oxalic acid has been mostly adsorbed during the first five minutes, regardless of the nanocomposite. Afterwards, only a slight increase of the intensity was detected, especially, the intensity of the shoulder between 1620 and 1580  $\text{cm}^{-1}$  changes slightly, and the equilibrium appeared to be reached after 25 min. The evolution of the integrated area of the peaks between 1800 and 1200  $\text{cm}^{-1}$  as a function of time is depicted in Fig. 8. Only slight changes of the integrated area corresponding to adsorbed oxalic acid was detected after the high value was obtained at 5 min. All the curves from the integrated spectra revealed a behavior similar to a Langmuir adsorption isotherm [40], despite the fact that the titanium dioxide was modified with rGO. Comparing the values of the integrated area reached by the studied photocatalysts a rise of the amount of adsorbed oxalic acid was detected when the rGO concentration in the  $\text{TiO}_2$  increased. This result may be attributed to the high surface area and high selectivity exhibited by rGO [42,43].

Subsequent to the adsorption process of oxalic acid on the photocatalyst surface, a series of spectra were recorded to track the oxalic acid degradation when the sample was irradiated by 365 nm light with an intensity of 1.0  $\text{mW cm}^{-2}$  for 2 h. The time evolution of the recorded spectra of the adsorbed organic compound during illumination with UV-A light is displayed in Fig. S.3. Following the first spectrum a decrease of the intensity in the wavenumber region between 1620 and 1550  $\text{cm}^{-1}$  was observed. This is related to removal of the least stable surface complex that represents the adsorption of oxalate [23,40]. On the other hand, the peak at 1300  $\text{cm}^{-1}$  barely suffered any changes under irradiation.

To better compare these results, the area under the peaks in the region between 1800 and 1200  $\text{cm}^{-1}$  was estimated for the spectra recorded every 5 min (Fig. 9). A pseudo-first order kinetic was observed for the oxalate surface photodegradation reaction. The obtained pseudo-first order rate constants were  $5.2 \cdot 10^{-3} \pm 2.3 \cdot 10^{-4}$ ,  $5.5 \cdot 10^{-3} \pm 2.1 \cdot 10^{-4}$ ,  $5.7 \cdot 10^{-3} \pm 1.2 \cdot 10^{-4}$  and  $6.8 \cdot 10^{-3} \pm 1.7 \cdot 10^{-4} \text{ min}^{-1}$  for P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5%, and P25-rGO 1%, respectively. The modified  $\text{TiO}_2$  with 0.5% and 1% yielded slightly higher values of the pseudo-first order kinetic constant than pure  $\text{TiO}_2$  (1.1 and 1.3 times higher respectively). This slight rise could be attributed to the higher adsorption capacity as a result of the introduction of rGO, previously mentioned above, and the more efficient separation of the photogenerated charge carriers according to the electrochemical characterization.

To further investigate the photocatalytic degradation of oxalic acid, reactions in which the photocatalysts were suspended in a 1 mM oxalic acid aqueous solution were conducted. UV-A light with an intensity of 1.08  $\text{mW cm}^{-2}$  was used to irradiate the reactor. No photolysis of oxalic

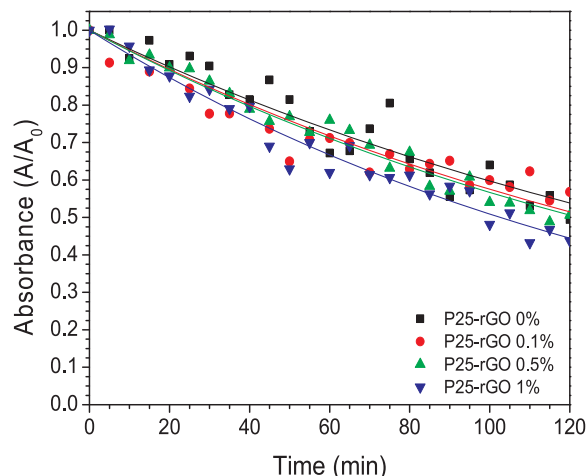


Fig. 9. Time evolution of the integrated area between 1800 and 1200  $\text{cm}^{-1}$ . A 365 nm LED with an intensity of 1  $\text{mW cm}^{-2}$  was used to illuminate the sample.

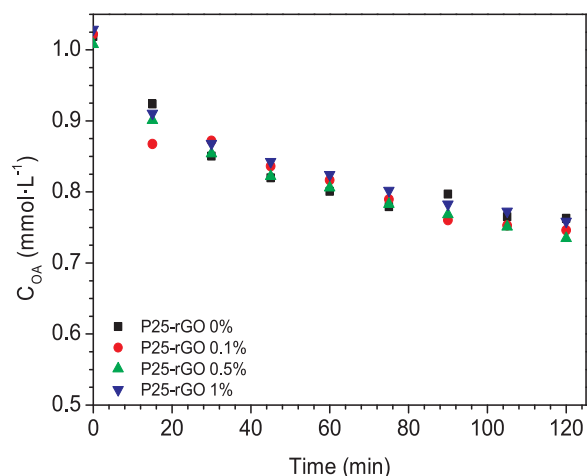


Fig. 10. Time evolution of the concentration of oxalic acid using P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1%. The sample was irradiated with UV-A light with an intensity of 1.08  $\text{mW cm}^{-2}$ .

acid was previously reported [44,45]. The photocatalytic degradation of oxalic acid over different studied photocatalysts is shown in Fig. 10 as the plot of the oxalic acid concentration versus illumination time. In this case, even smaller differences were observed in the photocatalytic degradation curves obtained for the nanocomposites compared to the studies using ATR-FTIR spectroscopy. One of the advantages of characterizing the photocatalytic oxidation using the ATR-FTIR technique is that differences of the effective path lengths are diminished as a thin layer is deposited on the ATR crystal. However, when the photocatalyst is suspended in the reaction medium, light-block effects occur. For instance, an excess of rGO can block the amount of light reaching the  $\text{TiO}_2$  nanoparticles [25], leading to lower photonic efficiencies in spite of the other beneficial properties of rGO. That might be the reason why P25-rGO 0.5% yielded the highest photodegradation in suspension, even though the surface photocatalytic reaction was faster for P25-rGO 1% as was shown by the ATR-FTIR experiments. Furthermore, an excessive amount of rGO could lead to the formation of clusters or agglomerates acting as recombination centers [25,46].

Despite the fact that the electrochemical characterization indicated that the modification of  $\text{TiO}_2$  with rGO led to much more efficient separation of the photogenerated charge carriers, similar photodegradation kinetics were observed for the different photocatalysts used in this study. In order to evaluate the effect of the mass doping ratio of rGO on the role played by the photogenerated electrons and holes and their

influence in the photocatalytic mechanism under UV light, EPR measurements were performed to detect the reactive oxygen species (ROS) involved in the photocatalytic process. Dissolved molecular oxygen plays a crucial role since it reacts with trapped electrons, subsequent to being photogenerated, forming superoxide anion radicals ( $O_2^{\cdot-}$ ) [37]. The generation of  $O_2^{\cdot-}$  was detected at room temperature by performing spin trapping technique using DMPO. The photocatalysts were suspended in DMSO instead of water to avoid the facile disproportionation of the superoxide radical that leads to a slow reaction between superoxide anion radicals or hydroperoxyl radicals and DMPO [47]. Moreover, using DMSO as a solvent favors the generation and trapping of  $O_2^{\cdot-}$  because of the stabilization effect of the aprotic solvent and the higher solubility of molecular oxygen [48]. Fig. S4 displays EPR spectra obtained at different irradiation times of the P25-rGO suspensions saturated with  $O_2$ . Under these conditions, for all the studied photocatalysts, a series of peaks were observed immediately after irradiation at around 337 mT and 340,5 mT for example. Then they decayed at the same time the intensity of other peaks at 336,5 mT and 338 mT increased. The simulation analysis of the EPR spectra (Fig. S5) revealed that the interaction of EPR signals could be ascribed to a combination of  $DMPO-O_2^{\cdot-}$  ( $a_N = 1.282$  mT,  $a_H^\beta = 1.035$  mT,  $a_H^\gamma = 0.132$  mT;  $g = 2.0058$ ) and  $DMPO-CH_3$  ( $a_N = 1.462$  mT,  $a_H^\beta = 2.093$  mT;  $g = 2.0057$ ) [48,49], where the two first signals mentioned above were attributed to the  $DMPO-O_2^{\cdot-}$  whereas the peaks at 3365 mT and 338 mT corresponded to the generation of  $DMPO-CH_3$ . The formation of  $CH_3^{\cdot}$  was previously reported as the result of the oxidation of DMSO by  $HO^{\cdot}$  radicals generated by the presence of adsorbed water onto the catalyst surface [48,50].

To delay the generation of  $DMPO-CH_3$  and achieve a better comparison of the ability to generate  $O_2^{\cdot-}$  radicals, the samples were irradiated for just two seconds, and afterwards, the EPR spectra was recorded (Fig. S6). The simulation confirmed the generation of  $DMPO-O_2^{\cdot-}$ , characterized by hyperfine splitting  $a_N = 1.282$  mT,  $a_H^\beta = 1.035$  mT,  $a_H^\gamma = 0.132$  mT;  $g = 2.0058$  [48,49]. Although the differences between these spectra are small, P25-rGO 0.1 and 0.5% exhibit a higher intensity. These results were attributed to the ability to reduce oxygen more easily when the  $TiO_2$  was modified by rGO, Fig. 7.

Valence band holes react with adsorbed hydroxide anions and water molecules giving rise to hydroxyl radicals, which together with holes are crucial oxidative species in the photocatalytic oxidation of dissolved organic matter [48]. Furthermore, hydroxyl radicals can be formed by consecutive reactions of photogenerated  $O_2^{\cdot-}$  with protons from the aqueous solution (reactions (4)-(7)):



The detection of hydroxyl radicals was performed upon irradiation of P25-rGO in  $O_2$  and  $N_2$  saturated aqueous suspensions at room temperature (Fig. S7). No signal was measured in the dark for any of the photocatalysts. However, when the sample was irradiated by a Xe lamp, a four-line EPR signal was identified. The simulation analysis, Fig. S8, confirmed the generation of  $DMPO-HO^{\cdot}$  ( $a_N = 1.497$  mT,  $a_H = 1.477$  mT;  $g = 2.0057$ ) [48,49].

It can be noticed that the experimental spectra perfectly corresponded with the simulated one. The signal appeared immediately after exciting the sample and suffered a decreased in intensity after 30 s (Fig. S7). No significant differences were observed among the spectra obtained for the studied photocatalysts, which indicates that a similar concentration of hydroxyl radicals were photogenerated in the presence of rGO. In order to discuss more easily the generation of reactive oxygen species in EPR experiments, the area of the EPR spectra signals, obtained under the different atmospheres, were calculated and plotted

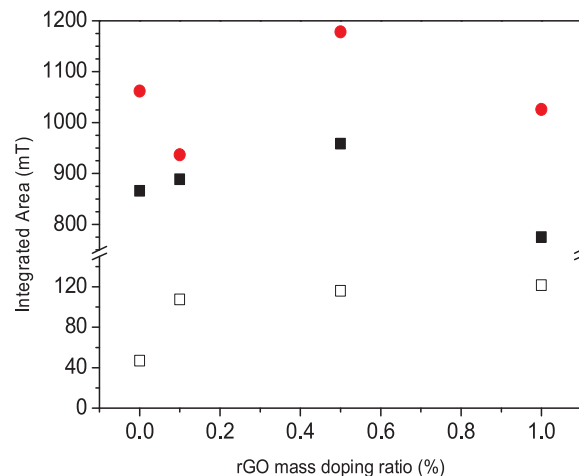


Fig. 11. Calculated area for  $DMPO-OH$  adduct in  $O_2$  (■),  $DMPO-O_2^{\cdot-}$  adduct in  $O_2$  (●),  $DMPO-OH$  adduct in  $N_2$  (□) for the studied P25-rGO photocatalysts. The area of the  $DMPO-OH$  and  $DMPO-O_2^{\cdot-}$  adducts were calculated from the EPR spectra obtained after illuminating for 30 and 2 s respectively.

versus rGO mass concentration (Fig. 11). Similar values for  $DMPO-HO^{\cdot}$  and  $DMPO-O_2^{\cdot-}$  were found regardless of the rGO doping ratio in  $O_2$  saturated suspensions, with P25-rGO 0.5% yielding the highest integrated area for both measured reactive oxygen species,  $O_2^{\cdot-}$  and  $HO^{\cdot}$ . The slight increase detected for some of these nanocomposites could be ascribed to the most effective separation of photogenerated charge carriers and the ability to achieve a more efficient reduction of oxygen. Regarding P25-rGO 1%, the integrated area values decreased as a result of the shielding effect caused by an excess of rGO that could also imply the formation of clusters acting as recombination centers [15,46], as was already pointed out in the above discussion about oxalic acid photodegradation. However, when the  $DMPO-HO^{\cdot}$  EPR spectra measured in  $N_2$  saturated suspensions was integrated, the integrated area was found to increase three times when 0.1% rGO was incorporated to  $TiO_2$ . Higher rGO concentrations only led to a slight increase. These results evinced the role played by rGO as an electron acceptor which enables the reaction between holes and adsorbed water to generate hydroxyl radicals whereas the electrons are dragged to rGO.

Even though electrochemical results indicated a great enhancement in separating electron-hole pairs, only a small improvement of photocatalytic activity was found in oxalic acid experiments and in ROS detection. To better understand of the processes occurring upon illumination transient absorption spectroscopy (TAS) has been conducted in the microsecond scale, which allows studying the reaction dynamics of the photogenerated charges. The TAS decays for the  $TiO_2$  and  $TiO_2$ -rGO powders under  $N_2$  or  $O_2$  were obtained after exciting the sample with laser pulses of light with a wavelength of 355 nm and energy of  $2.2$  mJ  $cm^{-2}$  per pulse (Fig. 12). Probe wavelengths at 400 nm and 660 nm were used to follow the decay kinetics of the trapped holes and electrons, respectively [5,51–55].

A kinetic model based on fractal surfaces [21] was applied to evaluate the effect of rGO and the atmosphere on the charge carriers dynamics:

$$\Delta J = \frac{A(1-h)}{(1-h) + Ak_f t^{1-h}} \quad (9)$$

Where  $k_f t^{-h}$  represents a rate coefficient and a time dependent factor,  $h$  is related to the fractal dimension of the surface and  $A$  represents the height of the transient signal. The  $k_f$  and  $A$  parameters are shown in Table 1.

Since rGO acts as an electron acceptor, electrons are transferred from  $TiO_2$  to rGO in the ps time regime [5,55]. That's why the A

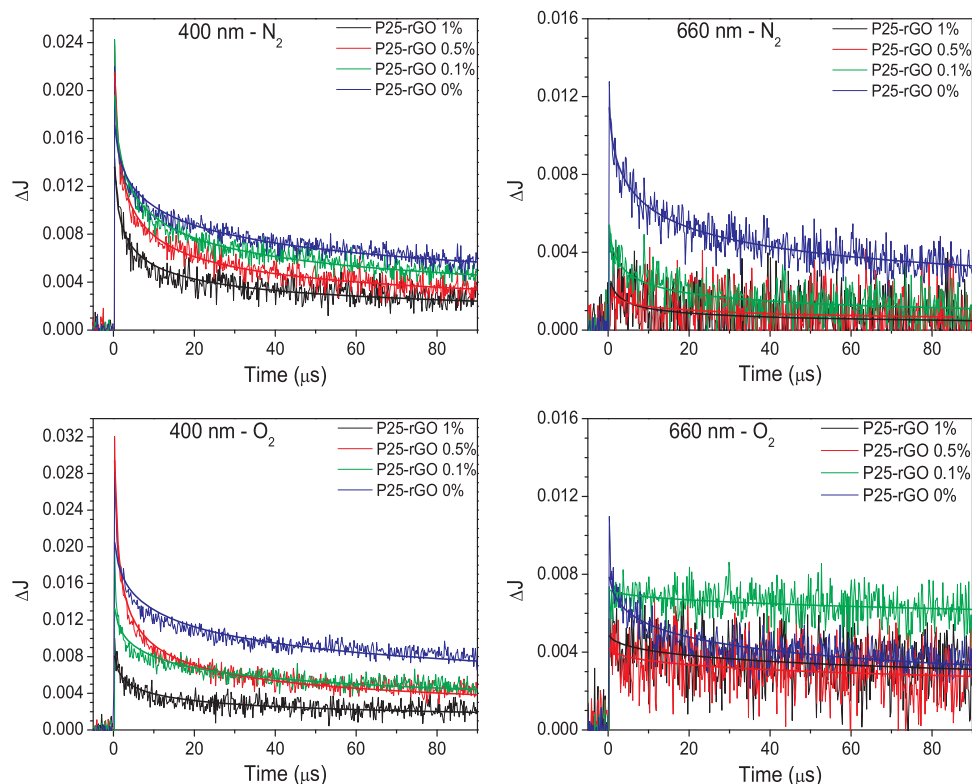


Fig. 12. Time profiles of transient absorption at 400 nm and 660 nm of P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1% under a  $N_2$  and  $O_2$  atmosphere.

parameters and the initial signals from trapped electrons (660 nm), observed in Table 1 and Fig. 12, were less intense compared to bare  $TiO_2$  in both atmospheres. It seems that 0.5% is the optimal rGO mass doping ratio because a higher addition of rGO does not mean a further reduction of the initial transient absorption signal. It is noteworthy that in  $O_2$  atmosphere the initial intensity obtained by bare  $TiO_2$  at 660 nm was lower than that obtained in  $N_2$  atmosphere. On the other hand, the initial height of the P25-rGO photocatalysts rose compared to the intensity observed in  $N_2$  atmosphere. The lowest initial intensity at 660 nm in  $O_2$  was observed for P25-rGO 0.5% indicating that a more electrons were transferred either to rGO or to  $O_2$ . All in all, the initial intensity difference between bare  $TiO_2$  and P25 modified with rGO, and therefore the electron transfer, was considerably decreased in the presence of  $O_2$ . These results agreed with the EPR results. Whereas low differences in  $DMPO-O_2^{\cdot-}$  and  $DMPO-HO^{\cdot}$  areas were noted in the presence of  $O_2$ , with P25-rGO 0.5% yielding the best results, the  $DMPO-HO^{\cdot}$  areas measured for the  $TiO_2$ -rGO nanocomposites was much higher than that obtained for P25-rGO 0% in  $N_2$  atmosphere.

As for the rate coefficients,  $k_f$  values estimated from the TAS decays in  $N_2$  atmosphere increased with the rGO content becoming between four and ten times higher than those for P25-rGO 0%. In TAS studies carried out in the  $\mu s$  time scale, the recombination between trapped electrons and holes was observed [5]. Thus, results indicates that in  $N_2$

atmosphere, where electrons cannot be released, rGO acts as a recombination center that leads to a faster charge carrier recombination rate [55]. On the other hand, in  $O_2$  atmosphere  $k_f$  values were reduced when rGO was added to  $TiO_2$ . Hence, the charge carrier recombination rate was decreased, and thus it could lead to higher  $O_2^{\cdot-}$  generation rate.

Concerning the 400 nm signal, it could be ascribed to deeply trapped holes that does not affect the photocatalytic activity [55]. This was verified since only small differences in the initial intensity were observed when rGO was added. In the presence of  $O_2$ , the initial height of the signal increased, due to the presence of an electron scavenger that reduced the recombination rate. Apart from that, the decay constants  $k_f$  increased with the addition of rGO and were similar in both atmospheres. However, it was previously corroborated that the charge carrier recombination rate was decreased in the presence of  $O_2$ . Hence, the decay rates observed at 400 nm was attributed to the migration of holes between different trapping sites (after electrons were transferred from  $TiO_2$  to rGO) [55].

To sum up, the presence of  $O_2$  hinders the transfer of free electrons from  $TiO_2$  to rGO but favors the electron transfer from bare  $TiO_2$ . In other words, the role of rGO as an electron acceptor is less significant in  $O_2$  atmosphere. As a consequence, lower differences in the  $O_2^{\cdot-}$  and  $HO^{\cdot}$  generation between bare  $TiO_2$  and P25-rGO photocatalysts were

Table 1

Estimated kinetic parameters of the transient decay signals dependent on the rGO (%) mass concentration and initial transient absorption obtained under  $N_2$  and  $O_2$  atmospheres.

	$N_2$ — 400 nm		$N_2$ — 660 nm		$O_2$ — 400 nm		$O_2$ — 660 nm	
	$k_f$ (au $\mu s^{-1}$ ) $\cdot 10^{-3}$	A $\cdot 10^2$	$k_f$ (au $\mu s^{-1}$ ) $\cdot 10^{-3}$	A $\cdot 10^2$	$k_f$ (au $\mu s^{-1}$ ) $\cdot 10^{-3}$	A $\cdot 10^2$	$k_f$ (au $\mu s^{-1}$ ) $\cdot 10^{-3}$	A $\cdot 10^2$
P25-rGO 0%	2.43	2.25	5.56	1.50	2.18	2.47	4.47	0.91
P25-rGO 0.1%	3.41	3.12	18.53	0.85	3.91	1.65	0.58	0.73
P25-rGO 0.5%	5.00	5.09	26.90	0.26	5.78	7.75	3.19	0.44
P25-rGO 1%	6.91	2.78	44.32	0.60	10.17	1.15	2.95	0.51

detected.

#### 4. Conclusions

TiO<sub>2</sub>-rGO photocatalysts were successively prepared by a hydrothermal method. The junction between TiO<sub>2</sub> and rGO involved a higher disorder degree as a consequence of the strong interaction between TiO<sub>2</sub> and rGO sheets. However, it did not mean a change of the surface area or the XRD patterns. Besides, the optical band gap and the conduction and valence band potentials were unchanged by the modification of TiO<sub>2</sub> with rGO, measuring values around -0.38 and 2.75 V vs. RHE, respectively. Electrochemical impedance spectroscopy (EIS) and photocurrent response measurements were carried out to evaluate the efficiency of charge separation. The addition of rGO led to a low charge transfer resistance across the electrode-electrolyte interface and even a tenfold increase in the photocurrent values was observed for P25-rGO 1%, indicating a more efficiency in the electron-hole separation.

A higher oxygen reduction current was found when increasing the rGO concentration. This could lead to an enhancement of the generation of reactive oxygen species (ROS). However, in the oxalic acid degradation only small differences were observed. Concerning the surface reaction measured using the ATR-FTIR technique, the higher the amount of rGO added, the higher the adsorption. As a consequence the surface reaction was faster for P25-rGO 1% thanks to a more efficient reduction of oxygen and lower charge transfer resistance, which suggests that this hybrid nanocomposite was also less limited by possible O<sub>2</sub> mass transfer limitations. Under slurry photoreactor conditions at oxygen excess, the oxalic acid photo-oxidation evolution was similar for all the studied catalysts. The EPR experiments revealed that only a slight increase of the generated HO· and O<sub>2</sub>·<sup>-</sup> for P25-rGO 0.5% as a result of slightly lower decay kinetics of the photogenerated electrons found in the TAS studies. On the other hand, regarding generation of HO· by N<sub>2</sub> saturated suspensions, the addition of only 0.1% rGO mass concentration was enough to detect a threefold increase of the EPR signal related to DMPO–HO·. Finally, to relate photocatalytic activity and EPR studies, the role played by rGO was investigated by conducting transient absorption spectroscopy (TAS) experiments under O<sub>2</sub> and N<sub>2</sub> atmospheres. TAS decay kinetics corroborated that rGO acts as an electron acceptor, occurring the electron transfer from TiO<sub>2</sub> to rGO in the ps time scale. This explained the higher DMPO–HO· signal obtained in N<sub>2</sub> atmosphere when rGO was added. However, the role played by rGO was not crucial in excess of dissolved O<sub>2</sub>, which meant lower differences in the O<sub>2</sub>·<sup>-</sup> and HO· generation detected by EPR between bare TiO<sub>2</sub> and TiO<sub>2</sub> modified with rGO.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: <https://doi.org/10.1016/j.apcatb.2018.09.070>.

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### **Procedure to prepare the photo-anodes by the screen-printing method**

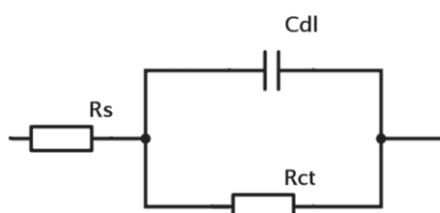
In brief, 15 mg of pure ethyl cellulose (EC) 10 CP was diluted in ethanol to yield 10 wt. % solutions. 0.6 g of the photocatalyst was mixed with 0.1 mL of acetic acid and the mixture was ground for 5 minutes. Afterwards, 0.1 mL of H<sub>2</sub>O was added and ground for 1 minute, repeating this step 5 consecutive times. 0.1 mL of ethanol was then mixed and the mixture was ground for another minute for 15 consecutive terms, and subsequently 0.25 mL of ethanol was mixed and the mixture was ground for another minute for 6 consecutive terms. This blend was added to a round bottomed rotavap flask diluting with 10 mL of ethanol. The mixture was magnetically stirred for 1 minute and further ultrasonicated for 2 seconds in an ultrasonic bath every 2 seconds 30 times. Afterwards, it was magnetically stirred for another minute. Subsequent to this step, 2 g of terpineol (anhydrous, Aldrich) were added and the previous step was repeated. 3 g of the ethyl cellulose 10 wt. % ethanolic solution previously prepared was then mixed and the stirring and sonicating step was repeated for 3 consecutive times. Ethanol and water were removed from the solution by rotary-evaporator (final pressure of 200 mmHg at 70 °C). Prior to preparing the photo-anodes, the FTO glass was cleaned by sonicating them in water, ethanol and acetone for 15 min each in a ultrasonic bath. After a layer of the paste was coated on the FTO glass by screen-printing, the electrodes were heated at 80 °C overnight. Only the electrodes used to determine the flat-band potential were calcined at 400 °C under Ar atmosphere with a heating rate of 4 °C·min<sup>-1</sup>.

### **Deposition of the TiO<sub>2</sub>-rGO layer on the ATR crystal**

To deposit a thin layer of the desired photocatalyst on the surface of the ATR ZnSe crystal the procedure reported by Mendive et al. [18] and H. Belhadj et al. [19] was followed. Firstly, an aqueous suspension of 5 g·L<sup>-1</sup> of P25-rGO was prepared and sonicated for 15 minutes in a ultrasonic bath. Before depositing of the TiO<sub>2</sub> films, the ZnSe surfaces (area = 6.8 mm x 72 mm) were cleaned by polishing with diamond paste (Metadi II, polishing grade) and rinsed with methanol and deionized water. Whilst stirring the suspension, 0.4 mL of the sample was taken and spread on the surface of the ATR crystal. A desiccator was then used to dry the suspension on the crystal at room temperature.

### **Nyquist plot explanation**

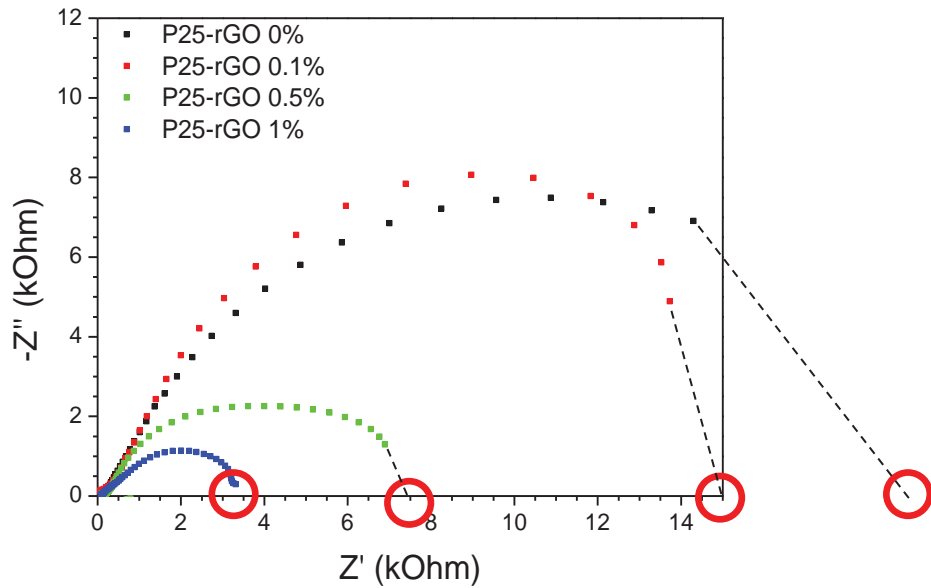
For a simple Randles circuit:



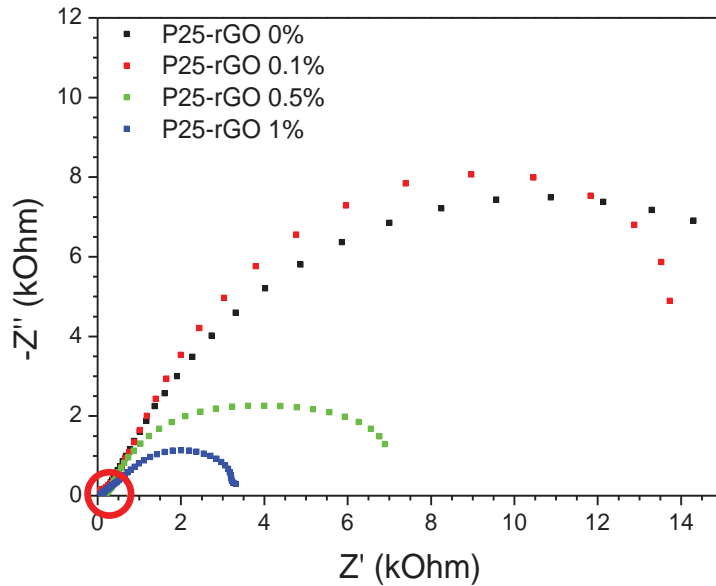
The impedance  $Z$  can be calculated as:

$$Z = Z_{Rs} + \left( \frac{1}{Z_{Cld}} + \frac{1}{Z_{Rct}} \right)^{-1} = R_s + \left( \frac{1}{j\omega C} + \frac{1}{R_{ct}} \right)^{-1}$$

When  $\omega \rightarrow \infty$  then  $Z = R_s + R_{ct}$  (right hand side of the semicircle)



When  $\omega \rightarrow 0$  then  $Z = R_s$  (left hand side of the semicircle)



For this reason, the diameter of the semicircle is  $(R_s + R_{ct}) - R_s = R_{ct}$  and gives an estimation of the charge transfer resistance.

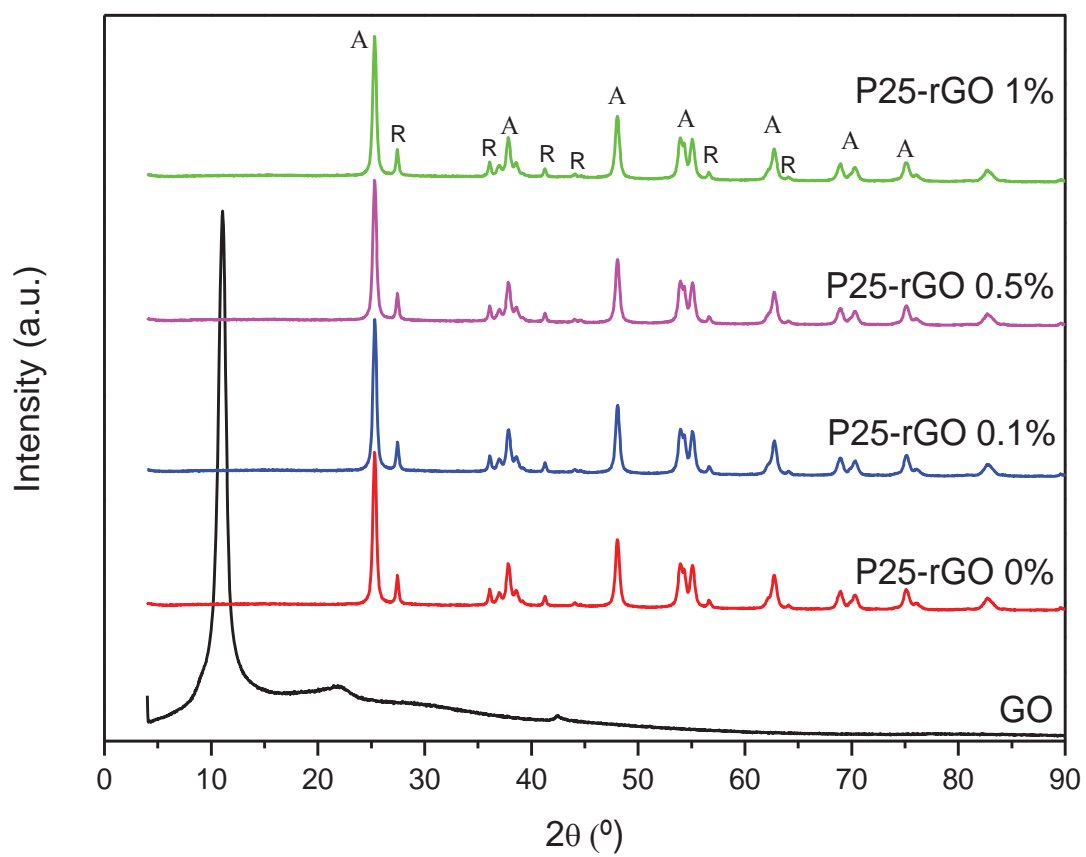
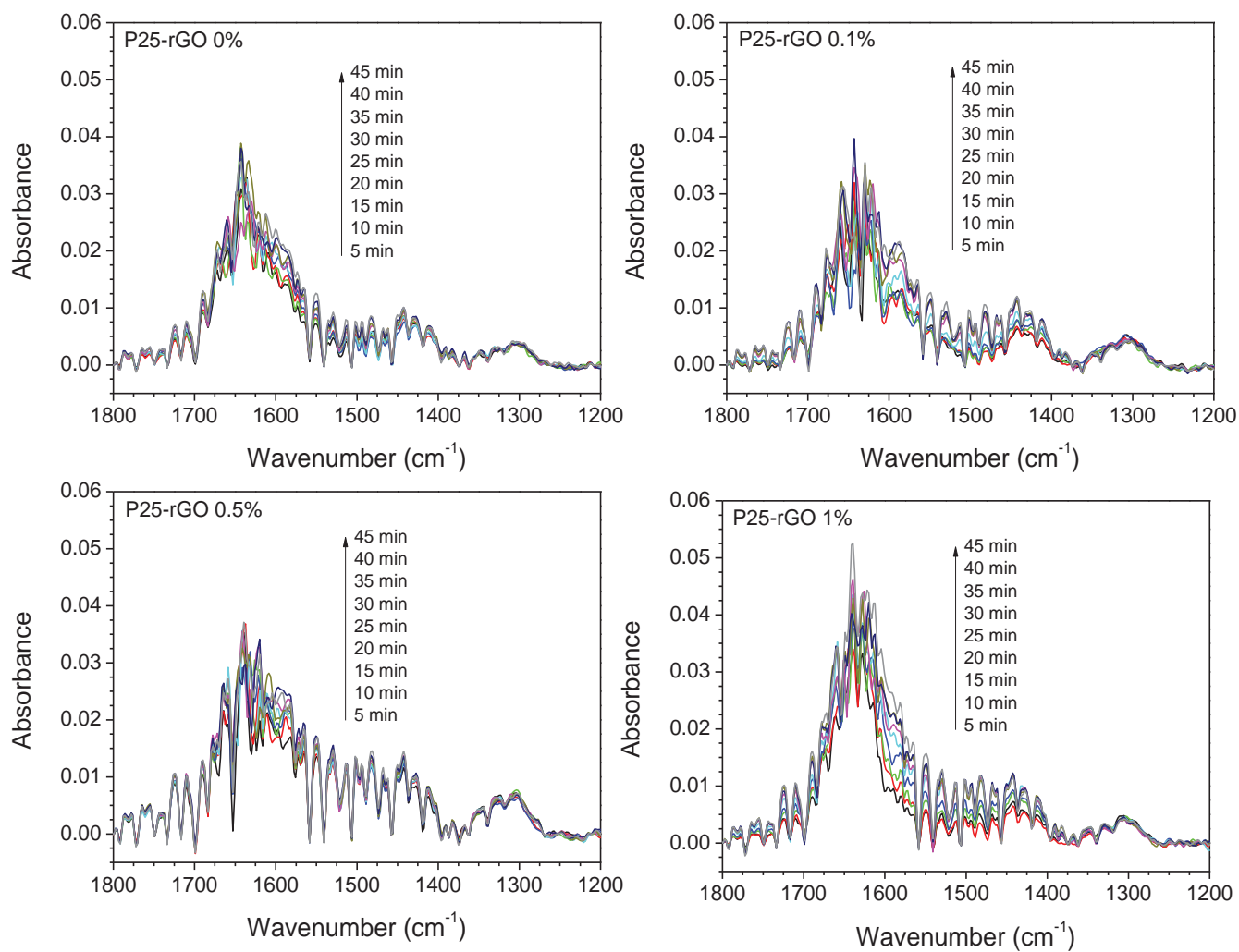
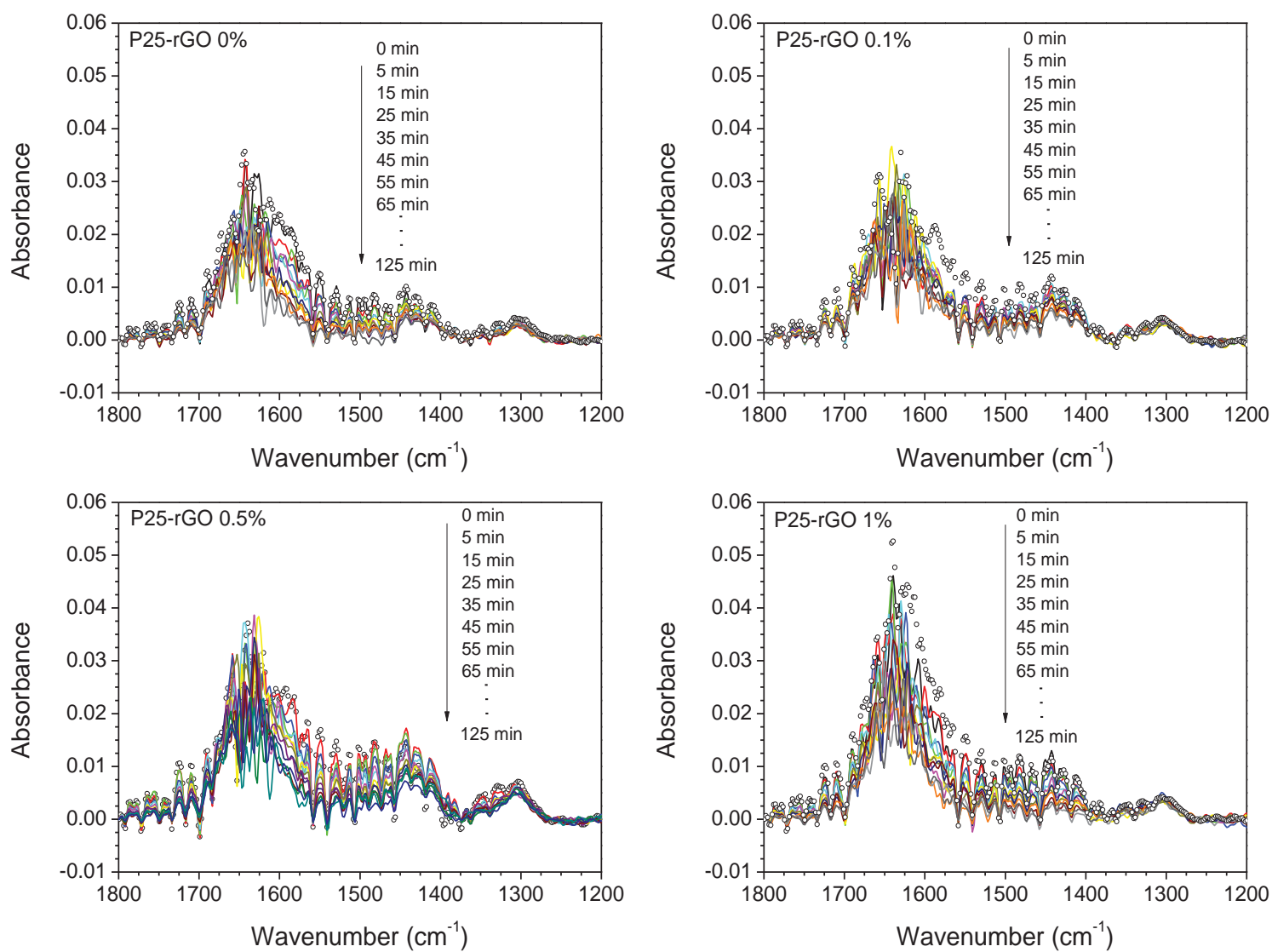


Figure S.1. XRD patterns of pure GO, P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1%.

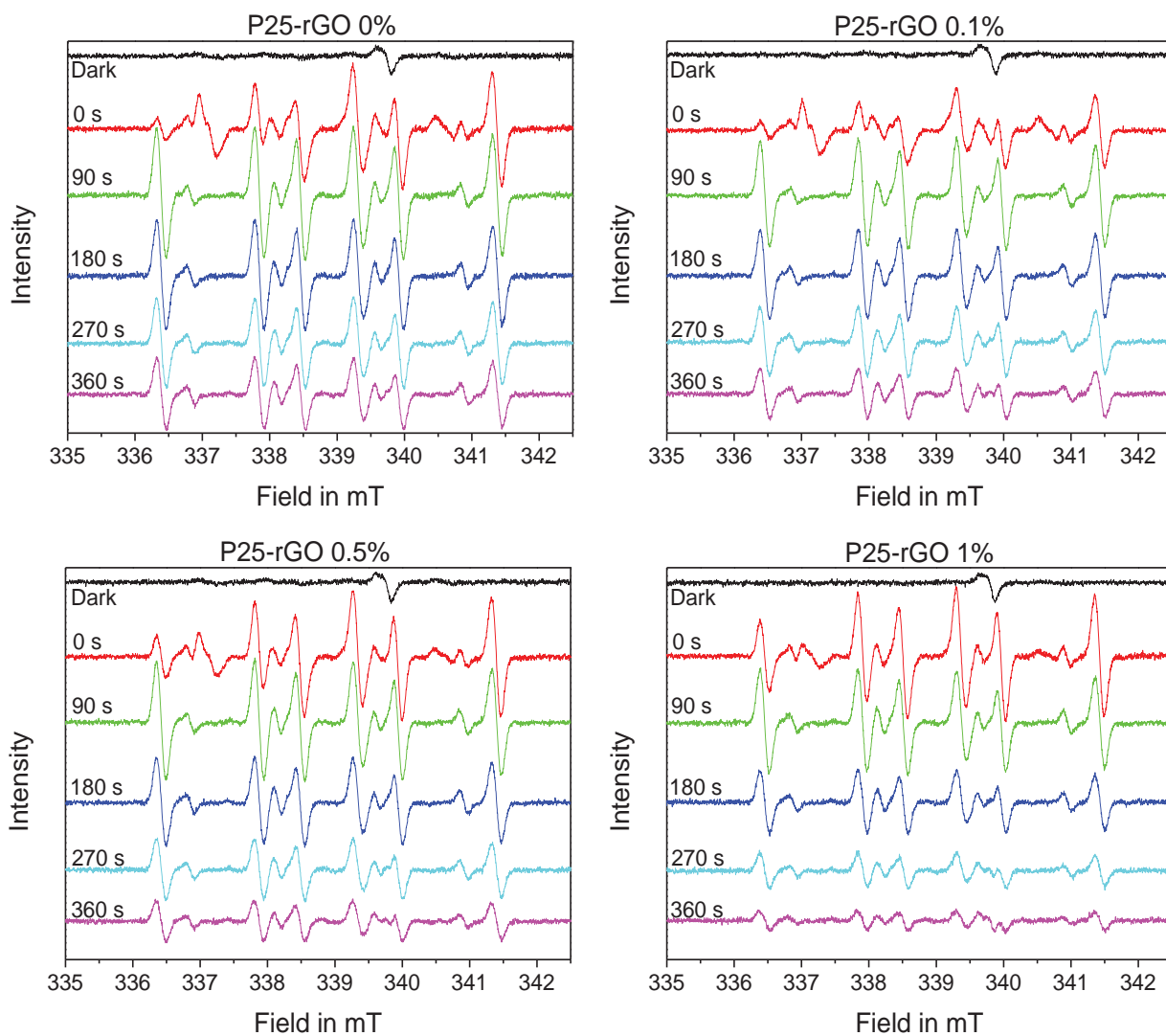


**Figure S.2. Time evolution of the FTIR spectra of oxalic acid adsorbed on the different P25-rGO in the dark. The initial oxalic acid concentration was 1 mM and the time interval between every spectra was 5 min.**





**Figure S.3.** Sequential FTIR spectra of oxalic acid adsorbed on the different P25-rGO under irradiation with a 365 nm LED and an intensity of  $1.0 \text{ mW}\cdot\text{cm}^{-2}$ . The initial oxalic acid concentration was 1 mM and the time interval between every spectra was 10 min.



**Figure S4. DMPO spin-trapping EPR spectra of the different P25-rGO photocatalysts suspended in DMSO in the dark and under UV-A light irradiation.**

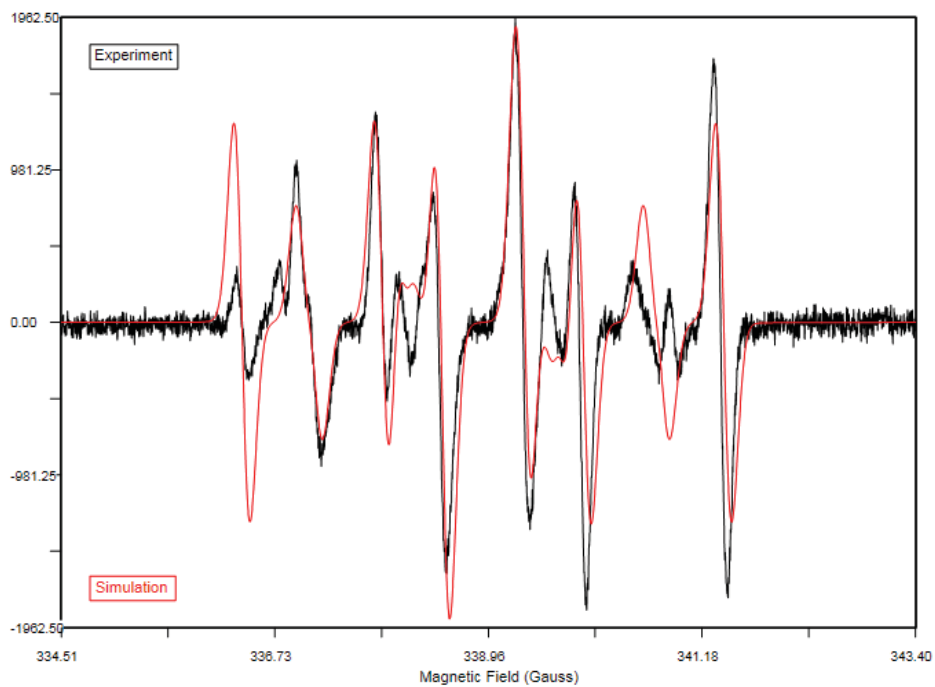


Figure S.5. Experimental and simulated EPR spectra measured just after irradiation for P25-rGO 0% suspended in O<sub>2</sub> saturated DMSO. The simulation represented a combination of DMPO–O<sub>2</sub><sup>•</sup> (a<sub>N</sub> = 1.282 mT, a<sub>H</sub><sup>β</sup>=1.035 mT, a<sub>H</sub><sup>γ</sup>=0.132 mT; g = 2.0058) γ •DMPO–CH<sub>3</sub> ( a<sub>N</sub> = 1.462 mT, a<sub>H</sub><sup>β</sup>=2.093 mT; g = 2.0057).

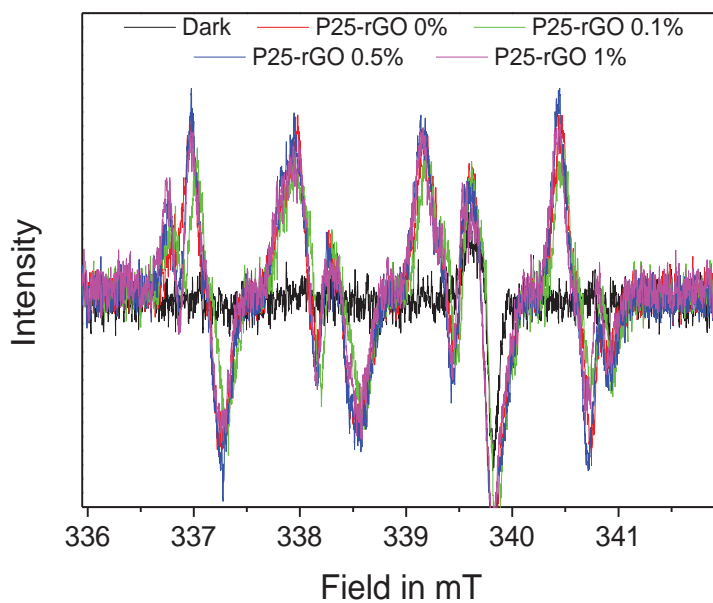
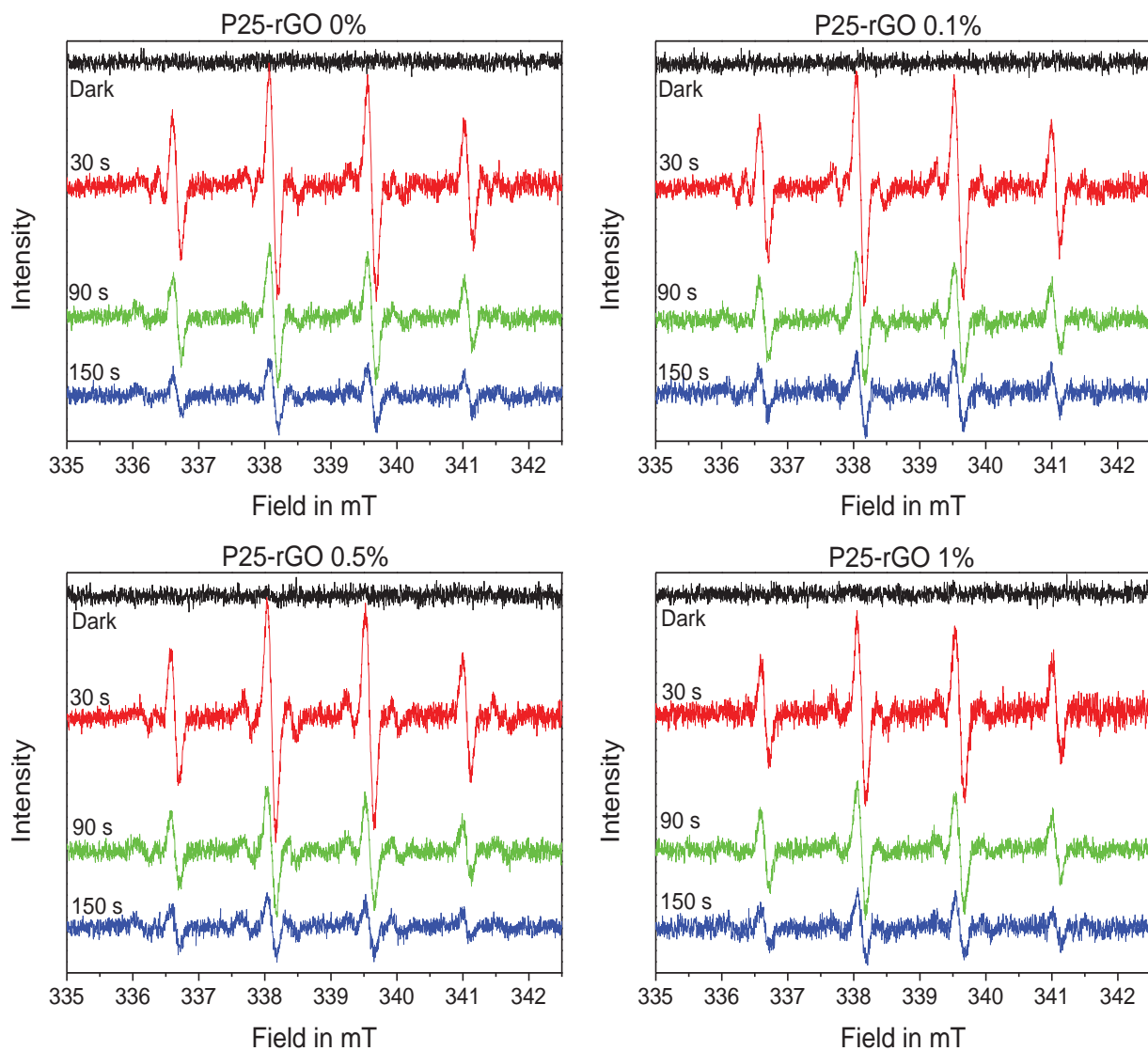
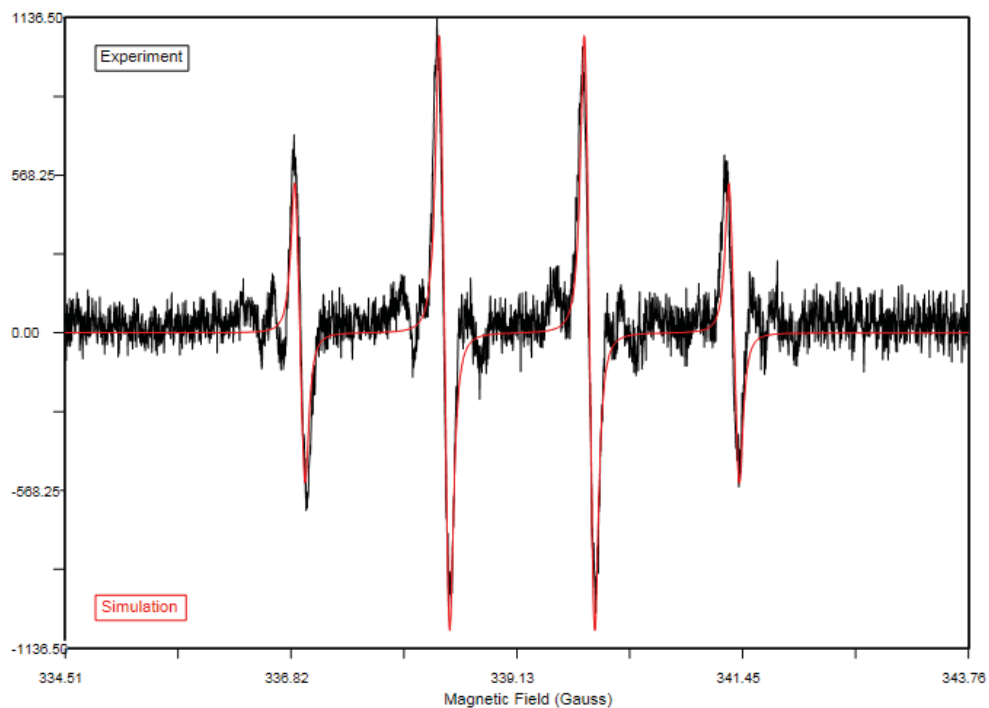


Figure S.6. DMPO spin-trapping EPR spectra of the different P25-rGO photocatalysts suspended in DMSO in the dark and just after two seconds of UV-A light irradiation.



**Figure S.7. DMPO spin-trapping EPR spectra of the different P25-rGO photocatalysts suspended in O<sub>2</sub> saturated H<sub>2</sub>O in the dark and under UV-A light irradiation.**



**Figure S.8. Experimental and simulated EPR spectra measured of P25-rGO 0% suspended in O<sub>2</sub> saturated H<sub>2</sub>O subsequent to being irradiated for 30 seconds. Simulation parameters \*DMPO-OH ( $a_N = 1.497$  mT,  $a_H^\beta = 1.477$  mT;  $g = 2.0057$ ).**

# Anexo V:

Influence of TiO<sub>2</sub>-rGO optical properties on the photocatalytic activity and efficiency to photodegrade an emerging pollutant



# Influence of TiO<sub>2</sub>-rGO optical properties on the photocatalytic activity and efficiency to photodegrade an emerging pollutant

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## ABSTRACT

TiO<sub>2</sub>-reduced graphene oxide (TiO<sub>2</sub>-rGO) photocatalysts with different mass ratios (GO:TiO<sub>2</sub> 0.1-0.5-1%) were synthesized via a hydrothermal method and compared through their physico-chemical properties and photocatalytic activity in the degradation of an emerging contaminant, clofibrac acid. The optical properties of the TiO<sub>2</sub>-rGO nanocomposites were first estimated in order to calculate the local volumetric rate of photon absorption inside a photocatalytic reactor. Radiation models were solved using the Monte Carlo method. The effect of rGO as well as the photocatalyst loadings on the radiation absorption was evaluated. The lowest photodegradation rate found in P25-rGO 1% was ascribed to an excess of rGO that could well favor charge carriers recombination leading to detrimental photoactivity. A GO/TiO<sub>2</sub> mass ratio of 0.5% provided the fastest initial photodegradation rate under the operating conditions studied here. Finally, the photo-efficiency of all these photocatalysts was also analyzed by calculating the quantum efficiency parameter. The highest value of quantum efficiency was achieved with P25-rGO 0.5% at 100 mg L<sup>-1</sup>, with an increase of 11% compared to the value obtained for P25-rGO 0%.

## 1. Introduction

Over the last decades, the ubiquitous presence of pharmaceutical compounds, considered as emerging contaminants (ECs), has increasingly become a matter for concern. These type of pollutants are being detected in drinking water, groundwater and surface water at concentrations ranging from ng·L<sup>-1</sup> to mg·L<sup>-1</sup> [1,2]. Even at these concentrations, they can pose a threat to aquatic environments and human health [1,3,4]. Sources of water contamination with ECs are sewage effluents from domestic and industrial facilities and industrial effluent discharges. Since conventional municipal (MWWTP) or industrial wastewater treatment plants (WWTP) were not designed to eliminate these compounds, low removal efficiency is achieved [5–7]. Pharmaceuticals can also be spread by applying the sewage sludge as a fertilizer or by landfill leakage favoring their ubiquity in groundwater [1–3]. Therefore, tertiary treatments are necessary to be implemented in WWTP to prevent the release of ECs into the natural waters [2,5,6,8,9].

In this context, advanced oxidation processes (AOPs), in which hydroxyl radicals (HO·) are generated, have been widely investigated

to remove water pollutants [2,6,10]. Among them, heterogeneous photocatalysis has received a lot of attention to degrade ECs. This process is based on the use of a semiconductor with wide band gap that involves the generation of electron-hole pairs when the semiconductor is irradiated with sufficiently energetic light (usually UV light). Electrons are promoted to the conduction band where they can react with oxygen to form oxidizing species such as superoxide radical anions (O<sub>2</sub><sup>-</sup>). Valence band holes can either directly oxidize an organic compound adsorbed on the catalyst surface or react with adsorbed water molecules to generate HO· radicals that further oxidize the pollutant [10–12]. Previous research on the use of photocatalysis to degrade pharmaceuticals has shown good results [2,13,14]. One of the most investigated semiconductors is TiO<sub>2</sub> because of its useful properties: resistance to chemical corrosion and photo-corrosion, high activity, cost-effectiveness and non-toxicity [10,15]. However, photocatalysis has some limitations that need to be solved prior to its commercial application: firstly, TiO<sub>2</sub> photocatalysts are only able to harvest photons from UV radiation leading to low efficiencies when solar light is employed; and secondly, more accurate procedures to

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Nomenclature	
$C_{cat}$	Mass catalyst concentration, $g L^{-1}$
$C_i$	Molar concentration of compound i in the bulk, $mmol L^{-1}$
CA	Clofibric acid
$e^a(x)$	Local volumetric rate of photon absorption, $Einstein \cdot cm^{-3} \cdot s^{-1}$
$E_g$	Band gap energy, eV
4-CP	4-Chlorophenol
g	Asymmetry factor, dimensionless
k	Apparent kinetic constant, $h^{-1}$
LVRPA	Local volumetric rate of photon absorption, $Einstein \cdot cm^{-3} \cdot s^{-1}$
p	Phase function, dimensionless
p-BQ	p-Benzoquinone
q	Radiation flux, $Einstein \cdot cm^{-2} \cdot s^{-1}$
R	Value of a reflectance spectrophotometric measurement
$(-r_i)$	Photodegradation rate of compound i, $mol \cdot cm^{-3} \cdot s^{-1}$
$S_{BET}$	Catalyst specific surface area, $m^2 \cdot g^{-1}$
T	Value of a transmittance spectrophotometric measurement
t	Time
V	Volume
VRPA	Volumetric rate of photon absorption, $Einstein \cdot cm^{-3} \cdot s^{-1}$
Y	Global transmission coefficient of the reactor windows
W	Wall thickness, cm
<i>Greek letters</i>	
$\alpha$	Absorption coefficient of the semiconductor, $cm^{-1}$
$\beta$	Extinction coefficient, $cm^{-1}$
$\eta$	Quantum efficiency, $mol \cdot Einstein^{-1}$
$\kappa$	Absorption coefficient, $cm^{-1}$
$\lambda$	Wavelength, nm
$\Gamma$	Global reflection coefficient of the reactor windows
$\theta$	Spherical coordinate, rad
$\sigma$	Scattering coefficient, $cm^{-1}$
$\omega$	Spectral albedo
<i>Subscripts</i>	
4-CP	Relative to 4-chlorophenol
0	Initial value or relative to the reactor window at $x=0$
$\lambda$	Indicates a dependence on wavelength
CA	Relative to clofibric acid
Cat	Relative to catalyst
L	Relative to the reactor window at $x=L$
p-BQ	Relative to p-benzoquinone
R	Reactor
T	Total
Tk	Tank
$V_R$	Relative to reactor volume
W	Wall
<i>Superscripts</i>	
*	Specific properties
+	Forward direction
-	Backward direction
<i>Special symbols</i>	
$\langle \rangle$	Average value over a defined space

design and scale-up photocatalytic reactors are necessary [15–19].

Because of the ineffective utilization of visible light by  $TiO_2$  and short lifetime of photogenerated charge carriers, new photocatalysts are being recently designed to overcome these limitations [11,20]. Among them, carbon-based  $TiO_2$  composites have been reported to reduce electron-hole recombination. However, in recent years, semiconductor-graphene has been widely investigated owing to the unique properties of graphene: good optical and thermal transmittance, chemical stability, large area, and high charge carrier mobility [20,21]. In this context, one of the most widely used techniques to synthesize  $TiO_2$ -graphene and  $TiO_2$ -reduced graphene oxide (rGO) nanocomposites is via a hydrothermal method [13,22–24]. Several studies have reported higher photocatalytic activity of these nanocomposites compared to pristine  $TiO_2$  [13,24–26]. The main advantages of the  $TiO_2$ -rGO junction are ascribed to a decrease of its band gap, which makes possible to harvest visible light, an increase in the specific surface area, and a reduction in the electron-hole recombination, since electrons can be transferred from the  $TiO_2$  conduction band to the reduced graphene oxide [20,21,27]. Thanks to these advantages Alamelu et al. [28] reported that  $TiO_2$ -graphene nanocomposites were able to increase organic dyes photodegradation by a factor between 3.5 and 15 compared to bare  $TiO_2$ . Similarly, Wu et al. [29] synthesized highly stable  $TiO_2$ -rGO photocatalysts. These photocatalysts proved to be effective to photodegrade organic dyes because of its stability, its charge separation efficiency and the high surface area of rGO. Furthermore,  $TiO_2$ -rGO photocatalysts have also been reported to improve antibacterial activity increasing sterilization rates by 1.4 times compared to the bare coating [30]. In this case, the improvement was ascribed to a higher hydroxyl radical formation rate. These nanocomposites have also been used to degrade pollutants from air. Wang et al. [31] reported that  $TiO_2$ -graphene exhibited higher photocatalytic activity (1.7 times higher than bare  $TiO_2$ ) in acetone photodegradation in air. The integration of

graphene allowed retarding electron-hole recombination and lead to a more effective electron transfer. On the other hand, new photocatalysts, such as ternary nanocomposites, were synthesized to achieve visible absorption and high photoactivity. A  $Ag_2CrO_4/g-C_3N_4$ /graphene oxide (GO) nanocomposite was used to photoreduce  $CO_2$  [32]. Thanks to the matched band structure, the ternary nanocomposite follows a Z-scheme mechanism which enhanced  $CO_2$ -conversion. This system showed improved light absorption, charge separation and higher amount of active sites provided by GO. However, to objectively compare the performance of the photocatalysts synthesized by different research groups in different experimental setups, it is useful to relate the photocatalytic activity to the radiation absorbed by the photocatalyst since photo-activation is the first step of the process. Therefore, the development of accurate models to describe radiation absorption has received a great deal of attention [17–19,33–40]. Firstly, in order to estimate the photons absorbed by the photocatalyst, information about the optical properties of the catalyst suspension is required: absorption and scattering coefficients, and phase function for scattering [18,41,42]. This information is further used to solve the radiative transfer equation (RTE) inside the photoreactor to calculate the local volumetric rate of photon absorption (LVRPA). Several methods can be employed to solve the RTE. Among the most frequently used, we found the discrete ordinate method (DOM), the Monte Carlo method, and the “two-flux” or “six-flux” radiation absorption-scattering models [17,18,38]. Over the last few years, the Monte Carlo method has been increasingly employed because of its accuracy and its simple application to model reactors with complex geometries and under uneven irradiation conditions [17,19,40,43]. Furthermore, only intrinsic kinetic models with an explicit dependence on the photon absorption rate are suitable to obtain predictive results independent of the experimental set up and, therefore, useful for the design and scaling-up of photoreactors [17,18,35,38,44]. Thus, the knowledge of the optical properties is a key



feature to calculate the photons absorbed by photocatalysts and, therefore, to determine the final efficiency of the photocatalytic process.

The main novelty of this work is the estimation of the optical properties of several hydrothermally prepared TiO<sub>2</sub>-rGO nanocomposites, with different GO doping ratios, and the evaluation of their activity in the photocatalytic degradation of clofibric acid, selected as model pollutant of ECs. Clofibric acid is the active metabolite of a pharmaceutical used as blood lipid regulator whose intermediates and degradation pathways have already been reported [14,45]. The influence of the presence of rGO and the photocatalyst concentration on the radiation absorption inside the reactor was evaluated by solving a radiation model using the Monte Carlo method. Finally, a comparison study of the photocatalytic performance of the TiO<sub>2</sub>-rGO nanocomposites was carried out by calculating the quantum efficiency parameter which relates moles of pollutant removed to moles of photons absorbed by photocatalyst in the reaction medium.

## 2. Experimental section

### 2.1. Chemicals

Graphene oxide (GO) water dispersions (0.4 wt% concentration) and titanium dioxide P25 Aeroxide® (80:20 anatase-rutile, BET specific surface area 54 m<sup>2</sup> g<sup>-1</sup>, average anatase and rutile crystal size of 21 and 33 nm, respectively) were provided by Graphenea and Evonik Company, respectively. Clofibric acid (CA > 97%) was purchased from Aldrich. 4-Chlorophenol (4-CP > 99%) and p-benzoquinone (p-BQ > 98%) were obtained from Aldrich and Fluka, respectively. All reagents were employed without further treatment and ultrapure water was used to prepare all the solutions.

### 2.2. Synthesis of P25-rGO

Titanium dioxide P25-rGO composites (P25-rGO) were prepared by a hydrothermal method. Briefly, 2 g of TiO<sub>2</sub> P25 were suspended in 400 mL of ultrapure water and stirred for 30 min at 500 rpm. Then, the desired amount of GO was added and the suspension was further stirred for 2.5 h to achieve a good dispersion of GO sheets. The mixture was then transferred to a 600-mL Teflon-lined stainless steel autoclave reactor and subjected to hydrothermal treatment for 3 h at 120 °C. Afterward, the composite was washed and centrifuged 3 times, and finally dried at 50 °C. The weight ratios GO:P25 were 0, 0.1, 0.5 and 1%, denoted as P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1%, respectively.

### 2.3. Photocatalyst characterization

Band gap and UV–vis absorption properties of the photocatalysts were studied after recording their diffuse reflectance spectra with a UV–vis Agilent-Varian, Cary 5000, equipped with an integrating sphere. The equation  $(\alpha \cdot h\nu)^{1/2} = A \cdot (h\nu - E_g)$  was used to obtain the band gap values of the samples, where  $\alpha$  is the absorption coefficient of the solid photocatalyst [46]. A Renishaw Micro Raman spectrometer ( $\lambda = 532$  nm) equipped with a 20 mW He-Ne laser emitting at 532 nm was used to obtain the Raman spectra of the samples. Spectra were recorded using 5 repetitions, 10 s of acquisition time and 0.2 mW of incident power. Energy Dispersive X-Ray Analysis (EDX) was performed on a Hitachi S-3000 N electron microscope equipped with Oxford Instruments INCA x-sight. To study structure and morphology of the TiO<sub>2</sub>-based materials, scanning electron microscopy (SEM) analyses and transmission electron microscope (TEM) studies were carried out using a Philips XL 30 S-FEG and a field emission gun JEOL 2100 F microscope operating at 200KV, respectively. Samples for TEM were prepared by dry deposition of the composites in a lacey carbon copper grid. Crystal structure of the photocatalysts were analyzed with a X-ray polycrystal

PANalytical X'Pert PRO using nickel-filtered Cu K $\alpha$  (1.541874 Å) radiation operating at 40 kV and 40 mA, with a 0.02° step size and accumulating a total of 50 s per point. Crystallite sizes were estimated by employing the Scherrer equation [47] and the crystalline phases were identified by comparison with ICDD PDF database [48]. The specific surface areas were determined by the Brunauer-Emmett-Teller (BET) method [49] from N<sub>2</sub> isotherm data measured at 77 K in a Micromeritics ASAP 2420 apparatus on samples previously outgassed overnight at 413 K to a vacuum of < 10<sup>-4</sup> Pa to ensure a dry, clean surface.

### 2.4. Measurement of optical properties

Extinctance, diffuse transmittance and diffuse reflectance measurements of the P25-rGO composites suspensions were carried out in an Optronic OL series 750 spectroradiometer. For diffuse measurements, an OL 740-70 integrating sphere reflectance attachment was used. All measurements were carried out in the range between 315 and 415 nm. The path length of the measuring rectangular quartz cuvette was 2 mm. Suspensions with photocatalyst concentrations of 50, 100, 250 and 400 mg L<sup>-1</sup> in distilled water were prepared and sonicated for 30 min prior to the measurements.

### 2.5. Photocatalytic experiments

Photocatalytic degradation experiments were carried out in a stainless steel reactor with an inner Teflon wall. The reactor geometry was cylindrical with two circular windows made of borosilicate glass (reactor length: 2.5 cm, diameter: 8.6 cm). Each window was irradiated by four tubular UV lamps (TL 4 W/08 Black Light UVA lamps from Philips). Both sets of lamps were positioned parallel to the flat windows. The emission of the lamps ranged from 315 to 415 nm, with a maximum around 355 nm. In order to obtain diffuse radiation at the reactor windows, ground glass plates were placed between the lamps and reactor. The radiation flux entering the reactor, determined experimentally by ferrioxalate actinometry [50], was 6.3 × 10<sup>-9</sup> Einstein·s<sup>-1</sup> cm<sup>-2</sup> (2.15 mW cm<sup>-2</sup>).

The reactor was part of a system operated in recirculation batch mode, as depicted in Fig. 1. The set up consisted of a peristaltic pump, the reactor and a 1 L storage tank with a water jacket to maintain the temperature constant at 25 °C throughout the experiments. The tank contained a thermometer, a sample withdrawal system and a gas inlet to continuously bubble oxygen to keep the solution saturated with O<sub>2</sub>.

Prior to experiments, a 1 L solution containing 20 mg L<sup>-1</sup> of CA and the desired amount of the photocatalyst were mixed and sonicated for 30 min. Then, the suspension was added to the storage tank and recirculated in the system for 30 min with a pump flow rate of 1.5 L·min<sup>-1</sup> in order to allow the mixture to reach adsorption equilibrium. O<sub>2</sub> was bubbled into the storage tank and the lamps were switched on to stabilize emission. Shutters were placed between the lamps and the reactor to prevent any radiation from arriving to the suspension. Subsequently, the first sample was withdrawn from the tank (t = 0), the shutters were removed, and the experiment started.

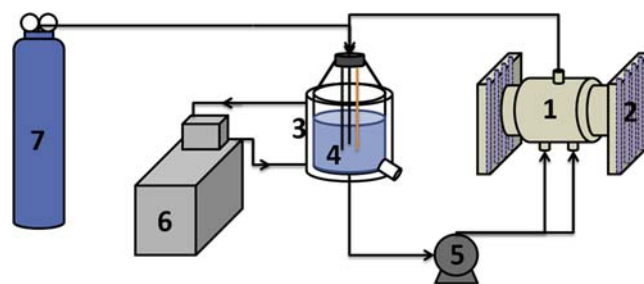


Fig. 1. Photoactivity experimental set-up: (1), photoreactor; (2), UV lamps; (3), water jacket; (4), storage tank; (5), pump; (6), thermostatic bath; (7), oxygen.

Samples withdrawn from the tank at different irradiation times were centrifuged and filtered through a 0.02 µm syringe filters (Anotop 25) to remove photocatalyst particles before analysis. Photocatalytic experiments were carried out at pH 5 (natural pH) [35] under different catalysts concentrations: 25, 50, 100, and 250 mg L<sup>-1</sup>.

### 2.6. Analysis

HPLC was used to quantify CA and the possible intermediates in a Waters chromatograph with a UV detector and a C-18 column. The mobile phase was a 70/30 mixture of acetonitrile/acidified water (with 0.1% v/v phosphoric acid). 20 µL of sample was injected with a flow rate of 1 mL·min<sup>-1</sup>. Detection of CA and 4-CP was made at 227 nm whereas p-BQ was detected at 254 nm.

## 3. Theoretical models

### 3.1. Estimation of the optical properties

In absorbing and scattering media, like photocatalysts suspensions, the distance travelled by a photon, the probability of being absorbed, and the directional distribution of the scattered radiation depend on the absorption coefficient ( $\kappa_\lambda$ ), the scattering coefficient ( $\sigma_\lambda$ ), and the phase function for scattering. It is important to note that optical properties depend on the wavelength of radiation,  $\lambda$ .

The extinction coefficient ( $\beta_\lambda = \sigma_\lambda + \kappa_\lambda$ ) was estimated from extintance measurements of the photocatalysts suspensions as  $\beta_\lambda = \frac{-\ln(T_\lambda)}{L}$ , where  $T_\lambda$  is the normal transmittance at wavelength  $\lambda$  and  $L$  is the measuring cuvette path. In order to minimize the amount of scattered rays that reach the detector, a slit was placed before the detector according to the procedure previously reported [41]. Then, the specific extinction coefficient  $\beta_\lambda^*$ , per unit of catalyst mass concentration  $C_{cat}$  ( $\beta_\lambda^* = \beta_\lambda / C_{cat}$ ), was obtained by applying linear regressions of the plots  $\beta_\lambda$  vs  $C_{cat}$ .

Diffuse reflectance and diffuse transmittance experimental measurements of the photocatalysts suspensions were carried out following the procedure described by Satuf et al. [42]. Simulation values of

diffuse transmittance and reflectance were calculated by solving the RTE in the measuring cuvette employing the Monte Carlo method. The adjustable parameters of the model were the absorption coefficient ( $\kappa_\lambda$ ) and the asymmetry factor ( $g_\lambda$ ) included in the Henyey and Greenstein (HG) phase function. Finally, a nonlinear regression procedure was employed to adjust simulation values to experimental measurements [19,40,43,51,52].

The Monte Carlo method is a stochastic simulation procedure that, applied to radiation problems, consists on tracking the trajectory of the photons in a domain, in this case the measuring cuvette, with the aid of random numbers ( $R_i$ ) between 0 and 1. The photocatalyst suspension inside the cuvette can be represented as a medium between two parallel infinite planes with azimuthal symmetry. Then, a one-dimensional, one-directional radiation transport model can be applied [41,42], i.e. the flight path of the photons can be traced with one spatial variable ( $x$ ) and one angular variable ( $\theta$ ). To describe the system, 1000 elementary volumes were considered in the simulations, in which photons could be either absorbed or scattered.

The main events considered in the Monte Carlo method to compute theoretical diffuse reflectance and transmittance values are detailed below and a scheme of the corresponding algorithm is shown in Fig. 2. In addition, a schematic representation of the radiation field inside the cuvette can be found in Figs. S1(A) and (B) of Supporting Information. The number of photons in the forward direction at  $x = 0$ ,  $n_\lambda^+(x = 0)$ , selected in the simulation was  $10^7$ :

- 1) The direction of the photon that arrives at the inner wall of the cuvette ( $x = 0$ ) is assumed to be  $\theta_0 = 0$  (collimated incident radiation)
- 2) Then, the length travelled by the photon in the catalyst suspension is calculated using the spectral extinction coefficient ( $\beta_\lambda$ ):

$$l = -\frac{1}{\beta_\lambda} \ln(1 - R_i) \quad (1)$$

And the new position is computed as:

$$x_{new} = x_{old} + e_x l \quad (2)$$

where  $x_{old}$  represents the previous position and  $e_x$  is the direction

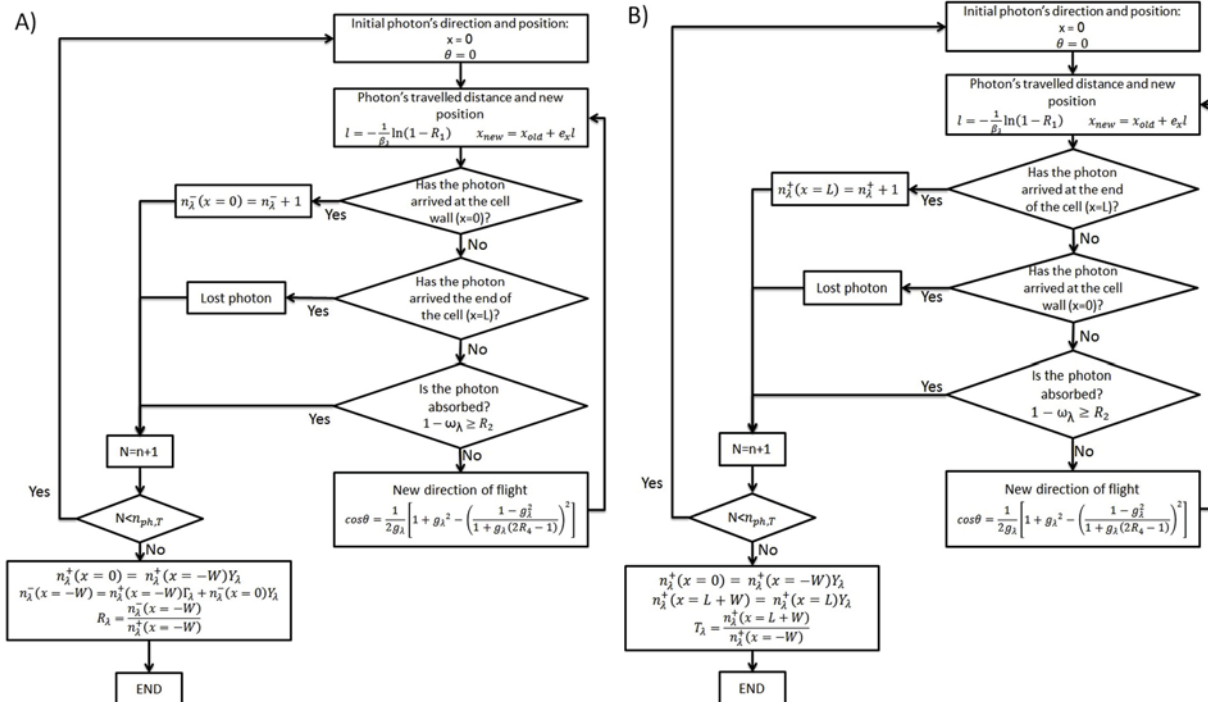
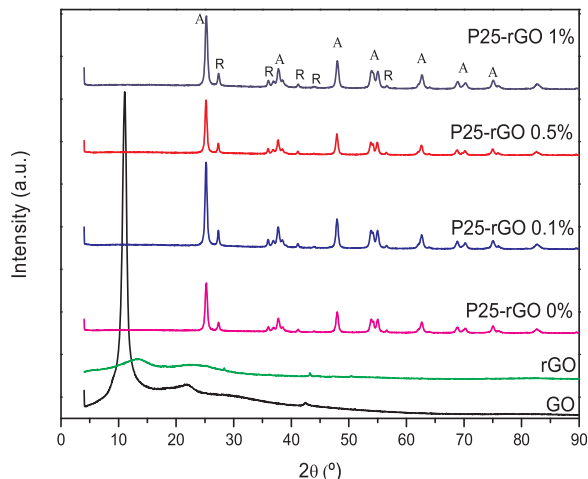


Fig. 2. Scheme of the Monte Carlo method used to calculate the theoretical diffuse reflectance (A) and diffuse transmittance (B) value.



**Fig. 3.** XRD patterns of pure GO, rGO, and P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1% photocatalysts.

cosine.

- 1) If the photon remains inside the quartz cuvette after travelling a distance  $l$ , the photon is considered to interact with a photocatalyst particle. The probability of absorption can be estimated with the albedo  $\omega_\lambda = \sigma_\lambda / \beta_\lambda$ . If

$$1 - \omega_\lambda \geq R_2 \quad (3)$$

the photon is absorbed, its trajectory ends and a new photon is generated. Otherwise, the photon is scattered and the new direction of the trajectory is calculated using the phase function. The Henyey and Greenstein (HG) phase function was adopted in this study since it provides suitable predictions of the photon trajectory in  $\text{TiO}_2$  suspensions [42,43,53].

$$p_{HG,\lambda}(\cos\theta) = \frac{(1 - g_\lambda^2)}{2(1 + g_\lambda^2 - 2g_\lambda \cos\theta)^{3/2}} \quad (4)$$

where  $g_\lambda$  is the asymmetry factor. Thus, the angle  $\theta$  that determines the new direction of the photon is given by:

$$\cos\theta = \frac{1}{2g_\lambda} \left[ 1 + g_\lambda^2 - \left( \frac{1 - g_\lambda^2}{1 + g_\lambda(2R_3 - 1)} \right)^2 \right] \quad (5)$$

Once the new direction is estimated, steps (2) and (3) are repeated until the photon is absorbed or it leaves the system through the cuvette walls.

- 1) If the new position of the photon is lower than 0 ( $x < 0$ ), the photon is considered to leave the measuring cuvette through the irradiated wall, and it is counted as part of the reflected photons,  $n_\lambda^-(x = 0)$ . On the other hand, if the new position of the photon is higher than the cell length ( $x > L$ ), the photon is stored inside the group of photons in the forward direction at the back wall of the cell,  $n_\lambda^+(x = L)$ .
- 2)  $n_\lambda^-(x = 0)$  denotes the number of photons in the backward direction

at the inner side of the front cuvette wall ( $x = 0$ ). To obtain the actual number of photons that leave the quartz cuvette at  $x = -W$  and reach the detector, the effect of the wall is accounted as

$$n_\lambda^-(x = -W) = n_\lambda^+(x = -W)\Gamma_\lambda + n_\lambda^-(x = 0)Y_\lambda \quad (6)$$

where  $Y_\lambda$  and  $\Gamma_\lambda$  represent the global wall transmission coefficient and the global wall reflection coefficient, respectively [42].

- 1)  $n_\lambda^+(x = L)$  represents the number of photons in the forward direction at the inner side of the back cuvette wall ( $x = L$ ). To obtain the actual number of photons in the forward direction that leave the quartz cuvette at  $x = L + W$  and reach the detector, the effect of the wall is accounted as

$$n_\lambda^+(x = L + W) = n_\lambda^+(x = L)Y_\lambda \quad (7)$$

Additionally, the incident photons that arrive at the inner side of the cuvette at  $x = 0$  ( $n_\lambda^+(x = 0)$ ) are calculated as

$$n_\lambda^+(x = 0) = n_\lambda^+(x = -W)Y_\lambda \quad (8)$$

Then, the theoretical value of diffuse reflectance and diffuse transmittance were calculated according to the following expressions:

$$R_\lambda = \frac{n_\lambda^-(x = -W)}{n_\lambda^+(x = -W)} \quad (9)$$

$$T_\lambda = \frac{n_\lambda^+(x = L + W)}{n_\lambda^+(x = -W)} \quad (10)$$

A mathematical algorithm based on a nonlinear, multiparameter regression procedure was applied to obtain the values of the absorption coefficient ( $\kappa_\lambda$ ) and the asymmetry factor ( $g_\lambda$ ) that minimize the difference between predictions and experimental data. The spectral scattering coefficient was determined by:

$$\sigma_\lambda = \beta_\lambda - \kappa_\lambda \quad (11)$$

Finally, the specific absorption ( $\kappa_\lambda^* = \kappa_\lambda / C_{cat}$ ) and specific scattering ( $\sigma_\lambda^* = \sigma_\lambda / C_{cat}$ ) coefficients were obtained from the slopes of linear regressions between the  $\kappa_\lambda$  and  $\sigma_\lambda$  data versus  $C_{cat}$ . The asymmetry factor was calculated as the average of the different  $g_\lambda$  values obtained for the different photocatalyst concentrations.

### 3.2. Calculation of the quantum efficiency

Numerous studies agree that the most suitable parameter to compare the intrinsic activity of a photocatalyst is the quantum efficiency ( $\eta$ ) when polychromatic radiation is used [18,54]. This parameter can be defined as the ratio of the observed initial molar reaction rate,  $\langle r_{CA}(x, t_0) \rangle_{V_R}$ , to the volumetric rate of photon absorption (VRPA) by the photocatalyst,  $\langle e^a(x) \rangle_{V_R}$ , both averaged over the reactor volume.

$$\eta = \frac{\langle r_{CA}(x, t_0) \rangle_{V_R}}{\langle e^a(x) \rangle_{V_R}} \quad (12)$$

$\eta$  describes the efficiency of the absorbed photons to contribute to the chemical reaction.

**Table 1**  
Physico-chemical properties of  $\text{TiO}_2$  and  $\text{TiO}_2$ -rGO photocatalysts.

Photocatalyst	Anatase (%)	Rutile (%)	$d_{\text{Anatase}}$ (nm)	$d_{\text{Rutile}}$ (nm)	Band gap (eV)	$A_D/A_G^a$ a.u.	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )
P25-rGO 0%	80	20	16.7	21.1	3.1	–	53
P25-rGO 0.1%	78	22	18.4	26.4	3.1	1.37	54
P25-rGO 0.5%	76	24	18.4	25.5	3.1	1.33	56
P25-rGO 1%	76	24	16.3	20.5	3.1	1.33	58

<sup>a</sup> The ratio  $A_D/A_G$  was 1.13 and 1.14 for GO and rGO respectively.

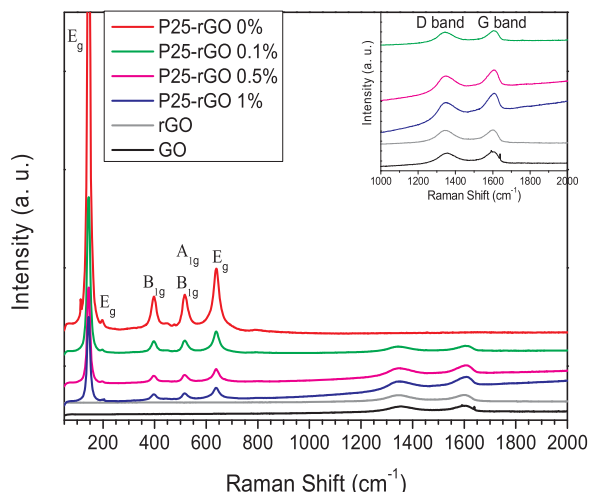


Fig. 4. Raman spectra of GO, rGO and P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5%, and P25-rGO 1% photocatalyst. (upper right) Raman magnified spectra ranging from 1000  $\text{cm}^{-1}$  to 2000  $\text{cm}^{-1}$ .

### 3.2.1. Volumetric rate of photon absorption (VRPA)

The VRPA in the photoreactor was calculated by solving a radiation model with Monte Carlo simulations, employing the previously estimated optical parameters of the photocatalysts. In the reactor, the incoming radiation is diffuse (there is no preferential direction) because of the ground glass plates, and the photocatalysts suspensions produce the extinction of radiation mainly along the axial coordinate. Thus, the propagation of the radiation can be modelled with one spatial variable ( $x$ ) and one angular variable ( $\theta$ ). The range of emission of the lamps was discretized in 11 wavelengths, every 10 nm from 315 to 415 nm, and the length of the reactor ( $L_R = 2.5$  cm) was divided into 1000 spatial

cells ( $\Delta x = 0.0025$  cm). In these simulations,  $10^7$  photons of each wavelength were generated and traced until they left the reactor or were absorbed, in which case their position was stored. The main events considered in the Monte Carlo simulation are:

- 1) The incoming radiation was diffuse and, therefore, photons at the inner side of the reactor window had the same probability to follow any direction [53]. The angle  $\theta$  that determines the direction of the photon was given by:

$$\sin \theta = 2R_1 - 1 \quad (13)$$

Steps 2) and 3) are the same as those detailed in Section 3.1.

The number of absorbed photons in each spatial cell  $\Delta x$  was stored as  $n_{abs,\lambda}(x)$ .

Finally the LVRPA in each cell was calculated by:

$$e^a(x) = \sum_{\lambda=315\text{nm}}^{\lambda=415\text{nm}} \frac{q_{w,\lambda} n_{abs,\lambda}(x)}{n_{tot} \Delta x} \quad (14)$$

where  $q_{w,\lambda}$  is the inlet radiation flux of wavelength  $\lambda$ , and  $n_{tot}$  is the total number of photons considered in the simulation.

Finally, the average volumetric rate of photon absorption (VRPA) in the cylindrical reactor was calculated according to the following expression:

$$\langle e^a(x) \rangle_{V_R} = \frac{1}{L_R} \int_{x=0}^{x=L_R} e^a(x) dx \quad (15)$$

### 3.2.2. Reaction rate

To calculate the quantum efficiency, apart from the VRPA, the initial volumetric reaction rate must be determined. For this purpose, the mass balance of clofibrac acid (CA) was considered assuming that: (1) conversion per pass in the photoreactor is differential, (2) the system is well-mixed, (3) chemical reactions occur at the solid-liquid interface,

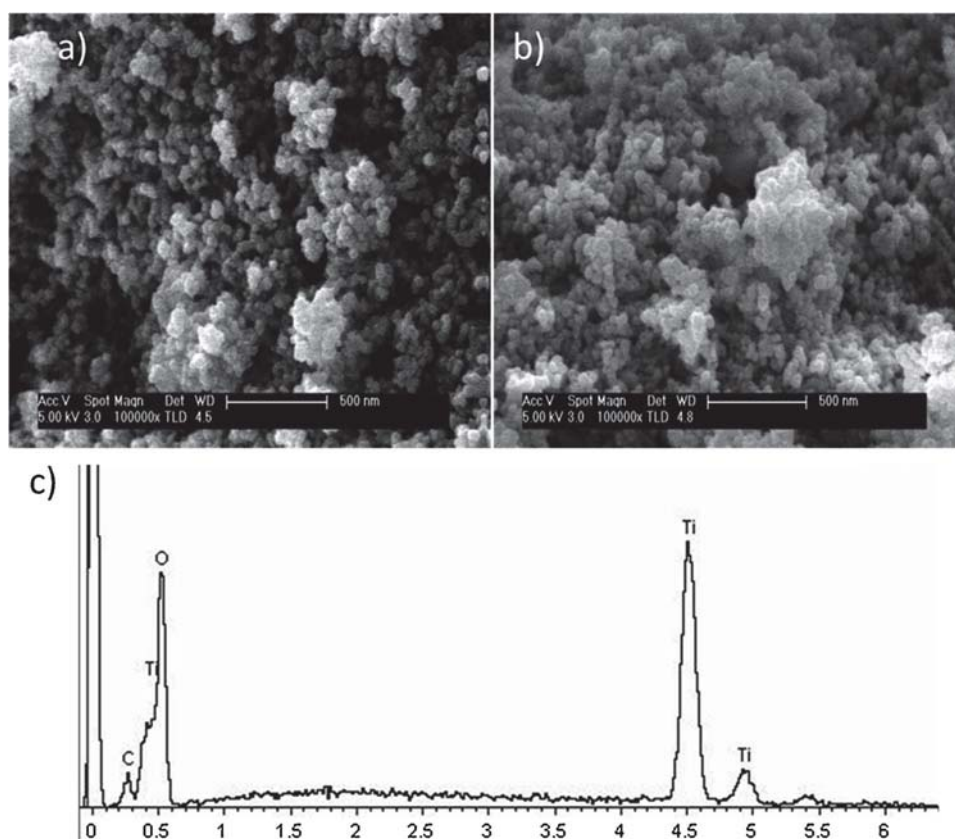
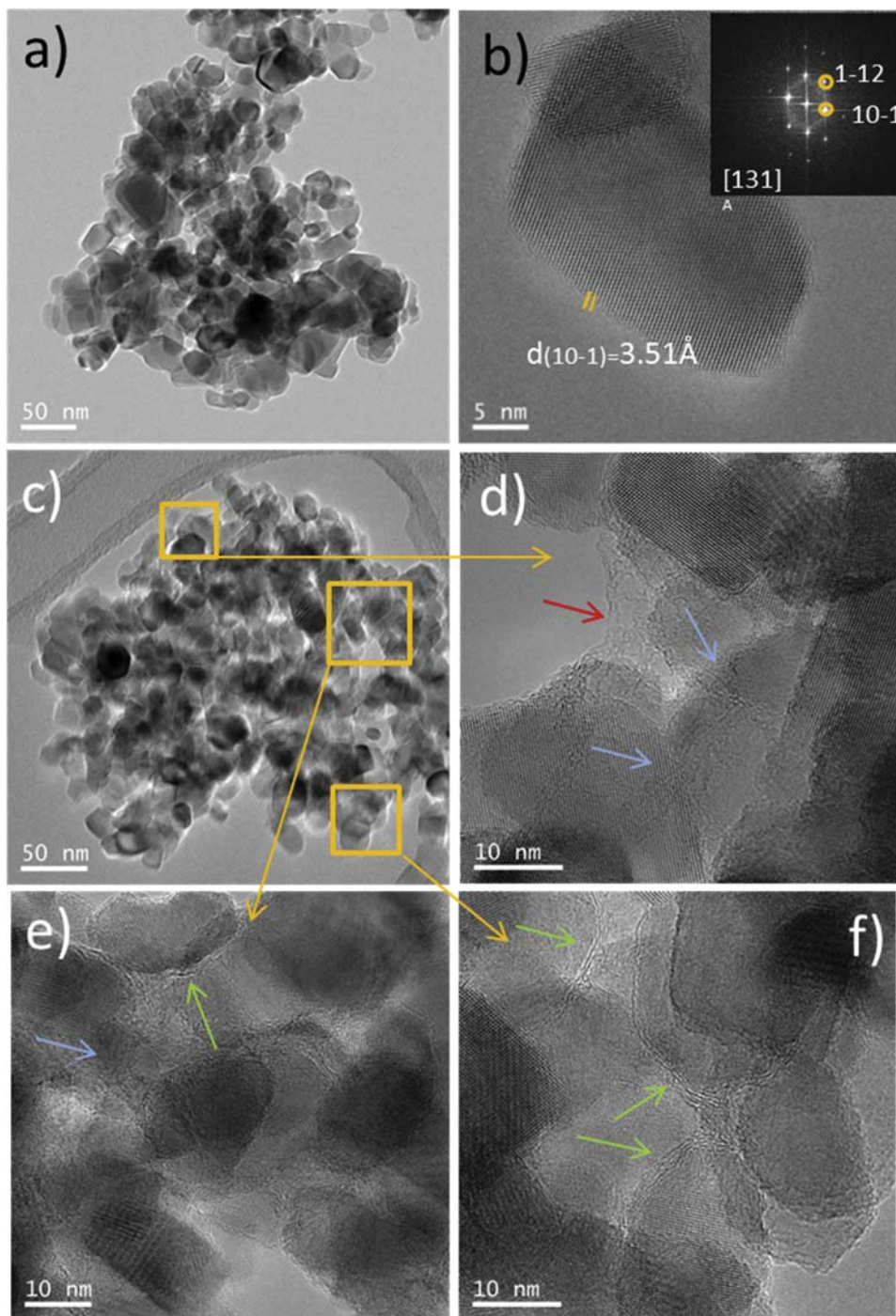


Fig. 5. SEM images of P25-rGO 0% (a) and P25-rGO 1% (b) EDX profile of P25-rGO 1% photocatalyst (c).





**Fig. 6.** TEM images of P25-rGO photocatalysts. (a) P25-rGO 0%; (b) HRTEM micrograph of the TiO<sub>2</sub> particles and the inset shows the Fast Fourier transform (FFT) pattern; (c) and (d–f) are TEM and HRTEM images of P25-rGO 1%, respectively.

(4) photolysis is negligible, and (5) there are no mass transfer limitations. Therefore, the mass balance for CA results:

$$\varepsilon_L \frac{dC_{CA}(t)}{dt} \Big|_{Tk} = -\frac{V_R}{V_T} \langle r_{CA}(x, t) \rangle_{V_R} \quad (16)$$

where  $\varepsilon_L$  is the liquid hold-up ( $\varepsilon_L \cong 1$ ),  $C_{CA}$  represents the molar concentration of clofibric acid,  $V_R$  is the reactor volume,  $V_T$  is the total volume of the system and  $Tk$  refers to the storage tank. Thus, the initial reaction rate of clofibric acid photo-oxidation can be derived from the plot of the CA concentration in the tank versus time as follows:

$$\langle r_{CA}(x, t_0) \rangle_{V_R} = -\varepsilon_L \frac{V_T}{V_R} \lim_{t \rightarrow 0} \frac{\Delta C_{CA}(t)|_{Tk}}{\Delta t} \quad (17)$$

## 4. Results and discussion

### 4.1. Photocatalyst characterization

From XRD patterns, shown in Fig. 3, bare TiO<sub>2</sub> have presented a mixture of anatase and rutile crystalline phases. The percentage of each crystalline phase and the crystallite sizes, determined by the Scherrer equation, are given in Table 1, where the main physico-chemical

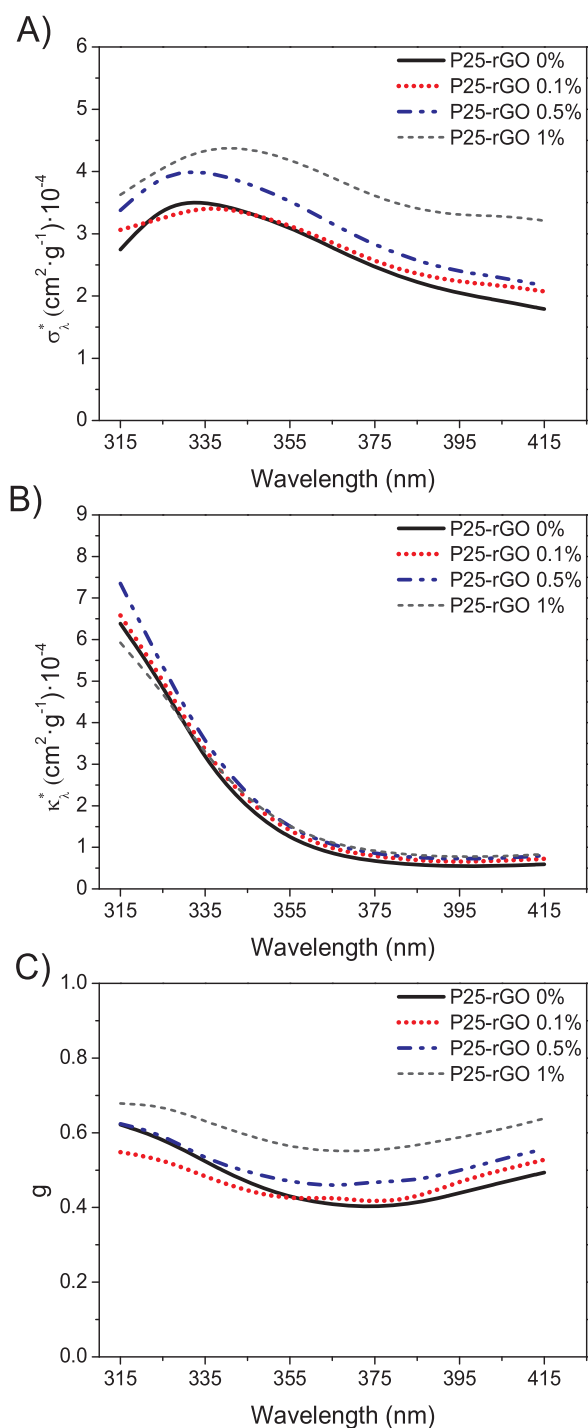


Fig. 7. Optical properties of the different  $\text{TiO}_2$ -rGO photocatalysts: (A), specific scattering coefficient ( $\sigma_{\lambda}$ ); (B), specific absorption coefficient ( $\kappa_{\lambda}$ ); (C), asymmetry factor ( $g_{\lambda}$ ).

properties of the  $\text{TiO}_2$ -rGO nanocomposites are also summarized. Bare  $\text{TiO}_2$  is mainly constituted by anatase (80%) with rutile (20%), with average crystallite sizes close to 17 and 21 nm, respectively. The presence of rGO in the nanocomposite did not introduce significant changes in both crystalline structure and average sizes of anatase and rutile, highlighting a slight increase in rutile crystalline phase when the rGO content was increased. Nevertheless, very similar XRD patterns were always found in all these P25-rGO nanocomposites in comparison to bare  $\text{TiO}_2$ .

Whereas the graphene oxide employed to prepare the

nanocomposites presents a clear diffraction peak at  $2\theta = 11.1^\circ$ , when GO was subjected to the hydrothermal treatment (rGO) a very broad peak at  $2\theta \sim 25^\circ$  was observed joined to the disappearance of the peak at  $2\theta = 11.1^\circ$ , which indicates the reduction of graphene oxide. Moreover, no typical diffraction peak of GO was detected in any of the  $\text{TiO}_2$ -rGO nanocomposites, probably because of the partial reduction of GO during the hydrothermal process and the low amount of GO added [22,55–57].

Raman spectra of the photocatalysts were measured to verify the coexistence of rGO and  $\text{TiO}_2$ . Fig. 4 shows the Raman spectra of GO, rGO, P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1%, respectively. Bare  $\text{TiO}_2$  and all P25-rGO nanocomposites have exhibited 5 distinct peaks at 143, 197, 399, 513 and  $641 \text{ cm}^{-1}$ , characteristic of the anatase crystalline phase [56,58]; whereas a small peak, detected at  $446 \text{ cm}^{-1}$ , was ascribed to rutile [58]. Regarding GO, rGO and P25-rGO nanocomposites, Raman spectra of the characteristic peaks of graphitized carbon species at  $1344$  and  $1602 \text{ cm}^{-1}$ , attributed to the D band and the G band respectively, were also observed. In Table 1 the ratio of the area of the D band to the G band is also reported ( $A_D/A_G$ ), which indicates the relative amount of defects compared to the  $\text{sp}^2$  hybridized graphene domains [25,56,57]. GO and rGO yielded an  $A_D/A_G$  value close to 1.1, indicating a disordered structure even after GO was reduced by the hydrothermal treatment [24,59], whereas values around 1.33 were estimated for the P25-rGO nanocomposites. The increase of the ratio is the result of the strong interaction between  $\text{TiO}_2$  and rGO sheets after the hydrothermal method, plus the contribution of remaining surface oxygenated functional groups [24,56,60,61].

Morphology of the synthesized photocatalysts was studied by SEM and TEM and the corresponding images are shown in Figs. 5 and 6, respectively.

SEM images of P25-rGO 0% and P25-rGO 1% can be seen in Fig. 5a and b, respectively. These photocatalysts, regardless the presence of rGO, are constituted by small spherical  $\text{TiO}_2$  nanoparticles with similar sizes, ranging from 20 to 40 nm. These primary particles led to the formation of densely packed agglomerates. Although isolated rGO sheets were hard to find probably because of the low amount of GO added to the  $\text{TiO}_2$ -rGO nanocomposite, exposed rGO surface without  $\text{TiO}_2$  nanoparticles should be easier to spot on increasing the rGO/ $\text{TiO}_2$  ratio [55].

Finally, in Fig. 5c is shown the EDX pattern of P25-rGO 1% photocatalyst. A peak ascribed to C was observed in the EDX spectrum which further evidences the presence of rGO in the nanocomposites.

In order to understand the morphology and microstructure of these photocatalysts TEM studies were also carried out. Fig. 6a shows a TEM micrograph of bare  $\text{TiO}_2$ , consisting in particles of  $\text{TiO}_2$  of around 20–40 nm size that form aggregates. The obtained results in XRD patterns, from which it was concluded that bare  $\text{TiO}_2$  and the corresponding  $\text{TiO}_2$ -rGO photocatalysts were constituted by a mixture of mainly anatase with rutile crystalline phases, were in accordance with the results obtained from TEM and electron diffraction studies where the predominant crystalline phase was always anatase. An HRTEM image of one of these anatase particles down the [131] zone axis is presented in Fig. 6b.

When rGO was present some features can be highlighted; a representative image of one aggregate can be observed in Fig. 6c. Different regions of this aggregate were analyzed in detail, marked with squares in Fig. 6c, and their corresponding HRTEM images are shown in the Fig. 6d, e and f. Attending to Fig. 6d, the rGO sheet can be seen isolated at the edge of the particles (red arrow), but also crumpled over them (blue arrows). This latter fact could be observed almost over the entire aggregate, as it is also noticeable in Fig. 6e. Here, it could also be appreciated that some particles seem to be wrapped with few layers of the rGO (green arrow). This intimate contact of the particles with the rGO sheets is more clearly observed in Fig. 6f, where some particles were at least partially if not completely surrounded by the rGO sheet. These observations evinced the good contact between the  $\text{TiO}_2$  particles

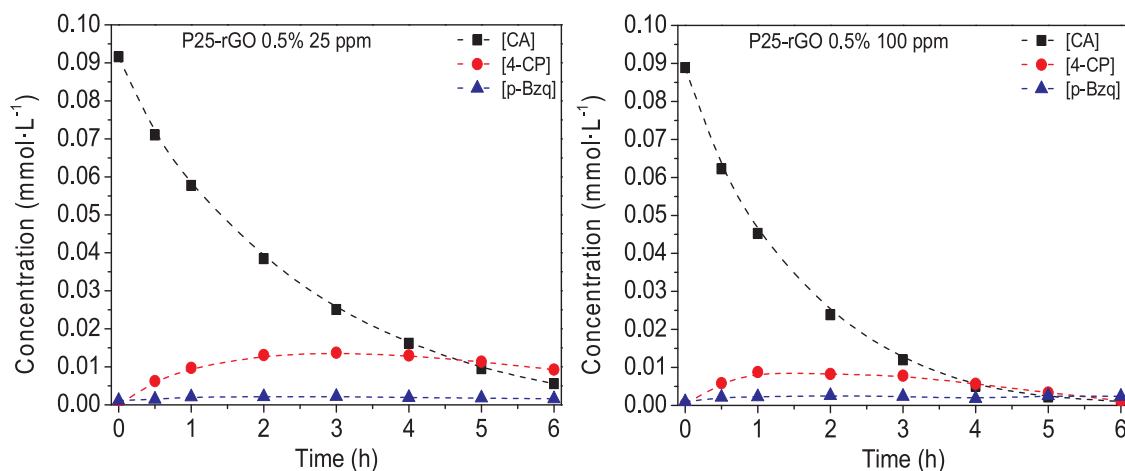


Fig. 8. Evolution of clofibrac acid (CA) concentration and the main intermediates, 4-chlorophenol (4-CP) and p-benzoquinone (p-Bzq), with 25 and 100 mg L<sup>-1</sup> of P25-rGO 0.5%.

Table 2  
Apparent kinetic constant *k* (h<sup>-1</sup>) for TiO<sub>2</sub> and TiO<sub>2</sub>-rGO photocatalysts.

C <sub>Cat</sub> (mg·L <sup>-1</sup> )	P25-rGO 0%	P25-rGO 0.1%	P25-rGO 0.5%	P25-rGO 1%
25	0.438	0.450	0.461	0.413
50	0.542	0.534	0.543	0.427
100	0.608	0.616	0.675	0.515
250	0.619	0.566	0.631	0.552

and the rGO.

UV-visible absorption properties of these photocatalysts powders were analyzed by measuring the UV-vis diffuse reflectance spectra (DRS). Band gap energy (E<sub>g</sub>) was estimated through the Tauc plot and the corresponding values are shown in Table 1 [46]. E<sub>g</sub> values of 3.1 ± 0.1 were obtained for all the photocatalysts, indicating that the presence of rGO did not entail the formation of new energy levels in the band gap.

Considering the BET surface area, no differences were observed among bare TiO<sub>2</sub> and the TiO<sub>2</sub>-rGO composites, with surface area values around 57 m<sup>2</sup> g<sup>-1</sup> (see Table 1).

#### 4.2. Optical properties of the photocatalyst suspensions

The plots of the specific scattering and absorption coefficients and the asymmetry factor as a function of the wavelength for P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1% suspensions are shown in Fig. 7 and the values corresponding to P25-rGO 0.5% can be found in Table S1 of the Supporting Information.

Regarding absorption coefficients, a notable increase is observed at short wavelengths, below 325 nm, when the GO:TiO<sub>2</sub> mass ratio increases up to 0.5%. In contrast, P25-rGO 1% photocatalyst exhibits slightly lower values of the absorption coefficient when is compared to P25-rGO 0%.

As to scattering coefficient, the higher the amount of rGO present in the nanocomposite, the higher the scattering coefficient values. In fact,

Table 3  
Influence of photocatalyst concentration on initial rate of CA photodegradation, VRPA and quantum efficiency for P25-rGO 0% and P25-rGO 0.5%.

C <sub>Cat</sub> (mg·L <sup>-1</sup> )	$\langle -r_{CA}(x, t_0) \rangle_{VR}$ (mol s <sup>-1</sup> ·cm <sup>-3</sup> ) × 10 <sup>11</sup>		VRPA (Einstein·s <sup>-1</sup> ·cm <sup>-3</sup> ) × 10 <sup>9</sup>		$\eta$ (mol·Einstein <sup>-1</sup> ) × 10 <sup>2</sup>	
	P25-rGO 0%	P25-rGO 0.5%	P25-rGO 0%	P25-rGO 0.5%	P25-rGO 0%	P25-rGO 0.5%
25	7.81	8.22	4.51	4.62	1.73	1.78
50	9.66	9.68	4.91	4.94	1.97	1.96
100	10.84	12.03	4.97	4.96	2.18	2.42

rGO seems to have greater effect on radiation scattering than on absorption.

It can also be noticed that below 335 nm (see Fig. 7), the values of the absorption coefficient exceeds those of the scattering coefficient. However, above that wavelength, opposite behaviour was found, with absorption coefficient values being nearly five times lower than the scattering coefficient.

A rise in the value of the asymmetry factor was observed when rGO was added to the TiO<sub>2</sub>. The asymmetry factor ranged between 0.4-0.63 for P25-rGO 0% and 0.55-0.68 for P25-rGO 1%. This positive value indicates that light scattered by the TiO<sub>2</sub>-rGO suspensions occurred mainly in the forward direction and the addition of rGO favours the scattering in that direction.

#### 4.3. Photocatalytic activity

The temporal evolution of clofibrac acid concentration and its main reaction intermediates, 4-chlorophenol (4-CP) and p-benzoquinone (p-BQ), using different loadings of P25-rGO 0%, 0.1% 0.5% and 1% can be found in Figs. 8 and S2-S5 of the Supporting Information. In all photodegradation runs the concentration evolution of the organic compounds was always very similar. 4-CP concentration was always higher than p-BQ concentration, and 4-CP concentration exceeded CA concentration after 4–5 h of photodegradation. Concerning the concentration evolution observed when P25-rGO 0.5% was used (Figs. 8 and Figures S4), negligible concentrations of CA and intermediates remained in the reaction medium after 6 h of irradiation time when catalyst loadings of 50 mg L<sup>-1</sup> or higher were used.

Under our experimental conditions, degradation of CA followed pseudo-first order kinetics. The effect of the photocatalyst concentration on the apparent reaction rate constant *k* for the different nanocomposites is presented in Table 2. The apparent kinetic constant always increased when increasing the catalyst concentration up to 100 mg L<sup>-1</sup>. Regarding the amount of rGO, the value of *k* increased when increasing the rGO content, reaching a maximum value with P25-



rGO 0.5%, and then decreased for P25-rGO 1%.

The performance of the catalysts presented the following order: P25-rGO 0.5% > P25-rGO 0.1% ≈ P25-rGO 0% > P25-rGO 1%. It could be noted that the addition of rGO to TiO<sub>2</sub> led to a slight increase in the apparent reaction rate constant values. This improvement in clofibrac acid photodegradation can be ascribed to the role played by rGO, since it is able to lower the charge transfer resistance and act as an electron acceptor, which helps to decrease the recombination rate of electron-hole pairs [31,62–65]. As a consequence, a higher amount of charge carriers can enable to generate reactive species such as holes or hydroxyl radicals [28]. However, an excess on the rGO loading can lead to a reduction of the photocatalytic activity ascribed to two reasons: (1) a shielding effect caused by rGO that blocks light and prevents radiation from being absorbed by TiO<sub>2</sub>, and (2) when the amount of rGO is excessive, it could act as recombination center [31,61,66–68]. Because the highest photocatalytic activity was obtained with P25-rGO 0.5%, this nanocomposite was selected for further comparison with bare TiO<sub>2</sub>. It should be mentioned that experiments with catalyst concentrations of 250 mg L<sup>-1</sup> were also carried out, but no significant improvements in the photoreaction rates were observed when they were compared with 100 mg L<sup>-1</sup>.

Table 3 presents the values of initial reaction rate, VRPA, and quantum efficiency for P25-rGO 0% and P25-rGO 0.5% photocatalysts. Similar values of VRPA were obtained with bare and nanocomposite catalysts, both increasing with the catalyst concentration. Regarding the quantum efficiency, the highest value was achieved with P25-rGO 0.5% at 100 mg L<sup>-1</sup> whose quantum efficiency value was 11% higher than that obtained with P25-rGO 0%. Since the absorbed radiation estimated for both photocatalysts was nearly the same, it could be concluded that the improvement in the performance of the photocatalytic activity of P25-rGO 0.5% was due to a reduction of the charge carriers recombination rate [24–27,69].

## 5. Conclusions

In this work, TiO<sub>2</sub>-rGO nanocomposites were hydrothermally prepared and compared through their physico-chemical properties and photoactivity in the degradation of clofibrac acid. Raman spectra indicated a strong interaction between TiO<sub>2</sub> and rGO layers, further confirmed by TEM images.

The optical properties of TiO<sub>2</sub>-rGO nanocomposites were estimated from UV–vis measurements in the range 315–415 nm. The presence of rGO increased the scattering coefficient in the whole UV-A range, whereas the effect on the absorption coefficient was notable only at wavelengths lower than 325 nm. P25-rGO 0.5% exhibited the highest absorption coefficients and P25-rGO 1%, the lowest. The asymmetry factor (around 0.55) for all photocatalysts indicated that radiation is preferentially scattered in the forward direction.

Radiation absorption inside the photocatalytic reactor was computed by using the Monte Carlo method. Complete degradation of clofibrac acid was achieved after 6 h of irradiation time and the maximum initial reaction rates were obtained when 100 mg L<sup>-1</sup> of the photocatalysts were used. P25-rGO 0.5% and P25-rGO 1% led to the highest and lowest photocatalytic activities, respectively. The lowest photodegradation found in P25-rGO 1% was ascribed to an excess of rGO that could favor charge carriers recombination leading to detrimental photoactivity. The highest value of quantum efficiency was achieved with P25-rGO 0.5% at 100 mg L<sup>-1</sup>, with an increase of 11% compared to the value obtained for P25-rGO 0%.

## Acknowledgements

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.01.054>.

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## INFLUENCE OF TiO<sub>2</sub> OPTICAL PARAMETERS IN A SLURRY PHOTOCATALYTIC REACTOR: KINETIC MODELLING

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### SUPPORTING INFORMATION

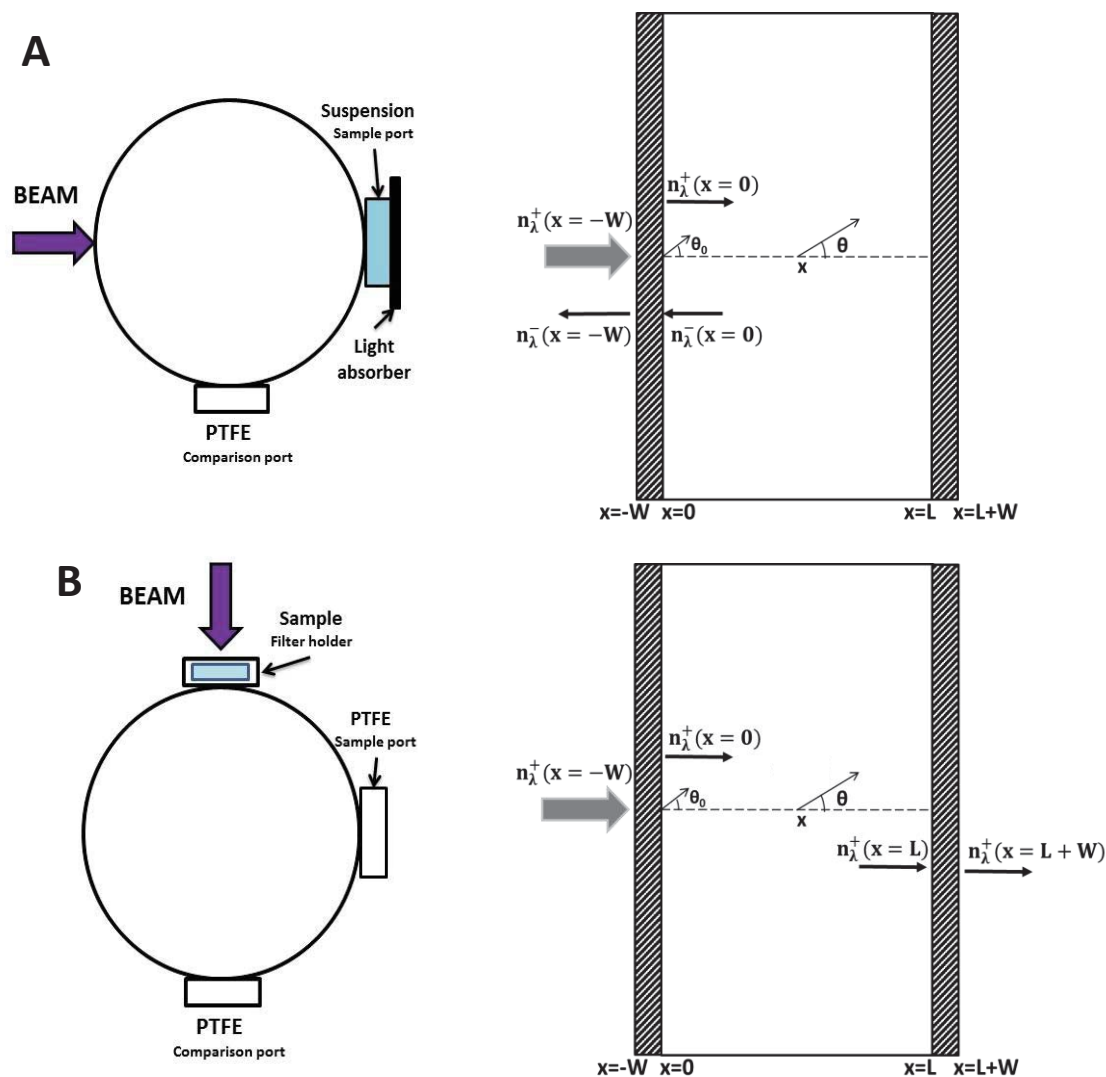
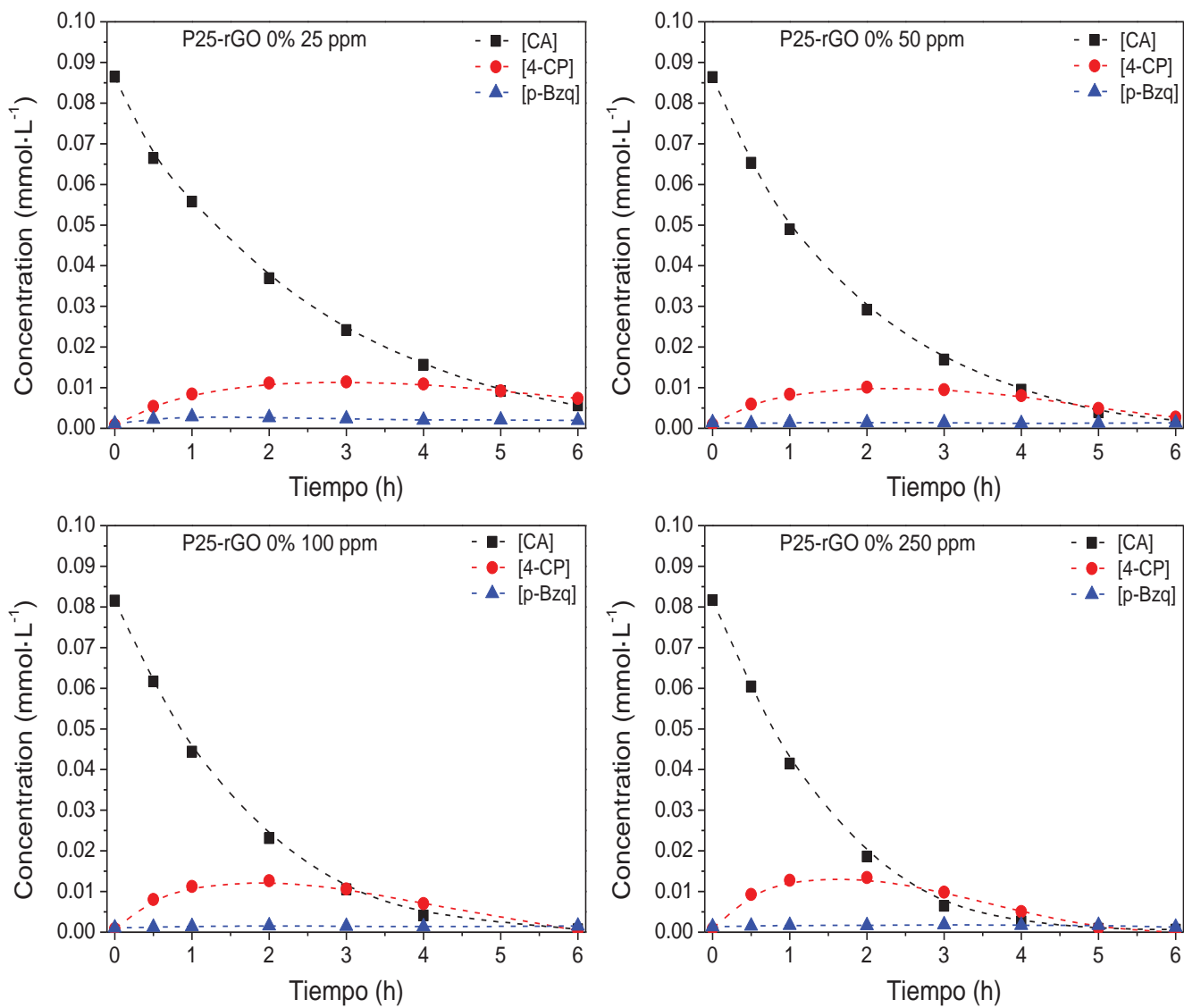


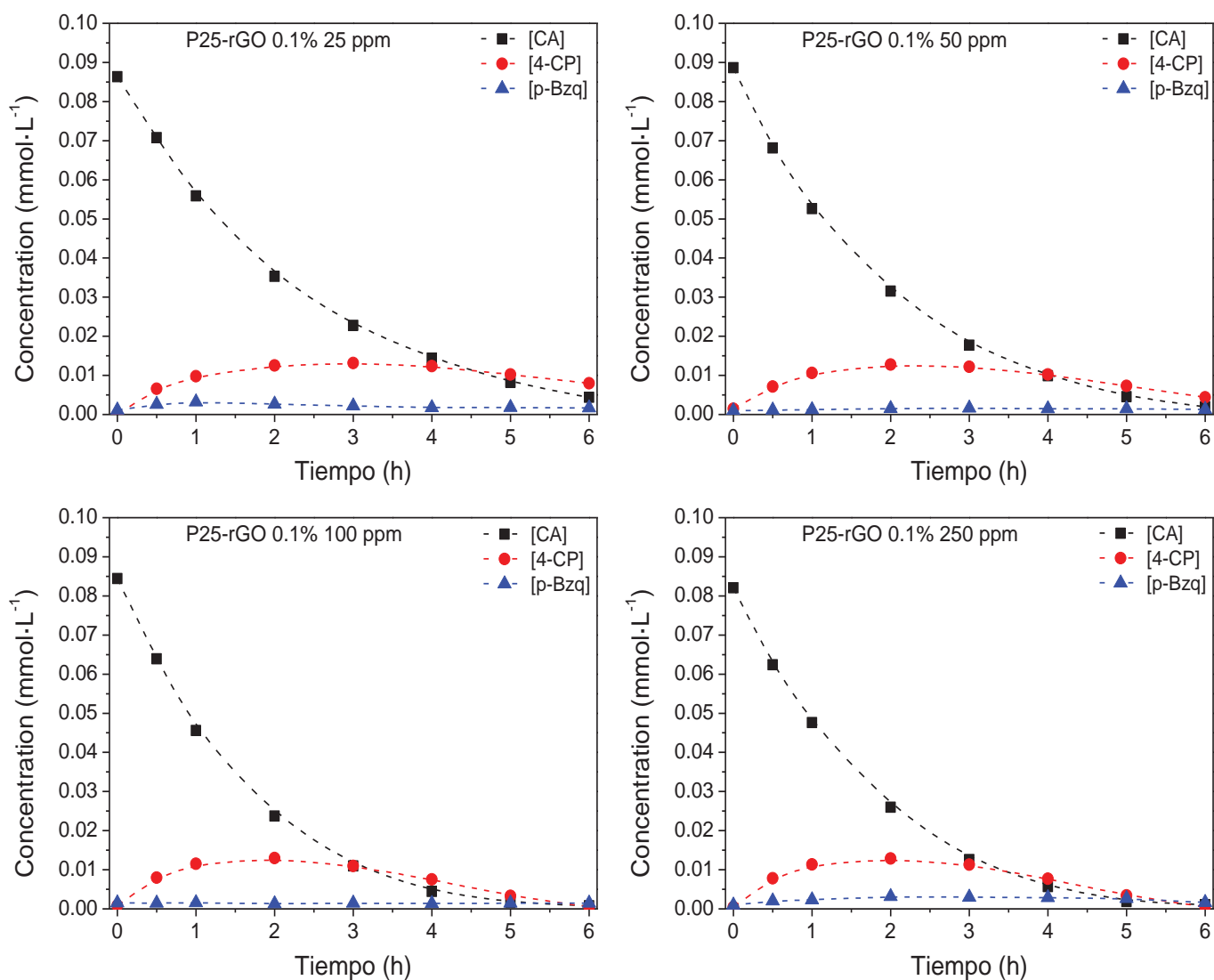
Figure S1. Schematic representation of the integrating sphere configuration and of the radiation field inside the cell for the diffuse reflectance (A) and diffuse transmittance (B) measurements.

**Table S1.** Optical properties for P25-rGO 0.5% nanocomposite.

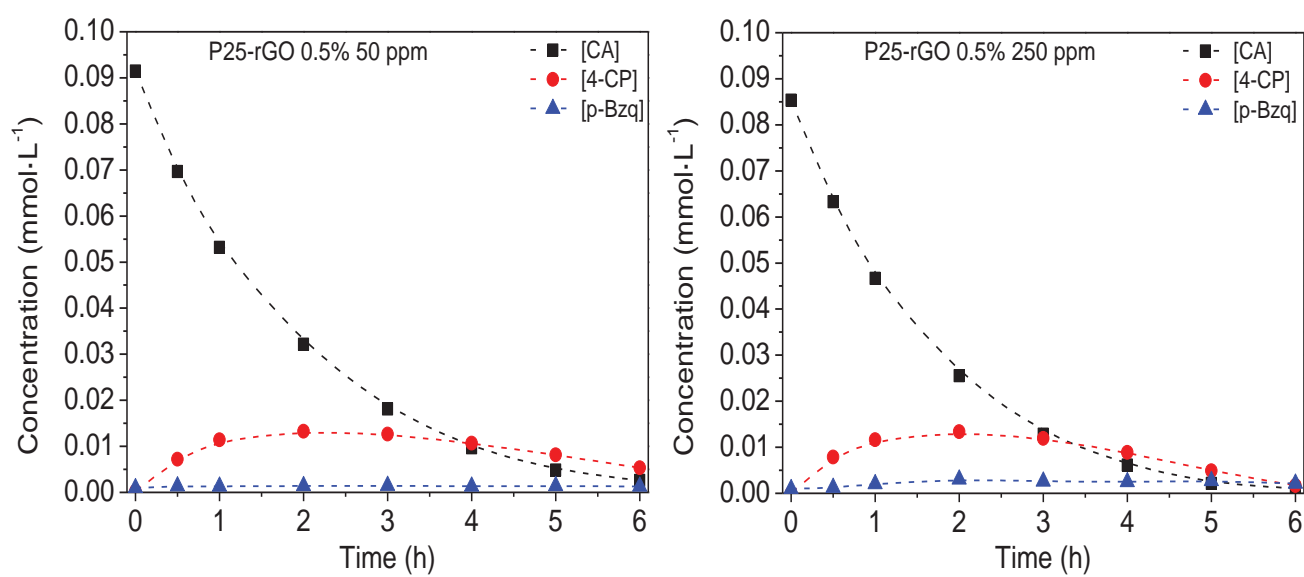
$\lambda$	$\beta^*$ (cm <sup>2</sup> ·g <sup>-1</sup> )	$\sigma^*$ (cm <sup>2</sup> ·g <sup>-1</sup> )	$\kappa^*$ (cm <sup>2</sup> ·g <sup>-1</sup> )	<b>g</b>
315	1.07E+05	3.38E+04	7.35E+04	0.624
325	9.31E+04	3.98E+04	5.33E+04	0.596
335	7.49E+04	4.02E+04	3.48E+04	0.530
345	6.04E+04	3.81E+04	2.22E+04	0.494
355	4.98E+04	3.53E+04	1.45E+04	0.468
365	4.20E+04	3.16E+04	1.04E+04	0.456
375	3.66E+04	2.82E+04	8.43E+03	0.469
385	3.30E+04	2.56E+04	7.44E+03	0.472
395	3.10E+04	2.39E+04	7.17E+03	0.498
405	3.03E+04	2.30E+04	7.38E+03	0.530
415	2.96E+04	2.16E+04	7.97E+03	0.557



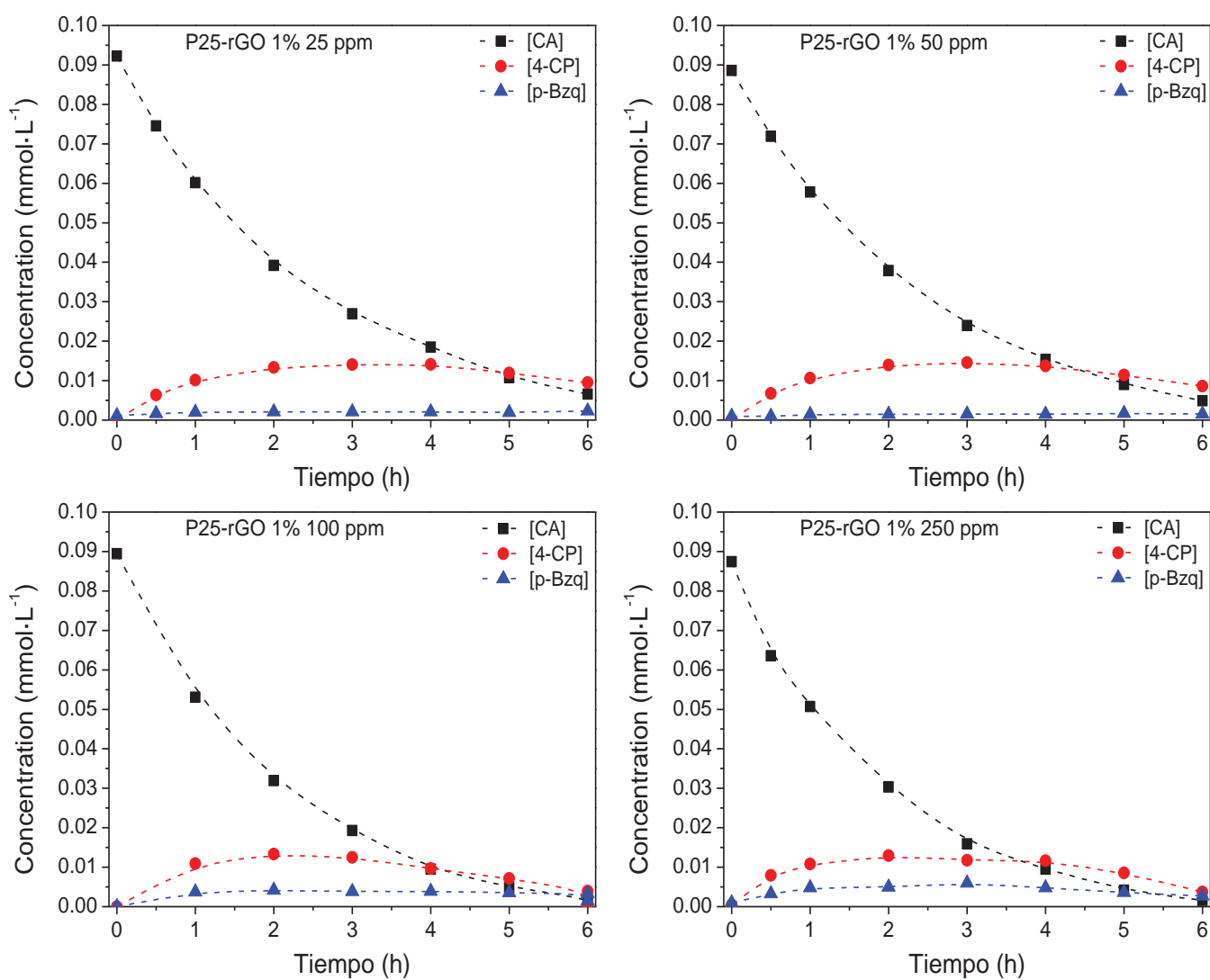
**Figure S2.** Evolution of clofibric acid (CA) concentration and the main intermediates, 4-chlorophenol (4-CP) and p-benzoquinone (p-Bzq), at different photocatalyst loadings of P25-rGO 0%.



**Figure S3.** Evolution of clofibrac acid (CA) concentration and the main intermediates, 4-chlorophenol (4-CP) and p-benzoquinone (p-Bzq), at different photocatalyst loadings of P25-rGO 0.1%.



**Figure S4.** Evolution of clofibric acid (CA) concentration and the main intermediates, 4-chlorophenol (4-CP) and p-benzoquinone (p-Bzq), with 50 and 250 mg·L<sup>-1</sup> of P25-rGO 0.5%.



**Figure S5.** Evolution of clofibric acid (CA) concentration and the main intermediates, 4-chlorophenol (4-CP) and p-benzoquinone (p-Bzq), at different photocatalyst loadings of P25-rGO 1%.



# Anexo VI:

TiO<sub>2</sub>-rGO photocatalytic degradation of an emerging pollutant: kinetic modelling and determination of intrinsic kinetic parameters

# TiO<sub>2</sub>-rGO PHOTOCATALYTIC DEGRADATION OF AN EMERGING POLLUTANT: KINETIC MODELLING AND DETERMINATION OF INTRINSIC KINETIC PARAMETERS

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ARTICLE INFO	ABSTRACT
<i>Keywords:</i> Photocatalysis TiO <sub>2</sub> -rGO kinetic model LVRPA Clofibric acid	A TiO <sub>2</sub> -reduced graphene oxide (rGO) nanocomposite has been used to photodegrade the active metabolite of a pharmaceutical drug, clofibric acid (CA), in a photocatalytic slurry reactor under a wide range of operating conditions, such as catalyst loading and irradiation level. This nanocomposite was prepared by a hydrothermal method with a GO/TiO <sub>2</sub> weight ratio of 0.5%, since it provided the highest quantum efficiency in a previous study. Absorbed radiation profiles inside the reactor were obtained by solving the radiation model with the Monte Carlo method. Higher photocatalyst loadings led to higher values of absorbed radiation close to the reactor windows. A photocatalyst loading of 100 mg·L <sup>-1</sup> provided the best results. Mass balances were proposed for the main pollutant and their detected intermediates, p-benzoquinone and 4-chlorophenol. An intrinsic kinetic model, based on a proposed reaction photo-mechanism and with an explicit dependency on the local volumetric rate of photon absorption (LVRPA), was developed. The kinetic model was able to accurately reproduce the photodegradation process. Good correlations were obtained between the theoretical and experimental concentrations of clofibric acid and its main intermediates, with a root-mean-square error below 11% when the main pollutant was considered.

## 1. INTRODUCTION

Because heterogeneous photocatalysis is considered a green and sustainable technology, in the last decades a lot of research has been focused on gaining knowledge and improving photocatalytic processes and reactors [1-3]. However, to be able to optimize the design and scale-up photoreactors, it is strictly necessary to develop full predictive models. In the case of photocatalytic reactors, mass balances and momentum balances must be solved. Since photocatalytic processes are initiated by the absorption of sufficiently energetic photons by a semiconductor, intrinsic kinetic equations with an explicit dependence on local photon absorption must be deduced to solve the mass balances of the main reacting species [4-13].

Great effort has been made to develop radiation models and mathematical tools to obtain the local photon absorption rates inside reactors with different geometries [9, 14-17]. The most

popular methods are the discrete ordinate method (DOM) [7-9, 18], the Monte Carlo method (MC) [8, 13-15, 19, 20], the “two-flux” or “six-flux” radiation absorption–scattering models (TFM and SFM, respectively) [6, 16, 21, 22]. The MC method is widely applied because of its simplicity, especially when applied to reactors with complex geometries and configurations. Nevertheless, other methods, such as the method of lines or the control curve method, can be found in the literature [23, 24]. Furthermore, commercial software based on multiphysics computational fluid dynamics (CFD) models are often used nowadays [12, 25-28] to simulate radiation intensities inside photoreactors with different geometries, e.g. annular reactors [11, 16, 22, 29], cylindrical reactors [13-15, 20, 30, 31], flat rectangular reactors [22, 24] or multi-tube reactor [28].

When the local photon absorption rates are known, intrinsic kinetic parameters involved in the kinetic equations can be

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estimated by comparing theoretical data obtained from the resolution of the mass balances with experimental data [5-7]. Intrinsic kinetic parameters obtained following this procedure are independent of the hydrodynamic and irradiation conditions and reactor geometry [16, 32]. Therefore, they can be employed to simulate the evolution of the pollutant concentration in different photoreactors. Kinetic parameters involved in the photodegradation of different organic compounds have been reported in the literature: phenolic compounds [6, 33], short-chain organic acids [10, 16, 24], cyanide [5, 34] and pharmaceuticals [13, 19, 20, 35]. Furthermore, some of these intrinsic parameters were employed to reproduce the evolution of the concentration of organic compounds with good accuracy [5, 6, 29, 35]. Thus, it has been proven that these parameters are suitable to optimize, design and scale-up photoreactors.

In addition, intrinsic kinetic parameters are useful to analyze the effect of TiO<sub>2</sub> modifications on the photocatalytic activity, for example, by the addition of metal oxides [23] or silver [22], or the immobilization of TiO<sub>2</sub> on different supports, such as silica particles [5]. In recent years, TiO<sub>2</sub>-graphene and TiO<sub>2</sub>-reduced graphene oxide (rGO) has been widely investigated owing to the unique properties of graphene: good optical and thermal transmittance, thermal conductivity, chemical stability, large area and high charge carrier mobility [36-38].

The aim of this work is to develop a kinetic model to simulate the photodegradation of the active metabolite of a pharmaceutical, clofibric acid, and the evolution of the concentration of the main reaction intermediates. The photodegradation of clofibric acid was performed under different irradiation conditions and using different loadings of a TiO<sub>2</sub>-rGO photocatalyst prepared by a hydrothermal process. The radiation profiles inside the reactor were calculated by solving the RTE using the Monte Carlo method. Mass balances were proposed and kinetic equations were derived according to a kinetic mechanism for clofibric acid photodegradation [39, 40]. Finally, the intrinsic kinetic model was applied to estimate the kinetic parameters and experimental values were compared with predicted results.

## 2. EXPERIMENTAL SECTION

### 2.1. Chemicals

Graphene oxide (GO) water dispersions (0.4 wt% concentration) and titanium dioxide P25 Aeroxide® (80:20

anatase-rutile, BET specific surface area 54 m<sup>2</sup>/g, average anatase and rutile crystal size of 21 and 33 nm respectively) were provided by Graphenea and Evonik Company, respectively. Clofibric acid (CA>97%), chosen as a model pollutant, was purchased from Aldrich. 4-chlorophenol (4-CP>99%) and p-benzoquinone (p-BQ>98%) were obtained from Aldrich and Fluka, respectively. All reagents were used without further treatment and ultrapure water was used to prepare all solutions.

### 2.2. Synthesis of P25-rGO

P25-rGO 0.5% was synthesized hydrothermally. To sum up, 2 g of P25 were stirred in 400 mL of ultrapure water for 30 minutes at 500 rpm. Subsequently, the necessary amount of GO to obtain a weight ratio GO/TiO<sub>2</sub> of 0.5% was added to the suspension and it was stirred for another 150 minutes to ensure that GO sheets were well dispersed and a homogenous suspension was obtained. The hydrothermal process was carried out in a 600-mL Teflon-lined stainless steel autoclave reactor for 3 h at 120 °C. After the reaction, the composite was washed and collected by centrifugation three times and finally dried at 50 °C.

Table 1. Description of the photoreaction system.

<b>Photoreactor</b>	
Length	2.5 cm
Inner diameter	8.6 cm
Reactor Volume (V <sub>R</sub> )	145.3 cm <sup>3</sup>
Total Volume (V <sub>T</sub> )	1000 cm <sup>3</sup>
<b>Lamps</b>	
Model	Philips TL 4W/08 Black Light UVA
Power	4 W
Number	8
Emission Wavelength	310-420 nm
Radiation flux (100%)	6.3·10 <sup>-9</sup> Einstein·s <sup>-1</sup> ·cm <sup>-2</sup>
Radiation flux (62%)	4.9·10 <sup>-9</sup> Einstein·s <sup>-1</sup> ·cm <sup>-2</sup>
Radiation flux (30%)	2.4·10 <sup>-9</sup> Einstein·s <sup>-1</sup> ·cm <sup>-2</sup>
<b>Operating conditions</b>	
Temperature	298 K
Flow rate	1.5 L·min <sup>-1</sup>
Catalyst loading (C <sub>Cat</sub> )	(0.025-0.25) g·L <sup>-1</sup>

### 2.3. Experimental set up and procedure

Photocatalytic experiments were carried out in a cylindrical stainless steel photoreactor with inner walls made of Teflon. The photoreactor windows consisted of circular borosilicate glasses at each side of the reactor. A four-lamp set (TL 4W/08

Black Light UVA lamps from Philips) was placed parallel to each glass windows, whose wavelength emission ranged from 310 to 420 nm, with a peak at 355 nm. A ground glass plate was located between the lamp set and the borosilicate window to produce diffuse inlet radiation. Radiation flux arriving at the reactor windows was measured by ferrioxalate actinometry [41]. The reactor dimensions and the main characteristics of the lamps are presented in Table 1.

In the experiments, the suspensions were continuously recirculated. The set up consisted of a peristaltic pump, the reactor and a 1 L storage tank. The storage tank was covered by a water jacket to keep the temperature constant at 25 °C throughout the experiments. A thermometer, a sample withdrawal system and a gas inlet, to continuously bubble oxygen to keep the solution saturated with O<sub>2</sub>, were included in the storage tank.

In photocatalytic experiments, 20 mg of CA was dissolved in 1 L of ultrapure water and mixed with the desired amount of P25-rGO 0.5%. The mixture was sonicated for 30 minutes in an ultrasonic bath to obtain a good dispersion of the photocatalyst. Afterwards, the suspension was transferred to the storage tank and recirculated for 30 minutes with a pump flow rate of 1.5 L·min<sup>-1</sup> to allow the mixture to reach adsorption equilibrium. O<sub>2</sub> was continuously bubbled into the storage tank and the lamps were turned on so that they could stabilize their emission. Shutters were placed between the lamps and the reactor to stop any radiation from arriving to the suspension. Then, the first sample was taken out of the storage tank (t=0) and the shutters were removed. Samples were centrifuged and subsequently filtered through a 0.02 μm syringe filters (Anotop 25) before analysis. Experimental conditions are summarized in Table 1. When the experiments were carried out under different irradiation levels, attenuation filters were placed between the lamps and the reactor.

#### 2.4. Analysis

Concentrations of CA and the main intermediates identified during the photodegradation, 4-CP and p-BQ, were measured by HPLC. The equipment used was a Waters chromatograph with a UV detector and a C-18 column as stationary phase. A 70/30% acetonitrile/acidified water (with 0.1 % v/v phosphoric acid) mixture was employed as mobile phase. 20 μL of sample was injected and the flow rate was 1 mL·min<sup>-1</sup>. CA and 4-CP were detected at 227 nm, whereas p-BQ was identified at 254 nm. Each sample was measured at least twice to ensure reproducibility.

### 3. RADIATION PROFILES INSIDE THE PHOTOREACTOR

To obtain the intrinsic reaction kinetics to design and scale up photoreactors, it is necessary to know the absorbed radiation distribution inside the photocatalytic reactor, i.e. the local volumetric rate of photon absorption (LVRPA,  $e^a(x)$ ). As a consequence, the radiation transport equation (RTE) must be solved. However, to obtain the boundary conditions of the RTE, the inlet radiation intensities arriving at the reactor must be determined either by using emission models or chemical actinometry [7, 9]. In this study, the spectral distribution of radiation arriving at the reactor windows is shown in Figure 1. Calculation of the radiation absorbed in the photoreactor demands the knowledge of the optical properties of the TiO<sub>2</sub>-rGO suspensions; they were determined in a previous study [42] and specific scattering ( $\sigma_\lambda$ ) and absorption ( $\kappa_\lambda$ ) coefficients of the P25-rGO 0.5% photocatalyst can be seen in Figure 1.

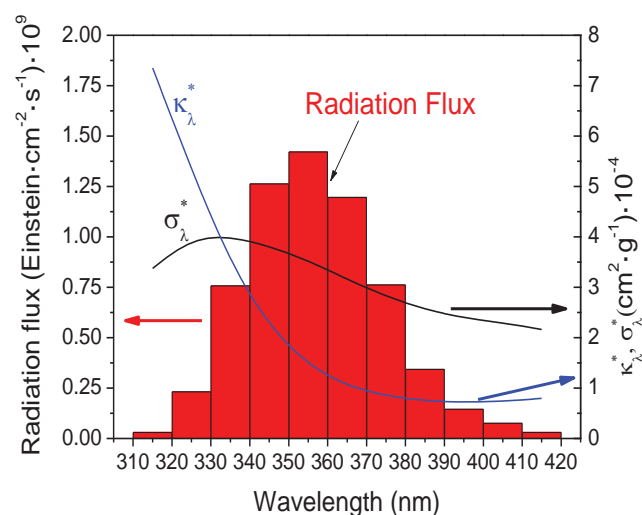


Figure 1. Spectral distribution of the incoming radiation and specific scattering ( $\sigma_\lambda$ ) and absorption ( $\kappa_\lambda$ ) coefficients of the P25-rGO 0.5% photocatalyst.

Given that the photoreactor featured ground glass plates, it was considered that the inlet radiation was diffuse. Therefore, assuming that the radiation was essentially attenuated along the longitudinal axis, a one-dimensional—one-directional model was considered to determine the LVRPA. Thus, the trajectory of the photon will be given by one spatial variable ( $x$ ) and one angular variable ( $\theta$ ). The Monte Carlo method was applied to obtain the absorbed radiation distribution inside the cylindrical photocatalytic reactor. This method consists of tracing the photon direction and trajectory since it enters the reaction space until it is absorbed or leaves the photoreaction system. For that purpose, random numbers ( $R_i$ ) between 0 and

are generated to determine the likelihood of each event. In these simulations,  $10^7$  photons of each wavelength were generated and traced until they left the reactor or were absorbed, in which case their position was stored. The range of emission of the lamps was discretized in 11 wavelengths and the length of the reactor ( $L_R=2.5$  cm) was divided into small cells ( $\Delta x=0.0025$  cm). The main events considered in the Monte Carlo method are shown schematically in Figure 2 and are detailed hereafter:

- 1) Firstly, it is necessary to know the direction of the photons emitted by the lamp. As it was assumed that the incident radiation was diffuse, all the directions had the same probability [43]. Hence, the zenith angle was determined by :

$$\sin \theta = 2R_1 - 1 \quad (1)$$

- 2) The length travelled by the photon inside the photocatalytic system without interaction is given by:

$$l = -\frac{1}{\beta_\lambda} \ln(1 - R_2) \quad (2)$$

where  $\beta_\lambda$  ( $\beta_\lambda = \sigma_\lambda + \kappa_\lambda$ ) is the spectral extinction coefficient of the reaction medium for a specific wavelength  $\lambda$ . After travelling a distance  $l$ , the new position is determined by:

$$x_{new} = x_{old} + e_x l \quad (3)$$

where  $x_{old}$  represents the previous position and  $e_x$  is the direction cosine.

- 3) If the new position lies within the reactor volume, the photon is assumed to strike a catalyst particle, and it can be either absorbed or scattered. The probability of each event depends on the albedo coefficient ( $\omega_\lambda$ ), which is the ratio of scattering to extinction coefficients,  $\omega_\lambda = \sigma_\lambda / \beta_\lambda$ . So, if

$$1 - \omega_\lambda \geq R_3 \quad (4)$$

the photon is absorbed and it is stored in the corresponding cell. If the photon is scattered, the scattering angle is calculated using the Henyey and Greenstein (HG) phase function [13, 14, 20, 44].

$$\cos \theta = \frac{1}{2g_\lambda} \left[ 1 + g_\lambda^2 - \left( \frac{1 - g_\lambda^2}{1 + g_\lambda(2R_4 - 1)} \right)^2 \right] \quad (5)$$

After establishing the new direction, the new length of flight and position are calculated following step 2.

- 4) If the new position of the photon lies outside the reactor volume, the photon is assumed to reach the

reactor windows, where it can be reflected or transmitted. If

$$\Gamma_{W,\lambda} > R_5 \quad (6)$$

where  $\Gamma_{W,\lambda}$  represents the global window reflection coefficient, the photon is reflected and it returns to the reaction space. Otherwise, the photon leaves the system, the sequence is finished and a new photon is generated.

Finally the LVRPA in each cell is calculated by:

$$e^a(x) = \sum_{\lambda=310 \text{ nm}}^{\lambda=420 \text{ nm}} \frac{q_{w,\lambda} n_{ph,\lambda,abs}(x)}{n_{ph,T} \Delta x} \quad (7)$$

where  $q_{w,\lambda}$  is the inlet radiation flux of a wavelength  $\lambda$ ,  $n_{ph,\lambda,abs}(x)$  is the number of photons of a given wavelength absorbed in a cell of position  $x$ ,  $n_{ph,T}$  is the total number of photons considered in the simulation, and  $\Delta x$  is the length of the cell.

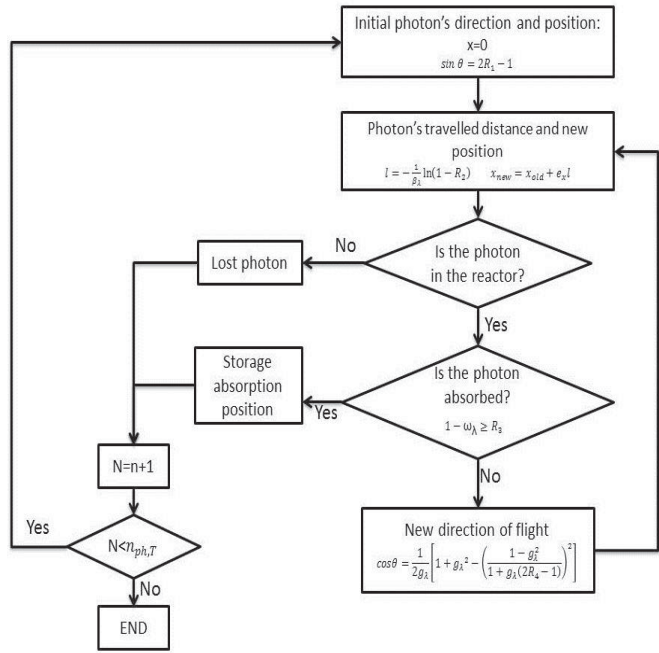


Figure 2. Scheme of the Monte Carlo method used to calculate the LVRPA.

#### 4. MASS BALANCES

In order to get the kinetic parameters to model the reaction and obtain the theoretical evolution of the pollutants concentrations, the mass balances of each organic compound must be solved. The conditions assumed to solve these mass balances were: (1) differential conversion per pass in the photoreactor, (2) the photocatalytic system is well-mixed, (3), chemical reaction occurs at the solid-liquid interface, (4) photolysis is negligible, and (5) there are no mass transfer limitations.

Regarding the reaction scheme considered by Manassero et al. [13], CA can be photodegraded by HO• either to produce 4-CP or p-BQ. Then, 4-CP can be further oxidized to generate more p-BQ or other organic intermediates (X<sub>i</sub>) that will eventually be turned into HCl, CO<sub>2</sub> and H<sub>2</sub>O. In the same way as 4-CP, p-BQ can be photodegraded to generate other organic intermediates (X<sub>j</sub>) that will be further oxidized until they are mineralized. Therefore, the following mass balances and their respective initial conditions are proposed:

$$\varepsilon_L \frac{dC_{CA}(t)}{dt} \Big|_{Tk} = -\frac{V_R}{V_T} a_v \{ \langle r_{CA,1}(x,t) \rangle_{A_R} + \langle r_{CA,2}(x,t) \rangle_{A_R} \} \quad (8)$$

$$C_{CA}(t=0) = C_{CA0}$$

$$\varepsilon_L \frac{dC_{4-CP}(t)}{dt} \Big|_{Tk} = \frac{V_R}{V_T} a_v \{ \langle r_{CA,1}(x,t) \rangle_{A_R} - \langle r_{4-CP,1}(x,t) \rangle_{A_R} - \langle r_{4-CP,2}(x,t) \rangle_{A_R} \} \quad (9)$$

$$C_{4-CP}(t=0) = 0$$

$$\varepsilon_L \frac{dC_{p-BQ}(t)}{dt} \Big|_{Tk} = \frac{V_R}{V_T} a_v \{ \langle r_{CA,2}(x,t) \rangle_{A_R} + \langle r_{4-CP,2}(x,t) \rangle_{A_R} - \langle r_{p-BQ}(x,t) \rangle_{A_R} \} \quad (10)$$

$$C_{p-BQ}(t=0) = 0$$

Where  $r_{CA,1}$  represents the photodegradation rate of clofibrac acid to form 4-chlorophenol,  $r_{CA,2}$  represents the reaction rate of clofibrac acid to produce p-benzoquinone,  $r_{4-CP,1}$  is the rate of 4-chlorophenol that is converted into organic intermediates,  $r_{4-CP,2}$  is the photodegradation rate to produce p-benzoquinone and  $r_{p-BQ}$  is the photodegradation rate of p-benzoquinone. All of them are superficial reaction rates averaged over the reaction area,  $A_R$ . The catalyst interfacial area per unit of suspension volume is  $a_v$ ,  $a_v = S_g C_{cat}$ , where  $S_g$  and  $C_{cat}$  are the catalyst specific surface area and the mass catalyst concentration, respectively;  $\varepsilon_L$  is the liquid hold-up ( $\varepsilon_L \cong 1$ );  $C_i$  represents the molar concentration of the organic compound;  $V_R$  is the reactor volume,  $V_T$  is the total volume of the system and  $Tk$  refers to the storage tank.

## 5. KINETIC MODEL

Once the mass balances were proposed, the kinetic equations were deduced using the reaction mechanism shown in Table 2

which was based on previous studies [39, 40, 43]. The following steps were considered in the reaction scheme: (1) activation of the photocatalyst by absorbing a photon with enough energy to generate an electron-hole pair, (2) adsorption of the different species on the photocatalyst surface, (3) recombination of the formed electron and hole, (4) electron transfer from TiO<sub>2</sub> to rGO, (5) reduction of oxygen by photogenerated electrons, (6) hole trapping by adsorbed water or hydroxyl ions, and (7) hydroxyl radical attack (HO•) to react with the different organic compounds, finally generating organic intermediates from 4-CP (X<sub>i</sub>) and p-BQ photodegradation (X<sub>j</sub>), or with inorganic species (Y) that can compete for hydroxyl radicals. It is important to point out that the production of hydroxyl radicals from photogenerated electrons was considered since it was reported that rGO can act as electron acceptor, favouring the transference of conduction band electrons and reduction of adsorbed oxygen to form superoxide radicals (O<sub>2</sub><sup>•-</sup>) [37, 45-47]. These radicals can further react to finally obtain hydroxyl radicals. In order to deduce the kinetic equations several assumptions were made: photocatalytic reaction takes place among adsorbed species on the photocatalyst surface and a dynamic equilibrium between adsorbed and bulk species was considered; oxygen is adsorbed at different active sites than the organic compounds; since clofibrac acid and its intermediates are adsorbed at the same type of sites, competitive adsorption was considered.

A complete description of the steps followed to obtain the equations of the kinetic model can be found in the Appendix. Thus, the following final expressions were obtained:

$$r_{CA}(x,t) = \frac{(\alpha_{2,1} + \alpha_{2,2})C_{CA}(x,t)}{1 + \alpha_3 C_{CA}(x,t) + \alpha'_3 C_{4-CP}(x,t) + \alpha''_3 C_{p-BQ}(x,t)} \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a(x)}{S_g C_{cat}}} \right\} \quad (11)$$

$$r_{4-CP}(x,t) = \frac{(\alpha_{4,1} + \alpha_{4,2})C_{4-CP}(x,t)}{1 + \alpha_3 C_{CA}(x,t) + \alpha'_3 C_{4-CP}(x,t) + \alpha''_3 C_{p-BQ}(x,t)} \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a(x)}{S_g C_{cat}}} \right\} \quad (12)$$



Table 2. Scheme of the proposed clofibric acid photodegradation mechanism.

Activation	$TiO_2 \xrightarrow{h\nu} e^-(TiO_2) + h^+(TiO_2)$	$r_{gs}$
Adsorption	$site_{O_2} + O_2 \leftrightarrow O_{2,ads}$	$K_{O_2}$
	$site_{H_2O} + H_2O \leftrightarrow H_2O_{ads}$	
	$site_{H_2O} + H_2O \leftrightarrow OH^-_{ads} + H^+$	
	$site_{CA} + CA \leftrightarrow CA_{ads}$	$K_{CA}$
	$site_{CA} + 4 - CP \leftrightarrow 4 - CP_{ads}$	$K_{4-CP}$
	$site_{CA} + p - Bzq \leftrightarrow p - Bzq_{ads}$	$K_{p-Bzq}$
	$site_{Y_l} + Y_l \leftrightarrow Y_{l,ads}$	
Recombination	$e^-(TiO_2) + h^+(TiO_2) \rightarrow heat$	$k_2[e^-][h^+]$
Electron transfer	$e^-(TiO_2) \rightarrow e^-(rGO)$	
Electron trapping	$O_{2,ads} + e^-(rGO) \rightarrow O_2^{*-}$	$k_3[e^-][O_{2,ads}]$
Holes trapping and HO <sup>•</sup> generation	$H_2O_{ads} + h^+(TiO_2) \rightarrow HO^{\bullet}$	$k_4[h^+][H_2O_{ads}]$
	$OH^-_{ads} + h^+(TiO_2) \rightarrow HO^{\bullet}$	
	$O_2^{*-} + H^+ \rightarrow HO_2^{\bullet}$	$k_5[H^+][O_2^{*-}]$
	$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	$k_6[HO_2^{\bullet}]^2$
	$H_2O_2 + O_2^{*-} \rightarrow HO^{\bullet} + O_2 + HO^-$	$k_7[O_2^{*-}][H_2O_2]$
Hydroxyl attack	$CA_{ads} + HO^{\bullet} \rightarrow 4 - CP_{ads}$	$k_{8,1}[HO^{\bullet}][CA_{ads}]$
	$CA_{ads} + HO^{\bullet} \rightarrow p - BQ_{ads}$	$k_{8,2}[HO^{\bullet}][CA_{ads}]$
	$4 - CP_{ads} + HO^{\bullet} \rightarrow X_{i,ads}$	$k_{9,1}[HO^{\bullet}][4 - CP_{ads}]$
	$4 - CP_{ads} + HO^{\bullet} \rightarrow p - BQ_{ads}$	$k_{9,2}[HO^{\bullet}][4 - CP_{ads}]$
	$p - BQ_{ads} + HO^{\bullet} \rightarrow X_{j,ads}$	$k_{10}[HO^{\bullet}][p - BQ_{ads}]$
	$Y_{l,ads} + HO^{\bullet} \rightarrow Y_{m,ads}$	$k_{11}[HO^{\bullet}][Y_{l,ads}]$

$$r_{p-BQ}(x, t) = \frac{\alpha_5 C_{p-BQ}(x, t)}{1 + \alpha_3 C_{CA}(x, t) + \alpha'_3 C_{4-CP}(x, t) + \alpha''_3 C_{p-BQ}(x, t)} \left( -1 + \sqrt{1 + \frac{\alpha_1 e^\alpha(x)}{S_g C_{cat}}} \right) \quad (13)$$

where  $\alpha_i$  are the intrinsic kinetic parameters.

Therefore, thanks to the electron transfer from TiO<sub>2</sub> to rGO, recombination of charge carriers might be decreased, and

therefore more holes could be available to oxidize water [45, 48]. Furthermore, the presence of rGO facilitates charge transfer to electron acceptors, which increases oxygen reduction [47].

## 6. RESULTS AND DISCUSSION

### 6.1. LVRPA profiles

LVRPA profiles along the longitudinal axis of the photoreactor using different catalyst loadings of P25-rGO 0.5% are depicted in Figure 3. Regardless of the photocatalyst concentration, it could be clearly observed that no radiation was absorbed by the suspension at the center of the



photoreactor. However, a rise of the photocatalyst loading led to a sharp increase of the radiation absorbed near the reactor windows. Thus, attenuation of light became more significant when using higher concentration of the nanocomposite.

The absorbed radiation profiles obtained for different irradiation levels are shown in Figure 4. These LVRPA profiles were calculated using 100 mg·L<sup>-1</sup> of P25-rGO 0.5% and different attenuation filters that allowed the pass of 62% and 30% of the incoming radiation. These experiments were carried out using 100 mg·L<sup>-1</sup> of P25-rGO 0.5% because of the higher activity achieved compared to other photocatalyst loadings and other initial GO/TiO<sub>2</sub> weight ratios analyzed previously [42]. It could be noted that the lower the radiation level, the lower the radiation absorbed near the window.

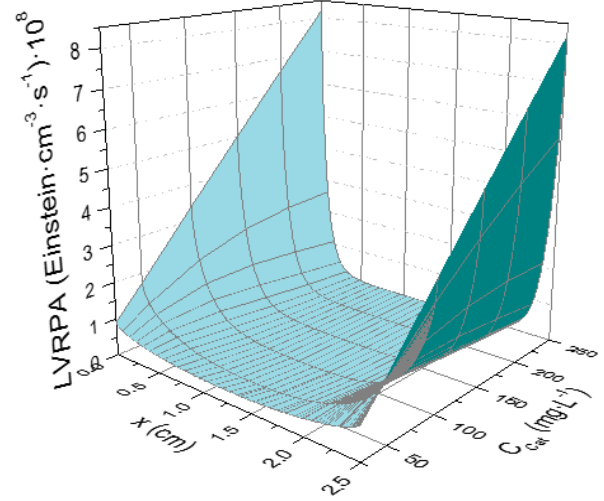


Figure 3. Local volumetric rate of photon absorption (LVRPA) for the studied P25-rGO 0.5% composite at different catalyst loadings.

Table 3. Estimated kinetic parameters.

	Parameter	Value	Units
6-Parameters model	$\alpha_1$	$5.77 \cdot 10^{11}$	$s \text{ cm}^2 \text{ Einstein}^{-1}$
	$\alpha_{2,1}$	$1.72 \cdot 10^{-6}$	$\text{cm s}^{-1}$
	$\alpha_{2,2}$	$2.62 \cdot 10^{-6}$	$\text{cm s}^{-1}$
	$\alpha_{4,1}$	$3.78 \cdot 10^{-6}$	$\text{cm s}^{-1}$
	$\alpha_{4,2}$	$1.67 \cdot 10^{-7}$	$\text{cm s}^{-1}$
	$\alpha_5$	$3.91 \cdot 10^{-5}$	$\text{cm s}^{-1}$
	RMSE	10.8	%
5-Parameters model	$\alpha'_{2,1}$	1.03	$\text{cm}^2 \text{ s}^{-1/2} \text{ Einstein}^{-1/2}$
	$\alpha'_{2,2}$	1.61	$\text{cm}^2 \text{ s}^{-1/2} \text{ Einstein}^{-1/2}$
	$\alpha'_{4,1}$	2.56	$\text{cm}^2 \text{ s}^{-1/2} \text{ Einstein}^{-1/2}$
	$\alpha'_{4,2}$	0.02	$\text{cm}^2 \text{ s}^{-1/2} \text{ Einstein}^{-1/2}$
	$\alpha'_5$	22.52	$\text{cm}^2 \text{ s}^{-1/2} \text{ Einstein}^{-1/2}$
	RMSE	16.3	%

## 6.2. Mass balances and kinetic model

A non-linear regression method based on the Levenberg–Marquardt algorithm was applied to estimate the kinetic parameters by comparing experimental values of clofibric acid, 4-chlorophenol and p-benzoquinone with those values obtained from the mass balances averaged over the whole reactor volume. Since values of the term  $[\alpha_3 C_{CA}(x, t) + \alpha'_3 C_{4-CP}(x, t) + \alpha''_3 C_{p-BQ}(x, t)] \ll 1$ , they were not considered and the denominator of the photodegradation rate expressions were disregarded.

On the other hand, since the value of  $\alpha_1$  was so high, it was assumed that  $\alpha_1 e^{\alpha_1 x} \gg 1$  for the different irradiation conditions, and therefore the kinetic equations could be simplified to obtain the following expressions:

$$r_{CA}(x, t) = (\alpha'_{2,1} + \alpha'_{2,2}) C_{CA}(x, t) \sqrt{\frac{e^{\alpha_1(x)}}{S_g C_{cat}}} \quad (14)$$

$$r_{4-CP}(x, t) = (\alpha'_{4,1} + \alpha'_{4,2}) C_{4-CP}(x, t) \sqrt{\frac{e^{\alpha_1(x)}}{S_g C_{cat}}} \quad (15)$$

$$r_{p-BQ}(x, t) = \alpha'_5 C_{p-BQ}(x, t) \sqrt{\frac{e^{\alpha_1(x)}}{S_g C_{cat}}} \quad (16)$$

where  $\alpha'_{2,1} = \alpha_{2,1} \sqrt{\alpha_1}$ ,  $\alpha'_{2,2} = \alpha_{2,2} \sqrt{\alpha_1}$ ,  $\alpha'_{4,1} = \alpha_{4,1} \sqrt{\alpha_1}$ ,  $\alpha'_{4,2} = \alpha_{4,2} \sqrt{\alpha_1}$  and  $\alpha'_5 = \alpha_5 \sqrt{\alpha_1}$ .

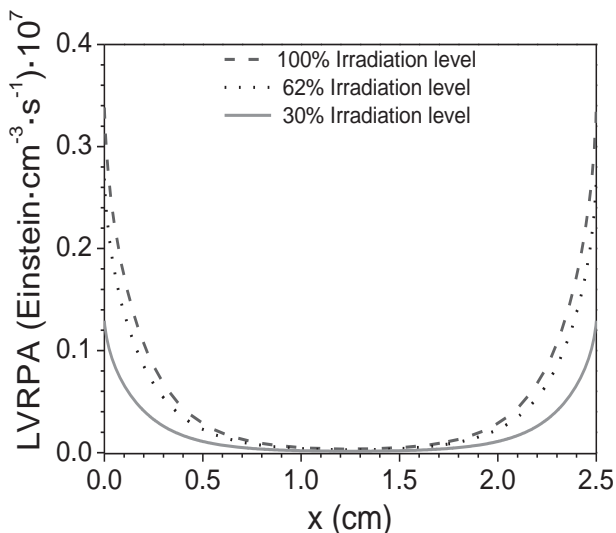


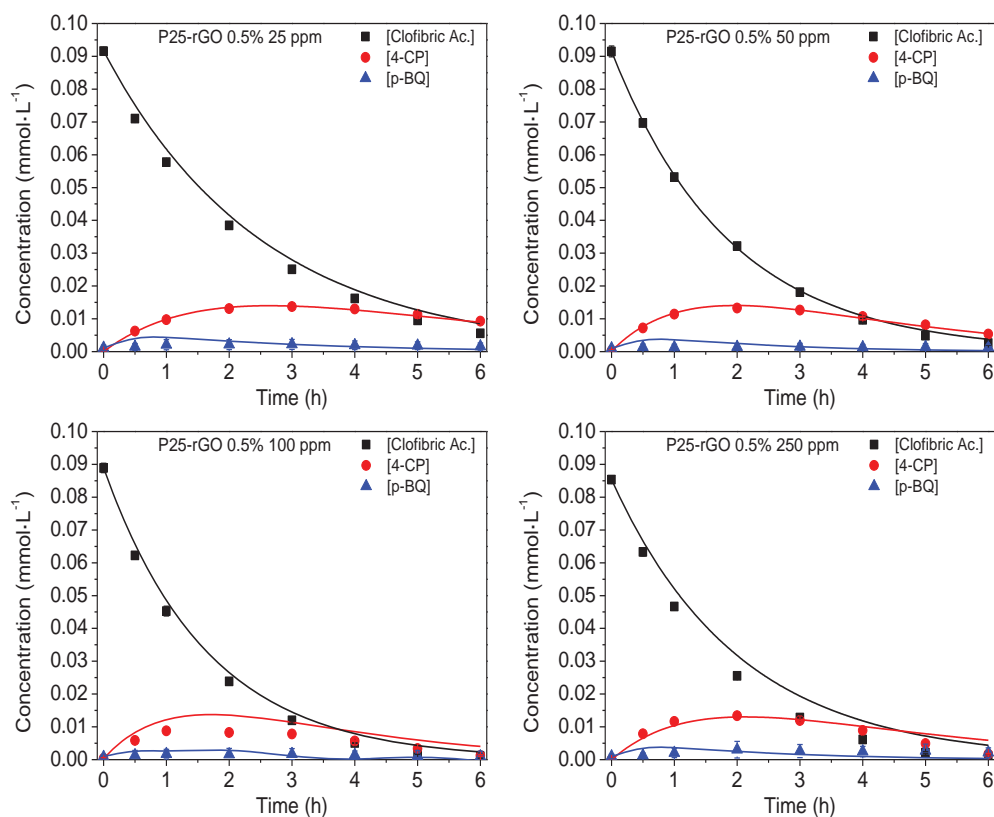
Figure 4. LVRPA profiles obtained using 100 mg·L<sup>-1</sup> of P25-rGO 0.5% at different irradiation levels.

The values of the kinetic parameters which provided the best fittings for both the complete (6-parameters) and simplified (5-parameters) kinetic models are shown in Table 3. From the values obtained with the 6-parameter and 5-parameter models, it could be observed that the kinetic parameter that represents the photodegradation of clofibric acid to form p-benzoquinone,  $\alpha_{2,2}$ , is slightly higher than that to generate 4-

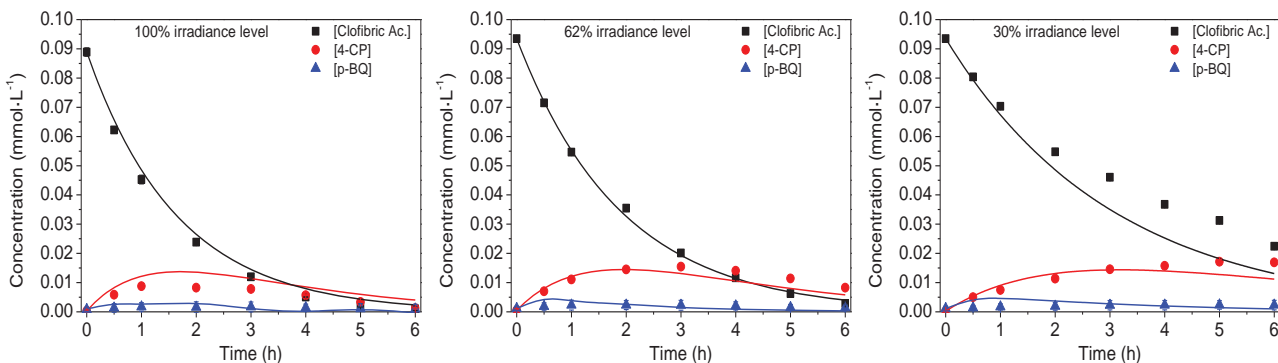
chlorophenol,  $\alpha_{2,1}$ . However, because of the higher value of the parameter related to p-benzoquinone photo-oxidation,  $\alpha_5$ , p-benzoquinone concentration was always very low. On the other hand, p-benzoquinone formation from 4-chlorophenol photo-oxidation was not kinetically favoured and other intermediates ( $X_i$ ) would be preferentially produced, as indicated the value of  $\alpha_{4,2}$ , which was far lower than  $\alpha_{4,1}$ .

Afterwards, the optimum photocatalyst loading (100 mg·L<sup>-1</sup>) was chosen and experiments with different irradiation levels are presented in Figure 6. When the irradiation level was decreased from 100% to 62%, 4-chlorophenol reached higher concentrations and, at the end of the experiment, 4-chlorophenol concentration exceeded the residual concentration of clofibric acid. Using an irradiation level of 30%, clofibric acid conversion after 2 h of treatment only reached 41%, while this value increased up to 73% for 100% irradiation. No meaningful differences in the evolution of p-benzoquinone concentration were detected under different irradiation levels.

In Figures 5 and 6 the theoretical values obtained with the 6-parameter model, for a wide range of operational conditions, were depicted for the three organic compounds detected.



Figures 5. Evolution of clofibric acid (CA) concentration and the main intermediates, 4-chlorophenol (4-CP) and p-benzoquinone (p-BQ), at different photocatalyst loadings of P25-rGO 0.5%. The predicted values of the concentrations (solid lines) were obtained with the 6-parameter model.



Figures 6. Evolution of clofibric acid (CA) concentration and the main intermediates, 4-chlorophenol (4-CP) and p-benzoquinone (p-BQ), at different irradiation levels using 100 mg·L<sup>-1</sup> of P25-rGO 0.5%. The predicted values of the concentrations (solid lines) were obtained with the 6-parameter model.

Concentrations predicted with the 5-parameter model were plotted in Figures S1 and S2 of the Supporting Information. It could be noted that good correlations between theoretical and experimental results were always obtained. To compare the ability of the model to predict the evolution of concentrations, total root-mean-square errors (RMSE) were calculated:

$$RMSE (\%) = \sqrt{\frac{\sum_{i=1}^N \left( \frac{C_{Exp}^i - C_{Mod}^i}{C_{Exp}^i} \cdot 100 \right)^2}{N}} \quad (17)$$

Values of RMSE can also be seen in Table 3. RMSE values of 10.8% and 16.3% were calculated for clofibric acid using the 6-parameter and 5-parameter models, respectively. Since concentrations lower than 0.01 mmol·L<sup>-1</sup> are within the experimental error, these low concentrations were not considered for the calculation of the RMSE. From these data, it can be concluded that, although simplified models with a small number of parameters are always preferred, the simplification leads to an increase in the error of the predicted values. Thus, the 6-parameter model was chosen to simulate the concentrations of the pollutants.

The proposed kinetic model was able to simulate accurately the experimental results of clofibric acid photodegradation using rGO-TiO<sub>2</sub> based photocatalysts.

## 7. CONCLUSIONS

In this work, an intrinsic kinetic model with an explicit dependence on radiation absorption was developed to model the photodegradation of clofibric acid and the main photogenerated intermediates, considering also the formation of hydroxyl radicals from photogenerated electrons. Firstly, the radiation absorbed by a nanocomposite, P25-rGO 0.5%,

was computed for different catalyst loadings and irradiation levels. The LVRPA was calculated by solving the RTE using the Monte Carlo method. Most radiation was absorbed near the photoreactor windows and it was not able to reach the centre of the reactor even using only 50 mg·L<sup>-1</sup> of photocatalyst. The intrinsic kinetic parameters were obtained for the complete (6-parameters) and simplified (5-parameters) models by comparing the experimental values and the theoretical concentrations of the organic compounds. The model proved to be able to predict with good accuracy the concentration evolution of clofibric acid and the main intermediates, 4-chlorophenol and p-benzoquinone, using different photocatalyst concentrations and irradiation levels. A very good correlation between calculated and experimental values of CA concentration was obtained with root-mean-square errors below 11%.

## Appendix. Derivation of the kinetic model

Firstly, competitive adsorption among the main pollutant, clofibric acid, and the intermediates was considered. The following equations can be written:

$$[CA_{ads}] = K_{CA} [site_{CA}] C_{CA} \quad (1)$$

$$[4-CP_{ads}] = K_{4-CP} [site_{CA}] C_{4-CP} \quad (2)$$

$$[p-BQ_{ads}] = K_{p-BQ} [site_{CA}] C_{p-BQ} \quad (3)$$

where  $[i_{ads}]$  is the superficial concentration of the adsorbed species,  $K_i$  is the equilibrium adsorption constant of each species,  $[site_i]$  represents the superficial concentration of vacant sites and  $C_i$  is the concentration of  $i$  in the bulk. The adsorption equation for oxygen can be expressed as:

$$[O_{2,ads}] = K_{O_2} [site_{O_2}] C_{O_2} \quad (4)$$

By making a balance of sites, the total concentration of sites  $[site_{i,T}]$  could be related to the concentration of vacant sites and concentration of occupied sites  $[site_{i,oc}]$  by oxygen or organic compounds:

$$[site_{O_2,T}] = [site_{O_2,oc}] + [site_{O_2}] \quad (5)$$

$$[site_{CA,T}] = [site_{CA,oc}] + [site_{CA}] \quad (6)$$

Introducing equation 4 into equation 5 and equations 1-3 into equation 6:

$$[site_{O_2}] = \frac{[site_{O_2,T}]}{1 + K_{O_2} C_{O_2}} \quad (7)$$

$$[site_{CA}] = \frac{[site_{CA,T}]}{1 + K_{CA} C_{CA} + K_{4-CP} C_{4-CP} + K_{p-BQ} C_{p-BQ}} \quad (8)$$

Since it was assumed that the organic compounds are mainly attacked by hydroxyl radicals and taking into account the photoreaction mechanism, the following photodegradation rates are proposed:

$$r_{CA} = k_{8,1}[HO^\cdot][CA_{ads}] + k_{8,2}[HO^\cdot][CA_{ads}] \quad (9)$$

$$r_{4-CP} = k_{9,1}[HO^\cdot][4 - CP_{ads}] + k_{9,2}[HO^\cdot][4 - CP_{ads}] \quad (10)$$

$$r_{p-BQ} = k_{10}[HO^\cdot][p - BQ_{ads}] \quad (11)$$

where  $k_i$  is the kinetic constant of the reaction between the compounds and hydroxyl radicals.

$$[HO^\cdot] = \frac{k_4[H_2O_{ads}][h^+] + k_7[O_2^-][H_2O_2]}{(k_{8,1} + k_{8,2})[CA_{ads}] + (k_{9,1} + k_{9,2})[4 - CP_{ads}] + k_{10}[p - BQ_{ads}] + \sum_l k_l[Y_{l,ads}]} \quad (20)$$

By applying the kinetic steady state approximation, the following superficial formation rates for electrons, holes, hydroxyl radicals, superoxide radicals, hydroperoxyl radicals and hydrogen peroxide were proposed:

$$r_{e^-} = r_{gs} - k_2[e^-][h^+] - k_3[e^-][O_{2,ads}] \cong 0 \quad (12)$$

$$r_{h^+} = r_{gs} - k_2[e^-][h^+] - k_4[h^+][H_2O_{ads}] \cong 0 \quad (13)$$

$$\begin{aligned} r_{HO^\cdot} = & k_4[h^+][H_2O_{ads}] + k_7[O_2^-][H_2O_2] - (k_{8,1} \\ & + k_{8,2})[HO^\cdot][CA_{ads}] - (k_{9,1} \\ & + k_{9,2})[HO^\cdot][4 - CP_{ads}] \\ & - k_{10}[HO^\cdot][p - BQ_{ads}] \\ & - \sum_l k_l[HO^\cdot][Y_{l,ads}] \cong 0 \end{aligned} \quad (14)$$

$$r_{O_2^-} = k_3[e^-][O_{2,ads}] - k_5[H^+][O_2^-] - k_7[O_2^-][H_2O_2] \cong 0 \quad (15)$$

$$r_{HO_2^\cdot} = k_5[H^+][O_2^-] - k_6[HO_2^\cdot]^2 \cong 0 \quad (16)$$

$$r_{H_2O_2} = k_6[HO_2^\cdot]^2 - k_7[O_2^-][H_2O_2] \cong 0 \quad (17)$$

where  $r_{gs}$  is the surface rate of electron-hole generation. Rearranging equations 12-17:

$$[e^-] = \frac{r_{gs}}{k_2[h^+] + k_3[O_{2,ads}]} \quad (18)$$

$$[h^+] = \frac{r_{gs}}{k_2[e^-] + k_4[H_2O_{ads}]} \quad (19)$$

$$[H_2O_2] = \frac{k_5[H^+]}{k_7} \quad (21)$$

$$[O_2^-] = \frac{k_3[e^-][O_{2,ads}]}{2k_5[H^+]} \quad (22)$$

From equations 18 and 19, the hole and electron concentrations could be obtained and operating with equation 20-22 the hydroxyl radical concentration is:

[HO]

$$= \frac{3k_3k_4[H_2O_{ads}][O_{2,ads}] \left\{ -1 + \sqrt{1 + \frac{4k_2r_{gs}}{k_3k_4[H_2O_{ads}][O_{2,ads}]}} \right\}}{4k_2\{(k_{8,1} + k_{8,2})[CA_{ads}] + (k_{9,1} + k_{9,2})[4 - CP_{ads}] + k_{10}[p - BQ_{ads}] + \sum_l k_l[Y_{l,ads}]\}} \quad (23)$$

Assuming that  $[H_2O_{ads}]$  and  $[O_{2,ads}]$  are constant and considering that there are no mass transfer limitations, the obtained photodegradation rate of clofibric acid was:

area is affected by the catalyst interfacial area per unit suspension volume,  $\alpha_v = S_g C_{cat}$ . Thus, the final expression is:

$$r_{CA} = \frac{(\alpha_{2,1} + \alpha_{2,2})C_{CA} \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a}{S_g C_{cat}}} \right\}}{1 + \alpha_3 C_{CA} + \alpha'_3 C_{4-CP} + \alpha''_3 C_{p-Bzq}} \quad (27)$$

$r_{CA}$

$$= \frac{(\delta_{2,1} + \delta_{2,2})[CA_{ads}] \left\{ -1 + \sqrt{1 + \delta_1 r_{gs}} \right\}}{\delta_3 \{(k_{8,1} + k_{8,2})[CA_{ads}] + (k_{9,1} + k_{9,2})[4 - CP_{ads}] + k_{10}[p - BQ_{ads}]\} + 1} \quad (24)$$

where:

$$\delta_1 = \frac{4k_2}{k_3k_4[H_2O_{ads}][O_{2,ads}]}$$

$$\delta_{2,1} = \frac{3k_3k_4k_{8,1}[H_2O_{ads}][O_{2,ads}]}{4k_2 \sum_l k_l[Y_{l,ads}]}$$

$$\delta_{2,2} = \frac{3k_3k_4k_{8,2}[H_2O_{ads}][O_{2,ads}]}{4k_2 \sum_l k_l[Y_{l,ads}]}$$

$$\delta_3 = \frac{1}{\sum_l k_l[Y_{l,ads}]}$$

where:

$$\alpha_1 = \delta_1 \bar{\phi}$$

$$\alpha_{2,1} = \delta_{2,1} K_{CA} [site_{CA,T}]$$

$$\alpha_{2,2} = \delta_{2,2} K_{CA} [site_{CA,T}]$$

$$\alpha_3 = \delta_3 (k_{8,1} + k_{8,2}) K_{CA} [site_{CA,T}] + K_{CA}$$

$$\alpha'_3 = \delta_3 (k_{9,1} + k_{9,2}) K_{4-CP} [site_{CA,T}] + K_{4-CP}$$

$$\alpha''_3 = \delta_3 k_{10} K_{p-BQ} [site_{CA,T}] + K_{p-BQ}$$

Substituting equations 1-3 and 8 into equation 24 and rearranging:

$$r_{CA} = \frac{(\alpha_{2,1} + \alpha_{2,2})C_{CA} \left\{ -1 + \sqrt{1 + \delta_1 r_{gs}} \right\}}{1 + \alpha_3 C_{CA} + \alpha'_3 C_{4-CP} + \alpha''_3 C_{p-BQ}} \quad (25)$$

By knowing that the surface rate of electron-hole generation takes the form:

$$r_{gs} = \frac{\bar{\phi} e^a}{\alpha_v} \quad (26)$$

where  $e^a$  corresponds to the local volumetric rate of photon absorption (LVRPA) and  $\bar{\phi}$  is the primary quantum yield averaged over all wavelengths. Reaction rate per unit catalytic

Following the same procedure, the expressions of the 4-chlorophenol and p-benzoquinone were obtained:

$$r_{4-CP} = \frac{(\alpha_{4,1} + \alpha_{4,2})C_{4-CP} \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a}{S_g C_{cat}}} \right\}}{1 + \alpha_3 C_{CA} + \alpha'_3 C_{4-CP} + \alpha''_3 C_{p-BQ}} \quad (28)$$

$$r_{p-BQ} = \frac{\alpha_5 C_{p-Bzq} \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a}{S_g C_{cat}}} \right\}}{1 + \alpha_3 C_{CA} + \alpha'_3 C_{4-CP} + \alpha''_3 C_{p-BQ}} \quad (29)$$

where:

$$\alpha_{4,1} = \frac{3k_3k_4k_{9,1}[H_2O_{ads}][O_{2,ads}]K_{4-CP}[site_{CA,T}]}{4k_2 \sum_l k_l [Y_{l,ads}]}$$

$$\alpha_{4,2} = \frac{3k_3k_4k_{9,2}[H_2O_{ads}][O_{2,ads}]K_{4-CP}[site_{CA,T}]}{4k_2 \sum_l k_l [Y_{l,ads}]}$$

$$\alpha_5 = \frac{3k_3k_4k_{10}[H_2O_{ads}][O_{2,ads}]K_{p-BQ}[site_{CA,T}]}{4k_2 \sum_l k_l [Y_{l,ads}]}$$

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### NOMENCLATURE

$a_v$  = interfacial area per unit suspension volume,  $m^{-1}$

$C_{cat}$  = mass catalyst concentration,  $g \cdot cm^{-3}$

$C_i$  = molar concentration of compound  $i$  in the bulk,  $mmol \cdot L^{-1}$

CA = clofibric acid

$e^a$  = averaged volumetric rate of photon absorption,  $Einstein \cdot cm^{-3} \cdot s^{-1}$

$e^a(x)$  = local volumetric rate of photon absorption,  $Einstein \cdot cm^{-3} \cdot s^{-1}$

4-CP = 4-chlorophenol

$g$  = asymmetry factor

$k$  = kinetic constant, its units depend on the step considered

$K$  = equilibrium constant

LVRPA = local volumetric rate of photon absorption,  $Einstein \cdot cm^{-3} \cdot s^{-1}$

$p$  = phase function, dimensionless

p-BQ = p-benzoquinone

$q$  = radiation flux,  $Einstein \cdot cm^{-2} \cdot s^{-1}$

$r_{gs}$  = surface rate of electron-hole generation,  $mol \cdot cm^{-2} \cdot s^{-1}$

$r_i$  = photodegradation rate of compound  $i$ ,  $mmol \cdot L^{-1} \cdot h^{-1}$

$S_g$  = catalyst specific surface area,  $m^2 \cdot g^{-1}$

$t$  = time, h

$V$  = Volume, L

VRPA = volumetric rate of photon absorption,  $Einstein \cdot cm^{-3} \cdot s^{-1}$

$X_i, X_j$  = secondary organic intermediates

$Y_l$  = inorganic species

### Greek letters

$\alpha_i$  = kinetic parameter

$\beta$  = extinction coefficient,  $cm^{-1}$

$\phi$  = primary quantum yield,  $mol \cdot Einstein^{-1}$

$\bar{\phi}$  = wavelength averaged primary quantum yield,  $mol \cdot Einstein^{-1}$

$\kappa$  = absorption coefficient,  $cm^{-1}$

$\lambda$  = wavelength, nm

$\Gamma$  = global reflection coefficient of the reactor windows

$\theta$  = spherical coordinate, rad

$\sigma$  = scattering coefficient,  $cm^{-1}$

$\omega$  = spectral albedo

### Subscripts

4-CP = relative to 4-chlorophenol

0 = initial value or relative to the reactor window at  $x=0$

$\lambda$  = indicates a dependence on wavelength

CA = relative to clofibric acid

Cat = relative to catalyst

Exp = experimental value

L= relative to the reactor window at  $x = L$

Mod = simulated value

p-BQ = relative to p-benzoquinone

R=reactor

T = total

Tk= tank reservoir

$V_R$  = relative to reactor volume

W=wall

### **Special symbols**

$\langle \ \rangle$  = average value over a defined space

$[ \ ]$  = relative to surface concentration



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# TiO<sub>2</sub>-rGO PHOTOCATALYTIC DEGRADATION OF AN EMERGING POLLUTANT: KINETIC MODELLING AND DETERMINATION OF INTRINSIC KINETIC PARAMETERS

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## SUPPORTING INFORMATION

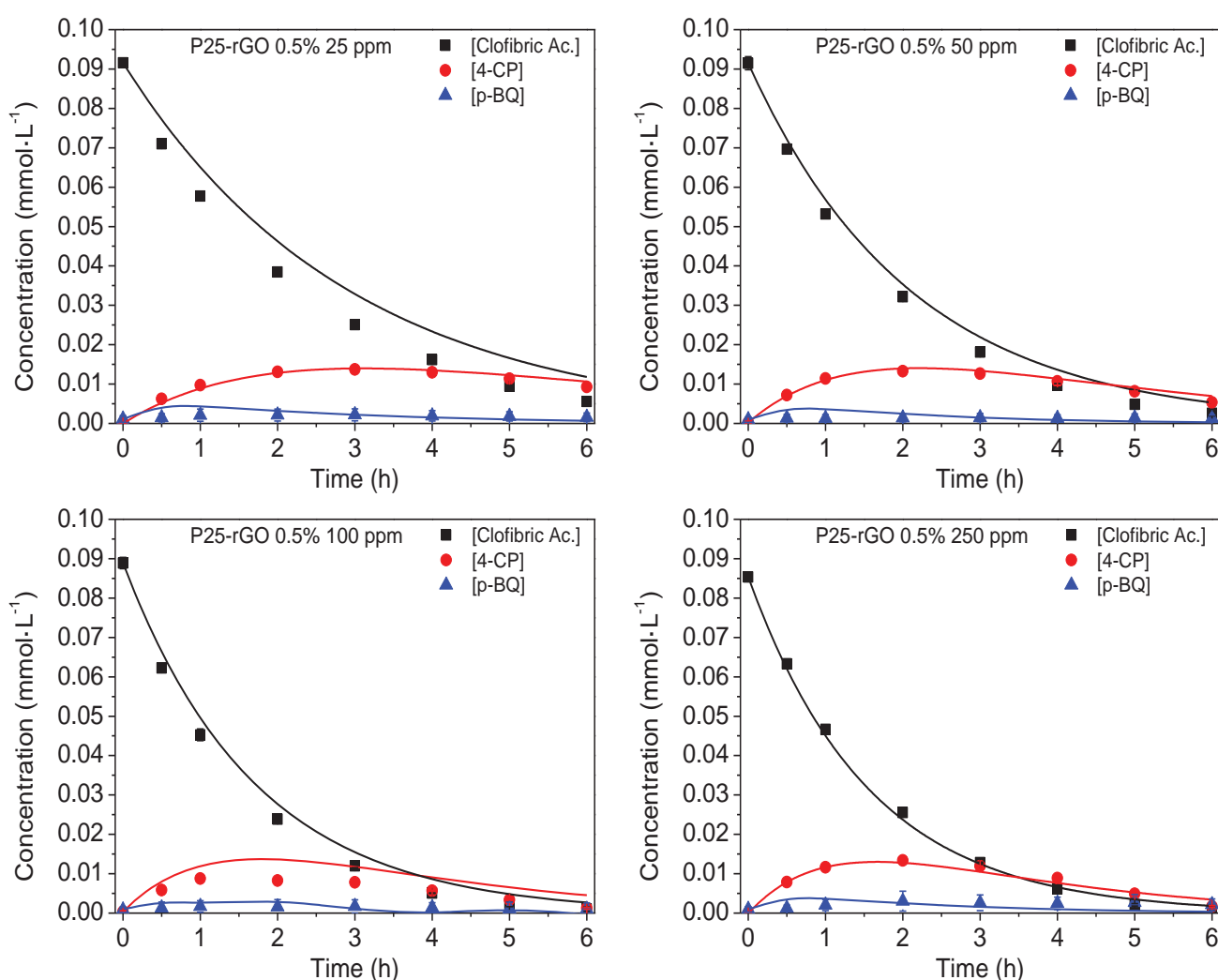


Figure S1. Evolution of clofibric acid (CA) concentration and the main intermediates, 4-chlorophenol (4-CP) and p-benzoquinone (p-BQ), at different photocatalyst loadings of P25-rGO 0.5%. The predicted values (solid lines) were obtained with the 5-parameter model.

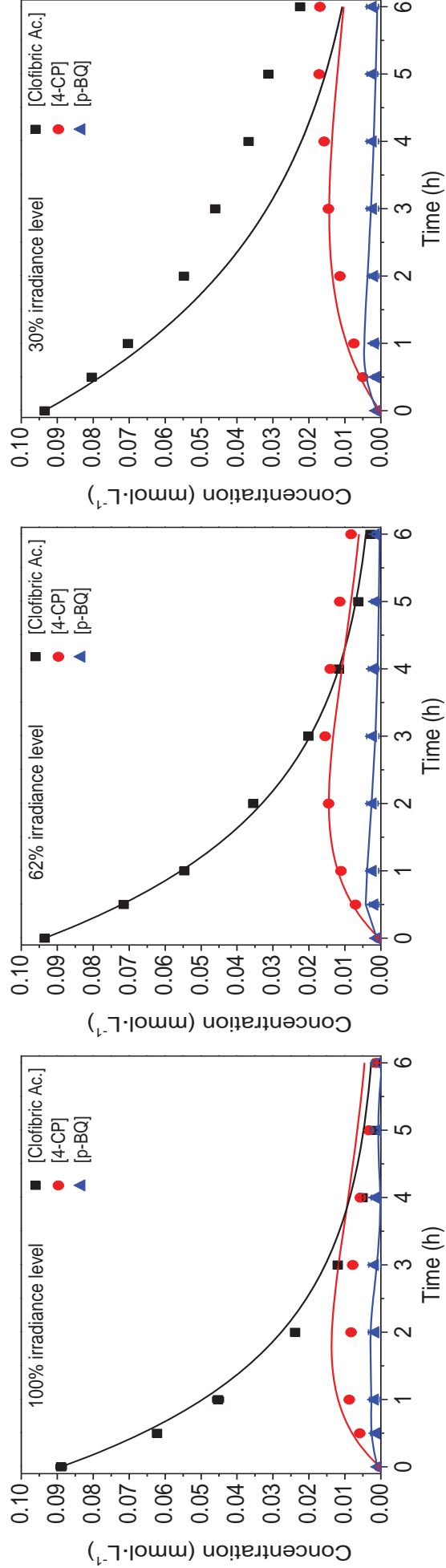


Figure 2. Evolution of clofibric acid (CA) concentration and the main intermediates, 4-chlorophenol (4-CP) and p-benzoquinone (p-BQ), at different irradiation levels using 100 mg.L<sup>-1</sup> of P25-rGO 0.5%. The predicted values of the concentrations (solid lines) were obtained with the 5-parameter model.

# Anexo VII:

Procedimiento experimental

En este capítulo se describen los métodos empleados para la modificación del  $\text{TiO}_2$  y para la preparación de los diferentes nanocomposites de  $\text{TiO}_2$ -rGO. Las técnicas de caracterización de materiales utilizadas se han seleccionado en función del grado de conocimiento requerido de las propiedades físicas y químicas más relevantes, con el objetivo de adquirir la mayor cantidad de información posible de los fotocatalizadores estudiados. Asimismo, se hace una descripción detallada de los sistemas experimentales, métodos de análisis y procedimientos utilizados en el análisis de la fotodegradación catalítica de todos los contaminantes orgánicos estudiados.

## 2.1. SÍNTESIS DE CATALIZADORES $\text{TiO}_2$ -rGO

Los nanocomposites de  $\text{TiO}_2$ -rGO fueron preparados mediante un método hidrotermal, como se representa esquemáticamente en la Figura 2.1. En el caso de los fotocatalizadores estudiados en el capítulo 6 (Figura 1 A), 2 g de  $\text{TiO}_2$  comercial P25 Aeroxide® fueron suspendidos en 400 mL de agua ultrapura y dispersados utilizando una sonda de ultrasonidos de 100 MHz (Misonix Microson 2000XL) durante 1 h. A continuación se añadió la cantidad correspondiente de óxido de grafeno, GO, (Graphenea, concentración de 0,4 wt% en peso) y la mezcla obtenida se sonicó durante una hora más, para homogeneizar el medio y dispersar el GO. Posteriormente la suspensión se llevó a un vaso de teflón de 600 mL que se introdujo en un reactor autoclave de acero inoxidable donde se realizó la síntesis hidrotermal durante 18 h a 120 °C. Por último, la suspensión se lavó exhaustivamente con agua ultrapura mediante centrifugación a 12.000 rpm durante 1 hora y el precipitado se secó en una estufa a 60 °C durante la noche (15 h).

La síntesis de los nanocomposites utilizados en el capítulo 7 (Figura 1 B) se optimizó para reducir la metodología de síntesis. En resumen, 2 g de  $\text{TiO}_2$  comercial P25 Aeroxide® fueron suspendidos en 400 mL de agua ultrapura y agitados durante 30 min a 500 rpm. A continuación se añadió la cantidad correspondiente de óxido de grafeno, GO, (Graphenea Company, concentración de 0,4 wt% en peso) y la mezcla se agitó durante otras 2 h y 30 min para homogeneizar el medio y dispersar el GO. Posteriormente la suspensión se llevó a un vaso de teflón de 600 mL que se introdujo en un reactor autoclave de acero inoxidable, donde se llevó a cabo la síntesis hidrotermal durante 3 h a 120 °C. Por último, la suspensión se lavó con agua ultrapura mediante centrifugación a 12.000 rpm durante 30 min y tras la tercera centrifugación, el precipitado obtenido se secó en una estufa a 50 °C durante la noche (15 h).



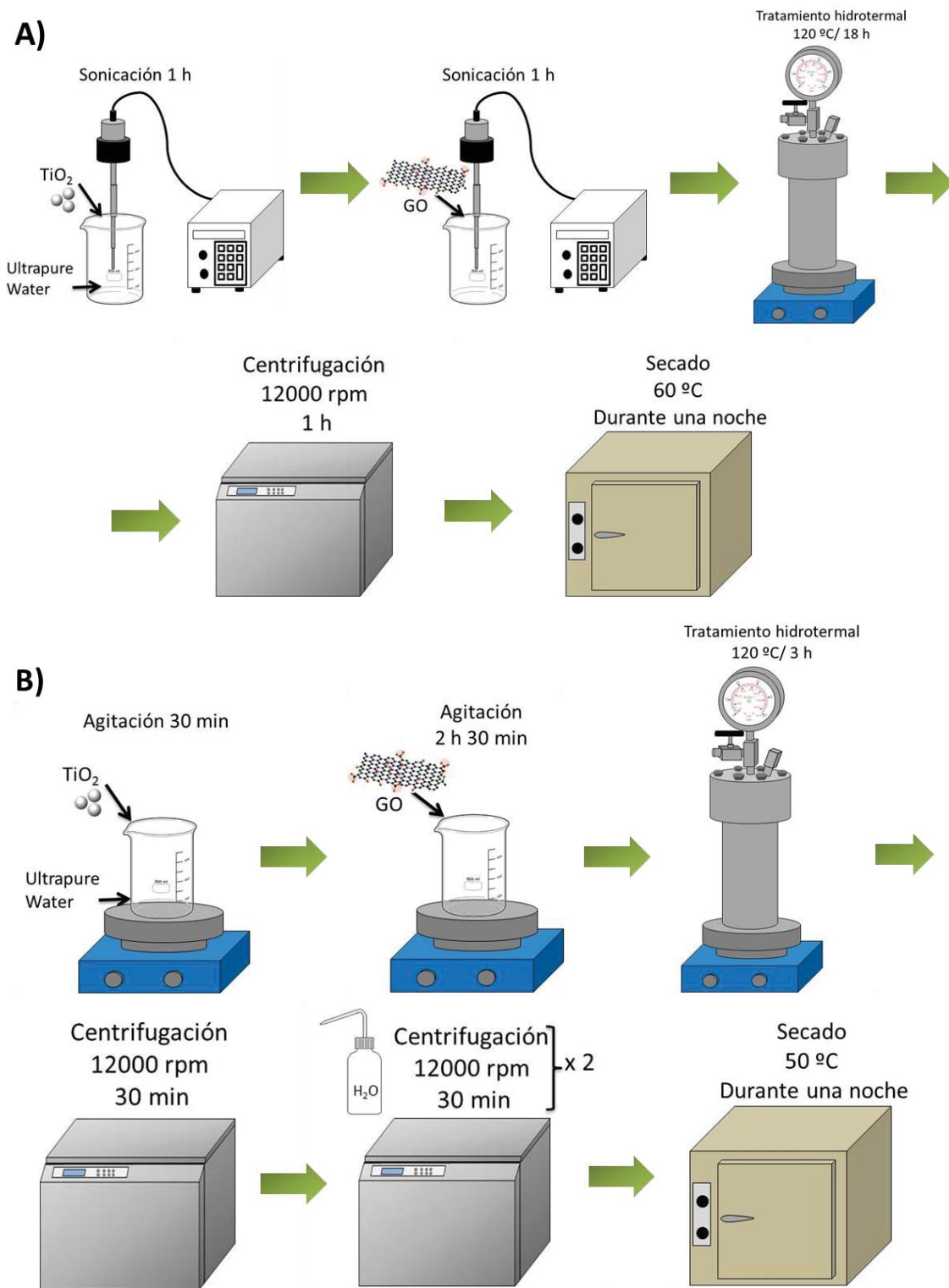


Figura 1. Procedimiento de síntesis de los fotocatalizadores P25-rGO utilizados en los capítulos 6 (A) y 7 (B).



## 2.2. TÉCNICAS DE CARACTERIZACIÓN QUÍMICO-FÍSICA

En esta sección se resumen las diferentes técnicas y equipos empleados para determinar las distintas propiedades de todos los fotocatalizadores estudiados, con el objetivo de poder correlacionar sus propiedades físico-químicas con su actividad fotocatalítica en el proceso en estudio. Además, en la Tabla 1 se resumen y clasifican las diferentes técnicas utilizadas en función del tipo de información que aportan.

Tabla 1. Clasificación y resumen de las técnicas de caracterización físico-química empleadas.

Análisis	Determinación	Técnica
Estructural	Fases cristalinas, tamaño de cristal, proporción de fases detectadas, etc.	Difracción de Rayos X Microscopía TEM Espectroscopía Raman
Textural y morfológico	Área superficial, Volumen y distribución de poros, topografía superficial	Isotermas adsorción-desorción de N <sub>2</sub> Porosimetría de mercurio Microscopía SEM
Superficial	Acidez	Isotermas de adsorción-desorción de NH <sub>3</sub>
	Grupos Superficiales	DRIFTS, FT-IR
Análisis Elemental	Composición química	EDX
Electrónico	Medidas del band-gap	UV-Visible de sólidos
	Dinámica de las cargas fotogeneradas	EPR Espectroscopía de absorción transitoria
Caracterización electroquímica	Transferencia de los pares e <sup>-</sup> /h <sup>+</sup>	Espectroscopía de impedancia Voltamperometría de Barrido Lineal Fotocorriente inducida
Suspensión en fase acuosa	Tamaño de partícula hidrodinámico, punto de carga cero, potencial zeta, etc.	Movilidad electroforética Difracción láser

## 2.2.1. ANÁLISIS ESTRUCTURAL

### 2.2.1.1. DIFRACCIÓN DE RAYOS X (XRD)

La difracción de rayos X (X-Ray Diffraction, XRD) es una técnica no destructiva que permite identificar y cuantificar las fases cristalinas presentes en un sólido. Esta técnica se basa en sólidos cristalinos, es decir, formados por átomos ordenados de forma tridimensional y periódica, que son capaces de difractar radiación electromagnética con longitud de onda similar a la distancia entre los átomos del cristal. Cada compuesto da lugar a un patrón de difracción específico, siendo posible la identificación de cada una de las fases cristalinas mediante su comparación con patrones de difractogramas de referencia existentes en bases de datos, como el *International Centre for Diffraction Data* (ICDD).

Además, la difracción de rayos X permite determinar el tamaño medio de cristal de cada una de las fases cristalinas presentes mediante la ecuación de Debye-Scherrer. Además, se puede cuantificar también la proporción de cada una de las fases en función del área o intensidad de los picos de difracción.

Para la obtención del difractograma de los diferentes fotocatalizadores empleados en esta memoria se ha empleado un difractómetro de rayos X X Policristal PANalytical X'Pert PRO, usando la radiación  $K\alpha$  del cobre ( $1.541874 \text{ \AA}$ ) con filtro de níquel y detector ultrarrápido X'Celerator. Las medidas de DRX de las muestras en polvo se registraron operando a 40 kV y 40 mA en el intervalo de  $2\theta$  de 40 a 90° con un paso de 0,02 °/s y un tiempo de acumulación de 50 s por punto. La cuantificación de cada una de las fases cristalinas identificadas se calculó de manera automática mediante el software X'Pert Highscore Plus utilizando el método RIR (*Reference Intensity Ratio*).

### 2.2.1.2. MICROSCOPIA ELECTRÓNICA DE TRANSMISIÓN (TEM)

La Microscopía Electrónica de Transmisión (*Transmission Electron Microscopy*, TEM) y de alta resolución (HRTEM) es una técnica que permite conocer la estructura y morfología de una muestra a escala nanométrica. Estos microscopios están formados por sistemas ópticos complejos capaces de generar imágenes de alta magnificación. Estas imágenes se generan tras incidir un haz de electrones sobre la muestra, siendo los electrones transmitidos y dispersados en la dirección del haz, recogidos y focalizados.

El análisis TEM de las muestras se realizó empleando un Microscopio electrónico de transmisión JEOL 2100F, operando a 200 kV. Las muestras en polvo se depositaron en una rejilla de cobre recubierta con un polímero orgánico.

### 2.2.1.3. ESPECTROSCOPIA RAMAN

La espectroscopía Raman se basa en la dispersión inelástica de luz monocromática, normalmente procedente de un láser. Los fotones emitidos por el láser son absorbidos por la muestra que reemite radiación con una frecuencia diferente a la de la radiación incidente (efecto Raman). Cuando el fotón reemitido tiene una frecuencia inferior a la original, debido a que la molécula original se relaja a un estado excitado, se denomina dispersión Raman *Stokes*. Si por el contrario el fotón reemitido tiene una frecuencia superior a la original, debido a que la molécula se encontraba inicialmente en un estado vibracional excitado, se denomina dispersión Raman *anti-Stokes*. La dispersión Raman *Stokes* es la más utilizada, debido a que es más probable de ocurrir a temperatura bajas y a que proporciona la misma información. Es importante señalar que la excitación de la muestra se puede realizar con un láser que trabaje en el intervalo UV, Vis o IR-cercano.

Los espectros Raman se registraron utilizando un espectrofotómetro Renishaw Micro equipado con un láser de He-Ne que emitía radiación a  $\lambda = 532$  nm con una potencia de 20 mW. Los espectros de las muestras en polvo se obtuvieron utilizando una potencia del láser de 0,2 mW, 5 repeticiones y un tiempo de adquisición de 10 s.

## 2.2.2. ANÁLISIS DE PROPIEDADES ELECTRÓNICAS

### 2.2.2.1. ESPECTROSCOPIA UV-VIS DE SÓLIDOS

Mediante la espectroscopía ultravioleta-visibles (UV-Vis) de sólidos se puede estudiar como interacciona la muestra con radiación electromagnética de la región UV-Vis. En el caso de sólidos semiconductores esta técnica permite estudiar las transiciones electrónicas desde la banda de valencia a la banda de conducción, siempre que la radiación incidente sea suficientemente energética. Además, a partir de los espectros UV-Vis se puede determinar cuantitativamente la energía del band-gap del semiconductor.

El espectro de muestras sólidas se obtiene mediante medidas de reflectancia difusa (R), la cual es definida como la fracción de radiación reflejada por la muestra con respecto a la radiación incidente. Para ello es necesario que el espectrofotómetro este equipado

con una esfera integradora, para que toda la radiación reflejada por la muestra alcance el detector.

Una vez obtenido el espectro, y tras haber realizado la transformación de Kubelka-Mulk, se puede determinar el valor del band-gap ( $E_g$ ) mediante el método de Tauc.

Las medidas de espectroscopía de reflectancia difusa se realizaron en un equipo UV-Vis-NIR Cary 5000 de Varian (Agilent Technologies) equipado con esfera integradora con referencia interna de Spectralon® en el intervalo de longitudes de onda entre 200 y 900 nm. La muestra en polvo, bien molida, fue preparada en una celda con ventana de cuarzo. Para calcular la energía del band-gap se asumió una transición indirecta.

En el caso del capítulo 6, los espectros de reflectancia difusa fueron registrados en un espectrofotómetro UV-Vis Cary 100 Bio UV-Vis de Varian equipado con esfera integradora.

#### **2.2.2.2. ESPECTROSCOPIA DE RESONANCIA PARAMAGNÉTICA ELECTRÓNICA (EPR)**

La espectroscopía de resonancia paramagnética (EPR) o espectroscopía de resonancia de espín electrónico (ESR) es una técnica analítica que permite la detección directa de radicales libres formados en sistemas químicos o biológicos. Para ello se estudia la absorción de radiación electromagnética (microondas) por parte de una muestra sometida a un campo magnético externo de frecuencia, intensidad y polarización adecuada. Para la detección del sistema catalítico de interés mediante EPR es necesario que tenga electrones desapareados. Cuando el campo magnético aplicado es adecuado, el espín del electrón se alinea de forma paralela o antiparalela al campo, teniendo cada orientación energías distintas, produciendo una separación de niveles discretos de energía (desdoblamiento Zeeman).

Aunque las aplicaciones de la técnica EPR son muy diversas, en el campo de la fotocatalisis destaca por su capacidad de detectar radicales libres en estado sólido, líquido o gaseoso y por la capacidad de detectar centros paramagnéticos generados al iluminar el semiconductor con radiación UV.

En el capítulo 6 de esta memoria se empleó esta técnica para poder evaluar la capacidad de los fotocatalizadores estudiados para generar especies oxidantes. Los huecos fotogenerados en la banda de valencia son capaces de reaccionar con el agua para dar lugar a radicales hidroxilo ( $\text{HO}^\bullet$ ). Por otro lado, los electrones fotogenerados son

capaces de llevar a cabo la reducción de oxígeno originando el radical superóxido ( $O_2^{\bullet-}$ ). Para la detección de estos dos radicales se empleó un atrapador de espín (5,5-dimetil-1-pirrolina N-óxido, DMPO) para de esa forma obtener el espectro de las especies DMPO- $HO^{\bullet}$  y DMPO- $O_2^{\bullet-}$  respectivamente. Los espectros EPR fueron registrados a temperatura ambiente utilizando un espectrómetro EPR MiniScope (MS400 Magnetech GmbH) operando en la frecuencia de banda X (9,43 GHz). Los parámetros de adquisición utilizados para detectar los espectros DMPO- $HO^{\bullet}$  y DMPO- $O_2^{\bullet-}$  fueron los siguientes: centro del campo: 339 mT; amplitud de barrido: 8/6 mT; tiempo de barrido: 25/15 s; número de escaneos: 1; amplitud de modulación: 0,1 mT; potencia: 10 mW; ganancia: 5. Las correspondientes simulaciones de los espectros EPR experimentales fueron obtenidos utilizando el software Winsim 2002.

Las muestras fueron preparadas suspendiendo  $1\text{ g}\cdot\text{L}^{-1}$  de fotocatalizador en agua o dimetilsulfóxido (DMSO) para detectar DMPO- $HO^{\bullet}$  y DMPO- $O_2^{\bullet-}$  respectivamente. Posteriormente las suspensiones se dispersaron en un baño de ultrasonidos. Tras llevar 1 mL de la suspensión a un tubo Eppendorf se añadió posteriormente 200  $\mu\text{L}$  de una disolución de DMPO 40 mM y la mezcla obtenida se agitó para homogeneizar la muestra. La suspensión se transfirió a un capilar de 50  $\mu\text{L}$  de borosilicato (Hirschmann ringcaps). La muestra fue irradiada directamente en el espectrómetro EPR a través de una ventana de cuarzo empleando una lámpara de xenón-mercurio (LC8, Hamamatsu, 200W).

### 2.2.2.3. ESPECTROSCOPIA DE ABSORCIÓN TRANSITORIA (TAS)

La Espectroscopía de Absorción Transitoria (TAS) es una técnica espectroscópica con resolución temporal, muy útil para cuantificar las especies transitorias generadas en reacciones iniciadas por la luz. En el caso de procesos fotocatalíticos permite caracterizar la dinámica de la generación, atrapamiento y recombinación de los huecos y electrones fotogenerados, dado que su resolución puede variar en la escala de cientos de femtosegundos hasta milisegundos. La técnica consiste en un pulso láser (con una duración inferior al tiempo de vida de la especie) que al irradiar la muestra con una longitud de onda adecuada provoca su excitación, generando una determinada cantidad de especies excitadas. A continuación, un segundo haz de luz ('sonda') irradia la muestra, permitiendo monitorear la cinética de la especie mediante la medición de su absorción.

Los estudios de espectroscopía de absorción temporal fueron realizados en un espectrofotómetro de fotólisis por destello láser LKS 80 de Applied Photophysics. Para

las medidas se utilizó el accesorio de reflectancia difusa para medir la reflectancia difusa. Las muestras se excitaron mediante un láser Nd-YAG (Quantel; Brilliant B; 3<sup>er</sup> armónico, 355 nm). Para analizar la absorción de las especies transitorias fotogeneradas la muestra se irradió con una lámpara pulsada de xenón (Osram XBO; 150 W). La radiación reflejada se condujo a un monocromador y al detector (Hamamatsu PMT R928). En todos los experimentos se usaron energías de excitación próximas a 2,2 mJ·cm<sup>-2</sup> por pulso, medida mediante un sistema contador de energía Maestro (Gentec-EO). Se empleó una resistencia terminal de 100 Ω para alcanzar un nivel de luz estable durante todo el experimento y se registraron y promediaron 12 pulsos del láser para reducir la relación señal/ruido. Se registraron datos durante 90 μs tras el pulso del láser. Todos los experimentos se realizaron a temperatura ambiente, empleando catalizador en polvo introducido en una cubeta plana de cuarzo de 2 mm de paso óptico, a la que se inyectaba N<sub>2</sub>, O<sub>2</sub> o N<sub>2</sub> saturado con CH<sub>3</sub>OH durante más de 30 minutos.

Se calcularon los valores correspondientes al cambio de la reflectancia óptica de la muestra ( $\Delta J$ ), a partir de los valores de absorbancia calculados por el software, para analizar los resultados obtenidos mediante reflectancia difusa:

$$\Delta J = 1 - 10^{-Abs} = \frac{I_0 - I}{I_0}$$

Donde  $\Delta J$  está relacionado con la absorción transitoria de las especies fotogeneradas y  $I_0$  e  $I$  representan la luz reflejada antes y después del pulso del láser, respectivamente.

### 2.2.3. ANÁLISIS TEXTURAL Y MORFOLÓGICO

#### 2.2.3.1. ISOTERMAS DE ADSORCIÓN-DESORCIÓN DE N<sub>2</sub>

La técnica más empleada para la determinación del área superficial y la estructura porosa de un sólido poroso es la fisisorción de gases, siendo el N<sub>2</sub> uno de los gases más utilizados.

En esta técnica, el gas en contacto con el sólido produce un equilibrio entre las moléculas adsorbidas y las moléculas en fase gas. La isoterma corresponde a la relación entre la cantidad de gas adsorbido en el sólido a diferentes presiones relativas del gas ( $P/P_0$ , donde  $P_0$  es la presión de saturación del N<sub>2</sub>), manteniendo constante la temperatura.

Para la determinación de la superficie específica ( $S_{\text{BET}}$ ) a partir de esta técnica, la IUPAC recomienda la metodología desarrollada por Brunauer, Emmet y Teller, que desarrollaron la ecuación que hoy se conoce como BET (método BET), que relaciona el volumen adsorbido en una monocapa del gas con la superficie específica.

Para determinar la distribución del tamaño de poro se empleó el método basado en el modelo BJH desarrollado por Barrett, Joyner y Halenda.

Las medidas experimentales de adsorción-desorción de nitrógeno y del área superficial, se llevaron a cabo en un equipo Micromeritics Asap 2420 a 77 K. Las muestras se desgasificaron previamente durante 20 horas a 413 K, con una presión residual de  $10^{-4}$  bar para asegurar que la superficie estuviera limpia, seca y libre de especies adsorbidas.

### 2.2.3.2. POROSIMETRÍA DE INTRUSIÓN DE MERCURIO

La técnica de porosimetría de intrusión de mercurio permite determinar el volumen y distribución del tamaño de poros en el intervalo de los mesoporos (próximo a su límite superior de 50 nm) y de los macroporos (diámetros mayores de 50 nm). Mediante la ecuación desarrollada por Washburn, en la cual se consideran poros cilíndricos, se relaciona los volúmenes de penetración con un radio de poro determinado a partir de un valor del ángulo de contacto ( $\theta=141^\circ$  según la IUPAC) y de la tensión superficial del mercurio ( $\gamma=484 \text{ mN}\cdot\text{m}^{-1}$ ).

Un porosímetro Fisons Instruments Pascal compuesto por los módulos 140 y 240 fue utilizado para llevar a cabo los análisis de la porosimetría de intrusión de mercurio, utilizando alrededor de 0,2 g de muestra, previamente secada a  $110^\circ \text{ C}$  durante 16 horas.

### 2.2.3.3. MICROSCOPIA ELECTRÓNICA DE BARRIDO (SEM)

La microscopía electrónica de barrido (*Scanning, Electron Microscopy, SEM*) permite conocer la morfología de la muestra así como su tamaño de partícula y estado agregación, es decir, permite obtener información morfológica a nivel micrométrico sobre el tamaño y la forma de las partículas que constituyen un material sólido.

Esta técnica consiste en la detección de electrones secundarios y electrones retrodispersados producidos tras interaccionar un haz de electrones con la muestra. La detección de los diferentes electrones permite la formación de una imagen de gran resolución.



El análisis de la morfología de los fotocatalizadores en polvo fue realizado en un microscopio electrónico de barrido Philips XL 30 S-FEG. Se empleó un voltaje de 5 kV y el máximo número de aumentos utilizado fue 20000x. Las muestras se dispersaron en un portamuestras recubierto de carbono y un adhesivo para mantener fijas las partículas de sólido.

## **2.2.4. ANÁLISIS SUPERFICIAL**

### **2.2.4.1. ESPECTROSCOPIA INFRARROJA DE REFLECTANCIA DIFUSA POR TRANSFORMADA DE FOURIER (DRIFTS)**

La espectroscopía infrarroja de reflectancia difusa por transformada de Fourier (DRIFTS) es un tipo de técnica de espectroscopía infrarroja (IR) usada para el estudio de materiales opacos o para medir sólidos cuya absorción es elevada.

En general, la espectroscopía infrarroja estudia la interacción de una muestra con radiación con una longitud correspondiente al intervalo IR del espectro electromagnético, habitualmente en el intervalo de número de ondas entre 400 y 4000  $\text{cm}^{-1}$ . Esta técnica se basa en la radiación IR absorbida que provoca una transición vibracional de la molécula. Es decir, la molécula comienza a vibrar de una determinada manera gracias a la energía que se le suministra mediante luz infrarroja. Las especies químicas se pueden identificar a través de las bandas de absorción detectadas a las diferentes frecuencias, características de las vibraciones asociadas a ciertos enlaces. Para la cuantificación de la intensidad y comparación de los espectros se emplea la función Kubelka-Munk.

En fotocatalisis, este tipo de espectroscopía es particularmente útil para la identificación de hidroxilos superficiales, de los enlaces presentes en la estructura o para obtener información sobre la interacción entre una molécula orgánica y el catalizador.

Los espectros DRIFTS fueron obtenidos utilizando un espectrofotómetro infrarrojo Shimadzu IRTracer-100 equipado con un detector MCT refrigerado por nitrógeno líquido. Los espectros fueron registrados en el intervalo 4000-1000  $\text{cm}^{-1}$ , empleando una resolución de 4  $\text{cm}^{-1}$  y una acumulación de 80 interferogramas. Los espectros de los compuestos fenólicos de referencia se midieron tras ser diluido con KBr.

#### 2.2.4.2. ISOTERMAS DE ADSORCIÓN DE NH<sub>3</sub>

Las isoterma de adsorción de amoníaco (NH<sub>3</sub>) es una técnica analítica que permite conocer la acidez superficial de un sólido, la cual influye en la adsorción de sustratos en un fotocatalizador y, por lo tanto, en su actividad fotocatalítica. Esta técnica se basa en la adsorción de NH<sub>3</sub>, una molécula básica, para evaluar la acidez superficial de un catalizador heterogéneo. De manera que a partir de la interpretación de las isotermas de adsorción de NH<sub>3</sub> se obtuvo el valor total de la acidez superficial del sólido catalítico.

La acidez superficial de los fotocatalizadores estudiados se midió en un equipo ASAP-2010C (Micromeritics). Tras la desgasificación previo durante 18 h a 613 K, las muestras se expusieron a una corriente gaseosa de NH<sub>3</sub> a presiones relativas entre 0,01-0,25 a 300 K (fisisorción + quimisorción). A continuación las muestras fueron nuevamente desgasificadas durante 4 h a 300 K y se realizó una segunda isoterma de adsorción de amoníaco (fisisorción de amoníaco). La diferencia del volumen de gas adsorbido, obtenido por diferencia entre las dos isotermas, corresponde al NH<sub>3</sub> retenido por quimisorción, que sirve para evaluar el número total de centros ácidos superficiales, expresados como meqH<sup>+</sup> por gramo de catalizador.

#### 2.2.5. ANÁLISIS DE LA COMPOSICIÓN QUÍMICA

##### 2.2.5.1. ANÁLISIS DE DISPERSIÓN DE ENERGÍA DE RAYOS X (EDX)

La espectrometría de dispersión de energía de rayos X es una técnica de microanálisis químico habitualmente acoplada a un microscopio electrónico. Esta técnica se basa en hacer incidir sobre la muestra un haz de electrones que provoca transiciones electrónicas entre diferentes niveles de energía. Como consecuencia de la relajación de un ion excitado a su estado inicial se produce la emisión de rayos X, debido a la transferencia de un electrón de un orbital exterior a una capa interior. Cada elemento presenta un espectro de emisión característico. El detector de EDX mide los fotones de rayos X según sus energías incidentes en todo el espectro simultáneamente, siendo el espectro de rayos X evaluado para determinar la composición elemental de la muestra.

Las medidas de EDX se realizaron utilizando un microscopio electrónico de barrido Hitachi S-3000N acoplado a un analizador EDX INCA x-sight de Oxford Instruments. Las muestras, sin modificación previa, se fijaron en el porta-muestras con una cinta adhesiva.

## 2.2.6. CARACTERIZACIÓN DE LA SUSPENSIÓN EN FASE ACUOSA

### 2.2.6.1. MEDIDA DE LA MOVILIDAD ELECTROFORÉTICA

Esta técnica permite determinar el punto de carga nula (PZC), definido como aquel pH en el que la carga superficial es neutra. Cuando el pH del medio es inferior al PZC la superficie estará cargada positivamente al aceptar  $H^+$ . Por el contrario, la carga será negativa cuando el pH del medio sea superior al PZC, debido a la aceptación de  $OH^-$ . Esta técnica se fundamenta en el hecho de que las partículas cargadas en una suspensión en un medio iónico se mueven cuando sobre ellas se aplica un campo eléctrico. Además la dirección en la que se mueven indica si éstas se encuentran cargadas positiva o negativamente.

La determinación del PZC es de gran importancia ya que influye en la interacción de los sustratos con la superficie del fotocatalizador y en el estado de agregación, lo cual afecta a su vez a la cantidad de radiación absorbida y a su sedimentación.

Las medidas del punto de carga nula se realizaron mediante medidas de movilidad electroforética. Para ello se utilizó un Zeta-Meter 3.0 acoplado a un microscopio estereoscópico Unitron FSB-4X, una celda de electroforesis de cuarzo (GT-2), un ánodo de Mo y un cátodo de Pt. Las medidas se llevaron a cabo suspendiendo 20-30 mg de muestra en 200 mL de una disolución 2 mM de KCl en un vaso conectado a un pH-metro. El voltaje aplicado durante las medidas fue 300mV. De este modo, para la determinación del PZC el análisis de la movilidad electroforética se llevó a cabo a través de la variación del pH de las suspensiones desde un pH ácido (pH~3) hasta un pH básico adicionando las cantidades necesarias de HCl y NaOH.

### 2.2.6.2. DIFRACCIÓN LÁSER

La difracción láser permite determinar el tamaño de partícula en una suspensión acuosa, que se denomina tamaño de partícula hidrodinámico. Esta técnica se basa en hacer pasar un rayo láser a través de una suspensión de partículas. La intensidad de la luz dispersada en diferentes ángulos se mide mediante detectores colocados a diferentes ángulos. Posteriormente, la distribución angular de la intensidad de la radiación dispersada es analizada, utilizando la teoría Mie de la dispersión de luz, para calcular el tamaño medio de las partículas. El tamaño de partícula se registra como un diámetro de esfera equivalente al volumen. Es importante destacar que esta teoría supone esfericidad de las partículas.

Las medidas se realizaron en un equipo Malvern MasterSizer S con láser de He-Ne ( $\lambda=632,8$  nm). Las suspensiones se prepararon a pH natural (pH~5,8) y se mantuvieron en agitación durante la medida.

## 2.2.7. CARACTERIZACIÓN ELECTROQUÍMICA

Para la caracterización electroquímica los fotocatalizadores estudiados se prepararon fotoánodos mediante el método “*screen printing*”, detallado en el capítulo 6. Todas las medidas electroquímicas fueron realizadas en una celda electroquímica constituida por tres compartimentos en las que se introducía el fotoelectrodo de trabajo, el contraelectrodo de Pt y el electrodo de referencia (Ag/AgCl/KCl (3 M)). Las medidas electroquímicas fueron realizadas utilizando un potenciostato Zennium y una celda fotoelectroquímica PECC-2 (Zahner-Elektrik GmbH & Co. KG).

### 2.2.7.1. ANÁLISIS DE LA FOTOCORRIENTE INDUCIDA

La evaluación de la fotocorriente inducida permite el estudio de las cargas fotogeneradas por el semiconductor al ser irradiado con luz suficientemente energética. Se trata de una medida similar a la cronoamperometría en la que la celda electroquímica es irradiada de forma intermitente. Por lo tanto, se puede estudiar la evolución de la intensidad de corriente en función del tiempo aplicando un potencial determinado.

Las medidas de la fotocorriente inducida se realizaron utilizando una disolución acuosa de  $\text{Na}_2\text{SO}_4$  0,1 M con 10% v/v de  $\text{CH}_3\text{OH}$  y se aplicó un potencial de 0,8 V vs. Electrodo Reversible de Hidrógeno (ERH). La celda electroquímica fue iluminada con una lámpara de Xe de 300 W y utilizando un filtro AM 1.5-global, proporcionando una intensidad de  $680 \text{ W}\cdot\text{m}^{-2}$  en el intervalo 280-1000 nm (LOT-Quantum Design GmbH). La celda fue irradiada con una frecuencia de 300 mHz.

### 2.2.7.2. ESPECTROSCOPIA DE IMPEDANCIA ELECTROQUÍMICA

Las medidas de impedancia electroquímica se basan en aplicar una perturbación eléctrica en la celda electroquímica (normalmente una onda sinusoidal de amplitud periódica pequeña) y medir su respuesta eléctrica en un intervalo de frecuencias de perturbación. Asumiendo un circuito equivalente al que se ajusta el espectro, se pueden obtener las principales características físicas o químicas del sistema electroquímico. La perturbación aplicada se produce en un generador de ondas procesado por un potenciostato.

Dado que en el sistema se produce la transferencia de electrones entre el electrodo y las especies redox, se produce una corriente faradaica. Esta corriente depende de la velocidad de transferencia de masa y de la velocidad de transferencia de electrones. Por tanto, es fundamental incluir dos resistencias en el circuito equivalente asumido para simular el comportamiento del sistema. Una de ellas representa la cinética de transferencia de carga (resistencia de transferencia de carga) y otra la cinética de transferencia de masa (impedancia de Warburg). Mediante la representación de Nyquist, que describe la respuesta de frecuencia de la celda a la perturbación, se puede conocer la resistencia a la transferencia de carga a partir del diámetro del círculo.

Además, a través de esta técnica, se pueden obtener parámetros tan importantes como el potencial de banda plana ( $V_{fb}$ ) o el tipo de semiconductor. El potencial de banda plana se puede definir como aquel para el cual la pérdida de potencial entre la superficie y el *bulk* de un semiconductor es cero y no hay región de carga espacial. La determinación del potencial de banda plana es fundamental, ya que permite conocer los potenciales de las bandas de conducción y valencia de un semiconductor y por tanto, permite conocer la viabilidad de que una fotorreacción determinada tenga lugar.

Para las medidas de espectroscopía de impedancia electroquímica se empleó una disolución acuosa de  $\text{Na}_2\text{SO}_4$  0,1 M como electrolito. Para determinar la resistencia a la transferencia de carga se realizaron una serie de experimentos donde se aplicó un intervalo de frecuencias entre 0,1-30000 Hz y un potencial fijo de 0 V vs. ERH. En el caso del potencial de banda plana, los espectros se obtuvieron en la región de 1 a 0,2 V vs. ERH con un paso de 25 mV. Cada espectro fue registrado a un potencial determinado en el intervalo de frecuencias entre 0,1-30000 Hz con 10 pasos por década. El circuito Randles fue seleccionado para ajustar el espectro registrado a cada potencial y obtener el valor de la capacitancia de la región de carga espacial ( $C_{sc}$ ). En esta memoria los valores de potencial de banda plana de los fotoánodos se calcularon a partir de la representación de Mott-Schottky ( $C^{-2}$  vs. Potencial aplicado). Para ello, en la representación se determinó el valor de potencial para el cual la tendencia lineal interceptaba con el eje X.

### 2.2.7.3. VOLTAMPEROMETRÍA DE BARRIDO LINEAL

La voltamperometría de barrido lineal se basa en la aplicación de un potencial al electrodo de trabajo, desde un valor inicial de potencial hasta un potencial final, con una determinada velocidad de barrido ( $\text{V}\cdot\text{s}^{-1}$ ). Mediante esta técnica se registra la corriente que circula a través del electrodo de trabajo en función del potencial. Como criterio

estándar la corriente presenta valores positivos, cuando se dan procesos de oxidación, y negativos, en procesos de reducción. La corriente generada en las medidas electroquímicas se debe a procesos faradaicos, que se rigen por la ley de Faraday, según la cual el alcance de una reacción es proporcional a la carga que circula por el electrodo.

En esta memoria se utilizó la voltamperometría de barrido lineal para analizar la corriente de reducción de oxígeno en presencia de los fotocatalizadores estudiados. Para ello, se midió la corriente en el intervalo de potencial de 0,8 V a -0,1 V vs. ERH (electrodo reversible de hidrógeno) en disoluciones saturadas con nitrógeno y oxígeno, con un paso de 10 mV y una velocidad de barrido de 1 mV·s<sup>-1</sup>. La diferencia entre ambos voltamperogramas da lugar a la corriente de reducción de oxígeno. Como electrolito se utilizó una disolución acuosa de Na<sub>2</sub>SO<sub>4</sub> 0,1 M.

## 2.3. MEDIDAS DE LA ACTIVIDAD FOTOCATALÍTICA

En esta sección se describen los reactivos, reactores fotocatalíticos, procedimientos y técnicas de análisis empleadas para evaluar la actividad fotocatalítica en los diferentes estudios incluidos en esta tesis.

### 2.3.1. FOTORREACTORES FOTOCATALÍTICOS

En este apartado se recogen los diferentes sistemas de reacción utilizados a lo largo de esta memoria. En primer lugar se ha empleado un fotorreactor sin recirculación de un 1 L de volumen, utilizado en los capítulos 3, 4 y 5. En el capítulo 6 se han utilizado dos fotorreactores distintos. El primero de ellos consistió en realizar la reacción *in situ* mientras se siguió la evolución del contaminante mediante Espectroscopía Infrarroja por Transformada de Fourier con un accesorio de Reflexión Total Atenuada (ATR-FTIR). El segundo de los reactores utilizados en el capítulo 6 consistió en un fotorreactor cilíndrico de 0,25 L sin recirculación. Por último, en el capítulo 7 se empleó un fotorreactor que formaba parte de un sistema con recirculación. Todos ellos fueron irradiados con fuentes de iluminación externa.

### 2.3.1.1. REACTOR SIN RECIRCULACIÓN DE 1 L

Este sistema de reacción fue empleado en los experimentos realizados en los capítulos 3, 4 y 5. Consiste en un reactor de mezcla perfecta tipo *slurry* discontinuo, de Pyrex con forma cilíndrica. Su diámetro interior es 7,6 cm y su altura 32 cm. Se trata de un reactor multifásico en donde el oxidante ( $O_2$  del aire) en fase gas es burbujeado continuamente a través de una frita de vidrio poroso. El fotorreactor (Figura 2) se sitúa en el centro de un equipo Multirays Apparatus (Helios Italquartz), consistente en una cámara con 10 posiciones de irradiación en las que se han fijado lámparas fluorescentes de dos tipos: 6 Narva LT-T8 BlackLight Blue de 15 W de potencia nominal cada una y con un rango de emisión entre 350-410 nm y 4 lámparas Osram Daylight de 15 W con emisión en el rango de longitudes de onda del visible. La superficie interior de la cámara está recubierta por una lámina de aluminio con elevado poder reflectante. Todas las reacciones fueron realizadas en un volumen de trabajo de 1 L, una irradiancia medida de  $38 \text{ W}\cdot\text{m}^{-2}$  en la región UV-A, pH natural de la suspensión, concentración inicial del compuesto orgánico (fenol, 4-clorofenol, 4-nitrofenol, metil 4-hidroxibenzoato) de  $50 \text{ mg}\cdot\text{L}^{-1}$  y agitación magnética (1000 rpm), empleando la concentración de catalizador deseada.

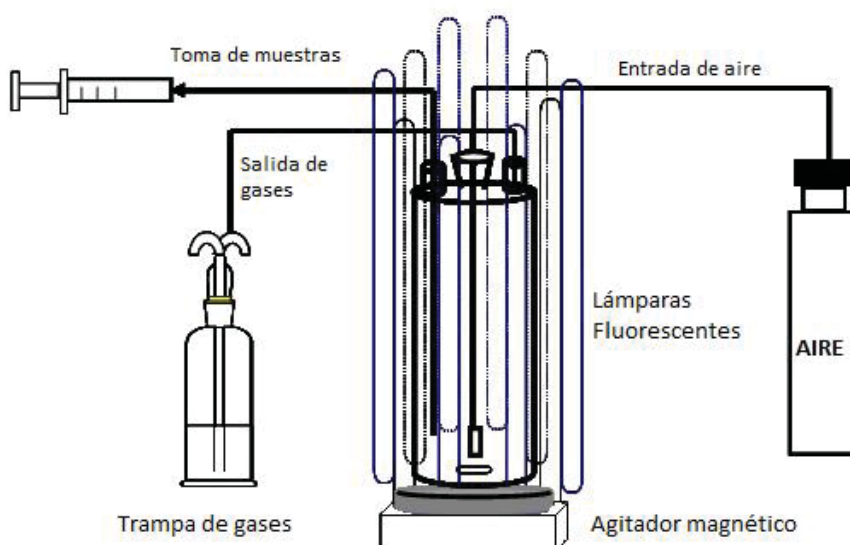


Figura 2. Esquema del fotorreactor slurry discontinuo de 1 L utilizado.

En los estudios de fotoactividad, la cantidad deseada de catalizador se suspendió en la disolución y la mezcla se mantuvo agitando durante 30 min en oscuridad. De esta manera se pretende tanto analizar el efecto de la adsorción del contaminante como alcanzar una mezcla homogénea. Una vez transcurrido este periodo se encendieron todas las lámparas y se comenzó a tomar muestras a diferentes tiempos de reacción.



Por último, antes de analizar las muestras, estas fueron filtradas mediante filtros de jeringa ( $\varnothing = 25$  mm,  $0,45 \mu\text{m}$  de tamaño de poro) con el fin de retener las partículas de  $\text{TiO}_2$ .

Para el estudio de la capacidad de generación de radicales hidroxilo ( $\text{HO}^\bullet$ ) se empleó ácido tereftálico (AT) en medio alcalino como molécula atrapadora. Esta molécula es capaz de reaccionar con los radicales  $\text{HO}^\bullet$  generados por el fotocatalizador, para producir ácido 2-hidroxitereftálico (ATOH), que puede medirse mediante espectroscopía de fluorescencia excitando a  $315$  nm y midiendo la emisión a  $425$  nm, como queda reflejado en la (Figura 3). En resumen,  $0,25 \text{ g}\cdot\text{L}^{-1}$  de  $\text{TiO}_2$  fueron suspendidos en una disolución de  $\text{NaOH}$   $2 \text{ mM}$  en la que se disolvió también una concentración  $0,5 \text{ mM}$  de AT. A continuación, tras agitar la mezcla en oscuridad durante  $30$  min, se encendieron las lámparas y se agitó continuamente el fotorreactor, tomando muestra a diferentes tiempos. Al igual que en el caso anterior, las muestras fueron filtradas antes de ser analizadas mediante filtros de jeringa ( $\varnothing = 25$  mm,  $0,45 \mu\text{m}$  de tamaño de poro) con el fin de retener las partículas de  $\text{TiO}_2$ .

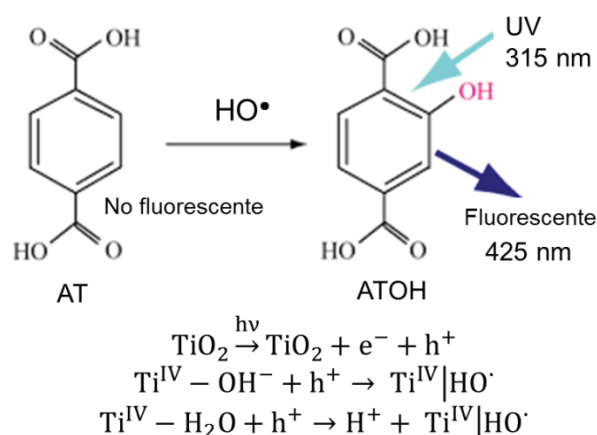


Figura 3. Representación esquemática de la formación y medición de ácido 2-hidroxitereftálico (ATOH) a partir de ácido tereftálico.

### 2.3.1.2. FOTORREACTOR *IN SITU* ACOPLADO A UN ESPECTROFOTÓMETRO INFRARROJO POR TRANSFORMADA DE FOURIER-REFLEXIÓN TOTAL ATENUADA (ATR-FTIR)

Este sistema de reacción fue utilizado en el capítulo 6 para realizar el seguimiento del ácido oxálico adsorbido en la superficie del fotocatalizador, inmovilizado en la superficie del cristal de  $\text{ZnSe}$  del accesorio de ATR. El recubrimiento se preparó suspendiendo  $5 \text{ g}\cdot\text{L}^{-1}$  de fotocatalizador en agua, que fue posteriormente sonicada durante  $15$  minutos en un baño de ultrasonidos. Antes de realizar el recubrimiento, la superficie de  $\text{ZnSe}$  se

limpió con pasta de diamante (Metadi II, polishing grade) y posteriormente se lavó con metanol y agua desionizada. Mientras la suspensión se agitaba, se tomaron 0,4 mL y se extendieron sobre la superficie del ATR. El accesorio fue introducido en un desecador para secar la suspensión a temperatura ambiente.

Para realizar una reacción en este accesorio se construyó un compartimento cerrado de polimetilmetacrilato (PMMA) que se fijaba al accesorio de ATR, como puede verse en la Figura 4. La celda fue irradiada con luz UV-A mediante una lámpara de LEDs (Model LED-Driver, THORLABS), con una longitud de onda máxima de 365 nm (FWHM = 7,5 nm). La lámpara se colocó aproximadamente 30 cm de la superficie de la solución para alcanzar, de esa manera, una intensidad en el intervalo UV-A de  $1,0 \text{ mW}\cdot\text{cm}^{-2}$ .

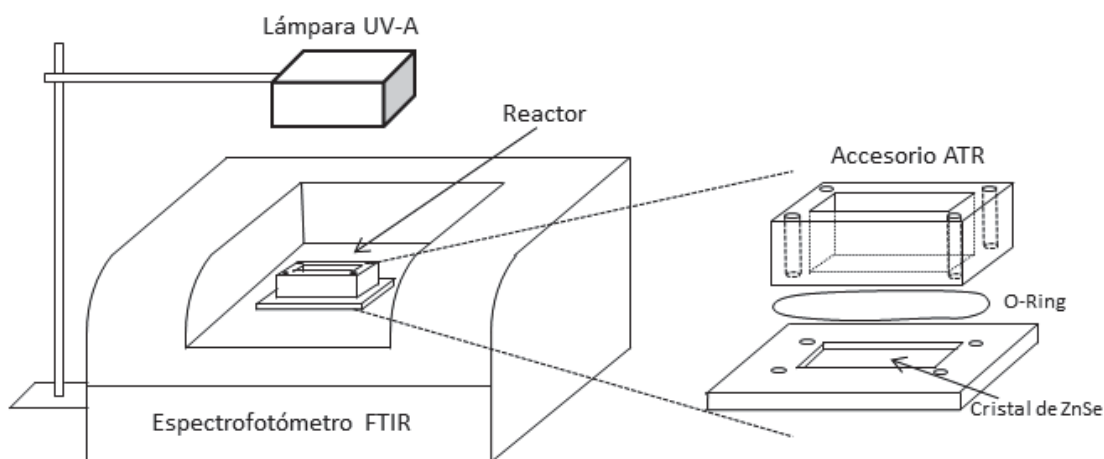


Figura 4. Esquema del sistema experimental usado para realizar la reacción *in situ* en el espectrofotómetro de infrarrojo FTIR con ATR.

Antes de empezar la reacción, se registró un espectro de la película sobre la superficie del cristal. A continuación, se añadieron en la celda 3 mL de agua Milli-Q y se registraron dos grupos de espectros de referencia; primero, se registraron espectros en oscuridad cada 300 s durante 45 min; e inmediatamente después, la celda comenzó a irradiarse, obteniéndose, cada 300 s durante 2 horas, los correspondientes espectros de referencia con iluminación de la muestra en contacto con agua. Tras ser registrados los espectros de referencia en contacto con agua, se sustituyó el agua por 3 mL de una solución 1 mM de ácido oxálico a pH 5 (ajustada con KOH). Dos nuevos grupos de espectros se registraron en presencia de la disolución de ácido oxálico, análogamente al caso del agua. Los espectros finales fueron obtenidos por sustracción del espectro de referencia correspondiente al del ácido oxálico obtenido a los diferentes tiempos.

### 2.3.1.3. FOTORREACTOR SIN RECIRCULACIÓN DE 0,25 L

Los experimentos realizados en el capítulo 6, para analizar la actividad fotocatalítica de los fotocatalizadores suspendidos se llevaron a cabo en un fotorreactor discontinuo. El reactor de vidrio borosilicato, representado en la Figura 5, presentaba geometría cilíndrica y un volumen de 0,25 L. Se situó debajo de 4 lámparas fluorescentes (PHILIPS CLEO 15 W, 365 nm, FWHM = 20 nm) y la distancia de las lámparas se ajustó para alcanzar una irradiancia de  $1,08 \text{ mW}\cdot\text{cm}^{-2}$  medida en el UV-A. En el fotorreactor se añadieron 0,2 L de una disolución 1 mM de ácido oxálico a pH 5 (ajustada con KOH) y  $0,2 \text{ g}\cdot\text{L}^{-1}$  de fotocatalizador. Las reacciones se realizaron a temperatura ambiente y presión atmosférica. La suspensión se burbujeada continuamente con aire mediante un compresor (Elite 801,  $1000 \text{ cm}^3\cdot\text{min}^{-1}$ ).

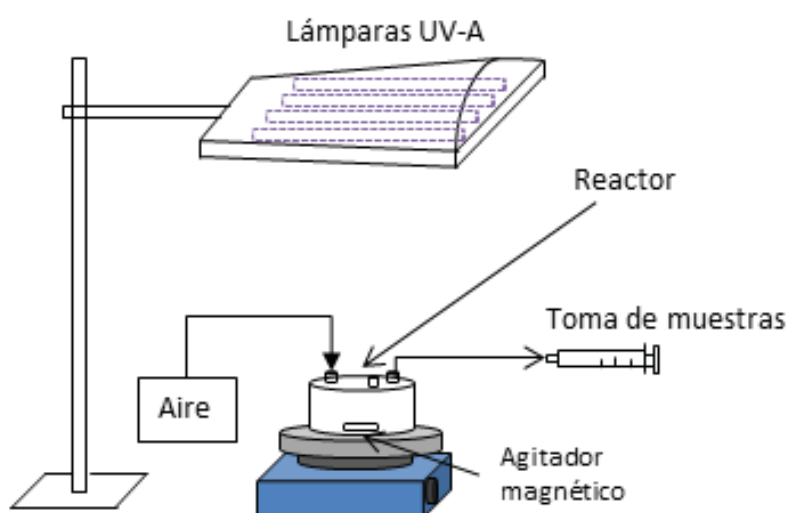


Figura 5. Representación del sistema de fotorreacción sin recirculación de 0,25 L.

Al igual que se ha descrito en los apartados anteriores, la mezcla se dejó agitando durante 4 h en oscuridad para permitir que se alcance el equilibrio de adsorción. A continuación, se encendieron las lámparas y se dejaron estabilizar antes de comenzar la reacción de fotodegradación, manteniendo el fotorreactor recubierto con una caja aislante de poliestireno, para impedir que la radiación incidiese en la suspensión. Tras este periodo, el reactor fue irradiado y se extrajeron muestras cada 15 min. Las muestras fueron filtradas con filtros de jeringa (PTFE,  $0,2 \mu\text{m}$  de tamaño de poro) antes de ser analizadas.

#### 2.3.1.4. FOTORREACTOR CON RECIRCULACIÓN

Este reactor fotocatalítico se utilizó en la obtención de los resultados presentados en el capítulo 7. El sistema consistió en un fotorreactor de acero inoxidable con una pared interior de teflón. Se trata de un reactor cilíndrico (longitud: 2,5 cm, diámetro: 8,6 cm) con dos ventanas circulares de vidrio borosilicato. Para irradiar todo el fotorreactor, en cada lado se colocaron 4 lámparas fluorescentes tubulares (TL 4W/08 Black Light UVA de Philips) paralelas a las ventanas. Estas lámparas presentaron un intervalo de emisión entre 315-415 nm, con un máximo situado alrededor de 355 nm. Para conseguir que la radiación incidente sea difusa, se colocó una pieza circular de vidrio esmerilado entre cada una de las ventanas del fotorreactor y el conjunto de lámparas. El flujo de radiación que llega al interior del reactor, medido mediante actinometría de ferrioxalato de potasio, fue de  $6,3 \cdot 10^{-9}$  Einstein $\cdot$ s $^{-1}$  $\cdot$ cm $^{-2}$  (21,5 W m $^{-2}$ ).

El esquema del sistema experimental utilizado está representado en la Figura 6. Este fotorreactor era parte de un sistema con recirculación, que operaba en modo discontinuo y estaba constituido por una bomba peristáltica, el propio fotorreactor y un depósito encamisado para mantener la temperatura constante a 25 °C durante el experimento. El depósito, en el que se colocaba un termómetro para la medición en continuo de la temperatura, disponía de un sistema de extracción de muestras y una entrada de O $_2$ , el cual se burbujeaba continuamente en la disolución.

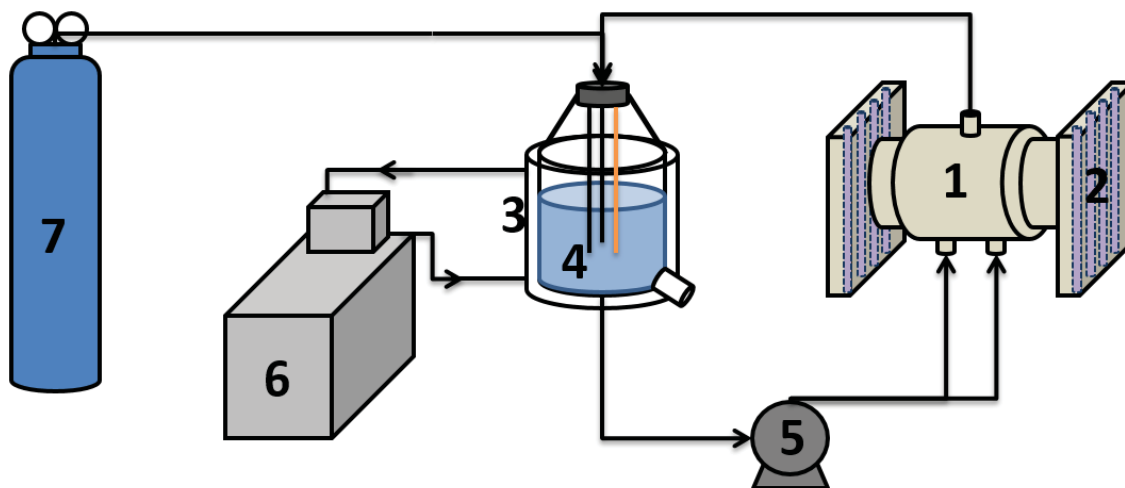


Figura 6. Esquema del sistema de reacción con recirculación: 1, reactor; 2, lámparas UV; 3, camisa del depósito; 4, depósito; 5, bomba; 6, baño termostático; 7, oxígeno.

En los experimentos, realizados a pH natural (pH~5), 1 L de disolución de ácido clorhídrico con una concentración de 20 mg $\cdot$ L $^{-1}$  se mezcló con la cantidad deseada de catalizador. La suspensión así preparada se sonicó durante 30 min en un baño de

ultrasonidos. A continuación, se llevó al depósito y se recirculó con un flujo de  $1,5 \text{ L}\cdot\text{min}^{-1}$  durante 30 min en oscuridad para alcanzar el equilibrio de adsorción. Antes de recircular la mezcla en oscuridad durante 30 min, se inició el burbujeo del  $\text{O}_2$  y se encendieron las lámparas para estabilizar su emisión. Para mantener el reactor en oscuridad y evitar que la radiación incidiese en el fotorreactor se utilizaron obturadores, que se colocaban entre las lámparas y las ventanas del fotorreactor. Después de los 30 minutos se retiraron los obturados y se comenzó la reacción fotocatalítica. Las muestras tomadas a diferentes tiempos fueron centrifugadas a 4000 rpm y filtradas a través de filtros de jeringa (Anatop 25,  $0,2 \mu\text{m}$  de tamaño de poro) antes de ser analizadas.

### 2.3.2. MÉTODOS Y EQUIPOS DE ANÁLISIS

En este apartado se describen y detallan los equipos y métodos de análisis utilizados para realizar el seguimiento de los distintos contaminantes estudiados, compuestos orgánicos, intermedios de reacción e iones presentes en el medio durante las reacciones fotocatalíticas estudiadas.

#### 2.3.2.1. CARBONO ORGÁNICO TOTAL (COT)

La concentración de carbono orgánico total (COT) en disolución se midió mediante un Analizador de Carbono Orgánico Total TOC-V CSH de Shimadzu que mide la concentración de carbono total, carbono inorgánico y de carbono orgánico total.

El COT se determina oxidando la muestra a analizar con aire a  $680 \text{ }^\circ\text{C}$  en un reactor de cuarzo en presencia de un catalizador de  $\text{Pt}/\text{Al}_2\text{O}_3$ . El  $\text{CO}_2$  formado en el proceso es cuantificado mediante un analizador de IR no dispersivo. Por otro lado, para la determinación de la concentración de carbono inorgánico, se inyecta una nueva alícuota de muestra en un depósito en el cual, por acidificación con ácido fosfórico al 25%, todos los carbonatos y bicarbonatos disueltos se desprenden en forma de  $\text{CO}_2$ , cuya concentración es de nuevo cuantificada en el detector de IR. Por diferencia se obtiene la concentración final de carbono orgánico total. Se han realizado calibrados para el carbono total con ftalato ácido de potasio y para el carbono inorgánico con carbonato y bicarbonato sódico anhidro.

### 2.3.2.2. CROMATOGRAFÍA LÍQUIDA DE ALTA RESOLUCIÓN (HPLC)

Para conseguir la separación y detección de la mayoría de los compuestos fenólicos y aromáticos estudiados se recurrió a la cromatografía líquida de alta resolución (HPLC). A lo largo de esta memoria se han utilizado dos equipos HPLC distintos:

- HPLC 1: Para la detección y cuantificación de fenol, 4-clorofenol, 4-nitrofenol, metil 4-hidroxibenzoato, así como de todos los posibles intermedios aromáticos generados durante la reacción fotocatalítica (capítulos 3, 4 y 5), como por ejemplo, hidroquinona, resorcinol, catecol, p-benzoquinona, 4-clorocatecol, 4-clororesorcinol, 4-nitrocatecol o ácido p-hidroxibenzoico, se empleó un cromatógrafo de líquidos de alta resolución HPLC de Varian (modelo 920-LC) equipado con un detector de matriz de fotodiodos. Como fase estacionaria se utilizó una columna Nucleosil C18 de 5  $\mu\text{m}$  de tamaño de partícula, 150 mm de longitud y 4,6 mm de diámetro, que se mantuvo a 40 y 30  $^{\circ}\text{C}$ . Para la cuantificación se ha utilizado la relación entre el área del pico y la concentración del compuesto correspondiente, obtenida previa calibración con disoluciones estándar del analito.

En el capítulo 3 la concentración de fenol y sus potenciales intermedios se determinaron utilizando un caudal de 0,8  $\text{mL}\cdot\text{min}^{-1}$  de una mezcla 20:80 metanol:0,1% ácido ortofosfórico en agua como fase móvil.

En el capítulo 5 y 6, los compuestos fenólicos y sus intermedios aromáticos se midieron utilizando como fase móvil una mezcla metanol:agua ácida (0,1 % v/v ácido ortofosfórico) en proporción 40:60 con un caudal de 0,6  $\text{mL}\cdot\text{min}^{-1}$  en el intervalo de 0-8 min y un caudal de 1  $\text{mL}\cdot\text{min}^{-1}$  de la mezcla metanol:agua ácida en proporción 20:80 en el intervalo de 8-18 min. La detección de los compuestos se realizó a 275 nm.

- HPLC 2: para detectar y cuantificar la concentración de ácido clofíbrico, 4-clorofenol y p-benzoquinona, del capítulo 7, se utilizó un HPLC de Waters equipado con un detector UV y una columna C18 a 30  $^{\circ}\text{C}$ . Como fase móvil se usó una mezcla de acetonitrilo:agua ácida (0,1% v/v ácido ortofosfórico) en proporción 70:30 con un caudal de 1  $\text{mL}\cdot\text{min}^{-1}$ . A 227 nm se identificó el ácido clofíbrico y el 4-clorofenol y a 254 nm la p-benzoquinona.

### 2.3.2.3. CROMATOGRAFÍA IÓNICA (IC) O CROMATOGRAFÍA IÓNICA DE ALTA PRESIÓN (HPIC)

La cromatografía iónica (IC) o la cromatografía iónica de alta presión (HPIC) se utiliza para la determinación y cuantificación de ácidos orgánicos de cadena corta, entre otros por ejemplo, ácido fórmico o ácido oxálico, así como distintos iones, por ejemplo nitratos, nitritos o cloruros.

En esta memoria se han utilizado dos equipos IC o HPIC:

- IC: Para detectar y determinar los ácidos orgánicos de cadena corta e iones presentes en el medio de reacción, como resultado de la fotodegradación de fenol, 4-clorofenol, 4-nitrofenol, metil 4-hidroxibenzoato, de los capítulos 3, 4 y 5, se utilizó un cromatógrafo iónico de Metrohm 883 IC con supresor y un detector de conductividad. Como fase móvil se usó una disolución 3,6 mM de  $\text{Na}_2\text{CO}_3$  con un caudal de  $0,7 \text{ mL}\cdot\text{min}^{-1}$ . La supresión se realizó con una disolución de  $\text{H}_2\text{SO}_4$  cuya concentración fue 100 mM. Como fase estacionaria se utilizó una columna modelo Metrosep A supp 7-250 (250 mm de longitud, 4 mm de diámetro) para medir aniones y una columna Metrosep C 6-250 (250 mm de longitud, 4 mm de diámetro) para medir cationes.
- HPIC: Se utilizó cromatografía iónica de alta presión para determinar la evolución de la concentración de ácido oxálico, en el capítulo 6, en un DIONEX ICS-1000 equipado con supresor y con un detector de conductividad. La temperatura del detector se mantuvo a  $35 \text{ }^\circ\text{C}$  durante todo el análisis. Se utilizó una columna Ion Pac AS9-HC (2x250 mm) y una precolumna Ion Pac AG9-HC (2 x 50 mm) de DIONEX. Como fase móvil se utilizó una disolución  $8\cdot 10^{-3} \text{ M}$  de  $\text{Na}_2\text{CO}_3$  y  $1,5\cdot 10^{-3} \text{ M}$  de  $\text{NaHCO}_3$ .

### 2.3.2.4. ESPECTROSCOPIA DE FLUORESCENCIA

La generación de radicales hidroxilo fue evaluada a partir del espectro de fluorescencia correspondiente al ácido 2-hidroxitereftálico (ATOH). Su emisión fue medida utilizando un espectrofotómetro de luminiscencia Perkin-Elmer LS-50B. La muestra se excitó utilizando una longitud de onda de 315 nm y el espectro de emisión se midió en el intervalo 325-650 nm, detectando su máximo de emisión a una longitud de onda de 425 nm.



### **2.3.2.5. ESPECTROFOTÓMETRO INFRARROJO POR TRANSFORMADA DE FOURIER-REFLEXIÓN TOTAL ATENUADA (ATR-FTIR)**

Para determinar la cantidad de ácido oxálico adsorbido en la superficie del catalizador y seguir su evolución durante las fotorreacciones realizadas en el capítulo 6, se utilizó un Espectrofotómetro de Infrarrojo de Transformada de Fourier. El equipo utilizado fue un espectrofotómetro FTIR IFS 66 BRUKER equipado con un detector de sulfato de triglicina deuterado (DTGS) y con un accesorio ATR. El ATR constaba de un cristal de ZnSe de 45° (área = 6,8 mm x 72 mm). Para evitar contaminación de H<sub>2</sub>O y CO<sub>2</sub>, el interferómetro y el camino óptico de la radiación infrarroja se purgaron continuamente con Argón. Los espectros FTIR se obtuvieron en el intervalo de 1200-1800 cm<sup>-1</sup>, con una resolución de 4 cm<sup>-1</sup> y un promedio de 300 escaneos.

# Anexo VIII:

Otras publicaciones

## OTRAS PUBLICACIONES

### Artículos:

- "Optimizing P25-rGO composites for pesticides degradation: Elucidation of photo-mechanism." G. Luna-Sanguino, A. Tolosana-Moranchel, C. Duran-Valle, M. Faraldos, A. Bahamonde. *Catalysis Today* (2019) 328: 172-177.
- "Analysis of photoefficiency in TiO<sub>2</sub> aqueous suspensions: Effect of titania hydrodynamic particle size and catalyst loading on their optical properties." J. Carbajo, A. Tolosana-Moranchel, J. A Casas, M. Faraldos, A. Bahamonde. *Applied Catalysis B: Environmental* (2018) 221: 1-8.
- "Solar-assisted photodegradation of isoproturon over easily recoverable titania catalysts." A. Tolosana-Moranchel, J. Carbajo, M. Faraldos, A. Bahamonde. *Environmental Science and Pollution Research* (2017) 24: 7821-7828.
- "Effect of water composition on the photocatalytic removal of pesticides with different TiO<sub>2</sub> catalysts." J. Carbajo, P. García-Muñoz, A. Tolosana-Moranchel, M. Faraldos, A. Bahamonde. *Environmental Science and Pollution Research*: (2014) 21: 12233-12240.

### Contribuciones a congresos:

- "New insights on environmental heterogeneous photocatalysis". **A.Tolosana-Moranchel**, G. Luna-Sanguino, M. Faraldos, A. Bahamonde. V Reunión Nacional de Grupos de Fotocatálisis (Islas Canarias, Septiembre 2018). Comunicación Oral.
- "Fotodegradación catalítica de NO<sub>x</sub> sobre recubrimientos autolimpiantes de TiO<sub>2</sub>-rGO: Interacción con el soporte". M. Faraldos, G. Luna-Sanguino, **A. Tolosana-Moranchel**, Q. Jin, K. E. Kurtis, A. Bahamonde. XXVI Congreso Ibero-Americano de Catálise, CICAT 2018 (Coimbra, Septiembre 2018). Comunicación póster.
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- “Optimizing the synthesis method of TiO<sub>2</sub>-rGO composites for enhancing the photodegradation of pesticides”. G. Luna-Sanguino, **A. Tolosana-Moranchel**, C. Durán-Valle, A. Bahamonde, M. Faraldos. 10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications, SPEA 10 (Almería, Junio 2018). Comunicación oral.
- “Photocatalytic-mechanism of phenolic compounds”. A. Montejano, A. **Tolosana-Moranchel**, J. A. Casas, M. Faraldos, A. Bahamonde. 10th World Congress of Chemical Engineering, WCCE10 (Barcelona, Octubre 2017). Comunicación póster.
- “Effect of UV-irradiation-sonication on TiO<sub>2</sub> hydrodynamic particle size and photocatalytic efficiency in aqueous suspensions”. A. **Tolosana-Moranchel**, J. Anderson, G. Luna-Sanguino, J. A. Casas, M. Faraldos, A. Bahamonde. 10th World Congress of Chemical Engineering, WCCE10 (Barcelona, Octubre 2017). Comunicación póster.
- “Effect of different substituents on the photodegradation of phenolic compounds over TiO<sub>2</sub> photocatalysts”. **A. Tolosana-Moranchel**, M. Peñas-Garzón, D. Ovejero-Roncero, J. A. Casas, M. Faraldos, A. Bahamonde. 10th World Congress of Chemical Engineering, WCCE10 (Barcelona, Octubre 2017). Comunicación póster.
- “Optimización de las condiciones de síntesis para composites TiO<sub>2</sub>-rGO aplicados a la fotodegradación de fenol en aguas”. G. Luna-Sanguino, **A. Tolosana-Moranchel**, J. A. Casas, A. Bahamonde, M. Faraldos. Congreso nacional de la Sociedad Española de Catálisis, SECAT (Oviedo, Junio 2017). Comunicación póster.
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- “Study of Chlorophenols abatement in aqueous effluents by Heterogeneous Photocatalysis”. B. Barco, **A. Tolosana-Moranchel**, J. A. Casas, J. J. Rodríguez, A. F. Mohedano, A. Bahamonde, E. Díaz, M. Faraldos. 9th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications, SPEA 9 (Estrasburgo, Junio 2016). Comunicación póster.
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- “Fotodegradación de una mezcla de pesticidas: evaluación de la recuperación del catalizador”. P.García-Muñoz, J.Carbajo, **A. Tolosana-Moranchel**, M. Faraldos, A. Bahamonde. Congreso nacional de la Sociedad Española de Catálisis, SECAT (Sevilla, Junio 2013). Comunicación oral.