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Photocatalytic degradation of pharmaceuticals in water: Design of nanocatalysts and study of by-products and mechanism
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Photocatalytic degradation of pharmaceuticals in water: Design of nanocatalysts and study of by-products and mechanisms

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CONTENTS

Acronyms and Abbreviations

AOPs	Advanced oxidation processes
CB	Conduction band
CIP	Ciprofloxacin
DC, DCF	Diclofenac
EDS	Energy dispersive X-ray spectroscopy
EG	Ethyleneglycol
ESI	Electrospay Ionisation
GC	Gas Chromatography
$g\text{-}C_3N_4$	Graphitic carbon nitride
h^+	Photogenerated holes
HAADF-STEM	High-angle annular dark-field scanning transmission electron microscopy
HPLC	High Performance Liquid Chromatography
HRTEM	High-resolution transmission electron microscopy
IBU	Ibuprofen
IR	Infrared spectroscopy
LC	Liquid chromatography
LOD	Limit of detection
NMR	Nuclear magnetic resonance
NPs	Nanoparticles
NPC	Nitrogen-doped porous carbon
NPX	Naproxen
NSAID	Nonsteroidal anti-inflammatory drug
$\cdot O_2^-$	Superoxide radicals
·OH	Hydroxyl radicals
PVP	Polyvinylpyrrolidone
Q	Quadrupole mass detector
QQQ	Triple quadrupole mass detector
ROS	Reactive oxygen species
STEM	Scanning transmission electron microscopy

TEM	Transmission electron microscopy
THF	Tetrahydrofuran
TiO_2	Titanium dioxide
ToF	Time-of-flying mass detector
UPLC	Ultra performance liquid chromatography
UV	Ultraviolet
VB	Valence band
vis	Visible
WWTP	Wastewater treatment plant
XPS	X-ray photoelectron spectroscopy

Summary/Resumen

SUMMARY

This PhD thesis pursues the photocatalytic degradation of different pharmaceuticals (paracetamol, ibuprofen, diclofenac, naproxen and ciprofloxacin) in water. For this purpose different photocatalysts were synthesised and characterised. Moreover, the photocatalytic performance of TiO_2 and g-C_3N_4 was tuned by grafting nanoparticles and creating unions between semiconductors to tailor the band gaps of the photocatalysts.

In some cases, the effect of pH in the degradations was assessed and the stability of g-C_3N_4 in some degradations was studied. Furthermore, the mechanism of degradation was studied introducing different scavengers in the degradations in order to identify which active species played a main role in the degradations. The by-products generated were also identified by high resolution mass spectrometry. And different set-ups (different water matrixes, different sources of irradiation, different catalytic systems...) were studied.

The noble metal nanoparticles enhanced the photocatalyst performance avoiding fast electron-hole pair recombination and thank to their plasmonic properties. All degradations followed kinetics of pseudo-first-order.

RESUMEN

Esta tesis doctoral se centra en la degradación fotocatalítica de diferentes medicamentos (paracetamol, ibuprofeno, diclofenaco, naproxeno y ciprofloxacino) en agua. Para este fin diferentes catalizadores fueron sintetizados y caracterizados. La capacidad fotocatalítica del TiO_2 y g-C_3N_4 se modificó depositando nanopartículas sobre ellos, o mediante uniones entre materiales, lo que aumentó su capacidad fotocatalítica.

En algunos casos se estudió el efecto del pH en las degradaciones y la estabilidad del g-C_3N_4 en algunas degradaciones. Además, los mecanismos de degradación fueron estudiados introduciendo capturadores de especies activas en las degradaciones para identificar que especies eran responsables de la degradación de los medicamentos. Los subproductos de degradación fueron identificados con espectrometría de masas de alta resolución y diferentes configuraciones (distintas matrices de agua, distintas fuentes de irradiación, diferentes sistemas catalíticos…) fueron estudiados.

Las nanopartículas metálicas mejoraron la actividad fotocatalítica de los catalizadores al evitar una rápida recombinación del par electrón-hueco gracias a las propiedades plasmónicas de los metales empleados. Todas las degradaciones siguen cinéticas de pseudo-primer orden.

Presentation/Presentación

PRESENTATION

This PhD thesis, entitled "Photocatalytic degradation of pharmaceuticals in water: Design of nanocatalysts and study of by-products and mechanisms" is presented as a compilation of publications. For the time being, most of them have already been published, whereas others have been written and presented in article format considering they will be submitted to journals shortly.

This research is focused on the development, synthesis and characterisation of nanomaterials based on TiO_2 and g-C_3N_4 to be used as photocatalysts to remove emerging pollutants (pharmaceuticals) in water. The former semiconductors were grafted with metal nanoparticles to enhance the photocatalytic performance. The by-products generated in each pharmaceutical degradation were also studied. Moreover, studies in the removal of diclofenac with micro-sized catalysts and sonocatalysis and sonophotocatalysis were also explored as result of a four-month predoctoral stay in the University of Milan (Italy).

A brief and comprehensive summary of each chapter of this thesis is presented below:

Chapter 1 is an introduction that depicts the pharmaceuticals occurrence in the environment, how pharmaceuticals end up in the environment, why this poses a dreaded risk for human health and ecology and different technologies to address this issue.

Chapter 2 is focused on the photocatalytic removal of paracetamol in ultrapure water with different nanocatalysts and irradiating with UV light and visible light. In this paper, two nanomaterials (TiO_2 and g-C_3N_4) grafted with gold nanoparticles were synthesised, characterised and evaluated in the degradation of paracetamol. The effect of pH and reusability of the catalyst in the degradation were also studied.

Chapter 3 deals with the degradation of nonsteroidal anti-inflammatory drugs (NSAIDs) such as ibuprofen, diclofenac and naproxen.

In chapter 3.1, the degradation of ibuprofen in ultrapure water and the identification of its by-products by high resolution mass spectrometry are addressed using two photocatalytic systems: TiO_2/UV and g-C_3N_4/visible light. Furthermore, the influence of pH in the degradations was evaluated. *(Published in Chemosphere).*

The chapter 3.2 presents another study on the ibuprofen photocatalytic degradation. In this work the nanocatalyst g-C_3N_4 decorated with AuAg nanoparticles was synthesised by a novel and simple method. This nanomaterial was broadly characterised, as well as the mechanism responsible of the pollutant degradation. The nanomaterial was evaluated in the degradation of ibuprofen in ultrapure water with visible light and natural sunlight. *(Submitted to Materials).*

The chapter 3.3 contains the results of the research work developed in the University of Milan during a predoctoral stay. It is focused on the photocatalytic, sonolytic and sonophotocatalytic degradation of sodium diclofenac in ultrapure water and drinking water with micro TiO_2 and TiO_2/Ag. In this article several set-ups were evaluated having in sight the implementation of this technology in real-life applications. *(Published in Ultrasonics–Sonochemistry).*

The chapter 3.4 is a continuation of the sodium diclofenac degradation research. In this work, the degradation of diclofenac using g-C_3N_4 as nanocatalyst in ultrapure and drinking water with visible light and natural sunlight was evaluated. Moreover, an exhaustive identification study of by-products was carried out by high resolution mass spectrometry and a degradation mechanism was proposed. To complete the study the active species involves in the degradation were identified by scavengers analysis. *(Published in Journal of Environmental Chemical Engineering).*

In chapter 3.5 the degradation of naproxen with g-C_3N_4 in ultrapure water and drinking water irradiating with visible light and natural sunlight was assessed and compared. The intermediate products were identified by high resolution mass spectrometry and a study to identify the active species involved in the degradation was performed in order to propose a plausible mechanism.

Chapter 4 is devoted to ciprofloxacin (an antibiotic) photodegradation by more complex hybrid nanocatalysts.

In the chapter 4.1 a study of intermediate by-products and mechanism of the photocatalytic degradation of ciprofloxacin in ultrapure water using g-C_3N_4 was carried out *(Published in Chemosphere)*. In chapter 4.2 a new nanohybrid catalyst, based on TiO_2@N-doped carbon core/shell grafted with AuAg bimetallic nanoparticles, was synthesised, characterised and evaluated in the photodegradation of ciprofloxacin.

*Disclaimer: as this thesis is presented as a compendium of publications the format of papers, style of references, usage of English (British or American) may be varied along the chapters depending on the Journals in which the articles were published.

PRESENTACIÓN

La siguiente tesis titulada "Photocatalytic degradation of pharmaceuticals in water: Design of nanocatalysts and study of by-products and mechanisms" es un compendio de publicaciones científicas, de las cuales la mayoría han sido publicadas hasta la fecha, sin embargo, otras han sido escritas en formato artículo y se enviarán a distintas revistas próximamente.

Esta investigación se centra en el desarrollo, síntesis y caracterización de nanomateriales basados en TiO_2 y g-C_3N_4 para ser usados como catalizadores en fotocatálisis con el objetivo de eliminar contaminantes emergentes en agua (medicamentos). Además, se han analizado e identificado los subproductos generados en la degradación de cada medicamento. Adicionalmente, se incluyen estudios sobre la eliminación de diclofenaco en agua con catalizadores micrométricos mediante sonocatálisis y sonofotocatálisis como resultado de una estancia predoctoral de cuatro meses en la universidad de Milán (Italia)

A continuación se resume brevemente el contenido de cada capítulo:

Capítulo 1: consiste en una introducción en la que se presenta el problema medioambiental de contaminación de aguas con medicamentos, como llegan los medicamentos a las aguas, por qué supone un grave problema para el medioambiente y distintas tecnologías para remediar este problema medioambiental.

Capítulo 2: se centra en la degradación fotocatalítica de paracetamol en agua ultra pura con diferentes nanocatalizadores e irradiando con distintas fuentes de luz (UV y visible). En este artículo dos tipos de nanomateriales (TiO_2 y g-C_3N_4) decorados con nanopartículas de oro han sido sintetizados y caracterizados. También se estudió la influencia del pH en la degradación de paracetamol y la vida útil del catalizador.

Capítulo 3: versa sobre la degradación de antiinflamatorios no esteroideos, como el ibuprofeno, diclofenaco y naproxeno.

En el capítulo 3.1 se aborda la fotodegradación del ibuprofeno en agua ultrapura con dos sistemas catalíticos: TiO_2/UV and g-C_3N_4/luz visible y la identificación de los subproductos mediante espectrometría de masas de alta resolución. También se estudió la influencia del pH en las degradaciones. *(Publicado en Chemosphere)*.

En el capítulo 3.2 se presenta otro trabajo sobre la degradación fotocatalítica del ibuprofeno. En este caso usando un catalizador que consiste en g-C_3N_4 dopado con nanopartículas de oro y plata que fue sintetizado mediante un método nuevo y sencillo a partir de un precursor organometálico. El material fue ampliamente caracterizado y se evaluó para la degradación de ibuprofeno con luz visible y luz solar. *(Enviado a Materials)*.

El capítulo 3.3 fue desarrollado durante la estancia predoctoral en la Universidad de Milán. Este trabajo compara la degradación fotocatalítica, sonocatalítica y sonofotocatalíctica del diclofenaco sódico en agua de grifo y agua ultra pura con TiO_2 y TiO_2-Ag como catalizadores e irradiando con luz UV. Además, se evaluaron distintos montajes de degradación enfocados a optimizar esta tecnología para su aplicación real. *(Publicado en Ultrasonics–Sonochemistry)*.

El capítulo 3.4 continúa con la investigación sobre el medicamento diclofenaco sódico. En este caso, se estudió la fotodegradación del diclofenaco con g-C_3N_4 en dos matrices de agua (de grifo y ultra pura) y dos fuentes de irradiación (luz visible y luz solar). Se realizó un estudio exhaustivo sobre los subproductos generados en la degradación mediante espectrometría de masas de alta resolución y se propuso un mecanismo de degradación gracias al estudio de las especies activas involucradas en la degradación. *(Publicado en Journal of Environmental Chemical Engineering).*

El capítulo 3.5 aborda y compara la degradación de naproxeno con g-C_3N_4 en agua ultra pura y de grifo y con luz solar y luz visible. Los productos intermedios fueron analizados e identificados. También se realizó un estudio sobre las especies activas involucradas y se propuso un mecanismo plausible que explica la degradación fotocatalítica.

Capítulo 4: se dedica a la fotodegradación de ciprofloxacino (un antibiótico) y a la síntesis de catalizadores nanohíbridos más complejos.

En el capítulo 4.1 se realizó un amplio estudio sobre los productos intermedios y el mecanismo de fotodegradación del ciprofloxacino en agua ultra pura con g-C_3N_4 como catalizador. *(Publicado en Chemosphere)*.

En el capítulo 4.2 se sintetizó y caracterizó detalladamente un nuevo catalizador de TiO_2 con nanopartículas metálicas y carbono dopado con nitrógeno. Su capacidad fotocatlítica se estudió en la degradación del ciprofloxacino.

*Aviso: Al ser esta tesis un compendio de publicaciones, el formato del los artículos, estílo de las referencias o el tipo de inglés usado (británico o americano) puede variar a lo largo de los capítulos dependiendo de la revista en la que ha sido publicado cada artículo.q

Objectives

OBJECTIVES

This thesis pursues the photocatalytic degradation of pharmaceuticals in water and studies the whole process involved in it. Subsequently, the PhD thesis was developed with the following objectives:

- To synthesise nanomaterials and characterised them to be used as photocatalysts in the degradation of pharmaceuticals in water.
- To synthesise and characterise novel visible-light-driven photocatalysts to take advantage of the solar spectrum (ca 43% visible light) for the degradations.
- To enhance the photocatalysts efficiencies under visible light by grafting noble metals nanoparticles on them.
- To detect and identify the by-products of each pharmaceutical generated in the degradations.
- To study the mechanism of degradation with different catalytic systems.
- To study degradations with different set-ups (tap water, solar light, dynamic assemblies, etc) to be implemented in real-life applications, apart from lab scale.

List of papers

The **published research papers** included in this PhD thesis are:

1. *Photocatalytic degradation of ibuprofen in water using TiO_2/UV and g-C_3N_4/visible light: Study of intermediate degradation products by liquid chromatography coupled to high-resolution mass spectrometry.* Chemosphere 215 (2019) 605-618. (Chapter 3.1). https://doi.org/10.1016/j.chemosphere.2018.10.053

2. *Sonophotocatalytic degradation of sodium diclofenac using low power ultrasound and micro sized TiO_2*. Ultrasonics - Sonochemistry 67 (2020) 105123. (Chapter 3.3). https://doi.org/10.1016/j.ultsonch.2020.105123

3. The *photocatalytic degradation of sodium diclofenac in different water matrices using g-C_3N_4 nanosheets: a study of the intermediate by-products and mechanism.* Journal of Environmental Chemical Engineering 9 (2021) 105827. (Chapter 3.4). https://doi.org/10.1016/j.jece.2021.105827

4. *Study of intermediate by-products and mechanism of the photocatalytic degradation of ciprofloxacin in water using graphitized carbon nitride nanosheets.* Chemosphere 247 (2020) 125910. (Chapter 4.1). https://doi.org/10.1016/j.chemosphere.2020.125910

Chapter 5

Conclusions/Conclusiones

CONCLUSIONS

The conclusions from each work have been exposed at the end of the corresponding scientific article. The general conclusions are reported below:

- Several families of pharmaceuticals (analgesics, NSAIDs and antibiotics) have been efficiently degraded in water (ultrapure and tap water) by photocatalysis using three sources of light (UVA, low power visible light and natural sunlight) and different photocatalysts (TiO_2, Au-TiO_2, g-C_3N_4, Au-g-C_3N_4, AuAg-g-C_3N_4, AuAg-PVP-TiO_2, TiO_2-N doped carbon, AuAg- TiO_2-N doped carbon). The fastest depletions were observed in tap water, with natural sunlight and with photocatalysts grafted with nanoparticles.

- A new approach for the synthesis of semiconductors grafted with metallic nanoparticles (Au NPs and AuAg NPs) through a fast and mild decomposition of an organometallic precursor has been developed. This method allowed the formation of composition-controlled NPs stabilised at the surface of the semiconductor, without the concurrence of any other growth directing ligand or polymer, leading to small-size plasmonic nanoparticles.

- The band gaps of the semiconductors TiO_2 and g-C_3N_4 used as photocatalysts have been tailored by heterojunctions to nanoparticles or union with other materials, which improved charge-carrier separation leading to enhance the photodegradation of the pharmaceuticals.

- The accurate mass and the elementary composition of by-products have been determined by high resolution mass spectrometry. Thanks to MS^2 data, it was possible to discern compounds. Some of the by-products proposed for the pharmaceuticals degradations have been reported for the first time.

- The toxicity of the by-products detected has been assessed according to Cramer rules. The by-products were as toxic as their precursor except for two by-products of ibuprofen which were more toxic. This evidence the need for not only pharmaceuticals degradation but also their by-products, since they can be more toxic than the pharmaceuticals itself and persist in the environment.

- The main active species involved in each degradation process depend on the pharmaceutical and the photocatalyst employed in the degradation. Since the conduction band edge and the valence band edge limit the formation of active species. However some of them might be formed indirectly, as it was the case of hydroxyl radicals with g-C_3N_4, they might be formed from $\cdot O_2^-$ in an indirect manner.

CONCLUSIONES

Las conclusiones de cada trabajo se resumen al final del correspondiente artículo científico. A continuación se muestran las conclusiones generales de la tesis:

- Distintas familias de medicamentos (analgésicos, antiinflamatorios no esteroideos y antibióticos) han sido eficientemente degradadas en agua (ultrapura y de grifo) mediante fotocatálisis usando tres fuentes de radiación (UVA, luz visible de baja potencia y luz solar) y diferentes fotocatalizadores (TiO_2, Au-TiO_2, g-C_3N_4, Au-g-C_3N_4, AuAg-g-C_3N_4, AuAg-PVP-TiO_2, TiO_2-Carbono dopado con nitrógeno, AuAg- TiO_2-Carbono dopado con nitrógeno). Las degradaciones más rápidas fueron observadas en agua de grifo, con luz solar y con catalizadores que contenía nanopartículas metálicas.

- Se ha desarrollado un nuevo método para la síntesis de nanopartículas de oro y oro/plata soportadas sobre semiconductores mediante la descomposición de precursores organometálicos. Este método permite controlar la formación de las nanopartículas sobre la superficie de los semiconductores sin necesidad de ningún ligando o polímero, dando lugar a pequeñas nanopartículas plasmónicas.

- El *band gap* de los semiconductores TiO_2 and g-C_3N_4 usados como fotocatalizadores se ha diseñado mediante heterouniones con nanopartículas o uniones con otros materiales, mejorando así la separación de cargas, lo que dio lugar a una mayor fotodegradación de los medicamentos.

- La masa exacta y composición elemental de los subproductos se determinó con espectrometría de alta resolución. Gracias a los análisis de MS^2 fue posible discernir entre compuestos y proponer sus estructuras. Algunos de los subproductos se detectaron por primera vez.

- La toxicidad de los subproductos se determinó de acuerdo a las reglas de Cramer. Los subproductos son tan tóxicos como los medicamentos de los que proceden, excepto dos subproductos del ibuprofeno que son más tóxico que el propio ibuprofeno. Esto evidencia la necesidad de degradar tanto los medicamentos como los subproductos, ya que algunos subproductos pueden ser más tóxicos que los propios medicamentos y persistir en la naturaleza.

- La principales especies activas involucradas en el proceso fotocatalítico dependen del medicamento y de los catalizadores empleados en la degradación. Los límites de la banda de conducción y banda de valencia de catalizador deben contener a los potenciales de formación de las especies activas. Aunque algunas especies activas se pueden formar de manera indirecta, como en el caso de los radicales hidroxilo con g-C_3N_4, que se pueden formar a partir de $\cdot O_2^-$.

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