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Role of reactive oxygen species on the activity of noble metal-doped TiO₂ photocatalysts

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Graphical abstract

HIGHLIGHTS

- The potential carcinogenic disinfection by-product DCA is removed by photocatalysis
- DCA degradation was achieved using TiO₂/Pt 0.5 wt% photocatalyst
- Role of O₂^{•-}, ·OH_{ads}, ·OH_{free} and h⁺_{VB} radicals is determined in DCA abatement
- DCA decomposition is conducted mainly by ·OH_{free} radicals using TiO₂ as catalyst
- ·OH_{free} radicals from O₂^{•-} play a key role in DCA removal using TiO₂/NM catalysts

Abstract

Modified TiO₂ catalysts are of interest in environmental water remediation since they can lead to efficient electron-hole separation and greatly enhance the photocatalytic properties of TiO₂. Reactive oxygen species (ROS), such as the superoxide radical (O₂^{•-}), hydroxyl radical (·OH), and positive valence band holes (h⁺_{VB}), have been reported as the main oxidative species involved in photocatalytic degradation processes. In this work, the role of these species using TiO₂, TiO₂/Pt 0.5 wt%, and TiO₂/Ag 10 wt% has been examined in order to clarify the oxidation pathways. For this purpose, the contribution of the main oxidative species was analyzed in the photocatalytic degradation of dichloroacetic acid (DCA) solutions using specific scavengers (benzoquinone, tert-butyl alcohol, and formic acid). Moreover, the hydroxyl radicals were quantitatively determined in order better understand the results. Regardless of the catalyst used, it is concluded that ·OH radicals are the major reactive species responsible for DCA degradation and no significant degradation is due to O₂^{•-} radicals. Nevertheless, different ·OH generation pathways were found, depending on the nature of the catalysts. Degradation using TiO₂ was conducted mainly via ·OH radicals generated in the positive holes, while noble metal-doped TiO₂ catalysts generated ·OH radicals through the transformation of O₂^{•-} radicals.

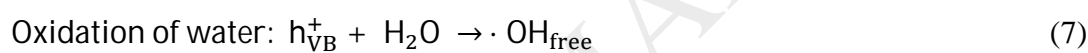
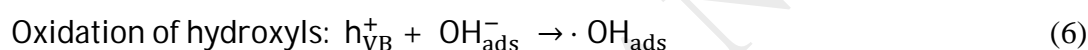
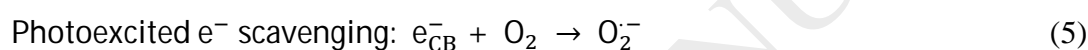
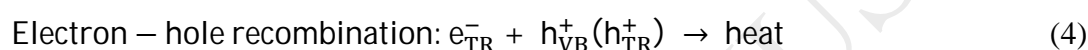
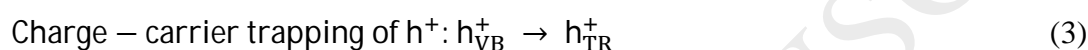
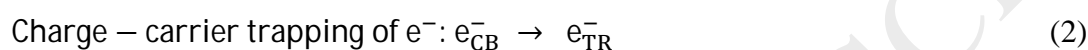
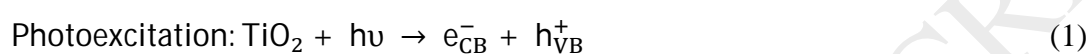
Keywords DCA removal; Reactive oxygen species; scavengers; TiO₂; noble metal

Introduction

Nowadays, water pollution is a worldwide issue for researchers and the global environmental safety community. Therefore, ensuring adequate water resources has become a very important challenge [1]. In this context, haloacetic acids (HAAs) represent the second most important disinfection by-product (DBPs) found in chlorinated drinking waters, after trihalomethanes [2-4]. DBPs are formed during chlorination of water sources due to the reaction between the chlorine and natural organic matter. Several health problems related to DBPs such as growth retardation, spontaneous abortion, cancer and congenital cardiac defects have been widely reported. [5]. Among these HAAs, dichloroacetic acid (DCA) has been classified by the US EPA as a probable human carcinogen (group B2), and has a higher concentration in drinking water than other HAAs [6,7]. Although in Europe the Drinking Water Directive 98/83/EC (DWD) does not currently propose any guideline values for HAAs in drinking water, US EPA drinking water regulations set a maximum contaminant level of 60 $\mu\text{g L}^{-1}$ for five HAAs (trichloroacetic acid (TCAA), dichloroacetic acid (DCA), monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA)) (US EPA, 1998). In addition, Japan's drinking water standards for MCAA, DCA, and TCAA are 20, 40, and 200 $\mu\text{g L}^{-1}$, respectively [8], while in Australia and New Zealand, the regulated limits for drinking water are: MCAA 150; DCAA 100; and TCAA 100 $\mu\text{g L}^{-1}$ [5].

New approaches incorporating the principles of sustainability have motivated the search for technological solutions to provide society with ample water sources while protecting existing resources. Heterogeneous photocatalysis is an advanced oxidation process (AOP) that is expected to play an important role in securing adequate water resources. Its most attractive features are the utilization of solar light as an energy source and the generation of highly reactive oxygen species (ROS) that allow the degradation of a wide range of organic pollutants with no secondary pollution [9]. ROS are relatively short-lived molecules that contain oxygen atoms and unpaired electrons that endow them with higher reactivity [10].

Compared to other semiconducting photocatalysts, titanium dioxide (TiO₂) is, so far, considered the most promising material because it is inexpensive, non-toxic, chemically and thermally stable, abundant, and environmentally friendly [11-14]. The photocatalytic mechanism of TiO₂ under UV light involves absorbing a photon with energy equal or greater to its band gap (3.2 eV) and exciting an electron from the valence band (h^+_{VB}) to the empty conduction band (e^-_{CB}) in femtoseconds, thus creating the electron-hole pair. These charge carriers, with sufficient reductive/oxidative power, can react with the surrounding oxygen-containing species, such as dissolved oxygen or H₂O (OH⁻), to produce ROS (1-7) [13-18].



Superoxide radicals (O₂⁻), hydroxyl radicals ($\cdot\text{OH}_{free}$ and $\cdot\text{OH}_{ads}$), and valence band holes (h^+_{VB}) are the main reactive species involved in organic pollutant degradation. However, the mechanistic implication of these species in photocatalytic processes is still under discussion.

Photocatalytic reactions over TiO₂ are strongly dependent on its surface and interfacial properties with recombination, trapping, and interfacial transfer of charge carriers being very fast processes. However, the rate of interfacial charge transfer to surrounding oxygenated species is much slower (nanoseconds to microseconds) than the rate of charge recombination in the bulk (nanoseconds), and on the surface (picoseconds) of the catalyst. Therefore, enhancing the interfacial charge transfer could minimize the recombination of photogenerated charges. Taking into account this fact, photocatalytic activity of TiO₂ can be improved by employing strategies, that prevent bulk and surface charge recombination and enhance charge transport to the surface sites of TiO₂, such as loading a co-catalyst or constructing nanostructured photocatalysts [19,20].

Noble metal-doped TiO₂ reports improved photocatalytic activity over TiO₂ catalysts due to the Schottky-barrier formation when semiconductor and noble metals are in contact. Noble metal nanoparticles act as electron trap, minimizing the electron-hole pair recombination. Moreover, localized surface plasmon resonance (LSPR) effect associated with noble metal nanoparticles leads to increased electron-hole formation in the semiconductor [21-24].

Previous work has focused on understanding the generation mechanism for ROS and their involvement in the degradation pathways of organic pollutants using selected chemical scavengers [17,25-32]. Research efforts have been aimed at the mechanistic study of the generation of ROS on TiO₂; however, varying results have been reported. Wang and co-workers (2010) [27] indicated that valence band holes were the main active species in the TiO₂ photocatalyst (P25), which could oxidize the adsorbed methylene blue under UV light. However, Raja and co-workers (2005) [28] concluded that superoxide radicals play an important role during the ring opening of a lignin model compound using a TiO₂-P25 semiconductor and UV-Vis light. On the other hand, Chen and co-workers (2005) [29] reported that the photocatalytic degradation mechanism under UV light consisted of the strong absorption of azo dye acid orange 7 molecules on the TiO₂ surface, and then the degradation reaction was mostly initiated by direct electron transfer between a positive hole and an organic molecule. When TiO₂-P25 was tested in recent work developed by Cavalcante and co-workers (2016) [17], a coupled influence of hydroxyl radicals (84%) and valence band holes (10%) was observed during the photocatalytic degradation of metoprolol employing a solar simulator as the light source. The improvement of TiO₂ activity, employing dopants, and constructing heterojunctions, is currently being studied. Nevertheless, how the TiO₂ modifications introduced influence ROS generation is still unclear. Moreover, when TiO₂ was coupled to different dopants, different ROS were involved in organic pollutant degradation pathways. Cruz-Ortiz and co-workers (2017) [30] studied the influence of the light source on ROS generation using TiO₂/rGO catalysts. They reported that superoxide radicals were the main species involved in *Escherichia coli* disinfection under visible light; however, hydroxyl radicals, hydrogen peroxide, and singlet oxygen (¹O₂) conducted the degradation process when UV-Vis light was used. Cavalcante and co-workers (2016) [17] examined the contribution of the main

active species to the photocatalytic degradation of metoprolol using a solar simulator and TiO₂/Boron 5% as the photocatalyst, indicating that ·OH radicals are the dominant reactive species, contributing around 80%, with O₂^{·-} radicals and holes contributing to a lesser extent. Nevertheless, the study developed by Yang and co-workers (2015) [31] showed that active photoinduced holes and O₂^{·-} radicals, rather than ·OH radicals, were the dominant species responsible for rhodamine B (RhB) degradation when P25/Ag₃PO₄/graphene oxide was used as the photocatalyst under visible light. For nitrogen and fluorine doped TiO₂ (NF-TiO₂), studies on the role of ROS suggested that O₂^{·-} and ·OH were involved in cyanotoxin degradation in visible and UV-Vis light, respectively [32]. Therefore, although some researchers have looked at the ROS generated in photocatalytic processes, the role of the reactive oxygen species still remains controversial due to the dependence on the nature of the photocatalyst, light source, and organic pollutant treated. In this context, the mechanisms and photocatalytic degradation pathways using noble metal-doped TiO₂ remain undefined.

The design of novel materials and an in-depth analysis of reaction mechanisms are among the scientific challenges that should be addressed before the full deployment of DCA photocatalytic degradation. This work therefore explores the formation of ROS under UV-Vis light activated TiO₂ catalysts doped with platinum (TiO₂/Pt) and silver (TiO₂/Ag) using selected chemical scavengers with the aim of gaining insight into the degradation pathways attributed to different properties of photocatalysts.

Experimental

Materials

Dichloroacetic acid (DCA), benzoquinone (BQ), and tert-butyl alcohol (t-BuOH) were purchased from Sigma-Aldrich. Titanium dioxide (P25, 20% rutile and 80% anatase) was supplied by Evonik Degussa. Formic acid 37-38% w/w (FA), and copper (II) sulfate 5-hydrate were purchased from Panreac.

Preparation and characterization of TiO₂/Pt and TiO₂/Ag

TiO₂/Pt 0.5 wt% and TiO₂/Ag 10 wt% binary catalysts were prepared using the polyol method; the selected noble metal loads were based on a previous work [23]. The novel

catalysts were characterized via several techniques reported in a previous work [23]. Moreover, X-ray photoelectron spectroscopy (XPS) measurements were performed using a SPECS Phoibos 100 MCD5 system with Mg K α radiation ($h\nu= 1253.6$ eV). The extinction coefficient was determined following the methodology proposed by Cabrera and co-workers (1996) [33] using an UV-1800 spectrophotometer (Shimadzu). The measurements were carried out using a sample cell (optical length, 1 mm) placed far from the detector position and introducing a narrow slit detector to minimize collected out-scattered radiation. Measurements were performed on sonicated suspensions at different catalyst loadings.

Photocatalytic activity

Photocatalytic experiments were carried out in a 1 l Heraeus Laboratory UV Reactor using a 150 W medium-pressure mercury lamp (Heraeus TQ-150, 200-600 nm) placed inside a quartz sleeve provided with a cooling tube to maintain a constant temperature of 20°C. An aqueous solution of copper sulfate (0.05 mol L⁻¹) was circulated to prevent overheating of the suspension and cut off the radiation below 300 nm. The irradiation on the reactor wall was measured with a PHD2102.11 radiometer (Delta OHM), with values of 229.2 W m⁻², 258.9 W m⁻², 27.54 W m⁻² and 961.3 W m⁻² for UV-A, UV-B, UV-C and visible light, respectively, being obtained.

The experimental methodology and analytical procedure of the photocatalytic DCA degradation have been already described in a previous work [23]. Moreover, this work explores the role of ROS during the photocatalytic process and with this aim, BQ, t-BuOH, or FA were added to 1000 mg L⁻¹ DCA solution containing the synthesized catalysts (0.3 g L⁻¹). The study was conducted with a suitable amount of each scavenger compound: 1 g L⁻¹ of BQ; 46.5 g L⁻¹ of t-BuOH; and 4 g L⁻¹ of FA.

•OH and H₂O₂ quantification

The method employed in this work to determine accumulated •OH_{free} radicals in the reaction medium was initially proposed by Tai and co-workers (2004) [34], and it has been already described in a previous work [9]. H₂O₂ measurements were carried out with hydrogen peroxide analytical test kit (photometric method 0.015 - 6.00 mg L⁻¹ H₂O₂ Spectroquant) provided by Merck KGaA. In the presence of a phenanthroline derivative

hydrogen peroxide reduces copper (II) ions to copper (I) ions. In the process an orange-colored complex is formed and it is determined photometrically.

Results and discussion

Catalyst characterization

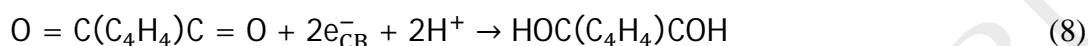
The characterization of the materials has been already discussed in a previous work [23]. Additionally, the surface compositions and elemental chemical states of TiO₂, TiO₂/Pt and TiO₂/Ag were characterized using XPS. Figure 1A shows two XPS peaks of Ti 2p_{3/2} and Ti 2p_{1/2} of Ti at 458.9 eV and 464.5 eV, respectively, in accordance with the binding energy of Ti⁴⁺ in TiO₂. Apart from the two peaks corresponding to Ti⁴⁺, the TiO₂/Pt photocatalyst presented two peaks of Pt 4f_{7/2} and Pt 4f_{5/2} at 70.5 and 73.8 eV, respectively, with a splitting energy of 3.3 eV (Figure 1B), related to the existence of metallic Pt [35]. Moreover, two additional peaks were observed at 72.1 and 75.4 eV attributed to Pt 4f_{7/2} and Pt 4f_{5/2} related to Pt²⁺ states. According to Hsieh and co-workers [36], this fact might be attributed to the formation of Pt-O bond on the TiO₂ surface, or metallic Pt atoms thermally diffusing into TiO₂ crystal lattice and oxidized to Pt²⁺ to substitute for Ti⁴⁺ or form the interstitial ions. XPS spectrum of TiO₂/Ag (Figure 1C) exhibits Ag 3d states in the catalyst surface. Specifically, peaks located at 364.65 eV and 370.29 eV correspond to the binding energy of Ag 3d_{5/2} and Ag 3d_{3/2}, respectively. This typical deviation (6 eV) of the binding energy between Ag 3d_{5/2} and 3d_{3/2} is the characteristic of silver [37]. However, these values are lower than the binding energies of metallic Ag (367.9 and 373.9 eV for Ag 3d_{5/2} and Ag 3d_{3/2}, respectively) and thus, they can be attributed to Ag⁺.

Photocatalytic ROS generation and ·OH_{free} quantification

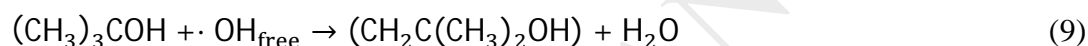
The influence of the O₂⁻, ·OH_{ads}, ·OH_{free}, and h⁺_{VB} radicals in the photocatalytic process using noble metal-doped TiO₂ catalysts was investigated through DCA degradation under UV-Vis light employing different scavengers. The excitation of the semiconductor provokes the generation of an empty unfilled valence band (h⁺_{VB}) and photogenerated electrons in the conduction band (1). In the valence band, the h⁺_{VB} can react directly with the adsorbed hydroxide ion (OH⁻) producing the ·OH_{ads} radical (6), or with water molecules to form the ·OH_{free} radical (7). Moreover, the h⁺_{VB} can act directly as an active degradation species. Finally, the photogenerated electrons of the conduction band result

in $O_2^{\cdot-}$ radical formation through the reduction of oxygen molecules by electron transfer (5).

BQ was used as a scavenger to test the role of $O_2^{\cdot-}$ radicals on photocatalytic degradation because it acts as a more efficient electron scavenger than molecular oxygen owing to its rather high inherent electron affinity. Therefore, BQ readily scavenges electrons at the surface of TiO_2 to form hydroquinone (HQ) [38], avoiding the formation of $O_2^{\cdot-}$ radicals according to the following equation (8).



In order to evaluate the role of $\cdot OH_{free}$ in the photocatalytic process, t-BuOH was used as it is very good at trapping $\cdot OH_{free}$ radicals due to the fact it generates inert intermediates; equation (9) [17].



Finally, FA was employed to assess the participation of the $\cdot OH_{ads}$, $\cdot OH_{free}$ and h^+_{VB} radicals due to its large capacity to be adsorbed onto the surface of the catalyst under acidic conditions and suppress the $\cdot OH_{free}$ radical process [17].



Dark adsorption experiments of DCA onto the catalysts surface were carried out without significant adsorption being recorded after 24 hours of contact. Therefore, direct degradation due to h^+_{VB} was ruled out for all catalysts.

Figure 2A shows the results of the addition of BQ, t-BuOH and FA to the photocatalytic degradation medium of DCA using bare TiO_2 as the catalyst. DCA degradation of 71.4% was reached after 480 minutes of irradiation time. No inhibition was observed when $O_2^{\cdot-}$ radicals were removed by BQ, indicating that these species do not participate in the photocatalytic degradation process. However, when t-BuOH or FA were added to the DCA solution, total inhibition was observed. Since the role of h^+_{VB} was not remarkable

due to its low adsorptive ability, together with the fact that the same inhibition was observed when either $\cdot\text{OH}_{\text{free}}$ or both $\cdot\text{OH}_{\text{free}}$ and $\cdot\text{OH}_{\text{ads}}$ were extracted, it was concluded that the $\cdot\text{OH}_{\text{free}}$ radicals play the most important role in DCA degradation when TiO_2 is used as the catalyst. In order to substantiate these results, Figure 2B shows the influence of scavenger molecules addition in the generation of $\cdot\text{OH}_{\text{free}}$ radicals. No decrease in the generation of $\cdot\text{OH}_{\text{free}}$ radicals was observed when BQ was added, but when FA was added the concentration of $\cdot\text{OH}_{\text{free}}$ was almost negligible.

After 420 minutes of irradiation, complete DCA degradation was achieved using TiO_2/Pt as the catalyst, corresponding to an enhancement of photocatalytic activity of about 34.6% compared to bare TiO_2 . In order to investigate the improved performance of TiO_2/Pt , Figure 3A shows the effects of BQ, t-BuOH and FA addition to the DCA degradation medium. A remarkable inhibition of the photocatalytic activity was seen when $\text{O}_2^{\cdot-}$ radicals were removed, contrary to the behavior observed with TiO_2 under the same conditions. A similar trend for DCA degradation was observed adding t-BuOH to trap $\cdot\text{OH}_{\text{free}}$ radicals. Moreover, the photocatalytic activity was suppressed when FA consumed $\cdot\text{OH}_{\text{ads}}$, $\cdot\text{OH}_{\text{free}}$ and h^+_{VB} radicals.

On the basis of the data obtained with TiO_2/Pt , the results seem to indicate that $\text{O}_2^{\cdot-}$ radicals are critical in the degradation process through disproportionation to H_2O_2 and the formation of $\cdot\text{OH}_{\text{free}}$ (12-16) [39-42]. According to previous studies, reaction (15) is the main contributor to the production of $\cdot\text{OH}_{\text{free}}$ radicals from H_2O_2 [39].



The difference between the inhibition observed with the addition of t-BuOH and that of FA, results in the direct contribution of the $\cdot\text{OH}_{\text{ads}}$ radicals since the involvement of h^+_{VB} was ruled out. Therefore, the degradation pathway using TiO_2/Pt was conducted mainly by free $\cdot\text{OH}_{\text{free}}$ radicals and, to a lesser extent, by $\cdot\text{OH}_{\text{ads}}$ radicals. In order to better understand these results, $\cdot\text{OH}_{\text{free}}$ radicals were quantified using TiO_2/Pt as the catalyst

together with the scavenger molecules (Figure 3B). When BQ was introduced into the DCA solution as an analysis tool for trapping $O_2^{\cdot-}$ radicals, there was a significant decrease in the photocatalytic generation of $\cdot OH_{free}$, supporting the assumption that the $O_2^{\cdot-}$ radicals were being transformed into $\cdot OH_{free}$ radicals (15-16) leaving, therefore, few $\cdot OH_{free}$ radicals in solution when the $O_2^{\cdot-}$ radicals were removed. A similar number of $\cdot OH_{free}$ radicals was detected when incorporating FA into the medium, meaning that $\cdot OH_{free}$ radicals were not photocatalytically generated when introducing BQ or FA. Finally, it should be noted that TiO_2/Pt generated 60.6% more $\cdot OH_{free}$ radicals than bare TiO_2 after 480 min. This can be attributed to the conversion of $O_2^{\cdot-}$ radicals to $\cdot OH_{free}$ radicals because platinum acts as an electron trap, making more electrons available for the photocatalytic process than with bare TiO_2 , leading to a decrease in the recombination rate of $e^- \cdot h^+$ (4).

The TiO_2/Ag catalyst was evaluated in order to compare the different ROS involved in the DCA degradation depending on the noble metal used as the dopant. The TiO_2/Ag photocatalyst resulted in 79.3% DCA abatement after 480 minutes, improving the degradation rate compared to bare TiO_2 . However, the results were worse than those obtained than with the TiO_2/Pt catalyst. Figure 4A shows the influence on DCA degradation depending on the scavenger added. Incorporating BQ or t-BuOH causes significant inhibition of the photocatalytic activity. Therefore, for silver-doped TiO_2 the major species involved in the degradation process are $\cdot OH_{free}$ radicals resulting from $O_2^{\cdot-}$ radical transformation. The TiO_2/Ag junction provokes the formation of the Schottky barrier, capable of efficiently transferring electrons from TiO_2 to Ag, providing electrons for the degradation. FA was used as a trapping molecule for $\cdot OH_{ads}$, $\cdot OH_{free}$ and h^+_{VB} radicals, as in previous studies, but anomalous behavior was noted in the DCA degradation. Chloroacetic acid was detected as a reaction intermediate using TiO_2/Ag but not when using either TiO_2 or TiO_2/Pt . This intermediate appears through the hydrogenation reaction between FA and DCA catalyzed by Ag [43]. Therefore, since the addition of FA modifies the DCA degradation pathway, it cannot be employed as a scavenger when TiO_2/Ag is used as the catalyst. The $\cdot OH_{free}$ radicals detected employing TiO_2/Ag (Figure 4B) presented an intermediate value between those measured with TiO_2/Pt and TiO_2 . $\cdot OH_{free}$ radicals were not photocatalytically generated when introducing BQ or FA into the reaction media, as was seen in the analysis carried out with TiO_2/Pt .

H₂O₂ was quantified in order to verify the presence of this compound as an intermediate in the formation of ·OH_{free} radicals (Figure 5). It can be observed that negligible concentrations of H₂O₂ were detected when TiO₂ was employed as photocatalyst; however, after two hours of irradiation time the presence of H₂O₂ was verified in the reaction medium containing TiO₂/Pt and TiO₂/Ag photocatalysts and its concentration increased with time. As it can be observed, higher amounts of H₂O₂ were formed using TiO₂/Pt than using TiO₂/Ag. This fact may be related to the higher ·OH_{free} radicals generation through H₂O₂ disproportionation using Pt-based photocatalyst compared to Ag-based photocatalyst.

Since ROS formation could also depend on the rate of photon absorption by the catalyst in suspension, and different optical properties for noble metal-doped TiO₂ photocatalysts could be anticipated, the specific extinction coefficient (β_λ) has been calculated per unit of catalyst mass concentration applying a standard linear regression with forced intercept at the origin. Figure S1 depicts the extinction coefficient for each photocatalyst as a function of the wavelength. Lower values for the specific extinction coefficient were obtained for TiO₂/Pt and TiO₂/Ag compared to TiO₂. However, using noble metal-based materials better photocatalytic activity and different degradation pathways compared to bare TiO₂ were observed.

According to Cassano & Alfano (2000) [44] the total extinction coefficient can be related to the absorption coefficient and the scattering coefficient through the following expression:

$$\beta_\lambda = \kappa_\lambda + \sigma_\lambda \quad (13)$$

where κ_λ is the absorption coefficient and σ_λ is the scattering coefficient. These optical parameters are related to the properties of the photocatalyst under irradiation and therefore, they are key to assess the photocatalytic activity of semiconductors regardless of the reactor set-up employed since they allow to understand the photon absorption rate of the semiconductor [45]. It can be concluded that from the optical point of view, TiO₂/Pt

and TiO₂/Ag show properties both qualitatively and quantitatively similar but, in addition, TiO₂ has a quantitatively higher response over the studied wavelength range compared to noble metal-based photocatalysts. The lower values of the extinction coefficient found for TiO₂/Pt and TiO₂/Ag compared to bare TiO₂ could be compensated by the higher absorption/scattering ratio provided by these catalysts compared to TiO₂.

Therefore, the enhancement of the photocatalytic activity due to electron-hole lifetime extension seems to be the main argument supported by the obtained results.

Role of ROS depending of the nature of the photocatalyst

Figure 6 shows the contribution of ROS to DCA degradation depending on the catalyst type. It can be observed that 100% of the DCA degradation was conducted by $\cdot\text{OH}_{\text{free}}$ radicals generated from water molecules reacting with h^+_{VB} when TiO₂ was used as the catalyst (Figure 6A). With regard to TiO₂/Pt, since Pt acts as an electron trap supplying a greater number of available electrons, approximately 78.2% of the degradation was conducted by $\cdot\text{OH}_{\text{free}}$ radicals formed from photogenerated O₂⁻ radicals (Figure 6B). O₂⁻ radicals are created when dissolved O₂ from the reaction medium accept a photogenerated electron (5). After that, H₂O₂ generation process is started through reaction (13) and reaction (14). Finally, the H₂O₂ can result in $\cdot\text{OH}_{\text{free}}$ radicals, mainly via electron transfer (15), which are involve in the DCA decomposition as they are powerful oxidants. Therefore, H₂O₂ can serve as a source of $\cdot\text{OH}_{\text{free}}$ radicals, playing a key role in the TiO₂/Pt photocatalytic process. Similarly, but contributing 64.9%, the DCA degradation using TiO₂/Ag was promoted by $\cdot\text{OH}_{\text{free}}$ radicals generated from the transformation of O₂⁻ radicals. Moreover, the $\cdot\text{OH}_{\text{ads}}$ radicals contributed with 35.1% to DCA oxidation in the study of the silver-doped catalyst (Figure 6B). These results are supported by the evidence of higher concentration of H₂O₂ using TiO₂/Pt than using TiO₂/Ag and the practically nonexistent generation when TiO₂ was employed as photocatalyst (Figure 5).

Conclusions

DCA has been reported as a disinfection by-product present in many chlorinated drinking waters and has a potentially carcinogenic effect. In this work, TiO₂/Pt 0.5 wt% and

TiO₂/Ag 10 wt% composite photocatalysts have been successfully synthesized and their performance in DCA degradation assessed, achieving 100% and 79.3% DCA removal, respectively. Moreover, and in order to gain insight into the degradation mechanisms, the contribution of different ROS to the oxidation kinetics of DCA using TiO₂ and noble metal-doped TiO₂ catalysts has been studied. Direct degradation via h^+_{VB} was ruled out for all the photocatalysts studied since there was no significant adsorption of DCA onto the solids. In the case of the TiO₂ catalyst, $\cdot OH_{free}$ radicals played the most important role in DCA degradation kinetics. The improved performance of noble metal-doped catalysts was seen in addition to the generation of ROS other than $\cdot OH_{free}$ radicals compared to bare TiO₂. DCA degradation in the presence of TiO₂/Pt and TiO₂/Ag was mainly due to the activity of $\cdot OH_{free}$ radicals from the transformation of $O_2^{\cdot -}$ and, to a lesser extent, $\cdot OH_{ads}$ radicals. The quantification of $\cdot OH_{free}$ radicals when $O_2^{\cdot -}$ radicals were removed from the reaction medium showed a significant decrease in the generation of $\cdot OH_{free}$ radicals. It was therefore assumed that $O_2^{\cdot -}$ radicals were critical in the formation of $\cdot OH_{free}$ radicals through disproportionation to H₂O₂. A higher contribution of these $\cdot OH_{free}$ radicals was seen with TiO₂/Pt (78.2% ± 0.5) than with TiO₂/Ag (64.9% ± 3.6). FA could not be used as a scavenger when TiO₂/Ag was employed as the catalyst due to the reaction between FA and the DCA catalyzed by Ag. In conclusion, this work contributes to the technical assessment of photocatalytic DCA degradation by analyzing the performance of newly synthesized photocatalysts while also providing insight into the mechanisms responsible for the photocatalytic degradation through an analysis of the role of different ROS.

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Figure 1. High-resolution XPS spectra of TiO₂ (A), TiO₂/Pt 0.5% (B) and TiO₂/Ag 10% (C) photocatalysts

Figure 2. Effect of BQ, t-BuOH and FA addition on the photocatalytic degradation of DCA (A) and ·OH generation (B) for bare TiO₂

Figure 3. Effect of BQ, t-BuOH and FA addition on the photocatalytic degradation of DCA (A) and ·OH generation (B) for TiO₂/Pt

Figure 4. Effect of BQ, t-BuOH and FA addition on the photocatalytic degradation of DCA (A) and ·OH generation (B) for TiO₂/Ag

Figure 5. H₂O₂ quantification using TiO₂, TiO₂/Pt and TiO₂/Ag photocatalyst

Figure 6. Proposed ROS mechanism in the photocatalytic degradation of DCA by TiO₂ (A), TiO₂/Pt, and TiO₂/Ag (B)