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ELUCIDATION OF THE PHOTOCATALYTIC-MECHANISM OF PHENOLIC COMPOUNDS

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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 TiO₂ 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 TiO₂ 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

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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).

Keywords: titania, photocatalyst, phenolic compounds, photo-mechanism, scavenger, quantum efficiency

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 determinate 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) 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, $\text{Cu}(\text{NO}_3)_2$ [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 $\text{HO}^\bullet$, 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_2 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_2 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. $\text{Cu}(\text{NO}_3)_3 \cdot 2.5\text{H}_2\text{O}$ (>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-Visible 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_2 photocatalysts after being in contact with the studied four organic substrates, the TiO_2 suspensions ($10\text{ g}\cdot\text{L}^{-1}$) in contact with $100\text{ mg}\cdot\text{L}^{-1}$ 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_2 photocatalysts in the presence of Cu^{2+} ions after the 4-nitrophenol photodegradation experiment in the presence of $\text{Cu}(\text{NO}_3)_3$ was measured. In this case the TiO_2 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. [25-27]. 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_2 photocatalysts in the photodegradation 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^2 , 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 [28]. 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 $1.4 \cdot 10^{-8}$ Einstein $\cdot$ cm⁻² $\cdot$ s⁻¹.

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 NmL $\cdot$ min⁻¹). All the reactions were performed with an organic compound and photocatalyst loading of 250 mg $\cdot$ L⁻¹ and 50 mg $\cdot$ L⁻¹. To avoid sedimentation of the photocatalyst the suspension was constantly stirred. The photocatalyst and the organic compound were mixed in the dark for 30 minutes before the lamps were turned on to ensure adsorption equilibrium. The used photoreaction system is described in deep detail in [29, 30].

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 μ m column (15 cm length, 4.6 mm diameter at 30 °C,) as stationary phase and 0.6 mL $\cdot$ min⁻¹ of 40:60 methanol:acidic water (0.1% phosphoric acid) in the range 0-8 min and 1 mL $\cdot$ min⁻¹, 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 TiO₂ catalysts P25 and Hombikat (HBK) on the degradation of four aromatic compounds (phenol, methyl 4-hydroxybenzoate, 4-chlorophenol and 4-nitrophenol) is depicted in Figure 1. Moreover, the corresponding initial reaction rates of

every aromatic compound were estimated by applying equation 1 for the first 45 minutes, 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 minutes of irradiation are shown in Figure 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 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, 31, 32]. 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, 31, 33]. An

isotropic phase function was chosen because it has been demonstrated that it provides good representation for the experimental LVRPA [4, 32, 34]. This model was already proved to be useful to simulate the radiation absorbed in our system [29]. The specific extinction, specific absorption and specific scattering coefficients for each TiO₂ catalyst were calculated as previously reported [26, 29] and are shown in Supplementary Information Figures 1. One million (10⁶) 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 Figure 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⁻¹ 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 Figure 2, using equation 2.

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

In Figure 3, LVRPA profiles along the reactor diameter (x) are plotted for each photocatalyst. The LVRPA calculated for the TiO₂ 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 Figure 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 ($\sim 275 \text{ m}^2$) is almost five times higher than that of P25 ($\sim 55 \text{ m}^2$). This could lead to a worse illumination and adsorption of the substrate on the TiO_2 particles. Furthermore, the smaller particle diameters of P25 will lead to greater values of the extinction, absorption and scattering coefficients [29, 35], as observed in Supplementary Information Figures 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 [36, 37]. When the size of the particle is comparable to the wavelength of the radiation absorbed by the TiO_2 , 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 equation 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 ($HO^\bullet$) 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 scavenger since recent studies have proved its excellent effectiveness [11, 13, 17]. Finally, Cu^{2+} was chosen as electron scavenger [13, 17, 18, 38]. In addition, $Cu(NO_3)_2$ was used because NO_3^- barely competes with the aromatic compounds for $HO^\bullet$ nor h^+ [17]. After a previous study, the employed concentrations of methanol, formic acid and $Cu(NO_3)_2$ were 125, 5 and 10 mM respectively. Ratios between scavenger concentration ($mmol \cdot L^{-1}$) and pollutant concentration ($mmol \cdot L^{-1}$) 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 Figures 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 photodegraded by HO• radicals using UV light as irradiation source [13].

However, HO• 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 TiO₂ surface and (ii) be produced from H₂O₂ formed by coupling reaction of hydroperoxyl radicals (HO₂•) [11, 15].

To study and establish the main pathway to form HO• radicals formic acid was used as hole scavenger, which avoids HO• radicals generation from water oxidation (equation 4).

In these conditions two different trends in the photodegradation process were observed (see Figures 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 CH₃OH 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 HCOOH as hole scavenger enhances this process and consequently, 4-nitrophenol photodegradation. This behavior was similar for both of the studied TiO₂, P25 and Hombikat.

When no HO• scavenger or when Cu(NO₃)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. Cu²⁺ presence showed a low contribution, which could be ascribed to the reduction of Cu²⁺ 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 Cu²⁺ ions on the oxidation rates is probably because the formation of H₂O₂ (equation 7) is low and the production of HO• by H₂O₂ decomposition is also very low. Nevertheless, HO₂• production seems to have a bigger contribution in the oxidation pathway of phenol since its disappearance rate is reduced by the presence of Cu²⁺ 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] :

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

represents the oxidation by HO• radicals generated from photo-induced holes (h⁺).

- $k_2 = k_{CH_3OH}/k$

represents direct photodegradation by holes (h^+), because reactive radicals formed from photogenerated holes ($HO^\bullet$ radicals) or electrons ($O_2^{\bullet-}$, $HO_2^\bullet$, $HO^\bullet$) were trapped.

- $k_3 = k_{HCOOH}/k$

represents oxidation by reactive oxygen species generated from electrons ($O_2^{\bullet-}$, $HO_2^\bullet$, $HO^\bullet$), as holes (h^+) were quenched by HCOOH [13, 39].

Where k_{CH_3OH} , k_{HCOOH} and $k_{Cu(NO_3)_2}$ are the pseudo-first order rate constants estimated for the reactions carried out in the presence of CH_3OH , HCOOH and $Cu(NO_3)_2$ respectively.

- 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 Figure 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 (equation 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 [40, 41]. 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 [42, 43]. Regarding methyl 4-hydroxybenzoate, 4-hydroxybenzoic acid is expected to be the primary hydroxylated intermediate in M p-HB photodegradation after $\text{HO}^\bullet$ radicals attack at $-\text{CH}_3$ and $-\text{H}$ in the aromatic ring. Afterwards, this product is oxidized to generate phenol and dihydroxybenzene [44].

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 Figure 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 Figures 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 denitrification and $\text{HO}^\bullet$ 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 [41, 45]. 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 $\text{HO}^\bullet$ radicals [41, 45], 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 Figure 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 [30] 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 Figure 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 Figure 5B) evidences the relevance of mechanisms mediated by photo-induced electrons for these both photocatalysts.

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[•] 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[•] 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 TiO₂ valence band (VB) to the conduction band (CB).

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5. REFERENCES

- [1] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, *Catalysis Today* 147 (2009) 1-59.

- [2] S. Ahmed, M.G. Rasul, R. Brown, M.A. Hashib, *Journal of Environmental Management* 92 (2011) 311-330.
- [3] W. Zhang, Y. Li, Y. Su, K. Mao, Q. Wang, *Journal of Hazardous Materials* 215–216 (2012) 252-258.
- [4] J. Moreira, B. Serrano, A. Ortiz, H. de Lasa, *Industrial & Engineering Chemistry Research* 49 (2010) 10524-10534.
- [5] A.E. Cassano, O.M. Alfano, *Catalysis Today* 58 (2000) 167-197.
- [6] M. de los Milagros Ballari, O.O. Alfano, A.E. Cassano, *Industrial & Engineering Chemistry Research* 48 (2009) 1847-1858.
- [7] A. Manassero, M.L. Satuf, O.M. Alfano, *Chemical Engineering Journal* 225 (2013) 378-386.
- [8] J. Marugán, R. van Grieken, A.E. Cassano, O.M. Alfano, *Catalysis Today* 129 (2007) 143-151.
- [9] A. Manassero, M.L. Satuf, O.M. Alfano, *Chemical Engineering Journal* 326 (2017) 29-36.
- [10] D. Hufschmidt, L. Liu, V. Selzer, D. Bahnemann, *Water Science and Technology* 49 (2004) 135-140.
- [11] J.F. Montoya, M.F. Atitar, D.W. Bahnemann, J. Peral, P. Salvador, *The Journal of Physical Chemistry C* 118 (2014) 14276-14290.
- [12] Y. Chen, S. Yang, K. Wang, L. Lou, *Journal of Photochemistry and Photobiology A: Chemistry* 172 (2005) 47-54.
- [13] M. Pelaez, P. Falaras, V. Likodimos, K. O'Shea, A.A. de la Cruz, P.S.M. Dunlop, J.A. Byrne, D.D. Dionysiou, *Journal of Molecular Catalysis A: Chemical* 425 (2016) 183-189.
- [14] L.M. Pastrana-Martínez, S. Morales-Torres, A.G. Kontos, N.G. Moustakas, J.L. Faria, J.M. Doña-Rodríguez, P. Falaras, A.M.T. Silva, *Chemical Engineering Journal* 224 (2013) 17-23.
- [15] T. Fotiou, T.M. Triantis, T. Kaloudis, K.E. O'Shea, D.D. Dionysiou, A. Hiskia, *Water Research* 90 (2016) 52-61.
- [16] B.R. Cruz-Ortiz, J.W.J. Hamilton, C. Pablos, L. Díaz-Jiménez, D.A. Cortés-Hernández, P.K. Sharma, M. Castro-Alfárez, P. Fernández-Ibañez, P.S.M. Dunlop, J.A. Byrne, *Chemical Engineering Journal* 316 (2017) 179-186.
- [17] A.O. Kondrakov, A.N. Ignatev, V.V. Lunin, F.H. Frimmel, S. Bräse, H. Horn, *Applied Catalysis B: Environmental* 182 (2016) 424-430.
- [18] S.A. Bakar, C. Ribeiro, *Journal of Molecular Catalysis A: Chemical* 421 (2016) 1-15.
- [19] Y. Nosaka, S. Komori, K. Yawata, T. Hirakawa, A.Y. Nosaka, *Physical Chemistry Chemical Physics* 5 (2003) 4731-4735.
- [20] R. Hazime, C. Ferronato, L. Fine, A. Salvador, F. Jaber, J.M. Chovelon, *Applied Catalysis B: Environmental* 126 (2012) 90-99.
- [21] J. Peral, J. Casado, J. Doménech, *Journal of Photochemistry and Photobiology A: Chemistry* 44 (1988) 209-217.
- [22] J. Araña, E. Pulido Melián, V.M. Rodríguez López, A. Peña Alonso, J.M. Doña Rodríguez, O. González Díaz, J. Pérez Peña, *Journal of Hazardous Materials* 146 (2007) 520-528.
- [23] S. Brunauer, P.H. Emmett, E. Teller, *Journal of the American Chemical Society* 60 (1938) 309-319.
- [24] H.N.D. Zhebo Chen, Eric Miller, *Photoelectrochemical Water Splitting Standards, Experimental Methods, and Protocols*, Springer New York, 2013.
- [25] A.E. Cassano, O.M. Alfano, *Catalysis Today* 58 (2000) 167-197.
- [26] M.I. Cabrera, O.M. Alfano, A.E. Cassano, *The Journal of Physical Chemistry* 100 (1996) 20043-20050.
- [27] M.L. Satuf, R.J. Brandi, A.E. Cassano, O.M. Alfano, *Industrial & Engineering Chemistry Research* 44 (2005) 6643-6649.
- [28] H.J. Kuhn, S.E. Braslavsky, R. Schmidt, *Chemical Actinometry*.
- [29] A. Tolosana-Moranchel, J.A. Casas, J. Carbajo, M. Faraldos, A. Bahamonde, *Applied Catalysis B: Environmental* 200 (2017) 164-173.

- [30] A. Tolosana-Moranchel, J.A. Anderson, J.A. Casas, M. Faraldos, A. Bahamonde, *Journal of Environmental Chemical Engineering* 5 (2017) 4612-4620.
- [31] A. Manassero, M.L. Satuf, O.M. Alfano, *Environmental Science and Pollution Research* 22 (2015) 926-937.
- [32] J. Moreira, B. Serrano, A. Ortiz, H. de Lasa, *Chemical Engineering Science* 66 (2011) 5813-5821.
- [33] A. Manassero, M.L. Satuf, O.M. Alfano, *Environmental Science and Pollution Research* 24 (2017) 6031-6039.
- [34] M.A. Mueses, F. Machuca-Martinez, A. Hernández-Ramirez, G. Li Puma, *Chemical Engineering Journal* 279 (2015) 442-451.
- [35] J. Carbajo, A. Tolosana-Moranchel, J.A. Casas, M. Faraldos, A. Bahamonde, *Applied Catalysis B: Environmental* 221 (2018) 1-8.
- [36] H. Xu, X. Chen, S. Ouyang, T. Kako, J. Ye, *The Journal of Physical Chemistry C* 116 (2012) 3833-3839.
- [37] M.-C. Tsai, J.-Y. Lee, P.-C. Chen, Y.-W. Chang, Y.-C. Chang, M.-H. Yang, H.-T. Chiu, I.N. Lin, R.-K. Lee, C.-Y. Lee, *Applied Catalysis B: Environmental* 147 (2014) 499-507.
- [38] N. San, A. Hatipoğlu, G. Koçtürk, Z. Çınar, *Journal of Photochemistry and Photobiology A: Chemistry* 146 (2002) 189-197.
- [39] Y. Li, B. Wen, C. Yu, C. Chen, H. Ji, W. Ma, J. Zhao, *Chemistry – A European Journal* 18 (2012) 2030-2039.
- [40] M.L. Satuf, R.J. Brandi, A.E. Cassano, O.M. Alfano, *Applied Catalysis B: Environmental* 82 (2008) 37-49.
- [41] M.H. Priya, G. Madras, *Industrial & Engineering Chemistry Research* 45 (2006) 482-486.
- [42] J. Carbajo, Thesis Dissertation: Application of Solar Assisted Photodegradation of Organic Pollutants in Aqueous Phase with Nanostructured Titania Catalysts, Universidad Autónoma de Madrid, Spain, 2013.
- [43] P. García-Muñoz, J. Carbajo, M. Faraldos, A. Bahamonde, *Journal of Photochemistry and Photobiology A: Chemistry* 287 (2014) 8-18.
- [44] Y. Lin, C. Ferronato, N. Deng, F. Wu, J.-M. Chovelon, *Applied Catalysis B: Environmental* 88 (2009) 32-41.
- [45] M.S. Dieckmann, K.A. Gray, *Water Research* 30 (1996) 1169-1183.