Effect of the irradiation wavelength on the performance of of nanoporous carbon as an additive to TiO₂

Marta A. Andrade^{1,2}, Ana S. Mestre¹, Rocío J. Carmona², Ana P. Carvalho^{1*}, Conchi O. Ania^{2*}

¹ Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

² ADPOR Group, Dpt. Chemical Processes for Energy and Environment, Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080 Oviedo, Spain

*Corresponding author. Tel./Fax: +353217500897 (Carvalho) / +34 985 118846 (Ania)

E-mail address: apcarvalho@fc.ul.pt (Carvalho); conchi.ania@incar.csic.es (Ania)

Abstract

We report the dependence of the photochemical activity of titania/carbon hybrid catalysts towards the degradation of phenol from solution using polychromatic light and filters. In all cases larger photooxidative efficiencies were obtained using light at 200 nm < λ < 600 nm. The incorporation of a carbon additive to TiO₂ increased the photocatalytic performance regardless the illumination conditions, although the effect was more pronounced at λ > 200 nm. The photocatalytic runs carried out with the nonporous carbon alone confirmed a certain level of intrinsic photoactivity under both irradiation conditions. Nevertheless, a clear deactivation was evident after 60 min of irradiation suggesting that the photoactive sites in the carbon are either consumed or deactivated in the course of the reaction. The composition of the catalyst and the illumination conditions also have a strong effect on the nature of the degradation intermediates, with a marked regioselectivity towards ortho-substitution at high energy photons and when the carbon component is added to the catalyst composition.

Keywords: sisal-based nanoporous carbons, TiO₂/carbon photocatalysts, UV and visible light, phenol photocatalytic degradation.

1. Introduction

Heterogeneous photocatalysis has become a popular topic in environmental remediation and energy conversion [1], and the low photonic efficiency of common semiconductors is still a challenge that calls out for research to be conducted on exploring novel materials [2]. Despite carbons are strong light absorbing materials, they have been extensively investigated in a number of photo-assisted reactions [3-9 and references therein]. The incorporation of carbon materials either as additives or supports to semiconductors has been long explored and many studies have shown that adding a carbonaceous component can enhance the performance of the photoactive material in a number of photocatalytic reactions. Furthermore, the use of carbon/semiconductor catalysts overcomes the operational drawbacks associated to the use of nanosized semiconductor powders that hinder the application in continuous flow systems due to limited recovery and reuse of the catalyst [6].

The origin of the increased photoconversion yields of carbon/semiconductor catalysts has been long speculated and mostly discussed in terms of: i) the enhanced visible light absorption of the carbon component, ii) an enhanced mass transfer of the adsorbed pollutant from the bulk solution to the photoactive particles through the interface between the two catalyst components, and iii) strong interfacial electronic effects between the substrate and the immobilized catalyst in the case of carbon nanostructures with high electronic mobility [3,4,10]. Also, it is considered that the photocatalytic response depends on the nature of the carbon; hence different mechanisms would apply for nanoporous carbons compared to nanostructured carbon nanotubes, fullerenes and graphene. Our recent investigations have also proved the photoactivity of semiconductor-free nanoporous carbons under UV and visible light [11-13] and their ability to photogenerate oxygen reactive species as the key aspect to achieve enhanced degradation yields of pollutants from solution.

The origin and dependence of the carbon/light interactions with the irradiation source still remains uncertain [14-16]. For instance, it is well known that only photons with $\lambda < 400$ nm can be absorbed by TiO_2 to induce the excitation of electrons from the valence to the conduction band and allowing the charge separation that would eventually lead to the desired pollutant's degradation reaction [1,2]. Simultaneously many organic compounds present a strong absorption of light at $\lambda < 400$ nm, leading to direct degradation in the absence of a catalyst (photolytic reaction). When using hybrid carbon/semiconductor catalysts, the situation is more complex due to the above-mentioned carbon/light interactions. Indeed, by

using monochromatic light we have recently reported the ability of certain semiconductor-free carbons to convert photons from the visible spectrum in chemical reactions [13].

Knowing this and since the use of carbon in photochemical applications has recently gained considerable attention, in this work we aimed at exploring the influence of the irradiation source on the photooxidative activity of a hybrid titania/carbon catalyst. Our approach consisted in exposing the catalysts to varied illumination conditions using filters to cut-off the light, while evaluating the effect on the photoconversion of phenol from aqueous solution and on the degradation mechanism. As additive to the semiconductor we have selected a nanoporous carbon prepared by chemical activation of a lignocellulosic precursor, in line with a current interest of our research group [17]. Furthermore, our previous studies have shown the good performance of this material as additive to titania with increased photooxidation conversions under sunlight [18]. We herein describe the performance of these materials under different illumination conditions, aiming at clarifying the role of the carbon matrix upon irradiation at high and low wavelengths. Thus the outcome of our previous studies is used only for data interpretation. Phenol was selected as model compound representing a toxic pollutant frequently found in wastewater and classified as a high environmental risk according to the European and American Environmental Protection Agencies.

2. Experimental

2.1 Materials synthesis

A nanoporous carbon prepared by chemical activation of a lignocellulosic industrial residue - discarded sisal ropes- was selected as carbon material for the preparation of the titania/carbon photocatalysts. Details on the synthesis of sisal-derived carbons have been reported elsewhere [18]. Briefly, 1 cm long sisal pieces were impregnated with a K_2CO_3 solution (weight ratio sisal: K_2CO_3 of 2:1) and activated in a horizontal furnace at 700 °C for 1 h under N_2 flow ($5\text{ cm}^3\text{ s}^{-1}$). After the activation, the sample was thoroughly washed with distilled water until pH 7 and dried at 100 °C. The sample will be labeled as S. Commercially available TiO_2 (P25 Degussa, Evonik) was used as a standard catalyst for the photocatalytic activity. The hybrid titania/carbon photocatalyst with a 1:1 weight ratio composition was prepared by physical mixture of TiO_2 and carbon powders in a mortar. The sample will be labeled as TiO_2/S .

2.2 Photodegradation runs

Phenol photodegradation experiments were carried out at room temperature using a photo-reactor of 0.5 L capacity and a loading catalyst ratio of 0.5 g L^{-1} . The irradiation source was

provided by a high pressure mercury lamp (Helios Italquartz, 125 W) emitting in the UV and visible light spectrum (between 200-600 nm, see Figure S1 in the Electronic Supplementary Information); the lamp was vertically suspended in a cylindrical, double-walled jacket cooled by flowing water, immersed in the solution. The water cell was used to control the temperature during the experiments, preventing any overheating of the suspension due to the irradiation. The reactor was open to air in all the experiments to ensure that enough oxygen was present in the reaction solution. The series of experiments were performed in the photoreactor with a quartz jacket ($\lambda > 200$ nm) or glass (pyrex) jacket ($\lambda > 360$ nm) that acts as a cut-off filter of the irradiation below 360 nm, and hence avoids the photolytic reaction in the catalytic runs (spectra in Figure S1). The incident photon flux emitted by the lamp and transferred to the photoreactor in both irradiation conditions was measured by chemical actinometry [19]. The values determined were 9.1×10^{-6} and 1.35×10^{-5} Einstein s^{-1} for the lamp with and without the pyrex filter, respectively.

In each run, the catalyst was added to the phenol solution under vigorous stirring (900 rpm) and allowed to equilibrate in dark conditions for 30 min. This step accounts for the adsorption on the porous catalysts and assures a similar phenol concentration in solution when the catalysts are illuminated (86 mg L^{-1}) [18]. After the equilibration step, the suspension was irradiated for 360 min. During the irradiation, small aliquots of the solution ($\sim 1 \text{ cm}^3$) were taken out at predetermined time intervals, and analyzed by reverse-phase HPLC (Spherisorb C18 column 125 mm x 4 mm, methanol to water 5:95, 30 °C, $0.7 \text{ cm}^3 \text{ min}^{-1}$ flow rate, photodiode array detector using the corresponding wavelengths) to determine the residual concentration of phenol (269 nm) and its aromatic degradation products, namely quinones (1,4-benzoquinone -245 nm- and 1,4-dihydroxybenzene -288 nm-), 1,2-dihydroxybenzene (*o*-catechol, 275 nm), 1,3-dihydroxybenzene (resorcinol, 273 nm), 1,3,5-trihydroxybenzene (264 nm) and 1,2,4-trihydroxybenzene (482 nm) (all Aldrich 99% reagents). The samples were previously filtered using cellulose filters with mean pore size of $0.45 \text{ }\mu\text{m}$. All the experiments were done in duplicate with deviations below 5 % in all cases; reported data represent the average values. Total organic carbon (TOC) of the solution at the end of each run was also measured in a TOC-V analyzer.

Experiments were also carried out in the absence of irradiation (series *dark*), for further comparison between the extent of phenol photodegradation and the uptake due to adsorption. The stability of the photocatalysts under irradiation was also explored upon illumination of the catalyst's suspensions in water in the absence of phenol.

2.3 Characterization of the catalysts

The physicochemical and textural characterization was carried out on the fresh and used catalysts (after the photocatalytic runs). The porosity of the samples was characterized by measuring the N₂ and CO₂ adsorption isotherms at -196 and 0 °C, respectively (Micromeritics). Before the experiments, the samples were outgassed under vacuum (ca. 10⁻³ torr) at 120 °C overnight. The isotherms were used to calculate the specific surface area, A_{BET} , total pore volume, V_{total} , while the micropore volumes were analyzed using the Dubinin–Radushkevich formulism to the N₂ and CO₂ adsorption data (W_{0,N_2} , W_{0,CO_2}) [20]. For the characterization of the spent catalysts, the samples were recovered by filtration, dried overnight at 60 °C and then outgassed as detailed above. Elemental analysis was carried out in LECO CHNS-932 and LECO VTF-900 automatic analyzers. Fourier transformed infrared spectroscopy (FTIR) was carried out using a Nicolet Magna-IR 560 spectrometer with a high-sensitivity MCT/A detector. Spectra were obtained using the attenuated total reflectance method (ATR) on powdered samples, without KBr addition. Each spectrum was obtained by collecting 300 interferograms with 4 cm⁻¹ resolution. The optical features of the catalysts were determined by UV-Vis diffuse reflectance spectroscopy, recorded on a Shimadzu spectrometer (UV-2501) equipped with an integrating sphere and using BaSO₄ as a blank reference. Measurements were recorded in the diffuse reflectance mode (R) and transformed to a magnitude proportional to the extinction coefficient through the Kubelka-Munk function, $F(R_{\infty})$. The morphology of the samples was observed by Field Emission Gun Scanning Electron Microscopy (FEG-SEM) with an X-ray Energy-Dispersive System (EDS) in a JEOL JSM-7001F, and in a FE-SEM apparatus (QuantaSEM, FEI), using an accelerating voltage of 25 kV.

3. Results and discussion

Before the photocatalytic runs, the catalysts were thoroughly characterized by different techniques. A more elaborated discussion on the physicochemical properties of the nanoporous carbon used as additive was reported in a previous study [18], however selected properties are herein shown for data interpretation purposes. It should be pointed out that the carbon additive is a nanoporous material with high surface area and pore volume (Table 1), thus the hybrid carbon/titania photocatalysts also shows an outstanding porosity. The carbon material is also characterized by a slightly acidic character (surface pH of 6.3), in agreement with a quite large oxygen content (elemental analysis rendered 15.9, 82.2 and 1.2 wt.% of

oxygen, carbon and hydrogen, respectively, Table S1). Additional characterization of the carbon component was carried out by infrared and diffuse reflectance spectroscopy (Figure 1). The infrared spectra of the nanoporous carbon (Figure 1 (b)) showed the presence of the broad band between 3200 and 3600 cm^{-1} (representing the vibrations of OH moieties in water molecules and/or structural OH groups), a weak band at 1000 cm^{-1} , representing C-O vibrations, a more intense band at ca. 1400 cm^{-1} , representing C-OH groups and sharper band at 1672 cm^{-1} , accounting for C=C from the aromatic ring mode conjugated carbonyl and carboxylate groups. A similar infrared pattern was obtained for the carbon/semiconductor photocatalysts, as expected since it was prepared by physical mixture of both components. For the same reason, no changes were detected in the optical features of the catalysts; as seen in Figure 1(a), the reflectance spectrum of titania showed the characteristic absorption sharp edge of the anatase in the UV region lying above 400 nm; the incorporation of the carbon material results in a broader background absorption in the visible light region, while the absorption onset is the same.

In photocatalytic reactions involving porous materials, several reactions occur simultaneously upon irradiation of the catalysts (namely adsorption, direct photolysis and photocatalysis) and must be considered when comparing the performance of different systems. Due to the characteristics of our irradiation source (i.e., wavelength and incident flux, Figure S1), the photolytic breakdown of phenol at $\lambda > 200$ nm was quite large in terms of phenol conversion, reaching similar values of those obtained when the catalysts are irradiated (Figure 3). However, the mineralization extent of the photolysis -estimated from the TOC values in solution after 6 hours of illumination- was very poor (ca. 5% for direct photolysis and 55% in the presence of the catalyst, Table 2). This is important as it shows the need of an appropriate catalyst to further degrade the intermediates, thus enabling the comparison of the efficiency of both irradiation set-ups. Similar mineralization values have been reported in the literature for direct photolysis of phenol aqueous solutions at $\lambda > 200$ nm using much powerful irradiation sources (ca. 500 W) [21,22]. When the light below 360 nm was cut-off with the pyrex filter, the photolytic reaction was largely suppressed as inferred from the low phenol conversion after 6 hours (i.e. 3 %) with no noticeable mineralization. This finding was quite expected considering that the fraction of light absorbed by the aqueous phenol solution above 360 nm is negligible [13] and the dependence of the energy of the photons with the emission wavelength of the irradiation source [22].

As the yield of photolysis is highly dependent on the concentration of phenol in solution [23], controlling the extent of the non-catalyzed reaction is of paramount importance for comparing the performance of the catalysts. For this reason, the photocatalytic runs were carried out on catalysts previously exposed to phenol (pre-adsorption step), so as to allow the adsorption of the pollutant on the porosity at equilibrium conditions, and to maintain the same initial concentration of phenol in the solution at the beginning of the illumination period. This procedure also enables to discriminate between the adsorption and photooxidation reactions, as both may take place simultaneously in porous catalysts.

The first step then consisted on evaluating the adsorption capacity of the catalysts at dark conditions (series dark) and the time needed for reaching the equilibrium during the pre-loading step. Phenol adsorption kinetics was quite fast for all the catalysts, with the equilibrium being reached after 30 min (Figure S2). The amount adsorbed by titania powders was negligible (below 3%), in agreement with the low porosity of the semiconductor (Table 1). In contrast, it was quite large for the carbon (ca. 145 mg g⁻¹) and the carbon/titania photocatalyst (ca. 70 mg g⁻¹), which is attributed to the open porosity of the catalyst provided by the carbon component (Table 1). Along with surface area and micropore volume, the open pore structure of the carbon matrix is also seen in the SEM images (Figure 2) showing a globular structure with large cavities, characteristic of materials with high external area, hence favoring the adsorption kinetics. At converse, the uptake was almost negligible (below 3%) for bare titania, as expected based on its non-porous nature. Hence, the concentration of phenol in the solution was adjusted for each run considering the adsorption capacity of each catalyst, so as to obtain a constant value of 86 mg L⁻¹ phenol in solution after the pre-equilibration step.

Figures 3 and 4 show the evolution of phenol and its degradation intermediates in solution at different irradiation conditions. Several differences become clear; first, higher phenol conversions and mineralization were obtained when the catalysts are irradiated using light at $\lambda > 200$ nm (lamp without filter); this is consistent given the higher energy of the photons and the higher photon flux of the arriving radiation at the system measured by chemical actinometry. Secondly, phenol photooxidation conversion after 6 hours was higher for TiO₂/S compared to bare TiO₂ and regardless the illumination conditions (Table 2), although the effect was more pronounced at $\lambda > 200$ nm (Figure 3(a)). This is most remarkable bearing in mind that the amount of semiconductor in the catalyst (weight ratio 1:1) is half of the amount

used in the experiments with titania, since the photocatalytic runs were carried out using a constant total solid loading of 0.5 g L^{-1} .

The extent of mineralization followed a similar trend, being the beneficial effect of the carbon more significant when the catalysts are exposed to light at $\lambda > 200 \text{ nm}$ as seen in Table 2; while the values obtained for TiO_2 and TiO_2/S exposed to light at $\lambda > 360 \text{ nm}$ are rather similar, phenol mineralization increased by 1.5 times for the hybrid carbon/titania photocatalyst at $\lambda > 200 \text{ nm}$, with half the amount of titania as mentioned before. The higher efficiency of the photooxidation when the catalysts were exposed to more energetic light (lower wavelength) is in agreement with the light absorption features of the semiconductors, since it is well known that for titania only photons with energy above 3.2 eV (corresponding to $\lambda < 400 \text{ nm}$) are capable of promoting the electrons from the valence band.

For the carbon component, our previous studies using monochromatic light have shown that the intrinsic photochemical activity of nanoporous carbons (if any) is higher under UV light [13]. It is also interesting to note the distinct performance of the carbon material alone (in the absence of titania) with the irradiation source. When exposed to light at $\lambda > 200 \text{ nm}$ in the absence of the semiconductor, a relatively high photooxidation yield was obtained. In fact, similar results were obtained for the nanoporous carbon ($\text{S}_{\lambda > 200 \text{ nm}}$) and for carbon/titania ($\text{TiO}_2/\text{S}_{\lambda > 200 \text{ nm}}$) under the same illumination conditions, indicating that the carbon material presents a certain level of self-photochemical activity. The conversions however dropped significantly when the pyrex filter was used to cut-off the light (Table 2), particularly for the carbon alone.

To further explore the superior performance of the hybrid carbon/titania photocatalyst compared to bare titania, additional photocatalytic runs were carried out varying the total solids loading between 0.25 and 1 g L^{-1} (Figure 5 (a) and (b)). Data of photolysis corresponding to zero catalysts loading is also plotted for comparison. The beneficial effect of the carbon component in the catalyst is clearly seen; for the experiments performed using a titania loading of 0.25 g L^{-1} , phenol conversion was under 40 %, far below the 84 % obtained for the hybrid carbon/titania photocatalyst with a total solids loading of 0.5 g L^{-1} , thus using an identical amount of TiO_2 . When the total loading of the photocatalyst is raised to 1 g L^{-1} When the total loading of the photocatalyst is raised to 1 g L^{-1} (sample labeled as $2x\text{TiO}_2/\text{S}$, see Figure 5 (b)), for which the amount of semiconductor was doubled, a high and almost unchanged phenol conversion was observed, whereas the mineralization extent improved

(Table 1). An enhanced performance of the yield with increasing the catalyst loading is rather common in heterogeneous photocatalysis [24]; in this case it also seems consistent as both individual components of TiO₂/S show some photoactivity (although very different) under adequate irradiation (Table 2).

The analysis of the porous features of the catalysts after the photocatalytic runs also revealed interesting information. First of all, it is worth noting that the accessible porosity of the nanoporous carbon after the pre-equilibration step in darkness (S_{dark}) was largely reduced, which was expected considering the phenol uptake of this carbon. Secondly, the textural features of the used catalysts (after the photocatalytic runs) are larger than those of their corresponding counterparts after dark adsorption (Table 1), which indicates a lower pore clogging of the used catalysts after the photocatalytic runs than after the adsorption in dark conditions. The effect is similar for both illumination conditions, although it was more pronounced when the catalysts were exposed to light at $\lambda > 200$ nm.

This is more clearly evidenced in the analysis of the narrow microporosity by means of the CO₂ adsorption isotherms at 0 °C (Figure 6). According to literature the adsorption of phenolic compounds on hydrophobic nanoporous carbons at low coverage occurs preferentially on the narrow micropores [25,26]. Since the microporosity of the hybrid carbon/titania photocatalyst is inherited from the carbon component, investigating the evolution of the volume of narrow micropores allows clarifying the fate of the fraction of phenol initially adsorbed on the porosity of the carbon material in the course of the photocatalytic reaction.

The higher micropore volume of the catalysts illuminated for 6 hours compared to the accessible porosity after the pre-equilibration step in darkness (series dark) demonstrates that neither phenol nor its intermediates are accumulated (adsorbed) in the micropore network but rather decomposed due to the photocatalytic reaction. During the photocatalytic runs, a small fraction of the pollutants may be decomposed inside the carbon matrix, since the fraction retained in the porosity decreased compared to the starting of the illumination, and the concentration in solution does not rise. This is in agreement with our previous studies reporting the photodegradation of the adsorbed fraction for some nanoporous carbons [11,13].

Interestingly, the same trend was seen when the nanoporous carbon alone was exposed to light (Table 1), which points out to some level of photochemical activity for this carbon. Based on our previous studies [12], we attribute this to the ability of the carbon material to generate oxygen radicals when exposed to high energy light. The large amount of

polyhydroxylated degradation intermediates also corroborates this. The concentration decay curves of phenol and intermediates upon irradiation of sample S showed an interesting pattern. When exposed to light at $\lambda > 200$ nm (high energy), the conversion of phenol is quite similar to that obtained from direct photolysis (Figure 3), while the time evolution of intermediates detected in solution is markedly smaller (Figure 4). This behavior is not accompanied by a clogging of the pore structure of the carbon (Figure 6 and Table 1), which confirms that the disappearance of phenol (and intermediates) from the aqueous solution cannot be attributed to the accumulation in the porosity. Additionally, an outstanding mineralization was achieved (ca. 53 % for S $\lambda > 200$ nm), a value comparable to that of TiO₂/S and higher than that of direct photolysis and bare titania (Table 2).

When the filter is used (light at $\lambda > 360$ nm), the conversion of phenol obtained upon irradiation of the nanoporous carbon alone is quite small; the concentration decay curve displays an interesting shape with a sharp decrease at short irradiation times (Figure 3) followed by a steady conversion above 60 min. As discussed above, the accessible microporosity of the carbon after the photocatalytic runs is still higher than that after dark adsorption, indicating some photoactivity. However, the plateau indicates that the photochemical reaction is stopped after 60 minutes of illumination; under these illumination conditions (wavelength $\lambda > 360$ nm) the contribution of direct photolysis of phenol can be neglected, thus data suggests that the photoactive sites of the carbon under visible light are consumed or deactivated in the course of the reaction.

In a previous study [18] we observed that the incorporation of the nanoporous carbon in the catalyst does not affect the degradation mechanism of phenol under visible light. Indeed, as seen in Figure 4, similar intermediate patterns were obtained for TiO₂ and TiO₂/S when exposed to light at $\lambda > 360$ nm, with quinones (due to the pH dependence of hydroquinone and benzoquinone, these are discussed together as total quinones, QU) as predominant compounds. The concentration of intermediates steadily increases with time for titania; in contrast it reaches a maximum after ca. 3 h of irradiation for TiO₂/S, pointing out a faster degradation of phenol and its intermediates.

A different trend appeared when the samples were irradiated with light at $\lambda > 200$ nm. Overall, the intermediate products are the same as those detected when the filter is applied, although their amount and distribution is different. A marked regioselectivity is noticed towards the preferential oxidation in the *ortho* position to form catechol (over *meta* or *para* positions in

resorcinol and hydroquinone) in the case of samples S and TiO₂/S and for the non-catalyzed reaction (photolysis $\lambda > 200$ nm). In the case of TiO₂, the amount of CAT increased although QU are still the major intermediates. Interestingly, a similar regioselectivity to the formation of CAT over QU has been reported for other nanoporous carbons under UV illumination [11]. This is important since CAT has a higher reactivity over QU [27], which would account for the improved conversion of phenol upon irradiation at $\lambda > 200$ nm. Additionally, trace concentrations of trihydroxylated benzenes (i.e., 1,2,4-trihydroxybenzene and 1,3,5-trihydroxybenzene) were detected for all three catalysts, not seen in the photolytic breakdown under the same illumination conditions nor upon irradiation with light at $\lambda > 360$ nm. The formation of polyhydroxylated subproducts suggests that more hydroxyl radicals are involved when the reaction is carried out using light at $\lambda > 200$ nm and catalysts.

Doubling the amount of TiO₂ in the catalyst (sample 2xTiO₂/S) reversed the distribution of the intermediates (Figure S3 in Supplementary Information), showing again the predominance of QU over CAT, following the same trend as TiO₂. Thus it seems that the distribution of the intermediates depends on the composition of the catalysts, with QU being favored over CAT at low energy photons and when titania is the major component of the photocatalyst (either TiO₂ alone or high loadings in the catalyst), and vice versa when the carbon component is added to the catalyst composition. Both cases indicate that the photooxidation of phenol proceeds through the *ortho*- and *para*-substitution, which are the preferred positions in electrophilic substitutions of aromatic rings [27]. The formation of polyhydroxylated compounds along with the accumulated amounts of intermediates - suggesting lower photooxidation reactivity than phenol itself - are also characteristics of electrophilic mediated pathways.

Another distinctive aspect of the photocatalytic runs under different illumination conditions is the variation of the solution pH observed for all the studied systems (photolysis and photocatalysis). The initial solution pH decreased between 1-3 pH units within the first 3 hours of irradiation using light at $\lambda > 200$ nm, as opposed to a fall by 0.5 units when the filter was used (light at $\lambda > 360$ nm). Such pH variation is consistent with the difference between TOC and TOC_{HPLC} values (Table 2), which account for the amount of short-chain alkyl acids present in solution at the end of the reaction. In fact, a smaller difference between these values, that is, a lesser amount of acids, is observed when a higher mineralization is obtained. This is also consistent with the above-mentioned mechanism based on electrophilic additions

leading to the regioselective oxidation in the ortho-position, which are more favored at acidic pH [27].

Additionally, the stability of the catalysts was confirmed upon irradiation of suspensions in water in the absence of phenol. Regardless the illumination conditions (lamp with and without filter), the carbon component was found to be stable when illuminated alone or in the hybrid TiO₂/carbon catalysts, as inferred from the elemental analysis of the samples (Table S1). On the other hand, according to the results previously obtained with TiO₂ powders and TiO₂/carbon composites [28] the slightly acidic characteristics of the sisal based allow us to anticipate the re-use of the catalysts in consecutive phenol photooxidation cycles.

4. Conclusions

We have investigated the dependence of the photochemical activity of hybrid titania/carbon photocatalysts with the wavelength of the irradiation source, by using polychromatic light and a pyrex filter to remove the contribution at $\lambda < 360$ nm. Phenol photooxidative efficiencies were larger at $200 < \lambda < 600$ nm for both the photolytic and catalyzed reactions. The use of a nanoporous carbon as additive increased both the photoconversion of phenol and the mineralization extent using half of the amount of the semiconductor. The effect was more pronounced at $\lambda < 200$ nm. Photocatalytic runs carried out with the carbon material alone (in the absence of titania) demonstrated a certain level of intrinsic photochemical activity of the nanoporous carbon additive under both irradiation conditions. When the light is filtered at $\lambda > 360$ nm, the conversion of phenol upon irradiation of the nanoporous carbon alone dropped significantly with a steady conversion above 60 min, suggesting that the photoactive sites of the carbon under visible light are consumed or deactivated in the course of the reaction.

In all the studied systems the photooxidation of phenol follows an electrophilic mediated pathway, with a marked regioselectivity depending on the composition of the catalyst and the illumination conditions. Quinones are favored over catechol at low energy photons and when titania is the major component of the photocatalyst (either TiO₂ alone or high loadings in carbon/titania catalyst), and vice versa when the carbon component is added to the catalyst composition. At $\lambda > 200$ nm higher amounts of polyhydroxylated intermediates were detected, suggesting that more hydroxyl radicals are involved under these illumination conditions.

ACKNOWLEDGMENTS

The authors thank Cordex (Portugal) for kindly supplying sisal. The financial support of the pluriannual funding to CQB (UID/MULTI/00612/2013), and MINECO (CTM2014/56770-R, AIB2010-PT00209) is also acknowledged. MAA and ASM thank FCT for their PhD (SFRH/BD/71673/2010) and Post-Doc (SFRH/BPD/86693/2012) fellowships, respectively. RJC thanks PCTI Asturias Fondos Feder for her Severo Ochoa fellowship. The authors thank Dr. Matos for fruitful discussion.

References

- [1] N. Serpone, E. Pelizzetti, Photocatalysis: fundamental and applications; Wiley Interscience, New York, 1989.
- [2] M.A. Henderson, Surf. Sci. Reports 66(2011) 185-297.
- [3] R. Leary, A. Westwood, Carbon 49 (2011) 741-72.
- [4] J.L. Faria, W. Wang, Carbon materials in photocatalysis, in: P. Serp, J.L. Figueiredo (Eds.), Carbon materials for catalysis, John Wiley & Sons, New York, 2009, pp. 481-506.
- [5] J. Matos, J. Laine, J.M. Herrmann, Appl. Catal. B: Environ 91 (1998) 281–91.
- [6] J. Araña, J.M. Doña-Rodríguez, E. Tello Rendón, C. Garriga i Cabo, O. González-Díaz, J.A. Herrera-Melián, J. Pérez-Peña, G. Colón, J.A. Navío, Appl. Catal. B: Environ. 44 (2003) 161-172.
- [7] B. Tryba, A.W. Morwski, M. Inagaki, Appl. Catal. B: Environ. 41 (2003) 427–433.
- [8] Y. Yu, J.C. Yu, J.-G. Yu, Y.-C. Kwok, Y.-K. Che, J.-C Zhao, L. Ding, W.-K. Ge, P.-K. Wong, Appl. Catal. A: Gen. 289 (2005) 186-196.
- [9] R. Ocampo-Pérez R.; M. Sánchez-Polo, J. Rivera-Utrilla, R. Leyva-Ramos, Appl. Catal. B: Environ. 104 (2011) 177-184.
- [10] C.O. Ania, L.F. Velasco, T. Valdes-Solis, Photochemical response of carbon materials. in: J.M.D. Tascon (Ed.), Novel Carbon Adsorbents, Elsevier, London, 2012, pp. 521-547.
- [11] L.F. Velasco, I.M. Fonseca, J.B. Parra, J.C. Lima, C.O. Ania, Carbon 50 (2012) 249-258.
- [12] L.F. Velasco, V. Maurino, E. Laurenti, C.O. Ania, Appl. Catal. A: Gen. 453 (2013) 310-315.
- [13] L.F. Velasco, J.C. Lima, C.O. Ania, Angew. Chem. Int. Ed. 53 (2014) 4146-4148.

- [14] M. Haro, L.F. Velasco, C.O. Ania, *Catal. Sci. Tech.* 2 (2012) 2264-2272.
- [15] T.J. Bandoz, J. Matos, M. Seredych, M.S.Z. Islam, R. Alfano, *Appl. Catal. A: Gen.* 445 (2012) 159-165.
- [16] Y. Luo, Y. Heng, X. Dai, W. Chen, J. Li, *J. Solid State Chem.* 182 (2009) 2521-2525.
- [17] A.S. Mestre, A.S. Bexiga, M. Proença, M. Andrade, M.L. Pinto, I. Matos, I.M. Fonseca, A.P. Carvalho, *Biores. Technol.* 102 (2011) 8253-8260.
- [18] M.A. Andrade, R.J. Carmona, A.S. Mestre, J. Matos, A.P. Carvalho, C.O. Ania, *Carbon* 76 (2014) 183-192.
- [19] H.K Kuhn, S.E. Braslavsky, R. Schmidt, *Pure App. Chem.* 76 (2004) 2105-2146.
- [20] J. Rouquerol, F. Rouquerol, P. Llewellyn, G. Maurin, K.S.W. Sing, *Adsorption by Powders and Porous Solids. Principles, Methodology and Applications*, second ed., Academic Press, Amsterdam, 2014.
- [21] H. Chun, W. Yizhong, T. Hongxiao, *Chemosphere* 41 (2000) 120-1209.
- [22] B. Bayarri, M.N. Abellan, J. Gimenez, S. Esplugas, *Catalysis Today* 129 (2007) 231-239.
- [23] S. Shanmuga Priya, M. Premalatha, P. Subramanian, *IE(J) Chem. Eng.* 90 (2009) 10-16. *Journal of The Institution of Engineers (Chemical Engineering division)*, Vol: 90, September 2009, pp.10-16.
- [24] J.-M. Herrmann, *Appl. Catal. B: Environ.* 99 (2010) 461-468.
- [25] L.F. Velasco, C.O. Ania, *Adsorption* 17 (2010) 247-254.
- [26] C. Moreno-Castilla, *Carbon* 42 (2004) 83-94.
- [27] V. Prakash Reddy, G.K. Surya-Prakash, *Electrophilic reactions of phenols*. in: Z. Rappoport (Ed.), *The chemistry of phenols*, John Wiley & Sons, England, 2003 pp. 600-660.
- [28] L.F. Velasco, R.J. Carmona, J. Matos, C.O. Ania, *Carbon* 73 (2014) 206-215.

Tables Captions

Table 1. Phenol degradation, Total Organic Carbon values (TOC, in mg C L^{-1}) and mineralization degree after 6 hours irradiation of the catalysts under varied illumination conditions. Initial TOC values correspond to the phenol concentration in solution after the pre-adsorption step.

Table 2. Main textural parameters obtained from gas adsorption data of the fresh and used catalysts (after the photocatalytic runs) at different illumination conditions. Data corresponding to the materials after the pre-equilibration in the dark (adsorption) is also included for comparison.

Figures Captions

Figure 1. Diffuse reflectance (a) and infrared (b) spectra of the catalysts.

Figure 2. SEM images of the catalysts.

Figure 3. Phenol concentration decay curves with the illumination time after irradiation at (a) $\lambda > 200$ nm and (b) $\lambda > 360$ nm. Negative times highlighted in shaded correspond to the pre-adsorption period of 30 min to equilibrate each system. Catalyst loading 0.5 g L^{-1} ; 86 mg L^{-1} phenol in solution at the beginning of illumination.

Figure 4. Evolution of phenol degradation intermediates upon irradiation under different illumination conditions: QU-quinones; BZ-benzoquinone; CAT-catechol, RES-resorcinol; 124THB-1,2,4-trihydroxybenzene; 135THB-1,3,5-trihydroxybenzene. Catalyst loading 0.5 g L^{-1} ; 86 mg L^{-1} phenol in solution at the beginning of illumination.

Figure 5. Effect of the catalyst loading at different irradiation conditions: (a) effect of TiO_2 loading; (b) effect of the total catalyst loading (symbols represent experimental values while lines are guides for the eye). Catalyst loading 0.5 g L^{-1} ; 86 mg L^{-1} phenol in solution at the beginning of illumination.

Figure 6. CO_2 adsorption isotherms obtained at 0°C on the as-received and exposed catalysts at different illumination conditions.

Table 1. Phenol degradation, Total Organic Carbon values (TOC, in mg C L⁻¹) and mineralization degree after 6 hours irradiation of the catalysts under varied illumination conditions. Initial TOC values correspond to the phenol concentration in solution after the pre-adsorption step.

	Conversion (%)*	TOC (mg C L ⁻¹)	TOC _{HPLC} ^{**} (mg C L ⁻¹)	Mineralization (%)
Photolysis $\lambda > 360\text{nm}$	3	64.8	64.8	1
S $\lambda > 360\text{nm}$	21	61.5	61.5	5
TiO₂ $\lambda > 360\text{nm}$	54	51.3	39.2	21
TiO₂/S $\lambda > 360\text{nm}$	62	50.4	40.3	22
Photolysis $\lambda > 200\text{nm}$	81	62.1	17.4	5
S $\lambda > 200\text{nm}$	85	30.6	12.6	53
TiO₂ $\lambda > 200\text{nm}$	70	43.6	25.2	33
TiO₂/S $\lambda > 200\text{nm}$	84	29.3	11.4	55
2 x TiO₂/S $\lambda > 200\text{nm}$	88	24.6	15.3	62
*catalyst loading 0.5 g L ⁻¹ ; 86 mg L ⁻¹ phenol in solution at the beginning of illumination				
** Values calculated considering the aromatic intermediates detected by HPLC				

Table 2. Main textural parameters obtained from gas adsorption data of the fresh and used catalysts (after the photocatalytic runs) at different illumination conditions. Data corresponding to the materials after the pre-equilibration in the dark (adsorption) is also included for comparison.

	S_{BET} (m ² g ⁻¹)	V_{TOTAL} ^A (cm ³ g ⁻¹)	$V_{\text{MESOPORES}}$ ^B (cm ³ g ⁻¹)	W_{0,N_2} ^C (cm ³ g ⁻¹)	W_{0,CO_2} ^C (cm ³ g ⁻¹)
TiO₂	57	0.4	-	0.02	-
S	968	0.45	0.04	0.41	0.37
TiO₂/S	484	0.23	0.02	0.21	0.16
S dark	351	0.17	0.02	0.15	0.24
TiO₂/S dark	236	0.13	0.02	0.11	-
S $\lambda > 200\text{nm}$	354	0.17	0.02	0.15	0.29
TiO₂/S $\lambda > 200\text{nm}$	288	0.16	0.04	0.12	0.14
S $\lambda > 360\text{nm}$	388	0.18	0.03	0.17	0.29
TiO₂/S $\lambda > 360\text{nm}$	288	0.16	0.04	0.12	0.14
^A evaluated at $p/p^0 \sim 0.9$ to avoid the contribution of interparticle voids					
^B Difference between V_{TOTAL} and W_{0,N_2}					
^C Evaluated from the Dubinin-Raduskevich approach					

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Supplementary Information

Effect of the irradiation wavelength on the performance of of nanoporous carbon as an additive to TiO₂

Marta A. Andrade^{1,2}, Rocío J. Carmona², Ana S. Mestre¹, Ana P. Carvalho^{1*}, Conchi O. Ania^{2*}

¹ Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

² ADPOR Group, Dpt. Chemical Processes for Energy and Environment, Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080 Oviedo, Spain

Figure S1. Emission spectra of the high pressure mercury lamp used (Helios Italquartz, 125 W) with and without pyrex filter.

Figure S2. Phenol adsorption kinetics for the catalysts (in the same experimental conditions of the photocatalytic runs). For 2xTiO₂/S (catalyst loading 1 g L⁻¹) only the data corresponding the 30 min is shown, allowing the comparison of the amount adsorbed.

Figure S3. a) Phenol concentration decay curve, including the pre-adsorption step, for sample 2xTiO₂/S; b) Evolution of phenol degradation intermediates detected upon irradiation of sample 2xTiO₂/S: QU-quinones, CAT-catechol, RES- resorcinol; 124THB-1,2,4-trihydroxybenzene.

Table S1- Elemental analysis of carbon S and of the catalysts (after irradiation of the catalyst's suspensions in water in the absence of phenol).*-normalized per gram of carbon.

	C	H	O
S	82.8	1.2	16.0
S $\lambda > 200\text{nm}$	79.5	1.4	15.6
S $\lambda > 360\text{nm}$	81.0	1.1	15.4
*TiO₂/S $\lambda > 200\text{nm}$	82.4	1.4	16.2
*TiO₂/S $\lambda > 360\text{nm}$	82.9	1.2	15.9