

Green and low cost tetracycline degradation processes by nanometric and immobilized TiO₂ systems

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Abstract

Tetracycline accumulation in surface waters, due to its extensive use and ineffective removal by traditional remediation treatments, represents a major environmental problem, leading *e.g.* to increased antibiotic resistance. Here, photocatalysis by TiO₂, both as nanostructured powders and macroscopic immobilized systems, is proposed as an efficient procedure to totally degrade tetracycline to harmless compounds. Home-made TiO₂ powders were studied to clarify the role of synthetic and process parameters (light pre-treatment, calcination temperature) and to shed light on the role of radical species in promoting the reaction (tests with radical scavengers). The control of phase composition and wetting features appears to be essential in producing photocatalysts able to completely mineralize tetracycline in a short time scale (6 h). The knowledge acquired on the powder system was preparatory to the development of low cost, mechanically robust and highly active TiO₂ immobilized systems. Two different substrate geometries (laminas and pellets) were investigated to ease the photocatalyst removal from the treated effluent. Both immobilized systems proved efficient: in particular, the TiO₂-coated pellets promoted tetracycline degradation and mineralization on a time scale that is very competitive when compared to similar literature immobilized systems.

Keywords

photocatalysis, tetracycline, titania, TiO₂ immobilization, degradation intermediates

1. Introduction

Tetracyclines, among the most common antibiotics, are classified as emerging micro-pollutants since their accumulation in the environment can induce long-term effects such as endocrine disruption, antibiotic resistance and toxicity on living organisms [1]. Due to their extensive use over the years, traces of tetracycline and of their metabolites have been found in many different environments, like wastewaters, drinking waters and soils [2]. Moreover, these antibiotics, due to their physicochemical properties, are mostly excreted after use in the pristine un-metabolized form.

Conventional wastewater treatments for the removal of organic pollutants usually fail to achieve a complete degradation of tetracycline, favouring the production of toxic reaction intermediates. Moreover, by-products often maintain high antibacterial activity, preventing the use of biological remediation methods, even as post-treatments [3]. Consequently, the search for effective and economical processes to reduce tetracycline release into the ecosystem has become imperative.

Remediation methods based on adsorption and/or filtration, although being applied to tetracycline-polluted systems [4–6], have the only effect to move the pollutant from the liquid to the solid phase without degrading it. In the last few years, advanced oxidation processes have been proposed as efficient methods to perform tetracycline degradation. In this regard, photolysis, ozonation, inverse osmosis, electrochemical, Fenton and photo-Fenton processes have been studied [7–11]. However, photocatalysis is arguably the most promising technique, giving rise to by-products characterized by a lower toxicity [12]. Different materials have been investigated as photocatalysts for tetracycline degradation. Several complex multi-component materials have been recently proposed to improve the photocatalytic degradation of tetracyclines, such as carbon nanotubes/Bi₂WO₃ composites [13], BiOI microspheres [14] and Ag/Fe₂O₃/C₃N₄ magnetic materials showing visible-light absorption [15]. However, starting from the pivotal studies of Reyes *et al.* and Palominos *et al.* [16,17], the chemical and photochemical stability, natural abundance and

low cost have made TiO₂ one of the best choices for removing tetracyclines from the environment by photocatalytic processes [18–20]. In this respect, commercial powders were mainly adopted in literature works [21,22]. Zhu *et al.*, by using P25 TiO₂, studied the molecule degradation pathway and the changes in the tetracycline solution toxicity during the reaction [23]; the influence of interferences and the optimization of the physicochemical parameters affecting the photocatalytic efficiency were also investigated [17,24,25].

Here, the photocatalytic degradation of tetracycline was performed by TiO₂ powders prepared by a multi-step procedure and thermally treated at four different temperatures. The choice of the calcination temperature is not trivial when large organic target molecules are considered, since the pollutant/oxide interactions can be deeply affected by the physicochemical features of the photocatalyst. Higher calcination temperatures can produce diverging effects on the material, *e.g.* decreasing the surface area while increasing the crystallite size, reducing the hydrophilicity but increasing the regularity. To the authors' best knowledge, no results can be found in the literature concerning this aspect in the case of the photocatalytic degradation of tetracycline.

A second relevant point is addressed in the present work: the transfer of the knowledge acquired on powders to parent immobilized systems. The immobilization of the photocatalyst on removable or reusable substrates has become an urgent issue. Few literature works address this problem. Very recently, Pronina and coworkers used TiO₂-coated clay granules for the degradation of tetracycline, with low degradation efficiency due to the low surface area of the supports [26]. Lu *et al.* synthesized TiO₂/Fe₂O₃/carbon nanotubes composites removable with magnets [27]. Borosilicate glass was used as a support for TiO₂ by Lalhariatpuia *et al.* [25]. In this work, two different strategies are proposed as viable solutions to the longstanding problem of the removal of suspended photocatalysts from the stream after use: titania films were deposited, starting from a sol developed in our laboratory [28], on two different kinds of supports (metal laminas or ceramic pellets). For both powders and immobilized films, the degradation process was followed by monitoring both the pollutant disappearance and the mineralization degree. The reusability of the

photocatalyst and the role played by radical species in supporting the reaction were also investigated.

2. Experimental Section

2.1 Sample preparation

Reactants were purchased from Sigma Aldrich and were used without any further purification. Solutions and suspensions were prepared by using doubly distilled water passed through a Milli-Q apparatus.

TiO₂ nanostructured powders were prepared by a modification of the procedure reported by Behnajady *et al.* [29]. In a flask kept in an ice/water bath, 3.78 g of acetic acid (AcOH) was mixed with 18.38 g of titanium(IV) isopropoxide (97%) (TTIP). Then, 220 mL of water was added dropwise in about 30 min while stirring vigorously. The TTIP:AcOH:H₂O molar ratios were 1:1:200. The reaction mixture was stirred for 1 h and then stored in the dark overnight at room temperature. The suspension was subsequently dried in an oven at 70 °C for 3 h and then at 100 °C for 24 h. The ground powder was purified by osmosis, centrifuged and dried in an oven at 80 °C. Finally, the powder was calcined at different temperatures for 6 h under an O₂ flux (9 NL h⁻¹). The powder samples calcined at 200, 300, 400, 500 and 600 °C were labelled as T200, T300, T400, T500 and T600, respectively.

Immobilized titania samples were prepared by depositing two successive TiO₂ layers on two different commercial supports, starting from a sol whose preparation procedure has been previously reported [28]. Sandblasted Al laminas were used as cheap and recyclable supports since the native alumina film favours the adhesion of the titania layer. The second selected support consisted in alumina commercial pellets (AL60610300 Goodfellow). Al plates (5.5 × 15 cm²) and 10 g of the millimetric rods were dipped in 40 mL of titania sol for 1 h, then drained from the sol onto a steel grid and immediately calcined at 500 °C for 5 h in O₂ flux (9 NL h⁻¹). The entire procedure was

repeated twice. Before the layer deposition, laminas were cleaned by a previously reported procedure [30].

2.2 Sample Characterization

Details about the adopted characterization techniques are reported in the Supplementary Material.

2.3 Photocatalytic activity

Samples were tested under UV irradiation (Jelosil HG500 lamp) in the degradation of aqueous solutions of tetracycline hydrochloride. The effective input power density of the lamp was 30 mW cm^{-2} , while the radiation energy leaving the jacketed reactor was 5 mW cm^{-2} in the case of the TiO_2 suspension and around zero in the case of the Al lamina, respectively. A commercial TiO_2 nanopowder (Alfa Aesar) was also tested as a reference; this commercial sample was selected due to its similar phase composition (anatase plus rutile traces) and specific surface area ($141 \text{ m}^2 \text{ g}^{-1}$) with respect to the synthesized samples. The photocatalytic tests were performed in a closed Pyrex glass jacketed reactor with a volume of 600 mL. Tests were carried out at $20 \text{ }^\circ\text{C}$ and natural pH (ca. 3), with magnetic stirring and oxygen bubbling (9 NL h^{-1}). The initial pollutant concentration was 35 ppm.

Tetracycline adsorption on TiO_2 was quantified by a test performed in the dark. The system reached its equilibrium after 20 min, with a 30% maximum amount of adsorbed molecule for T400. Direct photolysis was also evaluated by a test in the absence of photocatalyst, leading to negligible mineralization (Tab. 1, line 2).

Tests with TiO_2 powders were performed in slurry, by suspending 300 mg of the photocatalyst (0.5 g L^{-1} , according to previous literature studies [16,19]). The suspensions were sampled using a syringe and filtered with a Millipore MF-membrane filter ($0.45 \text{ }\mu\text{m-HA}$). In the case of immobilized supports, either one Al lamina or 10 g of pellets (deposited at the bottom of the reactor) were utilized. The amount of TiO_2 -coated pellets (10 g) was specifically selected in order to

provide an amount of TiO₂ equivalent to tests with powders (300 mg). Both powders and immobilized supports were irradiated with UV light for 1.5 h before the photocatalytic test.

The disappearance of the target molecule was followed by UV-vis spectroscopy (Shimadzu UV-2600 spectrophotometer), measuring the intensity of the absorption peak at 357 nm, typical of tetracycline (Fig. S1). The mineralization degree was estimated by Total Organic Carbon (TOC) measurements (Shimadzu TOC-V CPN Analyzer) according to the following equation:

$$\text{mineralization degree} = \frac{TOC_0 - TOC_t}{TOC_0} \cdot 100$$

The procedures of reuse experiments and of scavenger tests are reported in the Supplementary Material, together with that of Electrospray Ionisation Mass Spectrometry (ESI-MS) analyses used to identify the reaction intermediates.

3. Results and Discussion

3.1 Powder TiO₂ photocatalysts

The first part of the work focuses on the role played by the calcination temperature on the physicochemical properties and on the photocatalytic activity of home-made titania powders. As the lowest calcinations temperature (200 °C) yielded samples containing significant amounts of organic contaminants (as revealed by the dark colour of the powders), the work will focus on the T300, T400, T500 and T600 samples.

Crystal Structure and Morphology. XRPD spectra of all samples show a good degree of crystallinity (Fig. 1), which increases with the calcination temperature (the highest signal to noise ratio was achieved by the T600 sample). In all samples, anatase is the main polymorph (Tab. 1, 2nd column). T300 and T400 are biphasic, containing both anatase and brookite. Due to the relatively low calcination temperatures, anatase crystallites have a diameter smaller than 10 nm (Tab. 1, 3rd column). On the contrary, T500 is composed of pure anatase with larger crystallites ($d_a^{101} = 14$ nm), as shown by the sharper diffraction peaks. T600 is the most crystalline sample, and it is

characterized by a 20% rutile content, as expected on the grounds of the calcination temperature. The anatase average crystallite dimension further increases, reaching a diameter of 50 nm. The commercial Alfa Aesar sample is mainly composed by anatase with rutile traces and shows a crystallite size of 15 nm. The N₂ adsorption-desorption isotherms in subcritical conditions of the four TiO₂ powders and of the commercial sample are shown in Fig. 2. T300, T400 and T500 samples reveal hysteresis loops characteristic of mesoporosity. The profile of the hysteresis loops is H2-type, characteristic of “bottle-neck”-shaped pores and the vast majority of the pores has a diameter smaller than 6 nm (Fig. 3). The different position of the isotherm “knee”, which identifies the creation of a N₂ monolayer on the solid surface, shows that the T400 specific surface area (162 m² g⁻¹) is about twice that of T500 (73 m² g⁻¹), as reported in Tab. 1. Interestingly, T300 showed a decrease in specific surface area and pore volume with respect to T400, which might be related to an uncompleted removal of organic residues at this low calcinations temperature, as also supported by the sample whitish colour (see DRS results). Sintering effects and crystallite growth are responsible for the marked decrease of specific surface area of T500, as well as for a remarkable decrease of total porosity (from 0.284 to 0.103 mL g⁻¹), especially concerning the smallest pores (< 6 nm). Further increasing the calcination temperature to 600 °C leads to a tremendous decrease in the specific surface area (2 m² g⁻¹) and to an almost complete disappearance of the pores smaller than 6 nm. The hysteresis loop of the T600 sample, probably of H3-type, is almost unappreciable. It is noteworthy that the amount of bigger pores (> 80 nm) is not dependent on the calcination treatment. The shape of the hysteresis loop of the commercial sample is different from the low temperature home-made ones and can be labelled as H3-type, typical of slit-shaped pores. This sample shows the largest total pore volume (Fig. 3 and Tab. 1, 5th column).

Optical Characterization. DRS spectra of T400, T500 and T600 samples (Fig. 4) show slight variations of the absorption edge among the different samples. This is testified by the apparent band gap values (Tab. 1, 6th column): T400 has the highest band gap value (3.15 eV), possibly due to the lower crystallinity and the slight amount of brookite, whose band gap is wider

with respect to anatase [31]. On the other hand, the presence of rutile in T600 results in a red shift of the absorption edge and a decrease in the sample band gap value (2.96 eV with respect to 3.07 eV for T500), as expected on the grounds of rutile smaller band gap [32]. Unlike the other samples, T300 shows a higher absorption in the visible region (400-700 nm), which may be indicative of the presence of carbonaceous contaminants, in agreement with BET results (*vide supra*). Figure 4 reports also the curve relative to the commercial sample which appears slightly blue-shifted, giving rise to the slightly higher band gap value.

Photocatalytic activity. The photocatalytic activity of the different samples was tested toward the degradation of tetracycline hydrochloride in aqueous solution at natural pH. Although literature works indicate that the molecule photodegradation is favoured by alkaline pH values [17], no pH correction was introduced in the present work to simplify at best the chemistry of the process. The target molecule degradation was followed by UV-vis spectroscopy on the grounds of an established method widely proposed in the literature [8,14,16,17] and previously validated by HPLC determinations [13,16]. The mineralization degree was obtained by TOC measurements as an indication of the complete oxidation of tetracycline to CO₂, H₂O and NH₄⁺.

All samples were submitted to a UV irradiation step (1.5 h) prior to the photocatalytic tests. This procedure was adopted after observing an appreciable promotion of the overall activity of the photocatalyst upon irradiation treatment, from both the molecule disappearance and the mineralization viewpoint (Figs. 5a and S2). The prolonged pre-irradiation step may favour the hydroxylation of the powder surface and promote a cleaning effect from adsorbed impurities [33–36]. The increase in the -OH population at the surface of the photocatalyst, in its turn, may allow a better water wetting and the ensuing formation of more stable suspensions. Further effects may be related to a possible surface reconstruction occurring upon prolonged UV irradiation [37]. These effects play also a relevant role in affecting the activity of reused samples. The reused T400 sample is even more active than the pristine irradiated sample (Fig. 5a). The total absence of inactivation of the sample could have been expected on the grounds of the complete mineralization of the pollutant,

as proved by FTIR spectra of the used photocatalyst (Fig. S3). However, the slight increase in performance can be possibly attributed to the further irradiation step received by the reused sample and to the prolonged wetting in water during the former reaction.

In order to investigate the role played by oxidant species and charge carriers on the mechanism of tetracycline degradation, photocatalytic tests were carried out in the presence of two different scavengers (isopropanol and Na-EDTA) adopting T400 as the reference photocatalyst. Isopropanol was used as OH^\bullet scavenger, according to other literature studies [13,17,23,25], while Na-EDTA was chosen as h^+ scavenger as proposed by Zhu *et al.* and Lalhriatpuia *et al.* [23,25]. The degradation profiles are compared in Fig. 5b. Both scavengers inhibit the degradation, implying that both OH^\bullet and h^+ species are responsible for the oxidation of tetracycline, but the addition of Na-EDTA produces a larger inhibition with respect to isopropanol. This occurrence can be the result of two parallel effects: the competitive adsorption between EDTA and tetracycline at the surface of the photocatalyst, and the depletion of holes which directly oxidize the target molecule. A combined role played by both holes and OH^\bullet on the photodegradation of tetracycline by TiO_2 was previously observed by Zhu *et al.* and by Palominos *et al.* [17,23], whereas Luo *et al.* [38] recently proposed a reaction mechanism not involving OH^\bullet species. Yue *et al.* [13], on the other hand, attributed a stronger effect on OH^\bullet species, adopting ammonium oxalate as a hole scavenger. The combined role played by OH^\bullet and h^+ species is supported, in the present case, by reaction intermediates investigated by ESI-MS analyses (Fig. S4). In the initial solution (Fig. S4a), the peak at $m/z = 445$ can be attributed to the molecular ion of tetracycline $[\text{M}+\text{H}]^+$, while the other peaks are relative to ionization products of the molecular ion [39]. By comparing the ESI-MS spectra before and after 1 h irradiation (Fig. S4b), several peaks relative to degradation intermediates can be identified (Fig. S4c). The two peaks at $m/z = 459$ and 477 have been previously observed by several authors as intermediates in the degradation of tetracyclines [7,12]. Maroga Mboula *et al.* proposed a mechanism implying an initial attack by OH^\bullet followed by the loss of NH_3 supported by the interaction with h^+ species [12]. The presence of a peak at $m/z = 495$ could be related to a further

attack by OH^\bullet to the intermediate at $m/z = 477$, as proposed by Zhu *et al.* [17]. The oxidation products at $m/z = 229$ and 287 revealed that the opening of the non-aromatic rings of tetracycline already occurred after 1 h of irradiation [40,41].

Fig. 6a compares the degradation curves of the different photocatalysts. All powder samples, except T600, produce a complete degradation of tetracycline in 2 h, with a fast kinetics. The initial rates were calculated as pseudo-first order constants (Tab. 2, Fig. 7) in agreement with literature results [23]. T400 exhibits the best performance, reaching 90% degradation after 35 min of irradiation. The T300 sample leads to a slightly slower pollutant disappearance, degrading 83% of the molecule after 35 min. Despite the carbon contamination, T300 presents a good photocatalytic performance, possibly due to its better stability in water ensuing the lower calcinations temperature. The degradation produced by T500 is somewhat lower (66% degradation in 35 min) while T600 gives rise only to a degradation of about 30% in the same time. These results are mirrored by the mineralization degrees obtained for the three samples (Fig. 6b): T400 and T300 produce complete mineralization after 6 h, similarly to T500 which achieves more than 95% mineralization. Again the activity of T600 appears to be the lowest, producing a mineralization lower than 40% after 6 h.

The elaboration of kinetic data of the commercial sample by a pseudo-first order law was not satisfactory. The experimental points (pink triangles) are however reported in Fig. 7 for the sake of comparison. In the case of this sample, the molecule disappearance is fast (Fig. 6a), however tetracycline traces still remained at the end of the test and an incomplete mineralization (92%, after 6 h) was achieved (Fig. 6b).

Our sol-gel powder samples proved very promising materials for the photocatalysis of tetracycline. T400, favoured by the large surface area, appears to be the most efficient material, especially for what concerns the molecule disappearance (Fig. S5). However, the mineralization produced by T500, characterized by half the surface area, is quite comparable to that produced by T400. The comparison of the behaviour of the two photocatalysts may suggest that the mechanism of degradation is different in the two cases: the large surface area of T400 favours the fast

disappearance of the pristine molecule, while the mineralization seems to be more direct in the case of T500. Some specific features of the latter sample, apparently, promote its photocatalytic activity, overcoming the decrease in active surface produced by the higher calcination temperature. A first aspect can be suggested on the grounds of DRS spectra (Fig. 4) showing for T500 a larger absorption of light between 350 and 450 nm, *i.e.* in the emission range of the adopted lamp (Fig. S6), improving light harvesting. Further, the higher calcination temperature promotes crystal growth and surface regularity, as suggested by the almost double value of crystallite size. A decrease in defectivity can be expected to reduce recombination between photogenerated holes and electrons [42], improving photocatalytic efficiency. T600 shows the lowest performance due to the very poor morphological features; however, it is worth noting that its mineralization curve (Fig. 6b) clearly exhibits an increasing trend for all the duration of the photocatalytic test. Despite the very low porosity and photoactive available surface, this fact suggests that the active sites of T600 are not completely inactivated either by tetracycline or by its reaction intermediates.

3.2 Immobilized photocatalysts

A titania sol, previously developed in our laboratory, was adopted to produce mechanically robust and highly photoactive anatase layers [43,44] on supports with two different geometries. A roughened aluminium lamina (Fig. S7a), covered by a native alumina layer, was chosen as a stable, eco-friendly and cheap substrate for the deposition of TiO₂. Then, a second system was developed with the aim of increasing the accessible surface area of the photocatalyst, while using a support with the same chemical composition: commercial alumina pellets (Fig. S7b) with a surface area of around 100 m² g⁻¹ were chosen. The weight of the TiO₂ deposit was estimated in 30 mg per gram of pellets. Interestingly, the pellet specific surface area did not change after the deposition of the TiO₂ layers. Fig. 8 reports cross-sectional SEM images of cut pellets before and after the deposition of TiO₂. The surface appears rough in both cases while the deposition of the titania layer does not

seem to produce appreciable heterogeneity at the surface of the pellet. The TiO₂ layer on commercial pellets was ca. 5 μm thick (Fig. S7c).

The TiO₂-immobilized systems were tested photocatalytically in the same experimental conditions of the TiO₂ nanostructured powders. The aluminium lamina was suspended in the reactor, while the alumina pellets were deposited at the bottom of the reactor forming a compact and stable layer. The photocatalytic degradation was slower with respect to the TiO₂ slurries commented above (Fig. S8, Tab. 2). Both systems, however, accomplished degradation of tetracycline accompanied by a partial mineralization in the short time scale of the test (6 h). The alumina pellets showed a better performance with respect to the Al lamina (Fig. S8, Tab. 2 lines 7-8). After two hours of irradiation, around 60% of tetracycline was degraded by pellets, while only 47% by the lamina. At the end of the reaction, both systems produced more than 80% degradation (93% for pellets). The mineralization trend of both supports (Fig. S8) did not give rise to a plateau, confirming the efficacy of these TiO₂-immobilized macroscopic devices. A complete oxidation of the target molecule has to be expected by prolonging the reaction time. The present results can be analyzed with respect to those reported by He *et al.* [45] concerning the photocatalytic degradation of various pharmaceuticals by titania deposited onto quartz sand. In the literature work the adopted concentration of the pollutant was much lower than in the present case (20 instead of 35 mg L⁻¹) and the degradation of the molecules was obtained by a larger amount of supported photocatalyst (25 instead of 10 g) and after much longer irradiation time (80-100 h for the best conditions). No mineralization data were reported. Although data by He *et al.* pertain to a different wavelength of irradiation with respect to the present ones (300-800 nm) the comparison of the photocatalytic activity of the two immobilized titania systems seems to strongly favour the present materials. Furthermore, the presented sol-gel-based coatings have been previously reported to be more robust and stable to deactivation than films from commercial powders [43].

4. Conclusions

The photocatalytic degradation of tetracycline by TiO₂ nanostructured powders and immobilized macroscopic systems was investigated. Powder samples provided an insight into the relevant physicochemical aspects at play in the process. Home-made sol-gel powders calcined at different temperatures were studied.

Prolonged UV irradiation of the photocatalyst was found to be beneficial for the photocatalytic performance. Such an observation could be related to an increased surface hydroxylation and/or to the occurrence of surface reconstruction upon irradiation. The beneficial effect of light irradiation is profitable for the reusability of the photocatalyst, as shown by recycle tests.

The calcination temperature had a complex effect on the photocatalytic behaviour of the samples. While increasing the calcination temperature to 600 °C proved detrimental, probably as a result of the drastic drop of surface area and porosity, lower calcination temperatures showed high activity with respect to both the molecule disappearance and mineralization. In particular, the sample calcined at 400 °C showed the best performance in tetracycline disappearance, whereas mineralization curves were comparable for both the 300, 400 and 500 °C treated samples. The photocatalytic activity seems to be the result of an interplay among morphology, crystallinity and absorption features of the oxide, which can possibly determine different reaction mechanisms. As a whole, photocatalytic results seem to point out that the rate of tetracycline disappearance increases with the photocatalyst surface area, while its mineralization is less dependent on the photocatalyst morphological features, being fully comparable for the T300, T400 and T500 samples. This latter observation is instrumental for the development of immobilized photocatalysts, since higher calcination temperatures lead to more robust photocatalyst coatings.

In this respect, the role of radical species and electron holes was investigated. The role of hydroxyl radicals in tetracycline photocatalytic degradation is in fact a debated topic in the literature. Our tests with radical scavengers showed that both OH[•] and h⁺ species take part in the tetracycline degradation, with the holes playing a more relevant role. The concomitant occurrence

of both OH^{\bullet} - and h^+ - mediated pathways was confirmed also by ESI-MS determinations of the degradation intermediates.

Finally, a crucial aspect for the real life application of the remediation test was considered: the immobilization of TiO_2 on macroscopic substrates. The immobilization of photocatalysts on macroscopic substrates enables their easier removal from the treated effluent; further, it allows to overcome the health concerns associated with volatile nanostructured materials. However, the lower number of active sites in immobilized systems leads to detrimental effects on the process efficiency and makes the photocatalyst more prone to poisoning phenomena. In this respect, we tested two possible geometries for the substrates: roughened laminas and macroscopic pellets. In order to keep the costs low while promoting the adhesion of the TiO_2 layer on the substrate, aluminium/alumina supports were chosen. The TiO_2 deposition was carried out starting from a stable sol in order to guarantee the formation of a mechanically robust anatase layer. Photocatalytic tests showed that both immobilized substrates present notable photoactivity. The most performing immobilized photocatalyst proved to be the TiO_2 -coated alumina pellets, possibly due to their higher available surface area. Despite the high pollutant content, no plateaus were observed in the mineralization curve, confirming the efficacy of these devices.

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Table 1 - Specific surface area (S_{BET}), total pore volume (V_{pores}), average crystallite dimension of the anatase phase (d_a^{101}), phase composition (A: anatase; B: brookite; R: rutile), and apparent band gap value (E_g) of the three powder samples.

Sample	Phase composition (%)	d_a^{101} (nm)	S_{BET} ($m^2 g^{-1}$)	V_{pores} ($mL g^{-1}$)	E_g (eV)
T300	95 A – 5 B	9	134	0.205	2.97
T400	98 A – 2 B	8	162	0.284	3.15
T500	100 A	14	73	0.103	3.07
T600	80 A – 20 R	50	2	0.018	2.96
Alfa Aesar	95 A – 5 R	15	141	0.456	3.30

Table 2 - Pseudo-first order constants, k , of tetracycline disappearance in the first 65 min of irradiation and mineralization degrees after 3 h of irradiation for powder samples and immobilized systems. Standard deviations were obtained by comparing 3 independent experiments.

Sample	k ($\times 10^{-3} \text{ min}^{-1}$)	mineralization (%)
photolysis	3.0 ± 0.4	5 ± 1
T300	49 ± 1	88 ± 1
T400	56 ± 2	89 ± 1
T500	31 ± 3	87 ± 1
T600	9.5 ± 0.9	17 ± 1
Alfa Aesar	-	88 ± 1
lamina	6.2 ± 0.5	11 ± 1
pellets	8.5 ± 0.4	44 ± 1

Figure captions

Figure 1 - XRPD patterns of the different powder samples. The most relevant peak of each phase is highlighted (A: anatase and R: rutile).

Figure 2 - N₂ adsorption-desorption isotherms in subcritical conditions of the home-made powder photocatalysts and of the commercial sample.

Figure 3 - Pore volume distributions of the home-made and commercial powder samples.

Figure 4 - DRS spectra of the powder samples.

Figure 5 - Effect of UV pre-irradiation and recycle (a) and of the radical and hole scavengers (b) on tetracycline disappearance curves of T400.

Figure 6 - Tetracycline disappearance (a) and mineralization degree (b) as a function of irradiation time during photocatalytic tests for all powder samples.

Figure 7 - Determination of the kinetic constant of tetracycline disappearance: logarithmic conversion plot as a function of the reaction time for powder samples (a) and the relative correlation coefficients, R² (b).

Figure 8 - SEM images of bare (a) and TiO₂-coated (b) alumina pellets.







