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Chapter 7

Photocatalytic Treatment Techniques using Titanium Dioxide Nanoparticles for Antibiotic Removal from Water

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Additional information is available at the end of the chapter

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Abstract

The increasing of emerging micropollutants presence in drinking water sources has brought new challenges to existing water treatment systems (WTS), highlighting the need of innovative and low-cost technological solutions. Recent advances in nanotechnology enable highly efficient and multifunctional processes, providing sustainable alternatives to current water treatment practices. This chapter presents the results of several pilot-scale studies developed to assess the effects of TiO_2 nanoparticles on antibiotic removal efficiency, using different low-cost photocatalytic reactors. The characterization of its photo-oxidation kinetics also performed considering different test scenarios in order to assess the effects of the major abiotic parameters on oxytetracycline (OTC) removal efficiency, which achieved the maximum values of 96% and 98% using the photocatalysis with TiO_2 and the photocatalytic filtration, respectively. It must be highlighted the surprising regeneration ability showed by the photocatalytic porous medium, developed at a lab-scale, which can completely recover its oxidative properties after few hours of simple sun exposure.

Keywords: heterogeneous photocatalysis, photo-oxidation kinetics, TiO_2 nanoparticles, photocatalytic filtration, antibiotic removal, safe drinking water

1. Introduction

Reliable access to clean and safe water remains a major worldwide challenge for the twenty-first century, in a global climate change context. In recent years, the classic problems associated with the presence in the ecosystems of priority pollutants have been extended to the detection of increasing amounts of micropollutants commonly called emerging. These, due to their

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toxicity and persistence in the environment (water column and sediments), have brought new challenges to existing water treatment systems (WTS) aiming to protect public health and the preservation of drinking water sources.

The Directive 2008/105/EC (PSD) lays down environmental quality standards (EQS) and presents the List of Priority Substances as afforded on the Article 16 and Annex X of the Water Framework Directive 2000/60/EC (WFD). However, the pharmaceuticals are not yet included among those compounds to be monitored, despite the increase in its occurrence reported in many European countries [1]. For urban water monitoring, possible priority pharmaceutical compounds (PhCs) should be the mainly analgesics, antidepressants, antibiotics, antineoplastics [2], synthetic estrogens, and hormones [3]. The inclusion of target PhCs in the EU List of Priority Substances implies the definition of their corresponding EQSs and the necessity to subject to monitoring EU aquatic ecosystems.

Recent advances in nanotechnology offer opportunities to develop next generation of WTS, as sustainable and safe alternative to current water treatment practices relied on centralized systems. The highly efficient and multifunctional processes, enabled by nanotechnological solutions, can also provide new capabilities allowing economic utilization of unconventional water sources on water-stressed regions [4]. Future water treatment systems in developing countries will most likely opt for nanotechnology-based water monitoring, treatment and reuse systems that can efficiently immobilize a wide variety of water emergent pollutants (for which existing technologies are inefficient or ineffective) coupled with affordability and ease of operation [5].

Advanced oxidation processes (AOPs) have been widelly studied because of their potential as a complementary or alternative process to conventional wastewater treatment. These AOPs have proven to be particularly efective in the degradation of many toxic pollutants [6–8] when nanomaterials are applied as photocatalyst. Photocatalytic oxidation with TiO_2 has been used in the removal of micropollutants (like antibiotics) and microbial pathogens from waters, as a useful pre-treatment and/or a polishing step to oxidize hazardous and recalcitrant organic compounds.

This chapter presents the development and results of several pilot-scale studies aiming to assess the effects of TiO_2 nanoparticles on antibiotic removal efficiency and to define its photo-oxidation kinetics, using different low-cost photocatalytic water treatment systems.

The antibiotic tested in this work was oxytetracycline (OTC) is a widely used broad spectrum antibiotic, especially employed in veterinary medicine [9, 10] and for human therapy [11]. It can be found not only in raw and treated wastewaters but also in surface water sources [12]. The catalyst used is Degussa (*Evonik*) P25 TiO_2, which was applied as suspended and immobilized nanoparticles exposed to UV and solar radiation in two photocatalytic reactors: water columns and columns filters with a granular porous medium coated by immobilized TiO_2 nanoparticles using a sol-gel method.

For both photo-oxidation reactors, different test scenarios are defined in order to assess the effect on OTC removal efficiency of the major abiotic parameters, such as hydraulic conditions, OTC initial concentration, pH, cumulate solar energy, and media granulometry.

The experimental results were very promising, because removal efficiencies in both reactors achieved the maximum value of 96% for water columns with suspended TiO_2 nanoparticles

[13] and 98% for the photocatalytic filtration performed by the porous medium coated with TiO_2 [14].

It must be also highlighted that the surprising regeneration ability showed by the developed photocatalytic porous media can completely recover its oxidative properties after a simple sun exposure [15], allowing a truly sustainable use of the developed photocatalytic filter.

2. Urban water cycle sustainability: new challenges to ensure safe water

Urban water cycle management involves the fields of water supply, urban drainage, wastewater treatment, reutilization, and sludge handling with a river basin scale approach.

Conventional approaches to urban water management for providing water supply and sanitation services are often costly, inefficient, and not integrated. Hence, there is a need for finding new ways for improving and assess the urban water systems to enable better sustainability of these systems [16] to face new challenges in a climate change context.

In an urban water systems context, life cycle assessment (LCA) can provide a pertinent holistic approach supporting the critical processes identification and the potential improvements of these systems, including the water and wastewater treatment facilities, as well as, its interactions with source or receiving waters. Several researchers used LCA approach for comparing water treatment technologies sustainability [17, 18], as well as the major environmental impact changes resulting from centralized wastewater treatment systems commutation to decentralized ones [19].

This kind of approaches allowed to identify new threats for the urban water cycle sustainability, concerning with the obligation to ensure safe drinking water in order to safeguard public health and urban aquatic ecosystems.

2.1. Occurrence of emerging micropollutants in urban water systems

Aquatic ecosystem pollution is particularly problematic due to the cumulative effect of pollutants on aquatic organisms during its life cycle. This cumulative effect can occur so slowly that major impacts may remain undetectable until the hatching of irreversible ecosystem changes [20]. The hydrodynamics and the longitudinal dispersion patterns presented by receiving water systems have a decisive role in its ability to self-regenerate [21] and to wash-out inflow pollutants like nutrients and xenobiotics [22].

During the last decades, the impact of chemical pollution has focused almost exclusively on the conventional priority pollutants, especially those acutely toxic/carcinogenic pesticides displaying persistence in the environment.

At the same time (but receiving much less attention), the anthropogenic activities increased the diversity and load discharge of another groups of bioactive hazardous chemicals into urban water systems (**Figure 1**), namely:

- Contaminants of emerging concern (CECs), such as pharmaceutical compounds (PhCs), diagnostic agents, steroids, phthalates, and disinfectants.

- Endocrine disrupting compounds (EDCs), like natural and synthetic estrogenic or androgenic chemicals.
- Personal care products (PCPs), such as fragrances, sun-screen agents, and cosmetics.

The widespread use of antibiotics as a therapy for bacterial infections in humans and animals (even for promoting it growth) has led to the concentration increase of antibiotic-resistant bacteria (ARB) in surface waters and urban waterways [23–25], used for domestic sewage, hospital wastewater, and livestock feeding operations drainage. As opposed to the conventional persistent priority pollutants, PhCs need not be (necessarily) "persistent" if they are continually introduced to surface waters, even at very low concentrations.

The use of conventional water treatment technologies against these emerging contaminants is limited due to their ineffectiveness and incomplete biodegradation of the waste products as outlined in the applicable EU directives.

The presence of PhCs, PCPs, and EDCs in drinking water indicates that conventional and most commonly used water treatment technologies may not be enough to completely eliminate these compounds from source waters [26], which can be polluted because existing Wastewater Treatment Plants (WWTPs) were usually not designed to remove antibiotics present at trace levels, implying the need for its urgent improvement. Indeed, if urban WWTPs play a vital role in minimizing the discharge of many water pollutants, including antibiotics [27] and pathogenic microorganisms [28] to the aquatic ecosystems, they are also potential breeding grounds and point sources for environmental dissemination of antibiotic resistance [29].

Indeed, the very high bacterial density into biological reactors (e.g., activated sludge) promotes selective elimination and/or changes in the proportions of phenotypes within effluent bacterial populations turning WWTPs into important reservoirs of enteric bacteria which

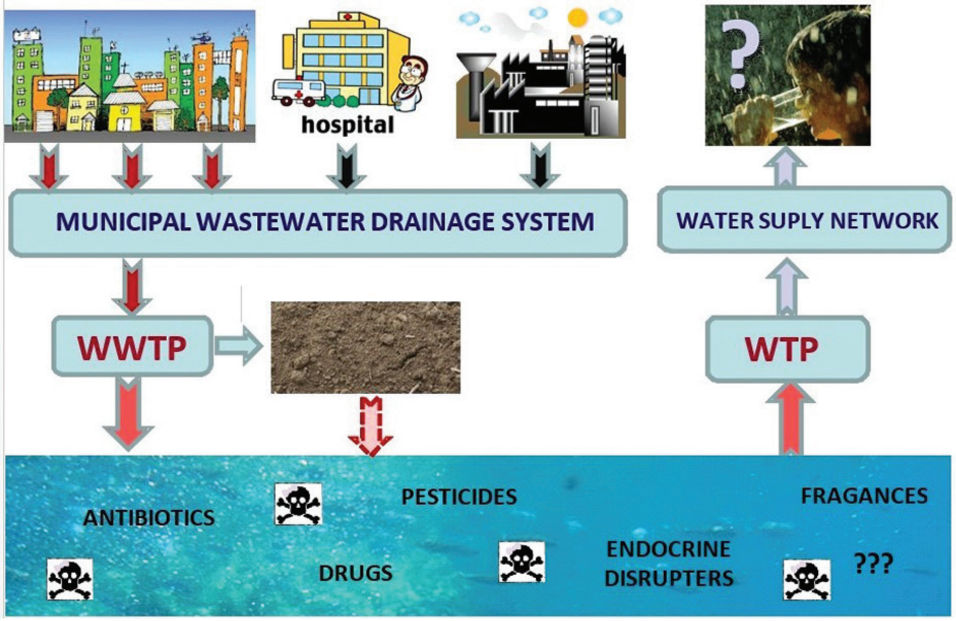

Figure 1. Threats to urban water cycle sustainability due to xenobiotic load increase.

carry potentially transferable resistance genes. For these reasons, higher frequency of multiple resistant coliform bacteria in treated sewage than in raw sewage [30, 31] for most antibiotics, especially for ciprofloxacin and tetracycline, have been found.

Human health risk characterization related to the pharmaceutical water ingestion exposure can be performed by the assessment of risk quotients (RQs). This risk index can be estimated dividing the maximum concentration of a pharmaceutical (MPC) found in the water matrix by the respective Drinking Water Equivalent Level (DWEL), which can be obtained as an exposure criteria based on other related parameters, such as acceptable daily intake; body weight, hazard quotient, and drinking water daily ingestion; gastrointestinal absorption rate; and frequency of exposure. So, a RQ value higher than 1 leads to a risk concern related to inadvertent exposure through drinking water, and measures must be considered in order to prevent public health.

A recent monitoring program performed along Lisbon's drinking water supply system [32] showed that appreciable risks to the consumer's health arising from exposure to trace levels of pharmaceuticals in drinking water were yet extremely unlikely, because all risk quotient (RQ) values were less than 0.001. Therefore, a high environmental risk was detected for *Erythromycin* (RQ = 1.55), the urgency of the study and development of new low-cost technologies for an effective removal of the most prevalent antibiotics in WTP raw waters.

2.2. Advanced oxidation processes: the role of photocatalysis as a *low-cost* alternative technology

Nanotechnology offers significant opportunities to revolutionize approaches toward drinking water treatment by enhancing the multifunctionality and versatility of treatment systems, while reducing reliance on stoichiometric chemical addition, shrinking large facilities with relatively long hydraulic contact times, and minimizing energy intensive processes [33]. So, it can provide low-cost, safe, and efficient water treatment systems with minimal energy requirements contributing for a more sustainable urban water cycle.

Nanomaterials properties have been explored for applications in water and wastewater treatment, due to its advantages related to the high specific surface area, fast dissolution, high reactivity, and strong sorption. Micropollutants' removal ability of new materials, such as carbon nanotubes, nanofibers, nanoscale metal oxide, nano-zeolites, and magnetic nanoparticles, is being tested and assessed when used in selected treatment unit processes, like adsorption, photocatalysis, membrane filtration, and disinfection.

Different advanced water treatment techniques for antibiotic removal have been studied, especially focus on membrane filtration, activated carbon adsorption, and advanced oxidation processes (AOPs). AOPs are recommended when water pollutants (such pharmaceuticals) have a high chemical stability and/or low degradability, allowing a more useful and cost-efficient combination with biological processes, namely in wastewater treatment [34].

The efficacy of AOPs depends on the generation of very reactive and nonselective free radicals—such as hydroxyl radicals ($^{\bullet}OH$), superoxide radical (O^{2-}), hydroperoxyl radical ($HO_2^{\bullet}$), and alkoxy radical ($RO^{\bullet}$)—involving chemical (e.g., O_3, O_3/H_2O_2), photochemical (UV/O_3, UV/H_2O_2), or photocatalytic (TiO_2/UV, ZnO/UV) oxidation processes. In recent years, semiconductor photocatalytic process has shown a great potential as a low-cost, environmental friendly, and sustainable treatment technology to align with the "zero" waste scheme in the water/wastewater industry. The ability of this advanced oxidation technology has been widely demonstrated to remove persistent organic compounds and microorganisms in water [35] and some hazardous inorganic micropollutants (e.g., arsenic, heavy metals, uranium).

Recent research works were mainly focused on AOPs assisted by solar radiation (a clean and renewable energy source), such as heterogeneous photocatalysis, in order to develop more sustainable and *low-cost* processes. The photocatalytic reactors can be divided into two main groups: with suspended nanoparticles (e.g., TiO_2, ZnO) in the reaction mixture (water and wastewater) and with immobilized nanoparticles on a carrier material (e.g., glass, quartz, stainless steel, zeolites).

When the catalyst is in suspension, the active surface is greater. However, its particles have to be removed from the treated water after the detoxification, and the manipulation of powdered semiconductors are difficult. To ensure complete rejection of TiO_2 nanoparticles, an extensive and relatively costly installation technology is necessary, including pumps. Very promising techniques for solving problems concerning separation of the photocatalyst as well as products and by-products of photo-degradation from the reaction mixture are the use of photocatalytic membrane reactors (PMRs) and the introduction of a magnetic into the nanocomposite [36]. However, the energy costs evolved in membrane processes can compromise the economic sustainability of the water treatment utilities, namely in medium and small water supply systems.

A solution for avoiding the contamination with the photocatalytic nanoparticles is their immobilization on the surface of specified materials by use of suitable coating techniques, as a wet chemical process. Quartz has been found to be the best support for titanium dioxide, because it is the most neutral and stable one at high temperatures. As a consequence, it has been chosen as the ideal support for new experiments with TiO_2 in the photodegradation of organic micropollutants in water [37].

3. Experimental methodology

During this research work, a set of experiments under different test scenarios were performed in order to assess the antibiotic removal efficiency and to characterize its photo-oxidation kinetics, using two different lab-scale photoreactors. In the first one (PR1), the heterogeneous photocatalysis was performed using suspended TiO_2 nanoparticles as catalyst to remove the antibiotic from water. In the second (PR2) one, a photocatalytic filtration was performed using a granular porous medium coated by immobilized TiO_2 nanoparticles.

In these experiments, the antibiotic used to prepare all synthetic solutions was the oxytetracycline hydrochloride (MW = 496.89, CAS# 2058-46-0), supplied by Sigma-Aldrich with a purity higher than 95%. The OTC concentrations were always measured using a UV-VIS spectrophotometer, Shimadzu UV-1800, at 354-nm wavelength. Titanium dioxide (TiO_2) used was Degussa (Aeroxide®) P-25 (80% anatase and 20% rutile).

The intensity of solar radiation is measured by a global UV radiometer (OHM – HD 9021), which was placed next to the solar reactors, in order to provide data in terms of incident solar radiation intensity (W/m^2). A reagent kit for rapid analysis of the amount of iron (Aquaquant®, E. Merck Darmstadt Germany) was also used.

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Test scenarios were defined aiming to assess the effect on OTC removal efficiency of some abiotic parameters (e.g., OTC initial concentration, pH, hydraulic conditions, UV radiation source, and water matrices).

3.1. Photo-oxidation experiments using suspended TiO_2

In reactor PR1, photo-oxidation experiments were performed, with and without suspended TiO_2 nanoparticles, using two different UV radiation sources: solar radiation and UV lamp reactor (**Figure 2**).

For the OTC photo-degradation under solar radiation, bottles of colorless polyester with a capacity of 1.5 L were used as reactor. These water bottles were placed vertically, being shaken manually every 10 minutes to prevent the deposition of TiO_2 at the bottom. The sun exposure time was 210 minutes for all photodegradation tests.

The UV reactor (*Heraeus Noblelight, System 2*) used in photodegradation assays consists of an UV immersion lamp TQ 150, an immersion tube, a cooling tube, and a reactor vessel. The UV

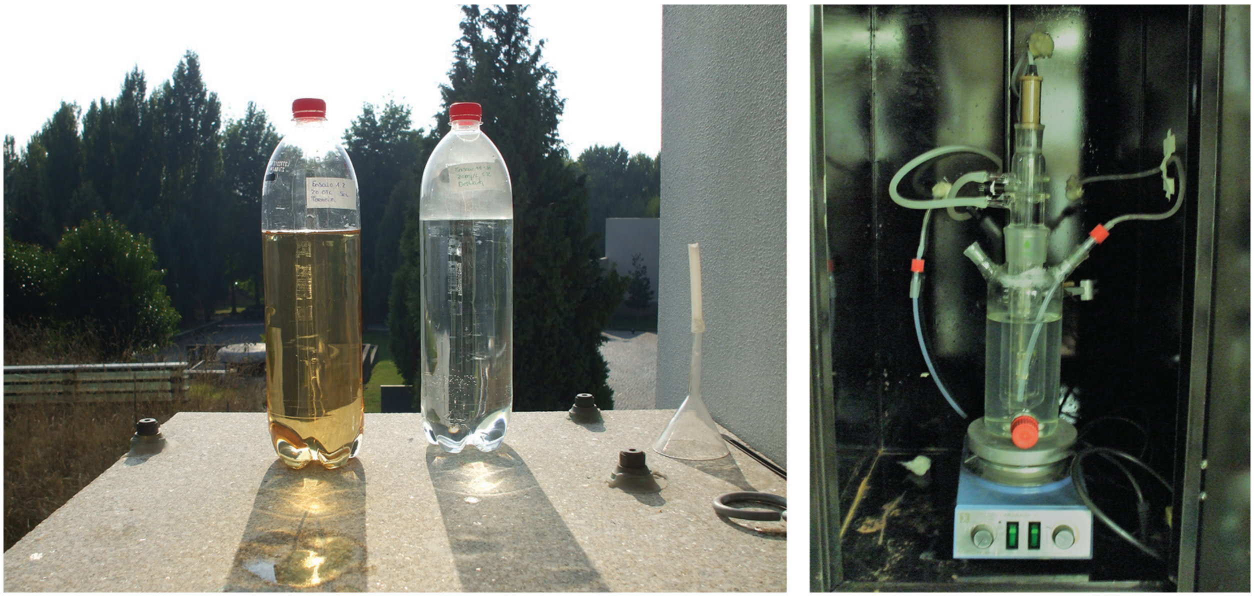

Figure 2. UV radiation sources used in OTC degradation experiments: solar (polyester bottles); UV reactor *Heraeus Noblelight*.

immersion lamp is a medium-pressure mercury vapor lamp with a broad emission spectrum in the UV range above 190 nm and lamp output of 150 W. The reactor vessel has a capacity of 0.8 L and three openings (one central and two sideways). In the central opening, the UV lamp tube is inserted, and only a side opening is used to carry out the extraction of the samples during the tests. The container is placed on a magnetic stirrer that was in operation throughout the test. The UV lamp exposure time was 60 minutes for all tests.

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Equation (1) allows the calculation of the amount of accumulated UV energy ($Q_{450\text{-}950n}$) received on any surface in the same position with regard to the sun, per unit of volume of water inside the reactor, in the time interval Δt.

$$Q_{450-950_n} = Q_{450-950_{n-1}} + \Delta t_n \times \overline{450-950} \times \frac{A_r}{V_t} \; ; \; \Delta t_n = t_n - t_{n-1} \tag{1}$$

Where t_n is the experimental time of each sample (s); V_t is the total reactor volume (L); A_r is the exposed surface area (m^2) of the reactor; and $\overline{450-950}$ is the average solar radiation $\left(\mathrm{W/m2}\right)$ measured during the period Δt_n (s).

Photolytic and photocatalytic experiments were carried out under static hydraulic conditions using 20 mg/L of OTC, as initial pollutant concentration, in all tests. For photocatalysis, the chosen initial suspended catalyst concentrations were 50 and 25 mg/L of TiO_2, in order to assess the effect of doubling the value of this parameter on OTC removal efficiency.

In order to assess the photocatalysis ability as post-treatment unit in WTPs for antibiotic removal, OTC solutions were prepared using two different water matrices (distilled and tap water) in order to assess the potential influence of other water supply constituents on OTC removal efficiency. The pH values measured in all experiments ranged between 4.3–4.9, for distilled water, and 6.6–7.3, for tap water.

To evaluate the influence of radiation in OTC degradation, at any given irradiation time interval, the dispersion was sampled (5 mL), filtered through a Millipore filter (pore size of 0.22 μm) to separate the TiO_2 particles, and the absorption was monitored to obtain OTC concentration.

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Table 1 summarizes the different assay conditions (scenarios) under which the OTC photodegradation tests, using suspended TiO_2, were performed (reactor PR1).

Most of the studies carried out on heterogeneous photocatalysis with TiO_2 have shown that the kinetics underlying the photo-oxidation of emerging pollutants can be represented by Eq. (2), according to the *Langmuir-Hinshelwood* model [38, 39].

$$r_0 = -\frac{dC}{dt} = \frac{k \times K \times C_0}{1 + K \times C_0} \tag{2}$$

Where r_0 is the initial rate of photo-oxidation (ppm minutes^{-1}); C_0 is the initial pollutant concentration (ppm); k is the reaction rate constant (ppm minutes^{-1}); and K is the pollutant adsorption coefficient (L/mg) measured during the period Δt_n (s).

Scenario	UV radiation	Water matrix	$[TiO_2]_0$ (ppm)
S1	Solar	Distilled	50
S2			25
S3		Tap	50
S4			25
S5		Distilled	–
S6		Tap	–
S7	UV lamp	Distilled	50
S8			25
S9		Tap	50
S10			25
S11		Distilled	–
S12		Tap	–

Table 1. Scenario analysis for OTC photo-oxidation in reactor PR1.

Considering that "$K \times C_0$" product can be a value quite low for photo-oxidation processes, which can be described by a pseudo-first order decay kinetics [35], the final pollutant concentration (C_t) is given by Eq. (3).

$$C_t = C_0 \times e^{-K_{aap} \times t} \tag{3}$$

Where K_{aap} is the apparent velocity reaction constant (minutes^{-1}).

So, the initial rate of photo-oxidation can be obtained by Eq. (4) when the pollutants present vestigial concentrations.

$$r_0 = K_{aap} \times C_0 \tag{4}$$

3.2. Photocatalytic filtration experiments using immobilized TiO_2

The lab-scale reactive filter applied on photocatalytic oxidation of OTC consists of two borosilicate glass cylinder (DURAN®) with 750 mm length, 70 mm external diameter, and 62 mm inner diameter. The filtration columns, with this quartz porous medium coated with TiO_2, are assembly as showed in **Figure 3**, and the OTC solution was feed to the columns by a peristaltic pump (Watson-Marlow 503U).

The porous bed consists of a quartz extracted from a quarry located in Ponte da Barca (Portugal), which was characterized by X-ray diffraction (XRD) (**Figure 4**).

The quartz was crushed and sieved in order to reduce its grains size till the desired granulometry, as well as, to facilitate the removal of the usual impurities. After sieving out, a grain

Figure 3. Filtration columns with a quartz porous media for OTC photo-oxidation.

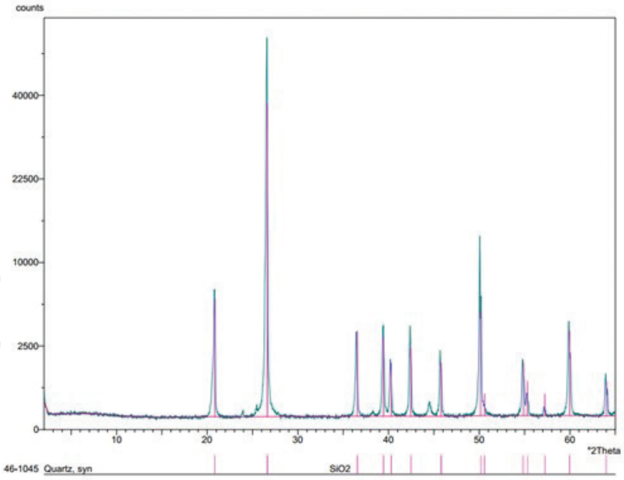

Figure 4. Characterization of a quartz sample by X-ray diffraction.

size distribution between 2.36 and 4.75 mm was dipped coated with TiO_2, also from Degussa (Aeroxide®), using the method described by Jeong et al. [40].

Prior to the start of the photocatalytic filtration tests, a study was carried out to optimize the hydraulic operation of the filter (e.g., flow rates ranges, head losses, hydraulic retention times) in order to select the most suitable flow rates: for photocatalysis, experiments were defined 4, 6 and 12 L/h; for adsorption, tests were defined 2, 4 and 6 L/h.

The selected range of flow rates for photocatalysis allows to simulate filtration (loading) rates similar to those occurring in WTP rapid and high rate filters (real scale hydraulic conditions) and also leads to OTC contact times with the TiO_2 that can provide an efficient photodegradation.

The hydraulic tests were performed both in open and closed (looped) circuit. An open circuit operation (without filtered water recycling) allows to maintain the initial OTC concentration constant and thus to evaluate the maximum capacity of retaining pollutant mass corresponding to the occurrence of porous medium saturation. A closed circuit operation allows to perform the number of loops (cycles) necessary to obtain the desired OTC contact time with the porous medium coated with TiO_2 nanoparticles.

The photocatalytic filtration tests of OTC solutions were performed in looped circuit during 270 minutes, considering different flow rates, initial OTC concentration (20 and 40 ppm), and aeration conditions. Final OTC concentrations were obtained by absorbance measurement using an UV-VIS spectrophotometer (Shimadzu UV—1800) at 354 nm wavelength. The effect of the aeration on the photo-degradation efficiency of OTC feed solution was also evaluated.

Table 2 summarizes the different test conditions (scenarios) under which the photocatalytic filtration was performed (reactor PR2)

Adsorption test was carried out under similar hydraulic conditions and the same duration of photodegradation tests, passing the OTC solution through the filter, first with quartz and after with quartz coated with TiO_2, in darkness to avoid any photodegradation contribute on final OTC removal.

3.3. Acute toxicity test

In order to assess the toxicity of OTC and oxidation by-products, it was used a simple toxicity test, not normalized but standardized by the international organization WaterTox Network [41]. In this toxicity assay, lettuce seeds (*Lactuca sativa*) are used.

Scenario	$[OTC]_0$ (ppm)	Flow rate (L/h)	Filter aeration
F1	20	4	No
F2	40	6	
F3	20		
F4		12	
F5			Yes

Table 2. Scenario analysis for OTC photocatalysis in reactor PR2.

Each of the lettuce seed root growth inhibition test was performed with 20 seeds in a Petri dish, containing a filter paper embedded in 2 mL of each sample dilution (100, 75, 50, and 25%). Root lengths were measured after 72 hours of incubation (**Figure 5**), and the average lethal concentration (LC50) was calculated as stated by Dutkka [42].

The samples used consisted of the oxytetracycline before and after photocatalytic treatment and, as negative control, distilled water. The tests were always carried out in triplicate.

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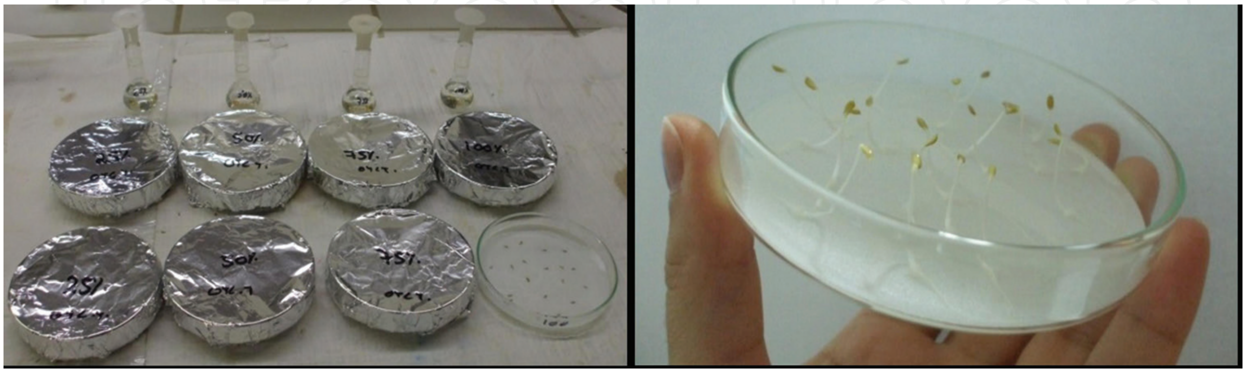

Figure 5. Preparation and final result of the acute toxicity bioassay using *L. sativa*.

4. Results and discussion

4.1. Photo-oxidation experiments (reactor PR1)

Figure 6 shows the degradation kinetics of OTC photocatalysis (scenarios S1–S4) and photolysis (scenarios S5 and S6) performed in two different aqueous matrices (distilled and tap water), always with an initial concentration of 20 mg/L and exposed to solar radiation (a free and renewable energy source) during 210 minutes (experimental).

For OTC degradation using solar radiation exposure, the maximum average value of 88% was reached for the scenarios S1 and S3 (different water matrix), which correspond to the highest TiO_2 concentration.

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The constituents present in the tap water, namely the iron, showed to have a significant effect on the OTC degradation efficiency, with special emphasis in photolysis experiments (almost quintupled), while in photocatalysis, this increase was only about 20%, under similar conditions of accumulated UV energy. Indeed, auxiliary control testing of tap water quality parameters detected the presence of iron concentrations in the range of 0.08–0.1 mg/L.

In order to assess a potential efficiency increase in OTC removal, due to an alternative UV radiation source (although with energy costs), those two photo-oxidative processes were also performed for the same aqueous matrices and OTC initial concentration but using the described UV lamp reactor with an exposure time of 60 minutes (scenarios S7–S12). The obtained results are depicted in **Figure 7**.

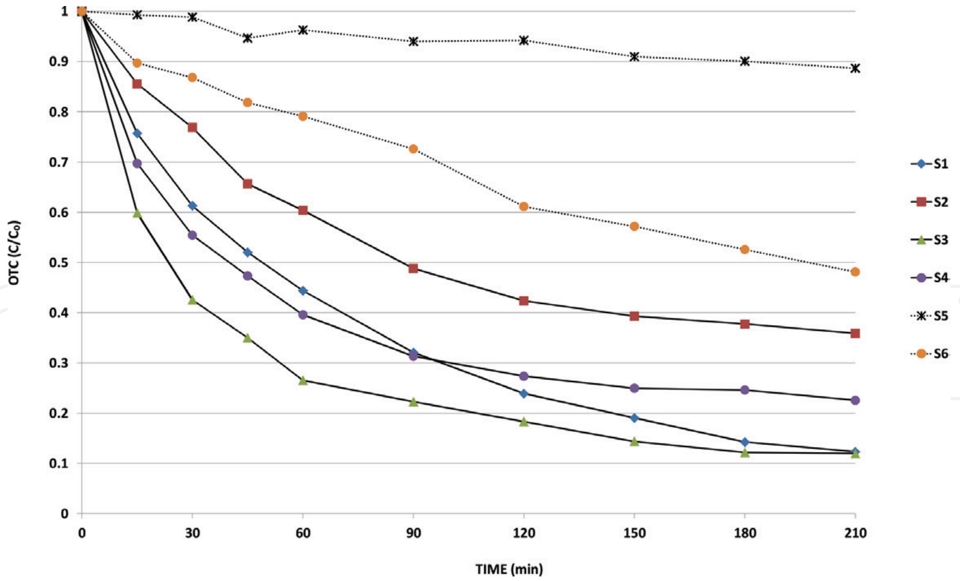

Figure 6. OTC photo-oxidation efficiency with solar radiation.

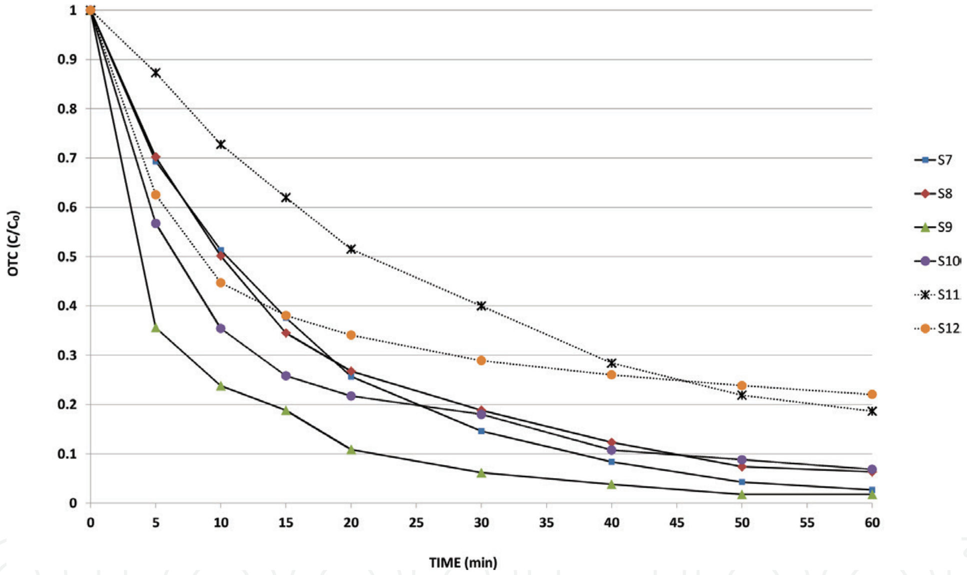

Figure 7. OTC photo-oxidation efficiency with UV lamp reactor.

For OTC degradation using UV reactor exposure, the same behavior was observed. The maximum efficiency (near 96%) was reached for the scenarios S7 and S9 (different water matrix), which correspond to the highest TiO_2 concentration. As depicted in **Figure 7**, the use of those two different aqueous matrices had a negligible effect on final OTC removal efficiency.

In this case (UV lamp reactor), the efficiency gains on OTC removal, related to the catalyst action, are much less significant than in the case of the solar radiation tests. Due to this finding the benefit of the use of photocatalysis would not be sufficiently attractive given the costs inherent to the necessary removal process of suspended TiO_2 nanoparticles.

Table 3 summarizes the major experimental results obtained for OTC removal using suspended TiO_2, namely the maximum average efficiencies, some photo-oxidation kinetic parameters, and the coefficient of determination (R^2) observed in the adjustment of the *Langmuir-Hinshelwood* model to the experimental data set obtained for each assay.

The obtained R^2 values (**Table 3**) allow to conclude that the *Langmuir-Hinshelwood* model adapts adequately to the kinetic behavior observed in the OTC photo-oxidation for any of those experimental scenarios tested and analyzed in this study.

For both water matrices solutions and in the scenarios using 50 mg/L of TiO_2, OTC removal efficiencies may achieve values higher than 88% if the accumulated solar energy quantity is higher than 113 kJ/L.

Comparing the results obtained using these two different UV radiation sources, the photocatalysis using TiO_2 with solar radiation seems to be a sustainable alternative for antibiotic removal in WTPs due to its minor energy costs and high efficiency removal, even requiring more exposure/retention time and achieving lower efficiencies, when compared with the ones observed in UV reactor tests.

4.2. Photocatalytic filtration experiments (reactor PR2)

The results of OTC removal efficiency by photocatalytic filtration performed in the reactor PR2 are depicted in **Figure 8**, considering the experimental scenarios F1–F5, which were defined aiming to assess the influence of different filtration fluxes, OTC initial concentration, and the OTC solution aeration in the feed tank.

The results showed that slower flux resulted in better OTC removal efficiency at the beginning of the experiment, due to longer retention times in the filter (curves F1, F3 and F4). Aeration is important for the oxidation reaction in photocatalytic processes. This process requires dissolved oxygen to act as an oxidant and to slow down the electron-hole recombination reaction. The curve F5 for the experiment with aeration shows the highest value for the initial photo-degradation rate.

In **Figure 8**, it can be seen that the experiments F1, F4, and F5 with 4 and 12 L/h had higher initial degradation rates, and these tests removed more than 96% of OCT by 270 minutes of solar irradiation time. The highest OTC removal efficiency obtained for photocatalytic filtration,

Parameter	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**	**S11**	**S12**
C_0 (ppm)	19.25	20.59	18.69	20.83	15.39	20.69	19.57	20.62	12.13	18.13	20.69	21.04
C_f (ppm)	2.48	4.80	2.48	7.60	13.67	10.06	0.86	2.16	0.48	1.43	4.02	3.22
K_{aap} (minutes^{-1})	0.013	0.009	0.011	0.006	0.001	0.004	0.061	0.047	0.078	0.052	0.030	0.040
R^2	0.844	0.909	0.974	0.987	0.931	0.982	0.899	0.866	0.816	0.807	0.992	0.321
r_0 (ppm·minutes^{-1})	0.25	0.19	0.21	0.12	0.01	0.08	1.19	0.97	0.95	0.94	0.62	0.84
OTC removal (%)	87	77	87	64	11	51	96	90	96	92	81	85

Table 3. Results synthesis of OTC photo-oxidation experiments in reactor PR1.

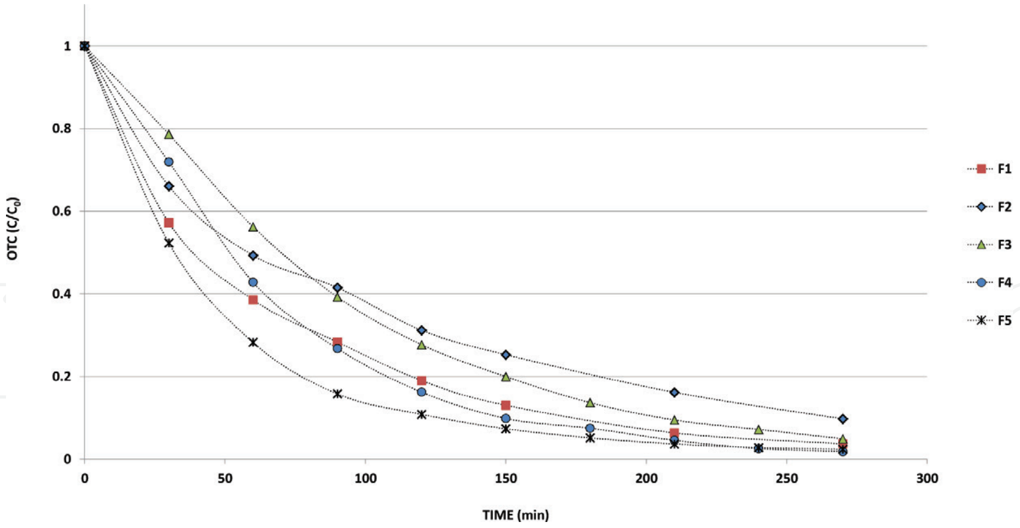

Figure 8. OTC removal efficiency using photocatalytic filtration with TiO_2 (PR2).

using a quartz porous medium coated with TiO_2, was 98% achieved for scenarios F4 and F5, which correspond to the higher flow rates tested (without and with filter aeration).

Table 4 summarizes the major experimental results of OTC removal experiments using photocatalytic filtration with a porous medium coated with TiO_2, namely the maximum average efficiencies, some photo-oxidation kinetic parameters, and the coefficient of determination (R^2) observed in the adjustment of the *Langmuir-Hinshelwood* model to the experimental data sets.

The results presented were obtained on different days with variations in the amount of accumulated energy from solar radiation received on the surface of the porous medium.

The calculated R^2 values (**Table 4**) allow to verify that the *Langmuir-Hinshelwood* model also adapts adequately to the kinetic behavior observed in the OTC photocatalytic filtration performed in this study for any of the analyzed experimental scenarios.

The effect of the flow rate variation on OTC adsorption was assessed using the reactor PR2 in darkness conditions and filtration with two different porous media (quartz without and with TiO_2 functionalization). The results of the OTC adsorption tests are depicted in **Figure 9**,

Parameter	F1	F2	F3	F4	F5
C_0 (ppm)	20.01	40.59	19.38	18.62	18.48
C_f (ppm)	0.74	3.94	0.95	0.33	0.47
K_{aap} (minutes^{-1})	0.011	0.009	0.007	0.010	0.013
R^2	0.941	0.956	0.999	0.999	0.958
r_0 (ppm·minutes^{-1})	0.44	0.36	0.14	0.38	0.51
OTC removal (%)	96.3	90.3	95.1	98.2	97.5

Table 4. Results synthesis of OTC photo-oxidation experiments in reactor PR2.

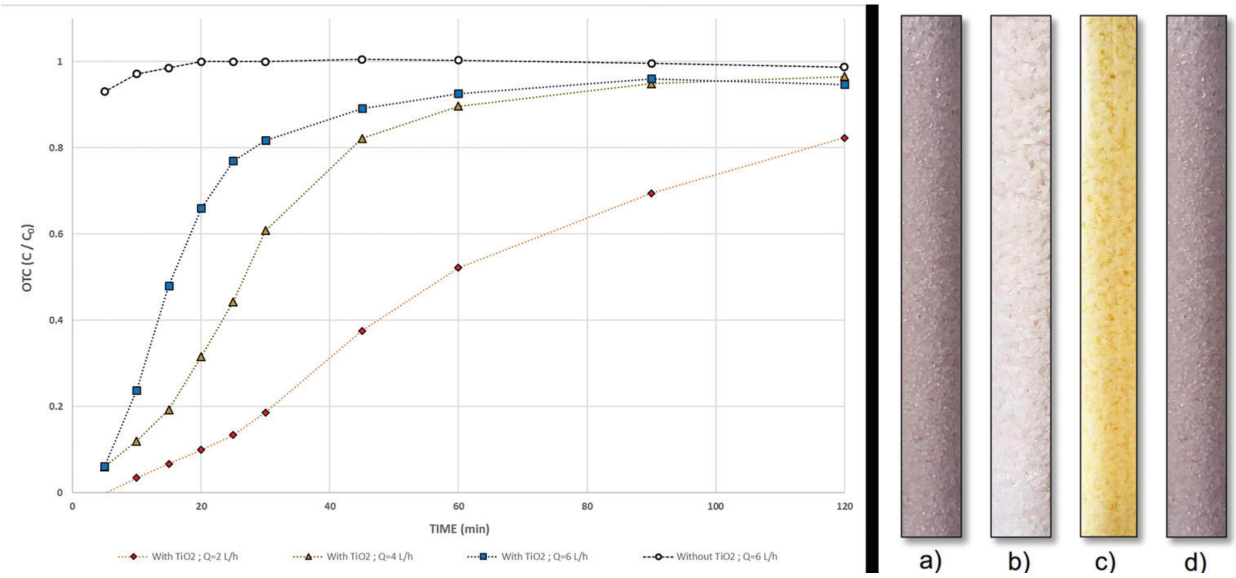

Figure 9. Results of the OTC adsorption tests and final look (color changes) of the porous medium.

as well as the final look (color changes) of the porous medium in the following four distinct situations:

a. Quartz without TiO_2

b. Quartz coated with TiO_2

c. Quartz coated with TiO_2 after saturation (OTC adsorption)

d. Quartz without TiO_2 after OTC adoption test.

In darkness and after 120 minutes, the quartz (without TiO_2) has a negligible OTC adsorption, but in the column filter with the coated quartz, the adsorption is function of the feed flow rate. With a flow rate of 6 L/h, the equilibrium concentration was reached within 90 minutes, and for 4L/h, the equilibrium concentration was only reached after 120 minutes.

Moreover, it was also observed a high regeneration ability by the photocatalytic porous medium, which can completely recover its oxidative properties after a simple solar radiation exposure of about 4 hours [15]. **Figure 10** presents the time evolution of saturation and regeneration processes observed in this photocatalytic filter.

As reported on item 3.3, the toxicity of the oxytetracycline both before and after the photocatalytic degradation (performed in each reactor – PR1 and PR2) was evaluated by using *L. sativa* seeds germination as a bioindicator.

The results of these toxicity tests toward lettuce seed growth showed a toxicity decrease after the photocatalytic OTC degradation, enabling the adoption of this emerging water treatment technique as an apparently safe alternative for the antibiotics removal challenge.

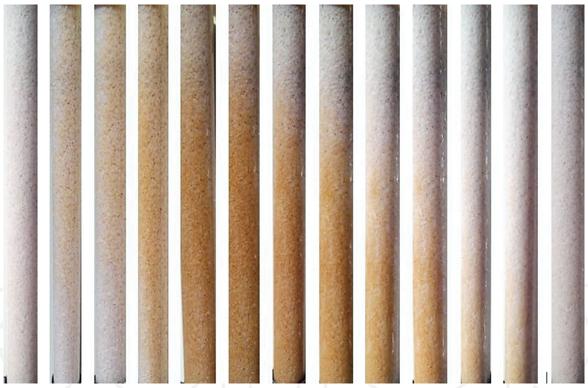

Figure 10. Saturation and regeneration processes evolution observed in the photocatalytic filter (PR2).

5. Conclusions

The chemical structure of OTC was effectively degraded by in both lab-scale photo-oxidation reactors, achieving very high OTC removal efficiencies for photocatalytic experiments (96–98%), even with small amounts of suspended and coated TiO_2 nanoparticles.

The results obtained in the photo-oxidation experiments using suspended TiO_2 indicate that:

- The photocatalytic tests were more effective than testing photolysis, which proves the high catalyzing power of TiO_2 particles described in the literature.
- OTC solutions exposed to UV-lamp radiation reached higher OTC removal efficiency (maximum about 96%) than those exposed to solar radiation (maximum about 88%). Nevertheless, the last one UV radiation source seems to be a more sustainable alternative for antibiotic removal in WTPs due to its minor energy costs and high efficiency removal.
- The overall efficiencies of the OTC degradation in distilled and tap waters are very close, namely when the iron concentration in water is low.
- The kinetics of OTC photo-oxidation reveals a faster degradation during the first 10–20 minutes.

The results obtained in the photocatalytic filtration experiments performed by a porous media coated with TiO_2 nanoparticles indicate that:

- The best OTC removal efficiency was 98%, achieved for an antibiotic initial concentration of 20 mg/L, a flow rate of 12 L/h in a looped hydraulic circuit, and for a cumulate solar energy near 805 kJ/L.
- Slower flux seems increase OTC removal efficiency at the beginning of the experiment, due to longer retention/contact time into the column filter.
- The experiment performed with aeration shows the highest value for the initial photo-oxidation rate, and one of the best final OTC removal efficiency.

- In darkness, the quartz (without TiO_2) has a negligible OTC adsorption, but in the column filter with the coated quartz the adsorption is relevant, and function of the feed flow rate increase.
- It must be highlighted the surprising regeneration ability showed by the developed photocatalytic porous media, which can completely recover its oxidative properties after a simple sun exposure for 4 hours, allowing sustainable use of the photocatalytic filter.

The *Langmuir-Hinshelwood* model was adequately adapted to the kinetic behavior observed in the OTC photo-oxidation processes in all of the analyzed scenarios, and for both used photocatalytic reactors.

The toxicity tests carried out showed that the use of heterogeneous photocatalysis with suspended TiO_2 does not induce the appearance of toxic by-products in the water, since the seeds of lettuce *L. sativa* always showed inhibition percentages lower than 22% after treatment.

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