Performance assessment of micropollutants removal from water using advanced oxidation processes

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Abstract: - In a global climate change scenario, reliable access to clean and safe water for all remains a great worldwide challenge for the twenty first century, as one of the most ambitious targets of several Sustainable Development Goals (SDG) established in the UN Agenda 2030. The increasing presence in the urban aquatic ecosystems of priority pollutants and contaminants of emerging concerning (CECs) have brought new challenges to the existing water treatment systems (WTS) concerning with public health protection and the of drinking water sources preservation. Advanced oxidation processes (AOPs) have been widely studied because of their potential as a complementary or alternative process to conventional wastewater treatment. Several AOPs using nanomaterials as photocatalyst can be particularly effective in the degradation of many toxic micropollutants, and enhance the multifunctionality, versatility and sustainability of WTS.

This work presents a synthesis of the major results obtained in several pilot and lab-scale studies aiming to assess the performance of different low-cost catalytic processes used for antibiotic and pesticide removal. For each photo-oxidation reactors, different test scenarios are defined in order to evaluate the effects of several abiotic and hydraulic parameters on process kinetics and removal efficiencies.

The experimental results were very promising, because antibiotic removal efficiencies achieved the maximum value of 96% for the photo-oxidation by water columns with suspended TiO_2 nanoparticles, and 98% for the photocatalytic filtration performed by a porous medium coated with TiO_2. In the photoelectrocatalytic reactor, the atrazine concentration has been fully removed for reaction times between 35 and 95 minutes.

Key-Words: Water treatment; micropollutants; advanced oxidation; photocatalysis; photoelectrocatalysis; TiO_2.

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1 Introduction

Urban waters pollution is particularly problematic due to the cumulative effect of pollutants on aquatic organisms during its life cycle. Life cycle assessment (LCA) can provide a pertinent holistic approach supporting the potential improvements of 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 [1, 2], and to identify new threats concerning with the obligation to ensure safe drinking water in order to safeguard public health and water sources.

The hydrodynamics and the longitudinal dispersion patterns presented by receiving water systems have a decisive role in its ability to self-regenerate [3] and to washout inflow pollutants, like nutrients [4] and emerging xenobiotic (e.g., pharmaceutical compounds (PhC), personal care products (PCP), endocrine disrupting compounds (EDC), pesticides). 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. Therefore, the anthropogenic activities increased the diversity and load discharge of another groups of bioactive hazardous chemicals into urban water bodies.

The Directive 2008/105/EC (PSD) lays down environmental quality standards (EQS) and presents twelve additional substances to the first Watch List of Priority Substances (PSs) as afforded on the Article 16 and Annex X of the Water Framework Directive 2000/60/EC (WFD). However, the pharmaceuticals were not yet included among those compounds to be monitored, despite the increase in its occurrence reported in many European countries [5]. Only in 2018, the EU presents its first proposal of regulation on minimum requirements, regarding contaminants of emerging concern (CECs).

The presence of PhCs, PCPs, and EDCs in drinking waters indicates that conventional and most commonly used water treatment technologies may not be enough to completely eliminate these compounds from source waters [6]. Therefore, the existing WWTPs were not designed to remove antibiotics present at trace levels, implying the need for its urgent improvement. Indeed, if urban WWTPs play a crucial role in discharge mitigation of many water pollutants (such antibiotics and pathogenic microorganisms) on receiving waters, they are also potential breeding grounds and point sources for environmental dissemination of antibiotic resistance [7].

Advances in nanotechnology offer opportunities to develop better sustainable and safe alternatives to current water treatment practices, based on chemical addition and energy needs reduction, allowed by multifunctional and highly efficient processes. Nanomaterials properties (high reactivity, fast dissolution, high specific surface area, strong sorption) can provide low-cost, safe, and efficient water treatment systems with minimal energy requirements contributing for a more sustainable urban water cycle.

Different advanced water treatment techniques for heavy metals, pesticides or antibiotic removal have been studied, especially focus on membrane filtration, adsorption on natural materials [8-9], and advanced oxidation processes (AOPs), which are recommended when water pollutants have a high chemical stability and/or low degradability.

Advanced oxidation processes (AOPs) have proven to be particularly effective in the degradation of many toxic pollutants [10-11] when nanomaterials are applied as photocatalyst. The efficacy of AOPs depends on the generation of very reactive and nonselective free radicals, such as hydroxyl radicals (•OH), superoxide radical (O_2^-), hydroperoxyl radical (HO_2•), and alkoxy radical (RO•).

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. Photocatalytic oxidation with TiO_2 has been successfully tested for micropollutants (antibiotics, pesticides) and microbial pathogens removal from raw waters.

The photocatalytic reactors can be divided into two main groups: with suspended nanoparticles (e.g., TiO_2, ZnO) and with immobilized nanoparticles on a support material (e.g., glass, quartz, stainless steel, zeolites). When the catalyst is in suspension, the active surface is greater, but its particles must be removed from the treated water and the manipulation of powdered semiconductors is usually complex. A solution for avoiding the contamination with the photocatalytic nanoparticles is their immobilization in a material surface using suitable coating techniques (e.g., sputtering, sol-gel method).

Quartz has been found to be a suitable support for TiO_2 nanoparticles due to its optical properties and stability even at high temperatures [12]. So, it has been chosen as the ideal support to be tested as a new reactive porous media performing a promising innovative water photocatalytic filtration with TiO_2 nanoparticles.

In order to overcome the obvious photolysis constraint inherent to its dependence of solar/UV radiation occurrence, it was considered pertinent to evaluate the performance of electrocatalysis in the micropollutants removal from water.

The electrochemistry achieves the organic pollutants oxidation by a chemical reaction with electrogenerated species from water discharge at the anode such as physically adsorbed "active oxygen" (physisorbed hydroxyl radical (•OH)) or chemisorbed "active oxygen" (oxygen in the lattice of a metal oxide (MO) anode). [13].

Electrochemical advanced oxidation processes (EAOPs) are emerging as a viable option for water and wastewater treatment. The major appeal of this technology is that electrochemical cells do not need the addition of chemical reagents and instead produce oxidizing species by the reactions that occur at the anode surface. So, this technology involves the use of a very clean reagent, the electron [14]. So, electrocatalysis (EC), photo-electrocatalysis (PEC) and solar assisted electrochemical processes (SPEC) are emerging and promising water treatment techniques that are received an increasing attention as environmentally friendly oxidation processes.

Recent research wok [15] reports the full atrazine removal, after 3 hours of reaction, by photo-electrocatalysis using a photoanode based on nanosheets of tungsten trioxide (WO_3).

This work presents and discuss the results of several pilot and lab-scale studies aiming to assess micropollutants removal efficiency using different low-cost photocatalytic (PC) and electrocatalytic (EC) treatment techniques, and to characterize their oxidation kinetics.

Two photocatalytic reactors were developed and tested: one constituted by a set of glass (borosilicate) columns using suspended TiO_2 nanoparticles mixed in water (heterogeneous photocatalysis); and the other one was made using similar columns to involve a granular porous medium coated by immobilized TiO_2 nanoparticles (photocatalytic filtration).

The selected antibiotic was oxytetracycline (OTC), a widely used broad spectrum antibiotic, especially employed in veterinary medicine and for human therapy. It can be found not only in raw and treated wastewaters but also in surface water sources [16].

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 photocatalytic reactors achieved maximum removal efficiencies between 96 and 98%.

Given that PC oxidation processes have an important limitation for its application at industrial scale, due to the need of a strong solar radiation, which doesn’t continuously occur throughout the year, PEC can constitute an interesting alternative to overcome this. So, a lab-scale photoelectrocatalytic reactor was developed to perform several experimental essays aiming to evaluate and compare the performance on atrazine (ATZ) removal by electrochemistry processes (EQ), photocatalysis (PC) and electrocatalysis (EC). The potential synergy of these processes was after tested using a photoelectrocatalytic reactor (PECR), which results are here presented.

Having verified the full ATZ removal for all tested scenarios, the goal was to identify the best set of several abiotic parameters (e.g., electrical voltage, incident illuminance, initial ATZ concentration, electrolyte concentration, and pH) that minimized the reaction time needed.

The best combination found for rehearsal conditions allows to achieve the total ATZ removal after 35 minutes of reaction, and an initial fast removal degradation decay.

2 Methods

2.1 Photocatalytic experiments

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 photocatalytic reactors.

In the first one (PCR1), the heterogeneous photocatalysis was performed using suspended TiO_2 nanoparticles as catalyst to remove the antibiotic from water. In the second (PCR2) 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 was 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.

Several 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).

2.1.1 Heterogeneous photocatalysis using suspended TiO_2 nanoparticles

In reactor PCR1, photo-oxidation experiments were performed, with and without suspended TiO_2 nanoparticles, using two UV radiation sources: solar radiation and UV lamp reactor (Fig. 1).

For the OTC photo-degradation under solar radiation, bottles of colourless 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 immersion lamp is a medium-pressure mercury vapour 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).

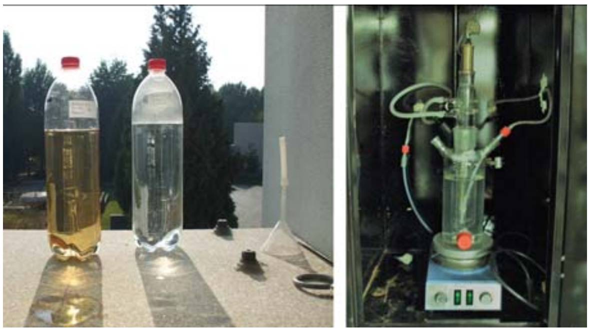

Fig. 1 UV radiation sources used for OTC degradation in photocatalytic experiments: solar (bottles); UV reactor

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.

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 adopted 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).

The *pH* values measured in all experiments ranged between 4.3-4.9 (distilled water), and 6.6-7.3 (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.

Table 1 summarizes the different assay conditions (scenarios) under which the OTC photodegradation tests, using suspended TiO_2, were performed (reactor PCR1).

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 depicted by equation 1, according to the *Langmuir-Hinshelwood* model [17].

Table 1. Synthesis of scenario analysis for OTC photocatalytic oxidation using reactor PCR1

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	-

$$r_0 = -\frac{dC}{dt} = \frac{k \times K \times C_0}{1 + K \times C_0} \qquad (1)$$

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

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 [17], the final pollutant concentration (C_t) is given by equation 2.

$$C_t = C_0 \times e^{-K_{aap} \times t} \qquad (2)$$

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

So, the initial rate of photo-oxidation by heterogeneous photocatalysis can be obtained by equation 3, when the micropollutants presents vestigial concentrations.

$$r_0 = K_{aap} \times C_0 \qquad (3)$$

2.1.2 Photocatalytic porous media (filter) using immobilized TiO_2 nanoparticles

A pilot-scale reactive filter was developed to perform photocatalytic oxidation of OTC, which consists of two borosilicate glass cylinder (DURAN®) with 750 mm length, 70 mm external diameter and 62 mm of inner diameter.

The filtrations columns, with this quartz porous medium coated with TiO_2, are assembly as showed on Figure 2, and the OTC solution was feed to the columns by a peristaltic pump (Watson-Marlow 503U).

Fig. 2 Filtration columns with a quartz porous medium for OTC photo-oxidation (solar radiation)

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 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. [19].

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 photocatalytic experiments, which chosen values were 4, 6 and 12 L/h. [20].

This selected range of flow rates allows to simulate filtration rates (hydraulic conditions) similar to those occurring in rapid and high rate filters of real WTP real, and also leads to OTC contact times with the coated TiO_2 nanoparticles that can provide an efficient photo-degradation.

The hydraulics tests were performed in open and closed (looped) circuits. 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 medium saturation occurrence. A closed circuit operation allows to perform the number of loops (cycles) needed to obtain the targeted OTC contact time 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 tests conditions (scenarios) under which the photocatalytic filtration was performed (reactor PCR2).

Table 2. Synthesis of scenario analysis for OTC photocatalytic oxidation using reactor PCR2

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

2.2 Photo-electrocatalytic experiments

Photo-electrocatalytic experiments were performed using an open reactor (PECR) composed of a circular borosilicate glass tub, 14 cm in diameter and 7.5 cm high, with a quartz granular medium coated with immobilized TiO_2 nanoparticles (similar to those one used in the reactor PCR2). Two graphite cathodes were installed in the granular medium 12 cm apart.

The solution of atrazine (Sigma-Aldrich, with 95% of purity) was prepared with ethanol addition to ensure a full water dilution. The PECR is placed on a magnetic stirrer operating throughout each test.

The UV radiation source used in the PECR: solar radiation and UV lamp reactor of 15 W (Fig. 3).

Fig. 3 UV radiation sources used for ATZ degradation in photoelectrocatalytic experiments: solar; UV lamp

The ATZ concentrations were also measure by absorbance measurement using the same UV VIS spectrophotometer (Shimadzu UV–1800), but at 220 nm wavelength.

Photoelectrocatalytic experiments aimed to analyze and evaluate the efficiency and kinetics of ATZ removal, under different test scenarios defined to assess the effect of three major abiotic parameters: electrolyte concentration (NaCl) (scenarios E1-E2 or E3-E4), *pH* of the initial solution (scenarios E1-E3 or E2-E4), and electrical voltage (scenarios E3-E5).

Considering the results obtained from exploratory electrochemical and photocatalytic assays [21] performed with both UV radiation sources (above described), in this work only the solar radiation was selected for all photoelectrocatalytic test scenarios here presented.

The initial ATZ concentration was similar (1.7-1.9 mg/L) for each set of scenarios used to assess the parameters effect on ATZ removal.

In PEC experiments, only a synthetic water matrix was used, to avoid cross effects/reactions due to the unknown concentration of all others water supply constituents. Table 3 summarizes the different test conditions (scenarios) performed in the PECR reactor.

Table 3. Synthesis of scenario analysis for ATZ removal by photoelectrocatalysis, using reactor PECR

Scenario	NaCl (mg/L)	pH	Electrical voltage (V)
E1	16.7	4.6	10
E2	8.3	4.5	10
E3	16.7	7.1	10
E4	8.3	7.0	10
E5	16.7	7.3	5

3 Results and discussion

3.1. Heterogeneous photocatalysis (PCR1)

Figure 4 shows the photodegradation results of OTC photocatalysis (scenarios S1 to S4) and photolysis (scenarios S5 and S6) performed in two different aqueous matrices (distilled and tap water), always with an initial OTC concentration of 20 mg/L and exposed to solar radiation during 210 minutes.

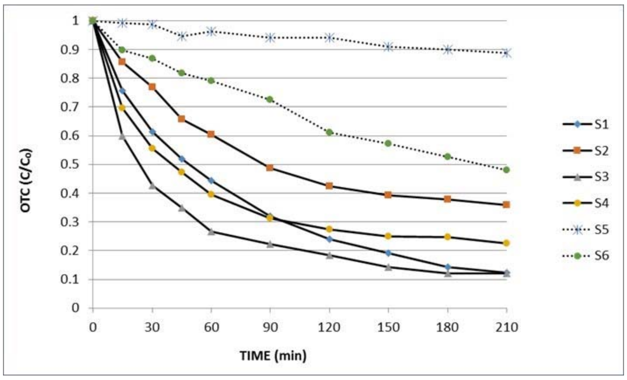

Fig. 4 OTC photo-oxidation efficiency with solar radiation using suspended TiO_2.

For photocatalysis experiments using solar radiation exposure, the maximum average efficiency removal was near 88% (scenarios S1 and S3) and corresponds to the highest TiO_2 concentration.

In the tap water, the iron presence (concentrations of 0.08-0.1 mg/L) 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.

Figure 5 presents the results obtained 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 to S12), much lower than the solar radiation tests.

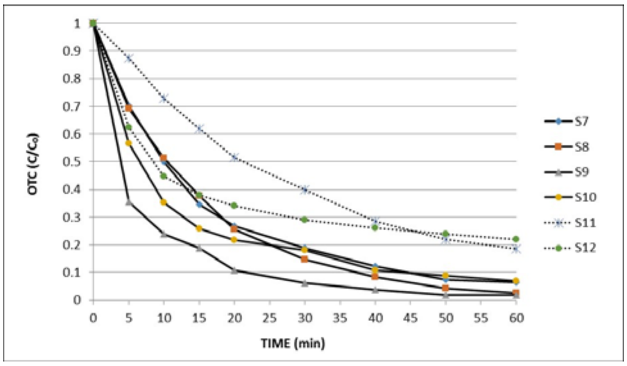

Fig. 5 OTC photo-oxidation efficiency with UV lamp reactor using suspended TiO_2

For OTC photo-oxidation with the UV lamp reactor similar kinetics were observed. The maximum efficiency value (96%) was reached for the scenarios S7 and S9, which also correspond to the highest TiO_2 initial concentration.

In this case (UV lamp reactor), the efficiency gains on OTC removal, due to the catalyst action, are much less significant than in the case of the solar radiation tests. So, the benefit of photocatalysis use would not be enough attractive, considering the costs inherent to the complementary treatment to remove TiO_2 suspended nanoparticles. As showed in last two figures, the use of those two different aqueous matrices had a negligible effect on the final OTC removal efficiency.

Table 4 summarizes the major experimental results obtained for OTC photo-oxidation using suspended TiO_2, such as the maximum average efficiencies, kinetic parameters, and the coefficient of determination (R^2) for adjustment evaluation of the *Langmuir-Hinshelwood* model to the experimental data set of each test.

Table 4. Results of heterogeneous photocatalysis experiments (reactor PCR1)

Scenario	K_{aap} (min^{-1})	R^2	r_0 (ppm/min)	OTC removal (%)
S1	0.013	0.844	0.25	87
S2	0.009	0.909	0.19	77
S3	0.011	0.974	0.21	87
S4	0.006	0.987	0.12	64
S5	0.001	0.931	0.01	11
S6	0.004	0.982	0.08	51
S7	0.061	0.899	1.19	96
S8	0.047	0.866	0.97	90
S9	0.078	0.816	0.95	96
S10	0.052	0.807	0.94	92
S11	0.030	0.992	0.62	81
S12	0.040	0.821	0.84	85

The obtained R^2 values allow to conclude that the *Langmuir-Hinshelwood* model is accurate to describe the kinetic behaviour observed in the OTC photo-oxidation for any of those experimental scenarios tested in both photocatalytic reactors.

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

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 operation simplicity, even requiring more exposure/retention time and achieving lower efficiencies, when compared with the ones observed in UV lamp reactor tests.

3.2. Photocatalytic filtration (reactor PCR2)

Figure 6 shows the results of OTC removal efficiency by photocatalytic filtration performed in reactor PCR2, considering the experimental scenarios F1 to F5, which were defined aiming to assess the influence of different filtration rates, OTC initial concentration, and the aeration induced in the feed tank.

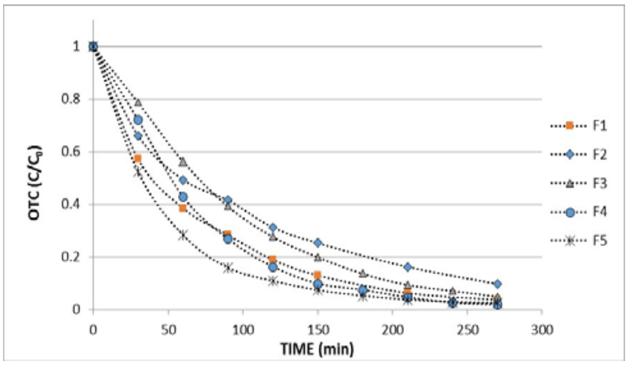

Fig. 6 OTC removal efficiency using photocatalytic filtration with immobilized TiO_2.

Results showed that slower filtration rates resulted in better OTC removal efficiency at the beginning of the experiment, due to longer retention times into the filter (curves F1, F3 and F4).

Aeration is important for the oxidation reactions during photocatalytic processes, because it requires dissolved oxygen to act as an oxidant and to slow down the electro-hole recombination reaction. Indeed, the curve F5 (test with aeration) shows the highest value for the initial photo-degradation rate, as expected.

Experiments corresponding to scenarios F1, F4 and F5 (for flow rates of 4 and 12 L/h) had higher initial degradation rates, and OTC removal efficiency achieves more than 96%, after 270 min of solar radiation.

The highest OTC removal efficiency obtained with the photocatalytic filtration reactor was 98%, observed for experimental scenarios F4 and F5, which correspond to the higher flow rates tested (without and with filter aeration).

Table 5 summarizes the major experimental results of OTC removal experiments using photocatalytic filtration, such as maximum average efficiencies, kinetic parameters, and the coefficient R^2 observed in the adjustment of the *Langmuir-Hinshelwood* model to the experimental data sets.

Compared with the heterogeneous photocatalysis, the calculated R^2 values are better than those obtained in PCR1 reactor.

Table 5 –Synthesis of OTC photocatalytic filtration results (reactor PCR2).

Scenario	K_{aap} (min^{-1})	R^2	r_0 (ppm/min)	OTC removal (%)
F1	0.011	0.941	0.44	96
F2	0.009	0.956	0.36	90
F3	0.007	0.999	0.14	95
F4	0.010	0.999	0.38	98
F5	0.013	0.958	0.51	98

Therefore, these highest values allow us to conclude that the *Langmuir-Hinshelwood* model is very accurate to describe the OTC oxidation kinetics observed in the photocatalytic filtration (reactor PCR2), for all analysed scenarios.

3.3. Electrocatalytic oxidation (reactor ECR)

Figure 7 shows the results of ATZ removal efficiency by photoelectrocatalysis performed in reactor PECR, considering the experimental scenarios E1 to E5, which were defined aiming to assess the influence of different NaCl concentrations, initial pH, and applied electrical voltage.

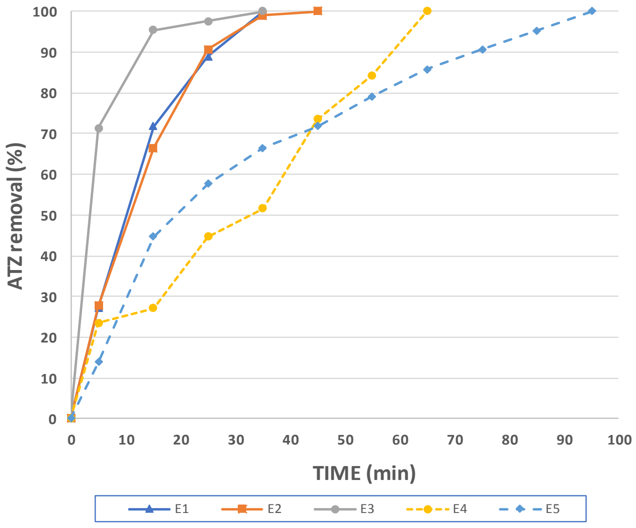

Fig. 7 Results of ATZ removal experiments using photoelectrocatalysis (PECR reactor).

Results showed the occurrence of full ATZ removal for all tested scenarios. Based on this finding, the experiment of minimum time reaction and fast ATZ decay rate allowed to identify the best tested scenario (E3).

So, for an incident illuminance of 90 *lux*, best parameter combination found for rehearsal conditions corresponds tested solution with pH = 7.1, 16.7 mg /L of electrolyte (NaCl) concentration, and an electrical voltage near 10 V.

Comparing the experimental results obtained in scenarios E1 and E2, it appears that (for a lower *pH* value, acid solution) the doubling of the electrolyte concentration lightly improves the pollutant degradation rate over time, allowing to reduce the reaction time needed for full ATZ removal by 30%. For a neutral *pH* value (E3-E4), this effects suffer a significant increase.

The *pH* variation doesn't seem to have any sensitive effect on the reaction time required to eliminate ATZ, but a value close to neutral made the removal rate faster (scenarios E1-E3).

A greater electric potential (voltage) applied to the aqueous solution increases energy available for any electrochemical reactions even if the electric current intensity is the same. Comparing scenarios E3-E5 results, we could confirm (as expected) that the final reaction time decreases dramatically when the value of the electrical potential is doubled.

Table 6 summarizes the major experimental results obtained for the experiments performed in PECR reactor, such as kinetic parameters, and the coefficient R^2 observed in the adjustment of a first order model to the experimental data sets. As described, for all analyzed scenarios the full ATZ removal was achieved.

Table 6 –Synthesis of ATZ removal using photoelectrocatalysis (reactor PECR).

Scenario	K_{ap} (min^{-1})	R^2	r_0 (ppm/min)
E1	0.039	0.93	0.058
E2	0.031	0.92	0.060
E3	0.048	0.67	0.090
E4	0.019	0.79	0.041
E5	0.025	0.96	0.0,40

The first order model was accurate the ATZ degradation kinetics observed in most scenarios, but not for the E3, which was identify as the best for reaction time minimization. So other models could be tested in future research developments. See also [22] and [23].

4 Conclusions

This research work can be a useful and innovative contribution to improve the effectiveness of WTS on emerging micropollutants removal using green chemical processes. Green chemistry must play an important role in support the development of sustainable water treatment technology. AOPs use should be increased in WTS to ensure safe drinking water, and to preserve water sources and public health as preconized on the challenging UN Sustainable Development Goals (like #3 and #6).

In both lab-scale photocatalytic reactors (PCR1 and PCR2), the photo-oxidation experiments achieved very high OTC removal efficiencies (96-98%), even with small amounts of suspended and coated TiO_2 nanoparticles. Therefore, the kinetic behaviour observed in the OTC photo-oxidation processes was accurately described by the *Langmuir-Hishelwood* for both photocatalytic reactors and all analysed scenarios.

The kinetics of OTC photo-oxidation by heterogeneous photocatalysis (using suspended TiO_2 nanoparticles) reveals a faster degradation during the first 10-20 minutes. In PCR1, the OTC solutions exposed to UV-lamp radiation reached higher OTC removal efficiency (96%), than those exposed to solar radiation (88%). Therefore, the overall efficiencies of the OTC degradation in synthetic and tap waters are very close, namely when the iron concentration in water is low.

In photocatalytic filtration experiments (PCR2), using a porous media coated with, the best OTC removal efficiency was 98%. This performance was achieved for an initial OTC 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. Due to longer retention/contact time into the column filter OTC removal efficiency seems to increase at the beginning of the experiment for slower filtration velocity. Therefore, filter aeration leads to highest value for the initial photo-oxidation rate, and one of the best final OTC removal efficiency.

The lab-scale photoelectrocatalytic experiments (PECR), using immobilized TiO_2 nanoparticles, are very promising, due to its ability to achieve the full ATZ degradation for a short reaction time, compared to the one reported in a previous research [15] using WO_3. The best abiotic parameter combination found in PECR tests corresponds to a solution with neutral pH, highest electrolyte (NaCl) concentration, and electrical voltage. So, it will be useful and interesting to develop new experiments in order to optimize energy costs as a function of operation time benefits.

Although this has not been described in the present work, we can reveal that toxicity tests were carried out for oxidation by-products resulting from all photocatalytic processes tested [20, 21]. Based on the potential growth´s inhibition of lettuce seeds (*Lactuca Sativa*), this simple bioassay showed very lower inhibition percentages, indicating that the solution toxicity had a strong decrease after the use of these AOPs.

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