



Treatment of emerging contaminants in wastewater treatment plants (WWTP) effluents by solar photocatalysis using low TiO₂ concentrations

L. Prieto-Rodríguez^a, S. Miralles-Cuevas^a, I. Oller^{a,c}, A. Agüera^{b,c}, G. Li Puma^d, S. Malato^{a,c,*}

^a Plataforma Solar de Almería-CIEMAT, Carretera de Senés Km 4, 04200 (Tabernas, Almería), Spain

^b Pesticide Residue Research Group, University of Almería, 04120 Almería, Spain

^c CIESOL, Joint Centre of the University of Almería-CIEMAT, 04120 Almería, Spain

^d Photocatalysis & Photoreaction Engineering, Department of Chemical Engineering, Loughborough University, Loughborough LE11 3TU, United Kingdom

ARTICLE INFO

Article history:

Received 4 June 2011

Received in revised form 31 August 2011

Accepted 3 September 2011

Available online 12 September 2011

Keywords:

Emerging contaminants

Xenobiotics

Photocatalytic

Solar photoreactor

CPC

P25

ABSTRACT

The optimal photocatalyst concentration for industrial wastewater treatment in current photoreactor designs is several hundreds of milligrams per liter. However, the elimination of emerging contaminants (ECs), which are present at extremely low concentrations in waste water treatment plants (WWTP) effluents might be accomplished at much lower catalyst (TiO₂) concentrations. One of the main drawbacks of reducing catalyst loading below the optimum is the loss of useful photons which instead are transmitted through the TiO₂ suspension without being absorbed by the catalyst. Accordingly, in this work, laboratory and solar pilot-scale experiments were performed with real WWTP effluents to evaluate the kinetics of photocatalytic degradation of 52 emerging contaminants under realistic (ppb) concentrations. The analysis of the samples was accomplished by solid phase extraction (SPE) followed by liquid chromatography–mass spectrometry (LC–MS). In view of the results, low concentrations of TiO₂ of the order of tens of milligrams per liter were found to be insufficient for the degradation of the ECs in photoreactors with a short light-path length (29 cm). However, it was established that solar reactors of diameters of several hundreds of millimetres could be used for the efficient removal of ECs from WWTP effluents. The results presented show a general methodology for selecting the most efficient reactor diameter on the basis of the desired catalyst concentration.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The occurrence of xenobiotics such as drugs, pesticides, pharmaceuticals and endocrine-disrupting compounds in wastewater has been widely investigated in the last decade [1–4]. Recently, pharmaceuticals, some personal care products, and especially endocrine-disrupting chemicals, have been labelled as emerging contaminants, which means they are still unregulated or in the process of being regulated [5]. These ECs have been found in treated wastewater, surface and ground waters, and even in drinking water, at concentrations ranging from 10 ng L⁻¹ to 20 µg L⁻¹ [6,7]. Their main source is through municipal sewage. Significant fractions of ECs are excreted in un-metabolized form or as metabolites (active or inactive) in wastewater treatment plants (WWTP) [4,8]. It is recognized that WWTP treatment technolo-

gies are very often unable to entirely degrade such persistent ECs. Consequently, ECs and metabolites accumulate in the aquatic environment where they may cause ecological risk [9], such as interferences with endocrine system of higher organisms, microbiological resistance and accumulation in soil, plants and animals [1,10,11]. Concern about the growing problem of the continuous rise of the concentrations of these compounds highlights that conventional wastewater treatments are not adequate to entirely remove many ECs. Consequently, alternative advanced technologies for tertiary treatment of WWTP effluents are necessary.

Advanced oxidation processes (AOPs) have been proposed as valuable methods for degrading persistent organic compounds, because unselective hydroxyl radicals are able to promote organic matter oxidation at high reaction rates. Among AOPs, heterogeneous photocatalysis (the irradiation of a semiconductor by photons with suitable wavelengths to promote electrons from the valence band to the conduction band, producing positively charged holes) is currently one of the most studied [12]. This process utilizes nanostructured photocatalysts to maximize the absorption of both photons and reactants. It presents recognized

* Corresponding author at: Plataforma Solar de Almería-CIEMAT, Carretera de Senés Km 4, 04200 (Tabernas, Almería), Spain. Tel.: +34 950387940; fax: +34 950365015.

E-mail address: sixto.malato@psa.es (S. Malato).

advantages, such as the low price and chemical stability of the most commonly used photocatalyst (TiO_2). However, its application to the treatment of large volumes of water is difficult due to the cost of artificial irradiation (UV lamps+electricity). Therefore, solar irradiation is considered a useful approach for reducing the cost of large-scale aqueous-phase applications [13–15]. The optimum catalyst concentration in current solar photoreactor designs for industrial wastewater treatment with typical tube diameters of a few inches is several hundreds of milligrams per liter [16]. However, the optimum catalyst concentration depends on reactor size (e.g., diameter of the tube) and the utilization of solar photoreactors with larger diameters could reduce the optimal amount of catalyst required in a solar photoreactor. This is because larger reactor diameters require lower catalyst loadings for optimal absorption of solar radiation [17]. In contrast, since the concentration of ECs in WWTP effluents is typically at ppb levels, high concentrations of TiO_2 should not be required as the objective of photocatalysis would be to remove a few tens of $\mu\text{g L}^{-1}$ of contaminants. Therefore, it might be possible to operate the solar photoreactor at catalyst concentrations much lower than the optimum that would favour an easier and more economical treatment of the effluents.

Among AOPs, solar detoxification by photo-Fenton has been described as a more efficient process than TiO_2 photocatalysis [16], but the need to operate at acidic pH (below 4 to avoid iron oxide precipitation) severely limits the use of the photo-Fenton process for the treatment of WWTP effluents. The treatment cost of adjusting the pH from near neutral to acidic and back to neutral would be too costly to treat large flowrates and in addition it raises water salinity. In contrast, detoxification by TiO_2 photocatalysis is relatively unaffected at near neutral pH, but it requires the separation and reuse of the photocatalytic particles from the slurry suspension [18–21]. Microfiltration membranes are used for this purpose but the treatment cost of this process increases when the concentration of the catalyst increases. Thus, the operation of photocatalysis at low TiO_2 concentrations would accomplish an easier recovery of the catalyst, would not require the addition of large amounts catalyst to the WWTP secondary effluents and overall should reduce the total treatment cost. Following these criteria, in this study, we selected TiO_2 loadings of few tens of mg L^{-1} for the treatment of WWTP effluents by solar photocatalysis. If TiO_2 at low concentrations were to be a feasible treatment alternative for ECs elimination, the process efficiency would have to be evaluated under these conditions. However, one of the main drawbacks of lowering the catalyst loading below the optimum is the loss of useful photons which are transmitted though the TiO_2 suspension at low optical thicknesses. In consequence, slower ECs degradation rates are realized. Accordingly, in this study, we performed laboratory-scale experiments of the degradation of selected ECs (sulfamethoxazole, flumequine, carbamacepine, 2-hydroxybiphenyl and progesterone) which were spiked to real WWTP effluents. These experiments were performed at different irradiances of constant simulated sunlight in a reactor having light-path lengths equal to those used in pilot-scale solar photoreactors. Experiments at TiO_2 concentrations of few tens of $\mu\text{g L}^{-1}$ were performed to determine, under controlled conditions, if the reduced rate of photon absorption due to the use of such low TiO_2 concentrations was very detrimental to the degradation rate of the ECs. Furthermore, the effectiveness of heterogeneous photocatalysis for the treatment of 52 ECs detected in real WWTP effluents was evaluated at pilot-plant scale using solar photoreactors having different diameters and optical thicknesses. The engineering considerations for optimal design of solar collectors for the photocatalytic degradation of ECs are presented.

2. Materials and methods

2.1. Reagents and real wastewater

The heterogeneous photocatalytic experiments were carried out with slurry suspensions of Evonik P-25 titanium dioxide (surface area $51\text{--}55\text{ m}^2\text{ g}^{-1}$). Sulphuric acid (PANREAC) was used for carbonate stripping and pH adjustment when necessary. Acetonitrile and methanol were HPLC grade from Merck and water was ultrapure Milli-Q grade. Formic acid was supplied by Merck. Analytical standards of sulfamethoxazole, flumequine, carbamacepine, 2-hydroxybiphenyl and progesterone were purchased from Sigma-Aldrich.

Real samples of wastewater effluents were collected downstream of the El Ejido WWTP secondary biological treatment in the province of Almería (Spain), and used within the following four days. Dissolved organic carbon (DOC), total inorganic carbon (IC) and chemical oxygen demand (COD) of the wastewater were in the 13–23, 110–132 and 43–63 mg L^{-1} ranges, respectively.

2.2. Analytical procedure

Dissolved organic carbon and total inorganic carbon samples were measured by a Shimadzu 5050A TOC analyzer immediately after sampling. The concentration of five emerging contaminants in the samples was monitored by high-performance liquid chromatography (HPLC, Agilent Technologies, Series 1100) fitted with a UV-DAD detector and a C-18 column (Phenomenex LUNA 5 μm , 3 mm \times 150 mm). The mobile phase (0.4 mL min^{-1}) was 10% acetonitrile and 90% water with 25 mM formic acid. Detection was performed at three wavelengths: 267 nm (sulfamethoxazole and carbamazepine), 248 nm (flumequine and progesterone) and 243 nm (2-hydroxy-biphenyl). Prior to HPLC analyses 10 mL of each sample was eluted through a 0.22- μm syringe filter to remove the catalyst, then 2 mL of HPLC-grade acetonitrile were eluted through the filter to extract the ECs adsorbed on the filter and on the TiO_2 retained in the filter.

Samples collected from the treatment of the real WWTP effluent were filtered and concentrated 100 times by solid-phase extraction (SPE) [11] and Waters Oasis HLB (divinylbenzene/*N*-vinylpyrrolidone copolymer) cartridges (200 mg, 6 cm^3). A Gilson ASPEC GX-271 automatic sample processor equipped with a 406 Single Syringe pump and VALVEMATE® II valve actuator was used. The extracts were then analyzed by a HPLC (Agilent Series 1100) and a 3200 QTRAP MS/MS system (Applied Biosystems, Concord, ON, Canada) [22] fitted with a reversed-phase C18 analytical column (Agilent Zorbax SB, 250 mm long and 3.0 mm i.d.). The analyses were performed with a turbo ion spray source in positive and negative modes. The Applied Biosystems/MDS Sciex Analyst software was used for data acquisition and processing.

2.3. Experimental set-up

2.3.1. Laboratory-scale experiments

Experiments were carried out in a Suntest solar simulator (Suntest XLS+ photoreactor, Atlas) equipped with a 765–250 W m^{-2} Xe lamp (61–24 W m^{-2} from 300 to 400 nm, $1.4 \times 10^{20}\text{--}5.5 \times 10^{19}$ photons $\text{m}^{-2}\text{ s}^{-1}$) and a cooler to keep the temperature at 35 °C. The laboratory-scale reactor consisted of a 170-mm-long Pyrex glass tube with a 32 mm O.D. (inner diameter 29.2 mm, thickness of the glass wall 1.4 mm, light transmission $\lambda < 400\text{ nm}$ 91%, illuminated volume, V_i , 120 mL), a glass container and connecting tubing to complete a total volume V_T of 1.2 L (see Fig. 1). The distance of the lamp axis to the reactor longitudinal axis was 250 mm. A peristaltic pump (Watson Marlow, 520S) was used to create a turbulent flow (0.5 L min^{-1}), and magnetic

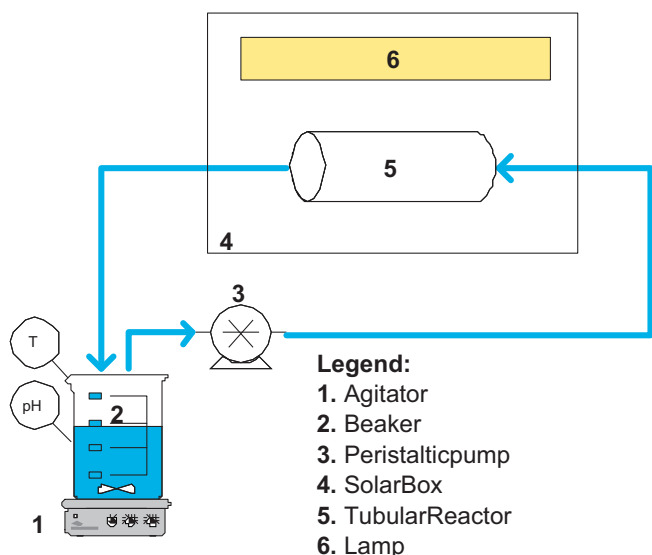


Fig. 1. Lab-scale photoreactor.

agitation ensured complete homogenization. Temperature and pH were monitored during the experiments by a Hanna check-temp 1 and a CRISON pH-meter respectively.

2.3.2. Pilot-plant experiments

Solar experiments were performed in two pilot-scale compound parabolic collector (CPC) solar plants [23] which had two different glass tube diameters, and therefore different light-path lengths. Photoreactor I was made of two 11-L modules with twelve Pyrex glass tubes each (32 mm O.D., the same used in the laboratory scale experiments) mounted on a fixed platform tilted 37° from the horizontal position. The total illuminated area was 3 m², the total volume was 35 L (V_T) and the illuminated volume was 22 L (V_i). Photoreactor II was composed of two modules with ten Pyrex glass tubes each (50 mm O.D., inner diameter 46.4 mm, thickness of the glass wall 1.8 mm). The total illuminated area was 4.5 m², the total volume was 60 L (V_T), and the illuminated volume was 45 L (V_i). Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3) mounted on a platform tilted 37°. Using Eq. (1) [23], the comparison of ECs degradation kinetics carried out in different experiments and different photoreactors was possible:

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV V_i}{30 V_T}; \quad \Delta t_n = t_n - t_{n-1} \quad (1)$$

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured during the interval Δt_n , and t_{30W} is a "normalized illumination time".

2.4. Experimental procedures

Laboratory-scale experiments were performed with a TiO₂ concentration of either 20 or 50 mg L⁻¹ under different solar simulator irradiances. When received, the WWTP secondary biological treatment effluents were pre-treated with H₂SO₄ under agitation to remove carbonates, which are known to scavenge hydroxyl radicals [24]. In these experiments, 1.2 L of real WWTP effluents were spiked with 100 µg L⁻¹ of ECs (sulfamethoxazole, flumequine, carbamacepine, 2-hydroxybifenyl and progesterone). After 15 min of homogenization, the concentrations of the original contaminants in the water was measured. Then the TiO₂ catalyst was added and a further 45 min were needed to ensure homogenization. Following this period, the lamp was turned on. Samples were collected every

15 min during the first 2 h of the experiment and then every hour until the end of the experiment.

Pilot plant experiments were performed with real WWTP effluents which was not spiked with ECs. Effluents, free of HCO₃⁻/CO₃²⁻ and at pH 6.5 were added to the pilot plant and recirculated through the solar collectors. During this phase the reactor was covered to avoid solar activation of the suspended catalyst. Then, 20 mg L⁻¹ of TiO₂ catalyst were added, and after 30 min of homogenization, the reactor was exposed to sunlight. 200-mL samples were collected every 20 min during the first 2 h and every hour for the rest of the experiment. Samples were concentrated by SPE prior to HPLC-QTRAP-MS analysis.

3. Results and discussion

3.1. Laboratory-scale mild heterogeneous photocatalysis with TiO₂

The reaction rate and efficiency of a photocatalytic process depend on factors governing the reaction kinetics, such as the concentration of ECs, the mass of catalyst and the incident radiant flux. In these experiments, the catalyst concentration used was ten times smaller (20 mg L⁻¹) than the concentration needed for optimum absorption of solar radiation in a 32-mm path length [17,25] tube. The concentration of the ECs in the water was in the µg L⁻¹ range. Fig. 2 shows the degradation of a mixture of five ECs (sulfamethoxazole, carbamacepine, flumequine, 2-hydroxybifenyl and progesterone) which were spiked to WWTP effluents. These laboratory-scale experiments were performed with 20 mg L⁻¹ TiO₂ at different light intensities and at 50 mg L⁻¹ TiO₂ over the normalized reaction time (t_{30W}). The degradation rate of the individual ECs and mixture at an irradiance of 24 W m⁻² was higher when 50 mg L⁻¹ of TiO₂ were used. The example for sulfamethoxazole is shown here for illustrative purposes in Fig. 2b. The total and individual degradation profiles are similar in all cases under the same experimental conditions, demonstrating that the degradation rate was controlled by the concentration of TiO₂ for all analytes. Other factors such as adsorption, pH, composition of the water matrix were judged to be of secondary importance compared to the optical thickness of the suspension. Although the adsorption of the contaminants using lower catalyst concentrations is diminished, we believe that the most important factor controlling the overall degradation of the contaminants is the poor absorption of the incident radiation since the reactor was operated at a very low optical thickness. As a result, a large fraction of useful photons was transmitted through the reactor since only a small fraction of these were absorbed by the catalyst slurry.

The absorption of radiation in a photocatalytic tubular reactor is influenced by the geometry of the reactor and by the optical properties of the photocatalyst. The modelling of the radiation absorbed in solar photoreactors (tubular reactors and compound parabolic collectors) has been recently reported in [17] for the optical properties of TiO₂ P25 averaged in the solar radiation spectrum which are: specific mass absorption $\kappa = 174.75 \text{ m}^2 \text{ kg}^{-1}$, scattering coefficients $\sigma = 1295.75 \text{ m}^2 \text{ kg}^{-1}$ and scattering albedo $\omega = 0.88$. Using these optical values, the optical thickness τ for the two catalyst loading configurations can be estimated from Eq. (2):

$$\tau = (\sigma + \kappa)c_{\text{cat}}d \quad (2)$$

where c_{cat} is the catalyst concentration and d is the internal tube diameter. For the catalyst concentrations used in these experiments, 20 and 50 mg L⁻¹, the optical thicknesses calculated from Eq. (2) for the 29.2 mm i.d. tube diameter were 0.86 and 2.15, respectively. Utilizing these two values of optical thicknesses and the results of photon absorption for tubular photocatalytic reactors

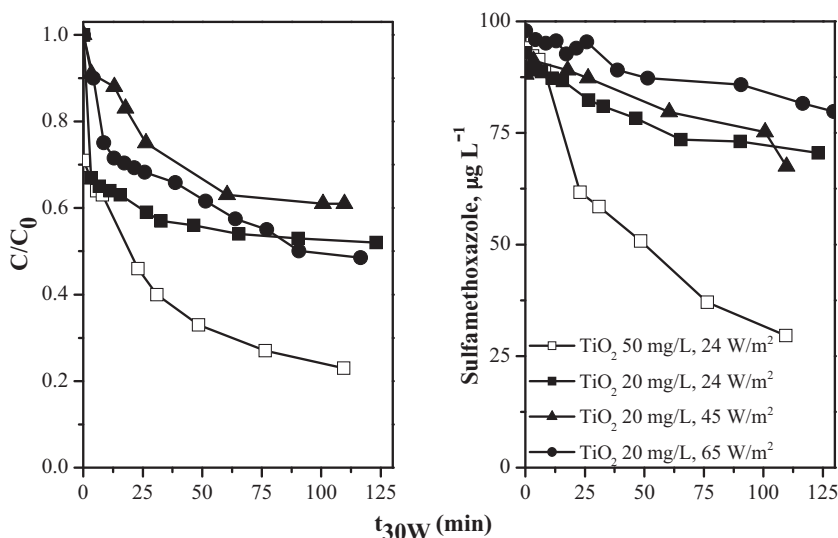


Fig. 2. (Left) Degradation of all five ECs ($100 \mu\text{g L}^{-1}$ each) in WWTP effluents during experiments performed with 20 mg L^{-1} TiO₂ at different light intensities and 50 mg L^{-1} TiO₂. (Right) Detail of the degradation of one of the contaminants (sulfamethoxazole) in the mixture.

with TiO₂ P25 presented in [17] it can be shown that for a scattering albedo $\omega = 0.88$ the radiation absorbed by the photocatalyst is 5.1 W/m in the reactor operated with 20 mg L^{-1} of TiO₂ and 10.0 W/m in the reactor operated with 50 mg L^{-1} . The results in reference [17] also show that the maximum rate of photon absorption per unit reactor length is 24.5 W/m which was obtained at the optimal catalyst concentration of 400 mg L^{-1} of TiO₂ P25 and at an optical thickness of 17.2. Either side of this catalyst concentration the absorption of radiation decreases due to either loss of radiation transmitted through the slurry suspension or because of insufficient irradiation of the entire reactor volume at very high catalyst concentrations. An efficiency for the absorption of solar radiation by a solar collector can be calculated by dividing the photon absorption realized in each reactor configuration by the maximum rate of photon absorption that could be absorbed in the photoreactor. Therefore, the reactor was 20.8% ($= 5.1 \text{ W}/24.5 \text{ W} \times 100$) efficient in terms of overall radiation absorbed when it was operated with 20 mg L^{-1} of TiO₂ and 40.6% efficient when it was operated with 50 mg L^{-1} . The results in Fig. 2 show that degradation rate of ECs and of sulfamethoxazole also doubled when the concentration of TiO₂ was varied from 20 to 50 mg L^{-1} which corresponds to the doubling of the rate of photon absorption when the concentration of TiO₂ was raised from 20 to 50 mg L^{-1} . However, the experiments performed at different radiant fluxes (Φ) with the lowest concentration of TiO₂ showed statistically insignificant differences under different photon fluxes. This is because of the large excess of photons that are available when the reactor is operated at optical thicknesses far from the optimum. Under these circumstances the photon flux remains at high values throughout the entire volume of the reactor and the photocatalytic particles are subjected to a large flux of photons. It is well-known that under these circumstances the rate limiting step is not electron/hole recombination, but the mass transfer of reactants to the photocatalyst surface, and therefore, the reaction rate is proportional to Φ^0 [13,26].

After 100 min of t_{30W} , 75% of all five contaminants were degraded with 50 mg L^{-1} of TiO₂, while 35–50% degradation was observed in the experiments with 20 mg L^{-1} of TiO₂. To achieve a more efficient degradation of ECs or their complete elimination using a low photocatalyst concentration, either a longer reaction time or some other improvement in the process would be necessary. However, it should be observed that a real WWTP effluent spiked with up to $500 \mu\text{g L}^{-1}$ is far from realistic, since WWTP

effluents often contain less than $50 \mu\text{g L}^{-1}$ of ECs. As a result, the treatment time should be much shorter with a total ECs concentration about ten times less than the experiments shown in Fig. 2. We therefore, investigated the effectiveness of solar photocatalysis under realistic conditions of ECs in WWTP effluents.

3.2. WWTP secondary biological treatment effluent

The efficiency of the “mild” photocatalytic experiment described above was tested at pilot-plant scale with un-spiked real WWTP secondary biological treatment effluents under natural sunlight. WWTP effluents were analyzed by HPLC-QTRAP-MS to quantify the degradation of each ECs. It is important to highlight that 52 target ECs out of 89 in the analytical protocol were quantified [22]. 16 of those present at an initial concentration of over 750 ng L^{-1} made up over 90% of the original total effluent pollutant load (PL, concentration of all ECs identified), which was in the range of $80 \mu\text{g L}^{-1}$. This group of 16 ECs consisted mainly of pharmaceuticals such as ibuprofen, hydrochlorothiazide, atenolol, diclofenac, ofloxacin, naproxen, trimethoprim, sulfamethoxazol. Another group was made up of dipyrone metabolites (4-methylaminoantipyrine (4-MAA), 4-formylaminoantipyrine (4-FAA), 4-aminoantipyrine (4-AA) and 4-acetylaminantipyrine (4-AAA)). The ECs detected at the highest concentrations were caffeine and paraxanthine ($\sim 17 \mu\text{g L}^{-1}$). Furthermore, other pharmaceuticals, pesticides (such as atrazine, even though now prohibited), metabolites and others, completed the list of 52 emerging contaminants quantified. The complete list and the initial concentration of each EC is shown in Table 1. The type and concentration of contaminants varied significantly from day to day but was always in the $\mu\text{g L}^{-1}$ range, therefore, the results presented in Table 1 should not be taken as representative of a monitoring study, but they were only useful for the purpose of the experiments described in this paper.

3.3. Mild solar heterogeneous photocatalysis with TiO₂ at pilot-plant scale

Fig. 3 shows the degradation of the 16 ECs with concentrations over 750 ng L^{-1} , as well as of the cumulative total concentration (ΣEC) of the remaining 36 ECs detected in the treated water. More than 85% of the PL (pollutants load) was degraded after 480 min,

Table 1
Contaminants identified in real WWTP secondary biological effluents by HPLC-QTRAP-MS.

Contaminant	C ₀ (ng L ⁻¹)	Contaminant	C ₀ (ng L ⁻¹)	Contaminant	C ₀ (ng L ⁻¹)	Contaminant	C ₀ (ng L ⁻¹)
4-AA	1315	Citalopram HBr	17	Ibuprofeno	726	Primidone	50
4-AAA	12,702	Clarithromycin	54	Indomethacine	437	Propranolol	17
4-FAA	4617	Codeine	192	Isoproturon	172	Propyphen.	32
4-MAA	2824	Cotinine	287	Ketoprofen	428	Ranitidine	710
Antipyrine	681	Diazepan	68	Lincomycin	192	Salbutamol	81
Atenolol	1241	Diclofenac	4425	Mefenamic acid	18	Simazine	704
Atrazine	305	Diuron	1081	Mepivacaine	28	Sulfadiazine	36
Azithromycin	69	Erythromycin	78	Naproxen	2968	Sulfamethazine	236
Benzafibrate	44	Famotidine	19	Nicotine	450	Sulfamethox.	999
Caffeine	17,175	Fenofibric acid	142	Norfloxacin	29	Sulfapyridine	131
Carbamazepine	114	Furosemide	100	Ofloxacin	1614	Terbutaline	85
Chlorfenvin	29	Gemfibrozil	2622	Paraxanthine	17,750	Trimethoprim	1661
Ciprofloxacin	305	Hydrochloro.	780	Pravastatin	75	Velafaxime	539

although some contaminants, such as caffeine and the dipyrone metabolites 4-AAA and 4-FAA were degraded at much smaller rates.

From these results, it appears that using such a low concentration of TiO₂ was inappropriate for an effective treatment of the ECs, as the reaction rate was too slow and the degradation was incomplete after such a long illumination time. This limitation was addressed by changing the geometry of the reactor which resulted in an increase of the rate of photon absorption while maintaining a low concentration of the catalyst. It has been reported [17,27,28] that the optimum photocatalyst concentration is mainly a function of photoreactor design and light-path length. Therefore, another series of experiments were performed in Photoreactor II using the same concentration of TiO₂, but with a 50-mm O.D. glass tube diameter. In these experiments, the WWTP secondary biological treatment effluents were sampled on a different day, and the contaminants composition differed significantly from the experiments performed in Photoreactor I. In these wastewater 50 ECs were identified. Fig. 4 shows the degradation of the most representative ECs, which differed from those observed in Fig. 3. Among the ECs the main contaminants (nicotine, 4-AAA, 4-FAA) and another

found in the µg L⁻¹ range (i.e., atenolol, 4-MAA, 4-AA, diclofenac and hydrochlorothiazide) were also identified in Fig. 3. In general, the degradation of most of the compounds was similar, but was different in the initial ECs concentrations. PL was approximately 60 µg L⁻¹. Fig. 4 also shows that the dark adsorption of the contaminants on the TiO₂ catalyst (data at *t* < 0) was insignificant for the purpose of this study. Over 90% of the PL was degraded after a reaction time of 300 min, which is significantly different compared to the PL degradation observed in Photoreactor I. Therefore, the difference in the reactor diameters was demonstrated to be a significant design parameter which would influence the photocatalytic treatment of ECs in under low-TiO₂ catalyst concentrations. It is anticipated, that new developments in CPC photoreactors with

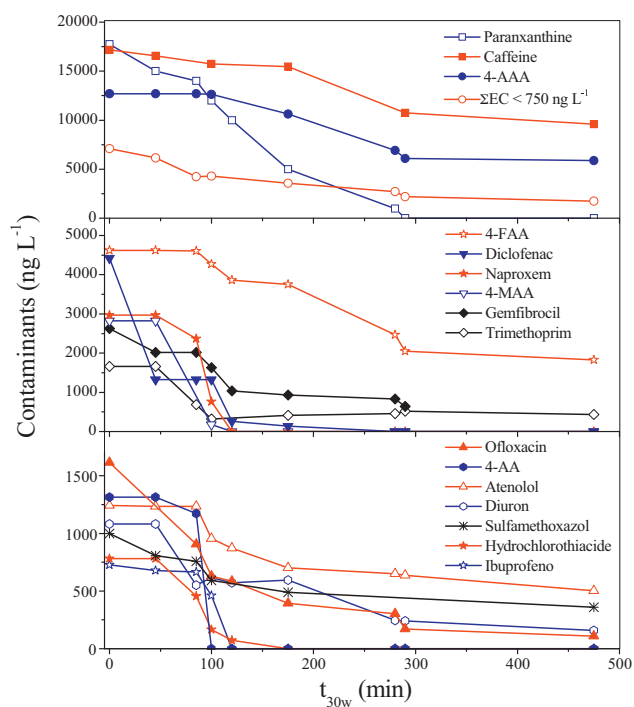


Fig. 3. Degradation by heterogeneous photocatalysis with 20 mg L⁻¹ TiO₂ in Photoreactor I of the 16 ECs with an initial concentration over 750 ng L⁻¹ and all ECs (ΣEC) under 750 ng L⁻¹.

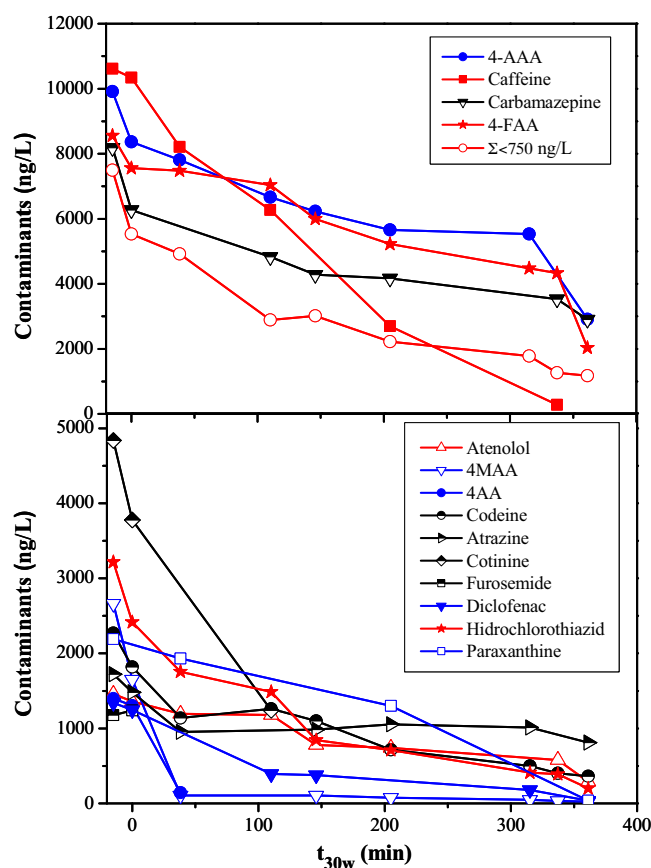


Fig. 4. Degradation by heterogeneous photocatalysis with 20 mg L⁻¹ TiO₂ in Photoreactor II of the 14 ECs with an initial concentration over 750 ng L⁻¹ and the sum of the rest of the ECs under 750 ng L⁻¹.

Table 2
Radiation absorption in the pilot scale photoreactors estimated from modelling the CPC by ray-tracing coupled with the six-flux absorption-scattering model [17].

	Photoreactor I	Photoreactor II
TiO ₂ P25 loading [mg L ⁻¹]	20	20
Inner tube diameter [mm]	29.2	46.4
Optical thickness, τ	0.86	1.36
Radiation absorbed per unit length [W/m]	12.6	36.9
Maximum rate of photon absorption [W/m] ^a	41.6	66.1
Radiation absorption efficiency [%]	30.3	55.8

^a This occurs when the reactors are operated at an optical thickness of $\tau = 13$.

much larger tube diameters could be necessary to substantially decrease the treatment time.

The results shown above can be rationalized by an analysis of the total solar radiation absorbed in each pilot-scale reactor configuration and by an estimation of the corresponding photon absorption efficiencies. In contrast with the tubular reactor configuration used in the laboratory-scale experiments, the CPC photoreactor is a much more efficient solar collector device due to the presence of the reflector. The CPC has been shown to have on average 70% higher photon absorption efficiency than a tubular reactor, and requires 39% less catalyst to operate under optimum conditions [17].

Table 2 shows the volumetric rates of solar radiation that were absorbed in the two pilot scale photoreactors estimated by modelling the CPC by ray-tracing coupled with the six-flux absorption-scattering model [17]. Photoreactor I was operated at an optical thickness of 0.86 and it absorbed 12.6 W/m, while Photoreactor II was operated at an optical thickness of 1.37 and it absorbed 36.9 W/m. As shown the radiation absorption efficiencies were 30.3 and 55.8% respectively. The results presented in Figs. 3 and 4 reflect this increase in the rate of photon absorption. Therefore, it may be concluded that an optimum treatment of the ECs in WWTP effluents can be accomplished by increasing the amount of solar radiation absorbed by the CPC photoreactor. In addition, the operational efficiency of Photoreactor II was not insignificant at 55.8% which could be increased further by using a reactor of an even larger diameter. A maximum rate of photon absorption is realized when the CPC reactor is operated at an optical thickness of about 13 [17]. Therefore, the corresponding reactor diameter can be estimated from Eq. (3) by using the desired concentration of catalyst.

$$d = \frac{\tau}{(\sigma + \kappa)c_{\text{cat}}} \quad (3)$$

For example, using a catalyst loading of 20 mg L⁻¹ the optimum diameter of the CPC which gives the maximum value of solar radiation absorption is 442 mm. However, 90% radiation absorption efficiency can be realized in a CPC operated at an optical thickness of 6.22 [17]. Therefore for a catalyst loading of 20 mg L⁻¹ the reactor diameter will be about half of the size and equal to 211 mm. The above considerations are important for the optimal design of photocatalytic solar collectors operated at low catalyst concentrations to reduce the overall treatment costs.

4. Conclusions

A mild photocatalytic tertiary treatment for the removal of 52 ECs from WWTP biological secondary treatment effluents was demonstrated under realistic conditions (real wastewater with contaminants in the $\mu\text{g L}^{-1}$ range). Although the low concentration of the catalyst limits the reaction rate due to the weak absorption of photons in current reactor designs, a higher extent of ECs degradation (>85%) is possible under natural sunlight when CPC reactors of larger diameters are used.

The use of low concentrations of TiO₂ could be a good, economical and simple alternative for the tertiary treatment of WWTP and for the removal of persistent ECs which are not degraded by traditional WWTPs. A strategy for increasing the absorption of solar radiation involves the use of tubular reactors and CPC with a wider tube diameter to allow optimal absorption of photons. However, further experimental validation is required to verify the model predictions and for the optimization of the conditions for effective removal of ECs and for the minimization of the overall treatment cost.

Acknowledgements

The authors wish to thank the Spanish Ministry of Science and Innovation for financial support under EDARSOL project (reference: CTQ2009-13459-C05-01). They also wish to thank Mrs. Deborah Fuldauer for English language correction. Lucía Prieto-Rodríguez would like to thank the University of Almeria and CIEMAT-PSA for her Ph.D. research grant. Sara Miralles would like to thank CIEMAT for her Ph.D. research grant.

References

- [1] N. Bolong, A.F. Ismail, M.R. Salim, T. Matsuura, A review of the effects of emerging contaminants in wastewater and options for their removal, *Desalination* 239 (2009) 229–246.
- [2] T. Heberer, Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, *Toxicol. Lett.* 131 (2002) 5–17.
- [3] M. Petrovic, S. Gonzalez, D. Barceló, Analysis and removal of emerging contaminants in wastewater and drinking water, *Trends Anal. Chem.* 22 (2003) 685–696.
- [4] J. Aleksandra, M. Gros, A. Ginebreda, R. Cespedes-Sanchez, F. Ventura, M. Petrovic, D. Barcelo, Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment, *Water Res.* 45 (2011) 1165–1176.
- [5] S.D. Richardson, T.A. Ternes, Water analysis: emerging contaminants and current issues, *Anal. Chem.* 83 (2011) 4614–4648.
- [6] D. Fatta-Kassinos, S. Meric, A. Nikolau, Pharmaceutical residues in environmental waters and wastewater: current state of knowledge and future research, *Anal. Bioanal. Chem.* 399 (2011) 251–275.
- [7] D. Barcelo, Emerging pollutants in water analysis, *Trends Anal. Chem.* 22 (2003) 14–16.
- [8] P. Amrita, K. Yew-Hoong Gin, A. Yu-Chen Lin, M. Reinhard, Impacts of emerging contaminants on freshwater resources: review of recent occurrences, sources, fate and effects, *Sci. Total Environ.* 408 (2010) 6062–6069.
- [9] P.D. Hansen, Risk assessment of emerging contaminants in aquatic systems, *Trends Anal. Chem.* 26 (2007) 1095–1099.
- [10] M.D. Camacho-Muñoz, J.L. Santos, I. Aparicio, E. Alonso, Presence of pharmaceutically active compounds in Doñana Park (Spain) main watersheds, *J. Hazard. Mater.* 177 (2010) 1159–2116.
- [11] N. Klammerth, S. Malato, M.I. Maldonado, A. Agüera, A.R. Fernandez-Alba, Application of photo-Fenton as tertiary treatment of emerging contaminants in municipal wastewater, *Environ. Sci. Technol.* 44 (2010) 1792–1798.
- [12] J.M. Herrmann, Photocatalysis fundamentals revisited to avoid several misconceptions, *Appl. Catal. B: Environ.* 99 (2010) 461–468.
- [13] J.M. Herrmann, Heterogeneous photocatalysis: state of the art and present applications, *Top. Catal.* 34 (2005) 48–65.
- [14] D. Bahnemann, Photocatalytic water treatment: solar energy applications, *Sol. Energy* 77 (2004) 445–459.
- [15] R.J. Braham, A.T. Harris, Review of major design and scale-up considerations for solar photocatalytic reactors, *Ind. Eng. Chem. Res.* 48 (2009) 8890–8905.
- [16] S. Malato, P. Fernandez-Ibañez, M.I. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, *Catal. Today* 147 (2009) 1–59.
- [17] J. Colina-Márquez, F. Machuca-Martínez, G. Li Puma, Radiation adsorption and optimisation of solar photocatalytic reactors for environmental applications, *Environ. Sci. Technol.* 44 (2010) 5112–5120.
- [18] H. Jiang, G. Zhang, T. Huang, J. Chen, Q. Wang, Q. Meng, Photocatalytic membrane reactor for degradation of acid red B wastewater, *Chem. Eng.* 156 (2010) 571–577.
- [19] L. Erdei, N. Arecrachakul, S. Vigneswaran, A combined photocatalytic slurry reactor-immersed membrane module system for advanced wastewater treatment, *Sep. Purif. Technol.* 62 (2008) 382–388.
- [20] D. Suryaman, K. Hasegawa, S. Kagaya, T. Yoshimura, Continuous flow photocatalytic treatment integrated with separation of titanium dioxide on the removal of phenol in tap water, *J. Hazard. Mater.* 171 (2009) 318–322.

- [21] W. Xi, S.-U. Geissen, Separation of titanium dioxide from photocatalytically treated water by cross-flow microfiltration, *Water Res.* 35 (2001) 1256–1262.
- [22] M.J. Martínez Bueno, A. Agüera, M.J. Gomez, M.D. Hernando, J.F. García Reyes, A.R. Fernandez-Alba, Application of liquid chromatography/quadrupole-linear ion trap mass spectrometry and time-of-flight mass spectrometry to the determination of pharmaceuticals and related contaminants in wastewater, *Anal. Chem.* 79 (2007) 9372–9384.
- [23] M. Kositz, I. Poullos, S. Malato, J. Cáceres, A. Campos, Solar photocatalytic treatment of synthetic municipal wastewater, *Water Res.* 38 (2004) 1147–1154.
- [24] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 1–84.
- [25] S. Malato Rodríguez, J. Blanco Galvez, M.I. Maldonado Rubio, P. Fernandez Ibañez, D. Alarcon Padilla, M. Collares Pereira, J. Farinha Mendes, J. Correia de Oliveira, Engineering of solar photocatalytic collectors, *Sol. Energy* 77 (2004) 513–524.
- [26] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C: Photochem. Rev.* 1 (2000) 1–21.
- [27] D.F. Ollis, Solar-assisted photocatalysis for water purification: issues, data questions, in: E. Pelizzetti, M. Schiavello (Eds.), *Photochemical Conversion and Storage of Solar Energy*, Kluwer Academic Publishers, Netherlands, 1991, pp. 593–622.
- [28] G. Riegel, J.R. Bolton, Photocatalytic efficiency variability in TiO₂ particles, *J. Phys. Chem.* 99 (1995) 4215–4224.