Water Air Soil Pollut (2023) 234:55
https://doi.org/10.1007/s11270-023-06075-4

Removal of Contaminants of Emerging Concern from a Wastewater Effluent by Solar-Driven Heterogeneous Photocatalysis: A Case Study of Pharmaceuticals

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Received: 13 October 2022 / Accepted: 5 January 2023 / Published online: 12 January 2023

Abstract The occurrence of emerging micropollutants (pharmaceuticals, pesticides, personal care products, industrial compounds, etc.) in the environment is considered a major threat to human health and aquatic ecosystems. These micropollutants enter the environment through anthropogenic actions and have been identified in surface, ground, waste, and even in drinking water, in quantities ranging from ng L^{-1} to μg L^{-1}. Currently, the pollution of the global water cycle with persistent organic pollutants remains one of the major challenges of the twenty-first century. Most of these organic substances are only partially removed by conventional wastewater treatment plants. Particularly, considerable amounts of pharmaceuticals are used in human and veterinary medicine, which are not efficiently removed during conventional wastewater treatments and subsequently continuously enter freshwater systems and even agricultural crops. Accordingly, we have evaluated the effectivity of TiO_2 as a photocatalyst in tandem with $Na_2S_2O_8$ as an oxidant for the treatment of a wastewater effluent polluted with pharmaceutical (atenolol, carbamazepine, clarithromycin, erythromycin, irbesartan, and ketoprofen) residues. Results show that the use of solar heterogeneous photocatalysis by means of band-gap semiconductor materials, especially TiO_2 in combination with a strong oxidant such as $Na_2S_2O_8$, significantly enhances their disappearance from the wastewater effluent. However, the selected pharmaceuticals show a slow degradation in wastewater effluent compared to pure water indicating that the occurrence of dissolved salts and organic carbon in wastewater effluent noticeably slows down the efficiency of the treatment. A single first-order model satisfactorily explains the photocatalytic degradation of the compounds studied for both, pure and wastewater. In the case of wastewater effluent, the highest DT_{50} values were observed for macrolides (13 and 16 min for erythromycin and clarithromycin, respectively), while the other compounds studied showed DT_{50} values below 10 min. This methodology has a notorious interest in some areas of the Mediterranean basin with water shortage, such as SE of Spain, where more than 3000 h of sunlight per year are recovered.

Keywords Advanced oxidation processes · Emerging micropollutants · Environmental risk · TiO_2

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1 Introduction

Numerous scientific papers published in the last 2 decades have reported the occurrence of emerging

pollutants (EPs), also called contaminants of emerging concern (CECs), in different aquatic environments, including wastewater (WW) (Gogoi et al., 2018; Noguera-Oviedo & Aga, 2016; Tang et al., 2019). CECs, including their transformation products, are chemicals without regulatory evaluation and whose effects on the environment and humans are poorly understood (Deblonde et al., 2011). The occurrence of these pollutants (mostly of organic in nature) and their harmful impact on aquatic and terrestrial ecosystems, as well as on human health, is now a matter of concern among the governmental institutions, scientific community, and citizens. CECs are not necessarily new substances. These compounds are present for a long time in environmental compartments, although their presence and involvement are currently being clarified. Despite guidelines established by national and local authorities, unregulated discharges often occur due to the lack of specific legislation and ecotoxicity data of CECs (Parida et al., 2021). Many of them are resistant to conventional treatments or have slow biodegradation rates (Choi et al., 2017). Uncontrolled release of CECs into the aquatic environment causes problems such as high persistence, ecotoxicity, and likely harm to human and animal health. Recent scientific studies and reports on WW composition have focussed attention on the presence in the environment of many chemicals derived from anthropogenic activities from urban, agricultural, and industrial sources (Pal et al., 2010; Deblonde et al., 2011; Archer et al., 2017; Wilkinson et al., 2017). The global occurrence of CECs in developed and developing countries shows the urgent need to address this type of contaminants. A compilation of worldwide occurrence of CECs detected in the environment has been recently published by Lee et al. (2021).

Although CECs are often present in the environment at low levels ranging from ng L^{-1} or µg L^{-1}, it is still unclear whether their concentrations in the aquatic environment can cause endocrine disruption in wildlife and humans. A lot of them are persistent in water, putting pressure on the wastewater treatment plants (WWTPs) for their operative removal (Archer et al., 2017). According to the NORMAN database, several thousand chemicals from 21 types have been identified in the European aquatic environment in recent decades (Norman, 2022). In addition, based on the number of chemical compounds listed by the European Chemical Agency, between 3×10^4 and 5×10^4 industrial chemicals are in daily use, and a large number are catalogued as potential CECs owing to their release into the environment (ECHA, 2022). Among them, pesticides also called plant protection products (herbicides, insecticides), personal care products (fragrances, parabens, UV filters), pharmaceuticals (analgesics, antibiotics, legal drugs, beta-blockers, steroids), drugs of abuse (cannabinoids, opioids) life-style compounds (nicotine, caffeine), or industrial additives and by-products (chlorinated solvents, plasticizers, polyaromatic hydrocarbons) among others have been found in WW worldwide over the last years (Tang et al., 2019).

Concretely, a pharmaceutical (PhMC), also called a medicine, pharmaceutical product, medication, or medicinal product, is "any substance or combination of substances which may be used in or administered to human beings either with a view to restoring, correcting or modifying physiological functions by exerting a pharmacological, immunological or metabolic action, or to making a medical diagnosis" (Vogler & Zimmermann, 2016). PhMCs include the active substance (a substance that, alone or in combination with one or more ingredients, is considered to fulfill the intended activity of a medicinal product) and excipients (substances, different from the active substance, that have been adequately evaluated for safety and are included in a medicine delivery system to protect, support, or enhance stability, bioavailability, or patient acceptability, among other functions). Many of them are regularly detected in high levels in the aquatic environment, possibly due to their unceasing release from WWTPs, which is meaningfully faster than their elimination rates. Consequently, they are considered as a group of pseudo-persistent contaminants with slow transformation rate, as pointed out by laboratory and field studies (Arnold et al., 2013; Bu et al., 2016). Even though PhMCs have been ubiquitous in aqueous media for a long time, the levels found in the environment have only recently begun to be monitored and recognized as potentially harmful to environmental ecosystems. This is due to the advance of new analytical techniques (mainly LC–MS/MS) that allow the identification and quantitation at very low levels (ng L^{-1}) of these compounds in waste, surface, and groundwater (Rivera-Utrilla et al., 2013). PhMCs have become an important public health issue as environmental pollutants over the last years (Kummerer, 2010). After ingestion, PhMCs are partially excreted unchanged and may subsequently reach the WWTPs via the sewer network.

Water shortage and the fitful terrestrial distribution of rainfall are disturbing concerns in arid and semiarid areas, where water management strategies promote the reuse of WW effluents for agricultural purposes because of climate change. Some papers have recently reviewed the occurrence and fate of a large number and variety of CECs likely to occur in agroecosystems (Boxall, 2012; Snow et al., 2020). Thus, PhMCs can enter in the agricultural environment directly (via therapeutic use in livestock and fisheries), as well as indirectly, through the cumulative use of reclaimed WW and the application of municipal biosolids and manure. Currently, WW is reused worldwide, particularly in semiarid areas like SE of Spain. Bearing in mind the extensive variety of CECs (many of them still unassessed) entering WWTPs, many compounds (transformed or not) can end up in agricultural soils with the consequent risk of plant intake. For this reason, the EU has focused on this issue with the reconsideration of the minimum requirements for water reuse according to Regulation 2020/741/EU (EC, 2020). The purpose of this regulation is to guarantee that reclaimed water is harmless for agricultural reuse, supporting resilience to climate change, promoting the circular economy, and contributing to the objectives of the Water Framework Directive (EC, 2000) by controlling water scarcity and the consequent pressure on water resources. Regarding this initiative, PhMCs are highlighted in the EU Strategic Approach on Pharmaceuticals in the Environment (EC, 2019).

In many cases, the conventional (biological) treatments are ineffective for their removal (Michael et al., 2013; Pérez-Lucas et al., 2022a). Consequently, there is a clear requirement to curb this problem by means of innovative and environmentally friendly technologies established in WWTPs to effectively remove these CECs. Membrane technology (nano, ultra, and microfiltration, reverse osmosis, adsorption dynamics on carbon nanotubes or graphene oxide, aerobic granular sludge, or gravity-driven) has been extensively applied during the last years to isolate micropollutants from wastewater in reactors (closed system) and in natural water system (open system). However, during its long-term process, the pollutants gradually accumulate into the adsorption materials, until they reached saturation, then it became inactive (Campo et al., 2021; Chen et al., 2019; Luo et al., 2022, 2023; Pronk et al., 2019), so that it is usually combined with ozonation, activated carbon, photodegradation, etc. (Vasilachi et al., 2021). In this context, relatively new treatment methods such as light-driven advanced oxidation processes (AOPs) need to be addressed (Rivera-Utrilla et al., 2013; Teixeira et al., 2015; He et al., 2016; Awfa et al., 2018; Almomani et al., 2018; Kanakaraju et al., 2018, Vasilachi et al., 2021). Light-based processes can be categorized into (i) UV/oxidant (H_2O_2, $S_2O_8^{2-}$), (ii) UV/O_3, (iii) photo-Fenton (Fe^{2+}) or photo-Fenton like (Fe^{3+}), and (iv) heterogeneous photocatalysis (with semiconductor materials, SC), each of which has a range of UV wavelengths and factors affecting their operation. Heterogeneous photocatalysis has special interest, which consists of the acceleration of a chemical reaction (photoreaction) by the action of a photocatalyst involving the combination of photochemistry and catalysis (Augugliaro et al., 2019). Both light (direct photolysis) and photocatalyst are needed to accelerate a chemical reaction. PhMCs are oxidized by highly reactive oxidant species (ROS), mainly hydroxyl radicals ($HO^{\bullet}$, $E^0 = 1.9–2.7$ V vs. normal hydrogen electrode, NHE) including others such as superoxide anion ($O_2^{\bullet-}$) and hydridodioxygen ($HO_2^{\bullet}$). Other radicals such as sulfate radical anion ($SO_4^{\bullet-}$, E^0 = 2.6–3.1 V vs. NHE) may also be implicated when using persulfate ($S_2O_8^{2-}$) to avoid electron (e^-)/hole (h^+) recombination (Yang et al., 2019). Commonly, light-driven heterogeneous photocatalysis is affected by different factors such as pH, temperature, UV/Visible absorbance and source, nature of catalyst and loading, nature and concentration of pollutant, and water matrix components (Malato et al., 2009). The impact of water composition especially affects the performance of light-driven processes because dissolved organic and inorganic compounds can adsorb on the SC surface reducing the number of active sites on it, can inhibit light penetration, and can act as ROS scavengers creating less powerful oxidants as is the case for some anions such as HCO_3^-, SO_4^{2-}, and/or Cl^- (Pérez-Lucas et al., 2022b; Ribeiro et al., 2019).

The main advantage of these processes is that they attain the removal or at least the reduction of PhMCs by mineralization, rather than transferring them from one place to another as with conventional processes (Miklos et al., 2018). Among various SCs, TiO_2 is the most widely used for water treatment, mainly due to its non-toxicity, photo-stability, corrosion resistance, availability, biological and chemical inertness, and chemical

and thermal stability over a wide pH range (Kanakaraju et al., 2014). With this aim, we have assessed the effectivity of TiO_2 as photocatalyst in combination with $Na_2S_2O_8$ as oxidant under natural sunlight for the treatment of a wastewater effluent (WWe) polluted with six PhMCs, atenolol and irbesartan (anti-hypertensives), clarithromycin and erythromycin (antibiotics), carbamazepine (anti-epileptic), and ketoprofen (anti-inflammatory) commonly used worldwide.

2 Methodology

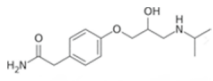
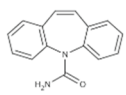
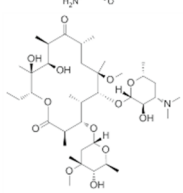
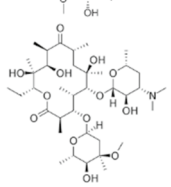
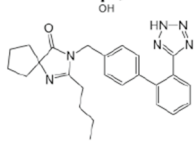
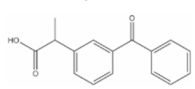
2.1 Pharmaceuticals and Reagents

Analytical standards of PhMCs with a purity > 95% were purchased from Fagron Ibérica (Barcelona, Spain). Table 1 shows their structures and main physicochemical properties. CH_3CN, CH_3OH and H_2O (HPLC-grade), $Na_2S_2O_8$, and NaCl, all with a purity > 98% were provided by Scharlab (Barcelona, Spain). Titanium dioxide (TiO_2, 99.5%, BET 55 $m^2\ g^{-1}$, size < 21 nm) Aeroxide® P25 was supplied by Nippon Aerosil Co Ltd. (Osaka, Japan). TiO_2 was previously characterized by *DRS*, *XRD*, *FE-SEM*, *XDS*, *ATR-FTIR*, and *BET* surface (Fenoll et al., 2016; Garrido et al., 2019).

2.2 Water Samples

Two different water samples were used: (i) deionized water (DW) and (ii) wastewater effluent (WWe). DW (18 MΩ cm resistivity, pH 6.8, EC < 1 µS cm^{-1}, and DOC < 20 µg L^{-1}) was obtained from a Millipore Milli-Q system (Bedford, MA, USA). WWe was obtained using a modular

Table 1 Main physicochemical properties of the used PhMCs (NIH, 2022)

Compound Formula Family	Structure	Therapeutic group	MW[a]	S_{H2O}[b]	log K_{ow}[c]	H[d]
Atenolol $C_{14}H_{22}N_2O_3$ Acetamide		Anti-hypertensive	266	13,300	0.2	1.37×10^{-18}
Carbamazepine $C_{15}H_{12}N_2O$ Carboxamide		Anti-epileptic	236	18	2.1	1.08×10^{-7}
Clarithromycin $C_{38}H_{69}NO_{13}$ Macrolide		Antibiotic	747	< 1	3.2	1.73×10^{-29}
Erythromycin $C_{37}H_{67}NO_{13}$ Macrolide		Antibiotic	734	< 1	3.1	5.42×10^{-29}
Irbesartan $C_{25}H_{28}N_6O$ Thiazide		Anti-hypertensive	429	< 1	5.3	7.04×10^{-15}
Ketoprofen $C_{16}H_{14}O_3$ Phenylacetic		Anti-inflammatory	254	51	3.1	2.12×10^{-11}

[a]*MW*, molecular weight (g mol^{-1}); [b]Water solubility (mg L^{-1}); [c]K_{OW}: partition coefficient octanol/water; [d]Henry's law constant (atm $m^3\ mol^{-1}$)

AT-8 WWTP purchased from August (Vilnius, Lithuania) with a capacity of 900 L day^{-1} including anaerobic and aerobic treatments. The main physicochemical parameters of WWe were as follows: pH=7.5; EC=1.1 dS m^{-1}; DOC=3.3 mg L^{-1}; Ca^{2+} =69 mg L^{-1}; Mg^{2+} =48 mg L^{-1}; Na^{+} =102 mg L^{-1}; K^{+} =7 mg L^{-1}; SO_4^{2-} =263 mg L^{-1}; Cl^{-} =150 mg L^{-1}; HCO_3^{-} =122 mg L^{-1}; NO_3^{-} =5 mg L^{-1}; NO_2^{-} =<0.5 mg L^{-1} and PO_4^{3-}=<5 mg L^{-1}.

2.3 Experimental Setup

Photocatalytic tests were performed in Pyrex glass vessels (110 mm length×80 mm i.d.) exposed to sunlight during September 2021 in Murcia, SE Spain. In all cases, 500 mL of water were spiked with PhMCs at 100 µg L^{-1} of each compound. Previously, the solution was homogenized for 20 min in darkness. Then, the appropriate amount of catalyst (250 mg L^{-1} of TiO_2) was added to the reaction solutions. The mixture was maintained for 30 min in the dark prior to illumination to achieve maximum adsorption of the PhMCs on the semiconductor surface as previously tested (Pérez-Lucas et al., 2022a). Subsequently, $Na_2S_2O_8$ (250 mg L^{-1}) was added, and the samples were exposed to natural sunlight for 240 min (10–14 h). The mean temperature measured during the photoperiod was 31.6±2.2 °C. UV-A and UV-B radiation values during the experiment varied from 21.2 to 26.3 W m^{-2} and 0.8–1.5 W m^{-2}, respectively. Three replicates were performed in each case, and several samples (50 mL) were taken during the photoperiod.

2.4 Analytical Determinations

The aqueous samples (50 mL) were adjusted to pH ≈ 3 with H_3PO_4 by adding 1 g of NaCl to increase the retention of the compounds on the adsorbent and the ionic strength, respectively. After homogenization, samples were passed through an Oasis® HLB 60 µm HLB extraction cartridge purchased from Waters (Milford, MA, USA) under vacuum, at a flow rate of ≈ 3 mL min^{-1}. Previously, the extraction cartridges were conditioned with CH_3CN (5 mL) and equilibrated with Milli-Q water (5 mL). Once the sample had passed through the cartridge, it was washed with Milli-Q water (5 mL), discarding the eluate and drying the cartridge with air. Finally, the target compounds were eluted with CH_3CN (5 mL) at a flow rate of 2 mL min^{-1}, collecting CH_3CN in a graduated tube and recording the total volume. After completion of SPE process, 2 mL were filtered through a nylon filter (20 µm). Chromatographic analyses were performed on an Agilent 1100 Series HPLC system (Santa Clara, CA, USA) comprising a reversed phase C8 analytical column (150 mm×4.6 mm and 5 µm particle size) (Zorbax Eclipse XDB-C8) coupled to an Agilent G6410A triple quadrupole mass spectrometer operating in ESI^{+} ion mode. A primary study of optimal selected reaction monitoring (SRM) transitions was carried out for each compound. Table 2 shows the MS/MS conditions used. A Thermo Scientific Dionex ICS-2100 ion chromatograph (Waltham, MA, USA) equipped with an AS19 column was used to determine anion concentrations. For cation measurements, an Agilent 5110 ICP-OES was used. Dissolved organic carbon (DOC) content was determined using an Analytik Jena Multi N/C 3100 TOC Analyzer (AG, Jena, Germany) after passing the samples through a nylon filter (0.45 mm).

3 Results and Discussion

3.1 Disappearance Kinetics

A simple comparison of the main important physicochemical parameters reveals substantial differences

Table 2 MS/MS parameters of the studied PhMCs

Pharmaceutical	SRM_1/SRM_2 (*m/z*)[a]	FV_1/FV_2 (V)[b]	CE_1/CE_2 (V)[c]
Atenolol	267→145; 267→190	110; 110	20; 10
Carbamazepine	237→194; 237→179	120; 120	20; 40
Clarithromycin	749→158; 749→590	150; 150	30; 20
Erythromycin	735→158; 735→83	150; 150	30; 50
Irbesartan	429→207; 429→195	150; 150	20; 20
Ketoprofen	255→77; 255→209	110; 110	50; 10

[a]Single reaction monitoring transition; [b]Fragmentor; [c]Collision energy

between the studied compounds (except macrolides) with different structures, functions, and therapeutic activities, as shown in Table 1. These compounds represent a wide range of PhMCs commonly present in WWTPs, including β-blockers, anti-epileptics, antibiotics, and anti-inflammatory drugs (Helwig et al., 2013; Lin et al., 2010; Yu et al., 2006).

An earlier test carried out under laboratory conditions using a photochemical reactor equipped with light emitting diode (LED) lamps (data not shown) demonstrated higher efficiency of TiO_2 compared to ZnO (with the same photocatalyst loading) in the photooxidation of the studied PhMCs. TiO_2 and ZnO are the most widely used photocatalysts for environmental applications. However, TiO_2 is a stable SC, while ZnO dissolves at acidic pH because it is not resistant to anodic photocorrosion (Pérez-Lucas et al., 2022a, b). Many photocatalytic studies using TiO_2 have investigated the effects of operating parameters, such as TiO_2 type and loading, initial pollutant concentration, solution pH, wavelength/light intensity, and water matrix composition, on the degradation kinetics of PhMCs (Carbajo et al., 2016). Thus, in the study carried out by Carabin et al. (2015), the most efficient TiO_2 type for carbamazepine degradation was P90, followed by P25, with removal efficiencies of 69% and 60%, respectively, after testing different TiO_2 materials (Hombikat UV 100, PC500, P25, P90, and ST01), which was attributed to the presence of a mixture of anatase and rutile in P90 and P25 materials. Dimitrakopoulou et al. (2012) examined the effect of eight different TiO_2 samples (Hombikat UV 100, Millennium PC50, Millennium PC100, Millennium PC105, Millennium PC500, Degussa P25, Tronox AK1, and Aldrich Anatase AA), on the degradation of the antibiotic amoxicillin showing P25 as the most suitable for its removal, which is due to its slower e^-/h^+ recombination rate and favorable proportion ratio of anatase and rutile phases. Another study carried out by Bianchi et al. (2017) examined the disappearance of paracetamol/aspirin mixtures in DW using TiO_2 P25 and micro-sized TiO_2 K1077 concluding that TiO_2 P25 achieved complete degradation and a mineralization efficiency around 90% (after 6 h) in contrast to TiO_2 K1077, which confirmed lower activity and poor mineralization (40% after 4 h).

In our study, the selected PhMCs show a slow degradation in WWe compared to DW, where the degradation was significantly very faster as shown in Fig. 1. After 5 min of sunlight exposure, the concentrations of all compounds strongly decreased in DW to values below 5% of their initial amounts. These results indicate that the occurrence of dissolved salts and organic carbon in WWe noticeably slows down the efficiency of the treatment.

It is well known that the point of zero charge (PZC) of TiO_2 is about 6.25 (Kosmulski, 2018). Therefore, when water pH is below it, the surface of TiO_2 is positively charged. Contrarily, when the pH is above it, the surface is negative. In our case, no significant differences ($p<0.05$) were found in the degradation of the studied compounds in the pH range 6–8. Depending on pH, $SO_4^{\bullet-}$/$HO^{\bullet}$ radicals can be present individually or simultaneously in the persulfate oxidation system (Liang & Su, 2009). Thus, at pH < 7, $SO_4^{\bullet-}$ is predominant; at pH = 9, $SO_4^{\bullet-}$ and $HO^{\bullet}$ are present; and at pH > 9, $HO^{\bullet}$ is the predominant radical. At circumneutral pH (pH of WWe used was 7.5), $SO_4^{\bullet-}$ can be more reactive than $HO^{\bullet}$, since the E^0 of $SO_4^{\bullet-}$ is detailed to be higher than that of $HO^{\bullet}$ (E^0 = 2.6–3.1 V and 1.9–2.7 V, respectively) (Oh et al., 2016). Ismail et al. (2017) found that at pH 7, $HO^{\bullet}$ and $SO_4^{\bullet-}$ radicals were involved in the degradation of sulfaclozine, whereas at pH 11, no contribution of $SO_4^{\bullet-}$ was observed.

In addition, $SO_4^{\bullet-}$ can generate more $HO^{\bullet}$ under neutral or basic conditions according to the following equations (Eqs. 1–3):

$$S_2O_8^{2-} + h\nu(\mathrm{UV}) \rightarrow 2SO_4^{\cdot-} \quad (1)$$

$$SO_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + HO^{\cdot} + H^+ \quad \left[k = 660 M^{-1}s^{-1}\right] \quad (2)$$

$$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + HO^{\cdot} \quad \left[k = 7 \times 10^7 M^{-1}s^{-1}\right] \quad (3)$$

The high solubility and non-toxic properties of persulfate are helpful for WW treatment, although the main disadvantage observed when it is used is the increase in SO_4^{2-} concentration generated by the reaction between $SO_4^{\bullet-}$ and PhMCs.

According to Liu et al. (Liu et al., 2014), the single first-order (SFO) kinetic model is regularly appropriate to describe the photooxidation rate of many organic pollutants using SC materials at low substrate concentration (Eq. 4):

$$-\frac{dC}{dt} = kC \rightarrow C_t = C_0 e^{-kt} \rightarrow lnC_t = lnC_0 - kt \rightarrow \ln\frac{C_0}{C_t} = kt \quad (4)$$

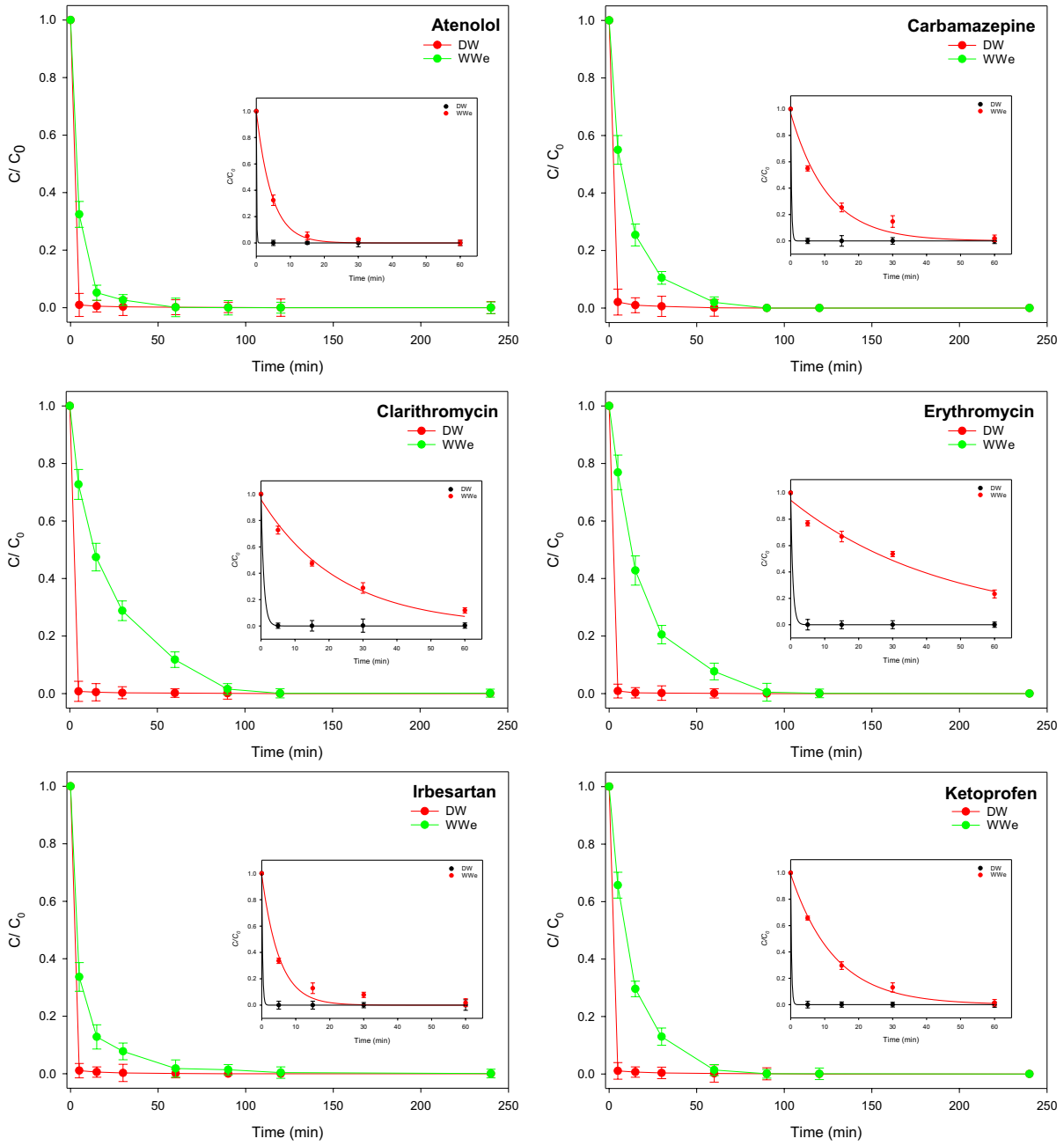


Fig. 1 Comparison of photocatalytic degradation of PhMCs in WWe and DW by solar heterogeneous photocatalysis ($TiO_2/Na_2S_2O_8$)

where t is the reaction time, C_0 is the initial concentration of PhMCs, C_t is the residual concentration at time t, and k is the rate constant. From the above equation, the time required for X % disappearance of PhMCs (disappearance time) from the water can be calculated according to Eq. 5:

$$DT_x = \ln\left(\frac{100}{100 - x}\right)/k \tag{5}$$

Consistent with the data shown in Tables 3 and 4, the SFO model satisfactorily explains the photocatalytic degradation of the compounds studied. As can

Table 3 Kinetic parameters obtained following an SFO model for photocatalytic degradation of PhMCs in DW

Pharmaceutical	$C_t = C_0\, e^{-kt}$				
	R^2	C_t/C_0	k (min^{-1})	$S_{y/x}$	DT_{50}/DT_{90} (min)
Atenolol	1.0000***	1.00	0.9210	0.003	0.8/2.5
Carbamazepine	0.9998***	1.00	0.7725	0.005	0.9/3.0
Clarithromycin	1.0000***	1.00	0.9656	0.003	0.7/2.4
Erythromycin	1.0000***	1.00	0.9421	0.002	0.7/2.4
Irbesartan	0.9999***	1.00	0.9019	0.003	0.8/2.6
Ketoprofen	0.9999***	1.00	0.9019	0.003	0.8/2.6

*** $p < 0.001$; $S_{y/x}$ standard error of estimation

be seen, R^2 values are very close to 1 in DW with a standard error of estimation ($S_{y/x}$) ≤ 0.005. In the case of WWe, PhMCs also fitted realistically to the exponential decay curve with $R^2 \geq 0.98$ in all cases and $S_{y/x} < 0.05$. In DW, DT_{50} (time required to reduce the concentration of a compound to exactly half of its original value) was in all cases < 1 min. In the case of WWe, the highest DT_{50} values were observed for macrolides, 13 and 16 min for erythromycin and clarithromycin, respectively, while the other compounds studied showed DT_{50} values below 10 min.

In the study carried out by Georgaki et al. (2014), photocatalytic conversion of carbamazepine was found to be generally slower, relative to ibuprofen using TiO_2 P25 and ZnO as photocatalyst under UV/Visible light irradiation, with TiO_2 showing better photocatalytic efficiency in the degradation of both pharmaceuticals compared to ZnO. Photocatalytic treatment of WWe using TiO_2 and high-intensity Xenon discharge lamps (55 W) to simulate solar light resulted in high removal efficiencies for poorly biodegradable PhMCs in WWe (100% for propranolol, 100% for diclofenac, and 76% for carbamazepine) after 96 h (He et al., 2016). In all cases, photodegradation followed SFO kinetics, and the rate constant of photocatalysis was much higher than that of photolysis in absence of TiO_2. Similar results were obtained by Eskandarian et al. (2016), where photocatalytic decomposition using TiO_2 and LED lamps was also much more significant than photolytic decomposition for different PhMCs such as acetaminophen, diclofenac, ibuprofen, and sulfamethoxazole.

3.2 Impact of Water Matrix Composition

On the other hand, the influence of the water composition on the photocatalytic process is crucial to assess its suitability for real WW treatment, and its effect can be complex. The surface charge of TiO_2 and the rate of ROS formation can be strongly affected by the components dissolved in the water matrix. The generated negative effect, mainly at high concentrations, is generally attributed to the occupancy sites on the photocatalyst surface by inorganic and organic components, the scavenging of $HO^{\bullet}$, and/or the aggregation of TiO_2 particles when the ionic strength is high

Table 4 Kinetic parameters obtained following an SFO model for photocatalytic degradation of PhMCs in WWe

Pharmaceutical	$C_t = C_0\, e^{-kt}$				
	R^2	C_t/C_0	k (min^{-1})	$S_{y/x}$	DT_{50}/DT_{90} (min)
Atenolol	0.9989***	1.00	0.2216	0.013	3.1/10.4
Carbamazepine	0.9925***	0.97	0.0958	0.034	7.2/24.0
Clarithromycin	0.9926***	0.96	0.0430	0.035	16.1/53.4
Erythromycin	0.9983***	1.00	0.0530	0.017	13.0/43.1
Irbesartan	0.9840***	0.99	0.1960	0.047	3.5/11.8
Ketoprofen	0.9989***	0.99	0.0779	0.017	8.9/29.6

*** $p < 0.001$; $S_{y/x}$ standard error of estimation

(Ahmed et al., 2011; Náfrádi et al., 2022). The unfavorable effects of some inorganic ions (mainly anions, such as Cl^-, CO_3^{2-}/HCO_3^-, NO_2^-/NO_3^-, and SO_4^-) can be explained by the fact that they decrease the oxidant power of the solution. The scavenging of $HO^\bullet$ by different anions originates the corresponding radicals such as $ClOH^{\bullet-}$, $Cl^\bullet$, $Cl_2^{\bullet-}$, $CO_3^{\bullet-}$, $HCO_3^{\bullet-}$, $Br^\bullet$, $Br_2^{\bullet-}$, $NO^\bullet$, $NO_2^\bullet$, $SO_4^{\bullet-}$, and/or $H_2PO_4^\bullet$, which have a lower oxidation potential (E^0) than $HO^\bullet$ (Ahmed et al., 2011; Bi et al., 2016; Ribeiro et al., 2019, Yang et al., 2019; Náfrádi et al., 2022). Figure 2 summarizes the generation mechanism of these radicals in presence of Cl^-, CO_3^{2-}/HCO_3^-, NO_2^-/NO_3^-, and SO_4^{2-}.

Bi et al. (2016) demonstrated a stronger inhibition effect of Cl^-, CO_3^{2-}, HCO_3^-, and NO_2^- on the oxytetracycline degradation, while NO_3^- did not influence its degradation. In our case, the most abundant anions of WWe were SO_4^{2-} (263 mg L^{-1}), Cl^- (150 mg L^{-1}), and HCO_3^- (122 mg L^{-1}), while NO_3^-, NO_2^-, and PO_4^{3-} contents were lower than 5 mg L^{-1}. The adverse effects of high Cl^- concentrations could favor the scavenging of $HO^\bullet$ and $SO_4^{\bullet-}$. Some authors have demonstrated that the removal of antibiotic oxytetracycline decreased at 0.4 mM of Cl^- (Bi et al., 2016). CO_2, CO_3^{2-}, and HCO_3^- are present in aqueous media at pH > 4. CO_3^{2-} and HCO_3^-, responsible of water alkalinity, can compete with PhMCs for $HO^\bullet$ and $SO_4^{\bullet-}$ radicals to generate weaker radicals, such as $CO_3^{\bullet-}$ and/or $HCO_3^{\bullet-}$. Above pH = 10.3, CO_3^{2-} is the predominant specie, but at pH below 8.3, all CO_3^{2-} has been converted to HCO_3^- (Manaham, 2010). As pH decreases, HCO_3^- also decreases and dissolved CO_2 increases. The relationship between CO_3^{2-}/ HCO_3^- and solution pH is represented as follows (Eq. 6):

$$\mathrm{pH} = \mathrm{pK_a} - \log\frac{[\mathrm{HCO_3^-}]}{[\mathrm{CO_3^{2-}}]}\mathrm{pK_a} = 10.3 \quad (6)$$

The high concentration of HCO_3^- strongly scavenges $HO^\bullet$, generating $CO_3^{\bullet-}$, a selective and less reactive reaction partner with a lower electrode potential ($E^0 = 1.6$ V) than $HO^\bullet$ ($E^0 = 2.7$ V).

On the other hand, the initial concentration of SO_4^{2-} (263 mg L^{-1}) increased to 315 mg L^{-1} at the end of the treatment because of the $S_2O_8^{2-}$ added (Eqs. 7 and 8):

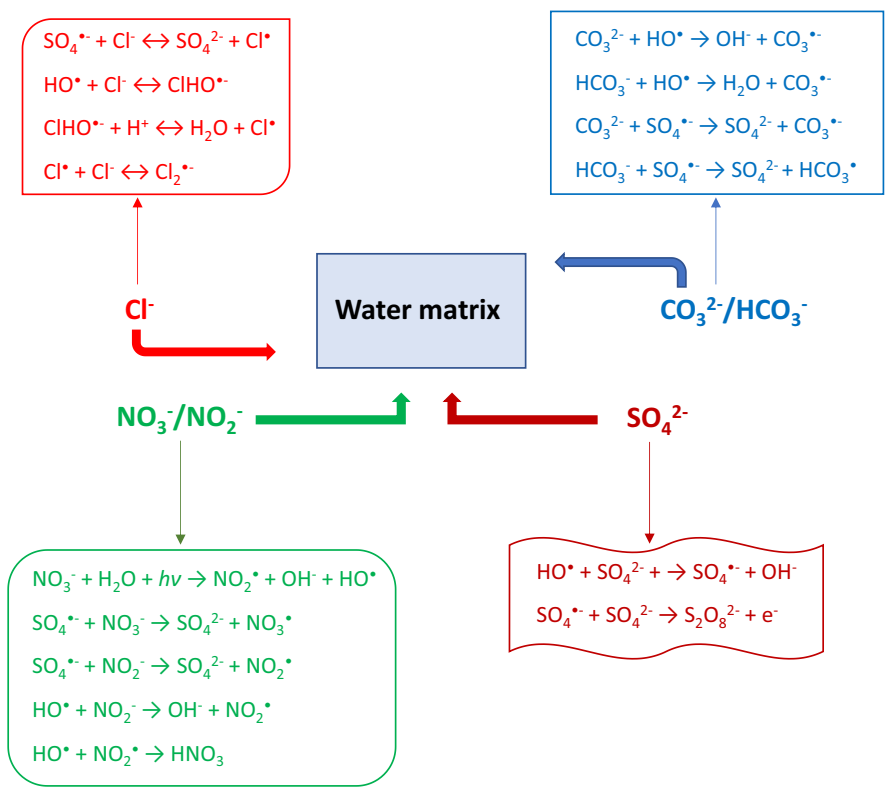


Fig. 2 Generation mechanism of radicals other than $HO^\bullet$ and $SO_4^{\bullet-}$ in presence of different anions (Cl^-, CO_3^{2-}/HCO_3^-, NO_2^-/NO_3^-, and SO_4^{2-}) in the water matrix

$$S_2O_8^{2-} + e^- = 2SO_4^{\cdot-} \quad (7)$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + HO^{\bullet} + H^+ \quad (8)$$

SO_4^{2-} is not a strong scavenger like Cl^- or CO_3^{2-}. Contrarily, it has been demonstrated that SO_4^{2-} can support the oxidative degradation of chloramphenicol to UV-activated $S_2O_8^{2-}$ (Ghauch et al., 2017).

The effect of NO_3^- on the photooxidation of pollutants in water is contradictory (Yang et al., 2019). On the one hand, it can absorb UV light by acting as an inner filter. On the other hand, some authors have reported that NO_3^- can generate $HO^{\bullet}$ in aqueous media, incrementing pollutant degradation. However, NO_2^- exhibits a notorious effect on the photooxidation process, which should be attributed to a group of complex reactions as specified in Fig. 2. However, in our case, the effect of NO_3^-/NO_2^- could be considered negligible due to their low concentrations in WWe.

Finally, both inhibitory and synergistic effects of dissolved organic carbon (DOC) on the degradation of different groups of CECs in water have been demonstrated as a function of the concentration and type of organic compounds involved, mainly humic (HA) and fulvic (FA) acids (Aliste et al., 2021; Tung et al., 2019; Yang et al., 2019). The presence of DOC may reduce PhMCs photodegradation, since the sensitizing (synergistic) effect is masked by quenching (inhibitory), a strong filter effect. DOC could act as an important sunlight absorber, suffering photolysis under UV–Visible light and consequently dissolved compounds can also react quickly with $HO^{\bullet}$ and $SO_4^{\bullet-}$. Aliste et al. (2021) found that a high DOC content considerably decreased the reaction rate constants observed for the photodegradation of some insecticides and their main intermediates in leaching water. However, in our case, the DOC content (3.3 mg L^{-1}) in WWe is very low, and consequently, its effect on the photooxidation of the target compounds should be negligible.

4 Conclusions

Currently, wastewater pollution constitutes a major environmental concern. Therefore, different wastewater treatment methods and techniques have been proposed to curb the problem, of which heterogeneous photocatalysis has proven to be one of the most effective and promising method standing out for its numerous advantages over other techniques. Solar-driven heterogeneous photocatalytic processes using photocatalyst materials such as TiO_2 have been widely applied for pharmaceutical drug degradation and have proven to be efficient, eco-friendly, and cost-effective methodologies to remove emerging micropollutants in wastewater. The present study shows the effect of the tandem TiO_2/$Na_2S_2O_8$ under natural sunlight on the degradation rate of different PhMCs in both WWe and DW. The rate is much faster in deionized water reaching 100% degradation in a few minutes compared to wastewater due to the matrix effect. Degradation experiments of the 6 investigated pharmaceutical compounds, consisting of atenolol, carbamazepine, clarithromycin, erythromycin, irbesartan, and ketoprofen, showed that the time required for 90% disappearance of PhMCs (DT_{90}) in WWe ranged from 10 to 53 min for atenolol and clarithromycin, respectively. Therefore, solar heterogeneous photocatalysis using TiO_2 in tandem with $Na_2S_2O_8$ constitutes a valuable tool for wastewater remediation, particularly in those areas that receive a large number of sunshine hours per year such as the Mediterranean basin.

Acknowledgements The authors are grateful to the Ministry of Science and Innovation of Spain for financial support (Project PID2019-106648RB-I00/AEI/https://doi.org/10.13039/501100011033) in the framework of the State Programs of Generation of Knowledge and Scientific and Technological Strengthening oriented to the Challenges of Society.

Author Contribution Gabriel Pérez-Lucas: methodology, writing—original draft, and revision editing. Abderrazak El Aatik: methodology, data curation, and revision editing. Marina Aliste: visualization, methodology, and data curation. Ginés Navarro: resource, validation, and formal analysis. José Fenoll: supervision, conceptualization, and validation. Simón Navarro: supervision, conceptualization, data curation, funding acquisition, writing—review and editing, and project administration.

Funding Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature. For open access charge: University of Murcia

Data Availability The datasets analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing Interests The authors declare no competing interests.

References

Ahmed, S., Rasul, M. G., Brown, R., & Hashib, M. A. (2011). Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review. *Journal of Environmental Management, 92*, 311–330. https://doi.org/10.1016/j.jenvman.2010.08.08

Aliste, M., Pérez-Lucas, G., Garrido, I., Fenoll, J., & Navarro, S. (2021). Mobility of insecticide residues and main intermediates in a clay-loam soil, and impact of leachate components on their photocatalytic degradation. *Chemosphere, 274*, e129965. https://doi.org/10.1016/j.chemosphere.2021.129965

Almomani, F., Bhosale, R., Kumar, A., & Khraisheh, M. (2018). Potential use of solar photocatalytic oxidation in removing emerging pharmaceuticals from wastewater: A pilot plant study. *Solar Energy, 172*, 128–140. https://doi.org/10.1016/j.solener.2018.07.041

Archer, E., Petrie, B., Kasprzyk-Hordern, B., & Wolfaardt, G. (2017). The fate of pharmaceuticals and personal care products (PPCPs), endocrine disrupting contaminants (EDCs), metabolites and illicit drugs in a WWTW and environmental waters. *Chemosphere, 174*, 437–446. https://doi.org/10.1016/j.chemosphere.2017.01.101

Arnold, K. E., Boxall, A. B., Brown, A. R., Cuthbert, R. J., Gaw, S., Hutchinson, T. H., et al. (2013). Assessing the exposure risk and impacts of pharmaceuticals in the environment on individuals and ecosystems. *Biology Letters, 9*, e20130492. https://doi.org/10.1098/rsbl.2013.0492

Augugliaro, V., Palmisano, G., Palmisano, L., & Soria, J. (2019). Heterogeneous photocatalysis and catalysis: An overview of their distinctive features. In G. Marcì & L. Palmisano (Eds.), *Heterogeneous photocatalysis* (pp. 1–24). Elsevier. https://doi.org/10.1016/B978-0-444-64015-4.00001-8

Awfa, D., Ateia-Ibrahim, M., Fujii, M., & Yoshimura, C. (2018). Photodegradation of pharmaceuticals and personal care products in water treatment using carbonaceous-TiO_2 composites: A critical review of recent literature. *Water Research, 142*, 26–45. https://doi.org/10.1016/j.watres.2018.05.036

Bi, W. L., Wu, Y. L., Wang, X. N., Zhai, P. P., & Dong, W. B. (2016). Degradation of oxytetracycline with $SO_4^{\cdot-}$ under simulated solar light. *Chemical Engineering Journal, 302*, 811–818. https://doi.org/10.1016/j.cej.2016.05.075

Bianchi, C. L., Sacchi, B., Pirola, C., Demartin, F., Cerrato, G., Morandi, S., & Capucci, V. (2017). Aspirin and paracetamol removal using a commercial micro-sized TiO_2 catalyst in deionized and tap water. *Environmental Science and Pollution Research, 24*, 12646–12654. https://doi.org/10.1007/s11356-016-7781-z

Boxall, A. B. A. (2012). New and emerging water pollutants arising from agriculture. Directorate for Trade and Agriculture. Organisation for Economic Co-Operation and Development. COM/TAD/CA/ENV/EPOC(2010)17/FINAL. Paris, France. Retrieved June 15, 2022. https://www.oecd.org/greengrowth/sustainable-agriculture/49848768.pdf

Bu, Q., Shi, X., Yu, G., Huang, J., & Wang, B. (2016). Assessing the persistence of pharmaceuticals in the aquatic environment: Challenges and needs. *Emerging Contaminants, 2*, 145–147. https://doi.org/10.1016/j.emcon.2016.05.003

Campo, R., Lubello, C., Lotti, T., & Di Bella, G. (2021). Aerobic granular sludge-membrane bioreactor (AGS-MBR) as a novel configuration for wastewater treatment and fouling mitigation: A mini-review. *Membranes, 11*, 261. https://doi.org/10.3390/membranes11040261

Carbajo, J., Jiménez, M., Miralles, S., Malato, S., Faraldos, M., & Bahamonde, A. (2016). Study of application of titania catalysts on solar photocatalysis: Influence of type of pollutants and water matrices. *Chemical Engineering Journal, 291*, 64–73. https://doi.org/10.1016/j.cej.2016.01.092

Chen, W., Mo, J., Du, X., Zhang, Z., & Zhang, W. (2019). Biomimetic dynamic membrane for aquatic dye removal. *Water Research, 151*, 243–251. https://doi.org/10.1016/j.watres.2018.11.078

Choi, Y. Y., Baek, S. R., Kim, J. L., Choi, J. W., Hur, J., Lee, T. U., et al. (2017). Characteristics and biodegradability of wastewater organic matter in municipal wastewater treatment plants collecting domestic wastewater and industrial discharge. *Water, 9*, e409. https://doi.org/10.3390/w9060409

Deblonde, T., Cossu-Leguille, C., & Hartemann, P. (2011). Emerging pollutants in wastewater: A review of the literature. *International Journal of Hygiene and Environmental Health, 214*, 442–448. https://doi.org/10.1016/j.ijheh.2011.08.002

Dimitrakopoulou, D., Rethemiotaki, I., Frontistis, Z., Xekoukoulotakis, N. P., Venieri, D., & Mantzavinos, D. (2012). Degradation, mineralization and antibiotic inactivation of amoxicillin by UV-A/TiO_2 photocatalysis. *Journal of Environmental Management, 98*, 168–174. https://doi.org/10.1016/j.jenvman.2012.01.010

EC. (2000). Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Official Journal of the European Union,* L327, 1–69. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32000L0060&from=en. Accessed 3 March 2022.

EC. (2019). Communication from the Commission to the European Parliament, the Council and the European Economic and Social Committee. European Union Strategic Approach to Pharmaceuticals in the Environment. Brussels, COM (2019) 128 final. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52019DC0128&from=EN. Accessed 3 March 2022.

EC. (2020). Regulation 2020/741/EU of the European Parliament and of the Council of 25 May 2020 on minimum

requirements for water reuse. *Official Journal of the European Union,* L177, 32–55. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32020R0741&from=EN

ECHA. (2022). Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). *European Chemicals Agency*. retrieved April 2, 2022. https://echa.europa.eu/es/regulations/reach/understanding-reach

Eskandarian, M. R., Choi, H., Fazli, M., & Rasoulifard, M. H. (2016). Effect of UV-LED wavelengths on direct photolytic and TiO_2 photocatalytic degradation of emerging contaminants in water. *Chemical Engineering Journal, 300*, 414–422. https://doi.org/10.1016/j.cej.2016.05.049

Fenoll, J., Garrido, I., Hellín, P., Vela, N., Flores, P., & Navarro, S. (2016). Photooxidation of three spirocyclic acid derivative insecticides in aqueous suspensions as catalyzed by titanium and zinc oxides. *Journal of Photochemistry and Photobiology a: Chemistry, 328*, 189–197. https://doi.org/10.1016/j.jphotochem.2016.06.003

Garrido, I., Pastor-Belda, M., Campillo, N., Viñas, P., Yáñez, M. J., Vela, N., Navarro, S., & Fenoll, J. (2019). Photooxidation of insecticide residues by ZnO and TiO2 coated magnetic nanoparticles under natural sunlight. *Journal of Photochemistry and Photobiology a: Chemistry, 372*, 245–253. https://doi.org/10.1016/j.jphotochem.2018.12.027

Ghauch, A., Baalbaki, A., Amasha, M., El Asmar, R., & Tantawi, O. (2017). Contribution of persulfate in UV-254 nm activated systems for complete degradation of chloramphenicol antibiotic in water. *Chemical Engineering Journal, 317*, 1012–1025. https://doi.org/10.1016/j.cej.2017.02.133

Georgaki, I., Vasilaki, E., & Katsarakis, N. A. (2014). Study on the degradation of carbamazepine and ibuprofen by TiO_2 & ZnO photocatalysis upon UV/Visible-light irradiation. *American Journal of Analytical Chemistry, 5*, 518–534. https://doi.org/10.4236/ajac.2014.58060

Gogoi, A., Mazumder, P., Tyagi, V. K., Tushara Chaminda, G. G., An, A. K., & Kumar, M. (2018). Occurrence and fate of emerging contaminants in water environment: A review. *Groundwater for Sustainable Development, 6*, 169–180. https://doi.org/10.1016/j.gsd.2017.12.009

He, Y., Sutton, N., Rijnaarts, H., & Langenhoff, A. (2016). Degradation of pharmaceuticals in wastewater using immobilized TiO_2 photocatalysis under simulated solar irradiation. *Applied Catalysis b: Environmental, 182*, 132–141. https://doi.org/10.1016/j.apcatb.2015.09.015

Helwig, K., Hunter, C., MacLachlan, J., McNaughtan, M., Roberts, J., Cornelissen, A., & Pahl, O. (2013). Micropollutant point sources in the built environment: Identification and monitoring of priority pharmaceutical substances in hospital effluents. *Journal of Environmental Analytical Toxicology, 3*, 1–10. https://doi.org/10.4172/2161-0525.1000177

Ismail, L., Ferronato, C., Fine, L., Jaber, F., & Chovelon, J. M. (2017). Elimination of sulfaclozine from water with $SO_4^{\bullet-}$ radicals: Evaluation of different persulfate activation methods. *Applied Catalysis B: Environmental, 201*, 573–581. https://doi.org/10.1016/j.apcatb.2016.08.046

Kanakaraju, D., Glass, B., & Oelgemöller, M. (2014). Titanium dioxide photocatalysis for pharmaceutical wastewater treatment. *Environmental Chemistry Letters, 12*, 27–47. https://doi.org/10.1007/s10311-013-0428-0

Kanakaraju, D., Motti, C. A., Glass, B. D., & Oelgemöller, M. (2018). Advanced oxidation process- mediated removal of pharmaceuticals from water: A review. *Journal of Environmental Management, 219*, 189–207. https://doi.org/10.1016/j.jenvman.2018.04.103

Kosmulski, M. (2018). The pH dependent surface charging and points of zero charge. VII. Update. *Advances in Colloid and Interface Science, 251*, 115–138. https://doi.org/10.1016/j.cis.2017.10.005

Kummerer, K. (2010). Pharmaceuticals in the environment. *Annual Review of Environment and Resources, 35*, 57–75. https://doi.org/10.1146/annurev-environ-052809-161223

Lee, B. C. Y., Lim, F. Y., Loh, W. H., Ong, S. L., & Hu, J. (2021). Emerging contaminants: An overview of recent trends for their treatment and management using light-driven processes. *Water, 13*(17), 2340. https://doi.org/10.3390/w13172340

Liang, C. J., & Su, H. W. (2009). Identification of sulfate and hydroxyl radicals in thermally activated persulfate. *Industrial and Engineering Chemistry Research, 48*, 472–475. https://doi.org/10.1021/ie9002848

Lin, A. Y., Lin, C. F., Tsai, Y. T., Lin, H. H., Chen, J., Wang, X. H., & Yu, T. H. (2010). Fate of selected pharmaceuticals and personal care products after secondary wastewater treatment processes in Taiwan. *Water Science Technology, 62*, 2450–2458. https://doi.org/10.2166/wst.2010.476

Liu, B., Zhao, X., Terashima, C., Fujishima, A., & Nakata, K. (2014). Thermodynamic and kinetic analysis of hetero geneous photocatalysis for semiconductor systems. *Physical Chemistry Chemical Physics, 16*, 8751–8760. https://doi.org/10.1039/C3CP55317E

Luo, Y., Han, Y., Xue, M., Xie, Y., Yin, Z., Xie, C., Li, X., Zheng, Y., Huang, J., Zhang, Y., Yang, Y., & Gao, B. (2022). Ball-milled bismuth oxybromide/biochar composites with enhanced removal of reactive red owing to the synergy between adsorption and photodegradation. *Journal of Environmental Management, 308*, e114652. https://doi.org/10.1016/j.jenvman.114652

Luo, Y., Wang, Y., Hua, F., Xue, M., Xie, X., Xie, Y., Yu, S., Zhang, L., Yin, Z., Xie, C., & Hong, Z. (2023). Adsorption and photodegradation of reactive red 120 with nickel-iron-layered double hydroxide/biochar composites. *Journal of Hazardous Materials, 443*, 130300. https://doi.org/10.1016/j.jhazmat.2022.130300

Malato, S., Fernández-Ibáñez, P., Maldonado, M. I., Blanco, J., & Gernjak, W. (2009). Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today, 147*, 1–59. https://doi.org/10.1016/j.cattod.2009.06.018

Manaham, S. E. (2010). *Environmental chemistry* (9th ed.). CRC Press.

Michael, I., Frontistis, Z., & Fatta-Kassinos, D. (2013). Removal of pharmaceuticals from environmentally relevant matrices by advanced oxidation processes (AOPs). *Comprehensive Analytical Chemistry, 62*, 345–407. https://doi.org/10.1016/B978-0-444-62657-8.00011-2

Miklos, D. B., Remy, C., Jekel, M., Linden, K. G., Drewes, J. E., & Hübner, U. (2018). Evaluation of advanced oxidation processes for water and wastewater treatment - A critical review. *Water Research, 139*, 118–131. https://doi.org/10.1016/j.watres.2018.03.042

Náfrádi, M., Alapi, T., Bencsik, G., & Janáky, C. (2022). Impact of reaction parameters and water matrices on the

removal of organic pollutants by TiO_2/LED and ZnO/LED heterogeneous photocatalysis using 365 and 398 nm radiation. *Nanomaterials, 12*, e5. https://doi.org/10.3390/nano12010005

National Institutes of Health (NIH). (2022). PubChem, an open chemistry database at the National Institutes of Health (NIH). Bethesda, MD. Retrieved February 10, 2022. https://pubchem.ncbi.nlm.nih.gov

Noguera-Oviedo, K., & Aga, D. (2016). Lessons learned from more than two decades of research on emerging contaminants in the environment. *Journal of Hazardous Materials, 316*, 242–251. https://doi.org/10.1016/j.jhazmat.2016.04.058

NORMAN. (2022). Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances. Retrieved January 13, 2022. http://www.norman-network.net

Oh, W. D., Dong, Z., & Lim, T. T. (2016). Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: Current development, challenges and prospects. *Applied Catalysis b: Environmental., 194*, 169–201. https://doi.org/10.1016/j.apcatb.2016.04.003

Pal, A., Gin, K., Lin, A., & Reinhard, M. (2010). Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects. *Science of the Total Environment, 408*, 6062–6069. https://doi.org/10.1016/j.scitotenv.2010.09.026

Parida, V. K., Saidulu, D., Majumder, A., Srivastava, A., Gupta, B., & Gupta, A. K. (2021). Emerging contaminants in wastewater: A critical review on occurrence, existing legislations, risk assessment, and sustainable treatment alternatives. *Journal of Environmental Chemical Engineering, 9*, e105966. https://doi.org/10.1016/j.jece.2021.105966

Pérez-Lucas, G., El Aatik, A., Aliste, M., Hernández, V., Fenoll, J., & Navarro, S. (2022). Reclamation of aqueous waste solutions polluted with pharmaceutical and pesticide residues by biological-photocatalytic (solar) coupling in situ for agricultural reuse. *Chemical Engineering Journal, 448*, e137616. https://doi.org/10.1016/j.cej.2022.137616

Pérez-Lucas, G., Aliste, M., Garrido, I., Fenoll, J., & Navarro, S. (2022). Solar reclamation of groundwater and agro-wastewater polluted with pesticide residues using binary semiconductors and persulfates for their reuse in crop irrigation. In M. H. Dehghani, R. R. Karri, & I. Anastopoulos (Eds.), *Pesticides remediation technologies from water and wastewater* (pp. 267–293). Elsevier. https://doi.org/10.1016/B978-0-323-90893-1.00013-1

Pronk, W., Ding, A., Morgenroth, E., Derlon, N., Desmond, P., Burkhardt, M., Wu, B., & Fane, A. G. (2019). Gravity-driven membrane filtration for water and wastewater treatment: A review. *Water Research, 149*, 553–565. https://doi.org/10.1016/j.watres.2018.11.062

Ribeiro, A. R. L., Moreira, N. F. F., Li Puma, G., & Silva, A. M. T. (2019). Impact of water matrix on the removal of micropollutants by advanced oxidation technologies. *Chemical Engineering Journal, 363*, 155–173. https://doi.org/10.1016/j.cej.2019.01.080

Rivera-Utrilla, J., Sánchez-Polo, M., Ferro-García, M., Prados-Joya, G., & Ocampo, R. (2013). Pharmaceuticals as emerging contaminants and their removal from water. *A Review. Chemosphere, 93*, 1268–1287. https://doi.org/10.1016/j.chemosphere.2013.07.059

Snow, D. D., Cassada, D. A., Biswas, S., Malakar, A., D'Alessio, M., Marshall, A. H. L., & Sallachm, J. B. (2020). Detection, occurrence, and fate of emerging contaminants in agricultural environments. *Water Environmental Research, 92*, 1741–1750. https://doi.org/10.1002/wer.1429

Tang, Y., Yin, M., Yang, W., Li, H., Zhong, Y., Mo, L., et al. (2019). Emerging pollutants in water environment: Occurrence, monitoring, fate, and risk assessment. *Water Environmental Research, 91*, 984–991. https://doi.org/10.1002/wer.1163

Teixeira, S., Gurke, R., Eckert, H., Kühn, K., Fauler, J., & Cuniberti, G. (2015). Photocatalytic degradation of pharmaceuticals presents in conventional treated wastewater by nanoparticle suspensions. *Journal of Environmental Chemical Engineering, 4*, 287–292. https://doi.org/10.1016/j.jece.2015.10.045

Tung, T. H., Xu, D., Zhang, Y., Zhou, Q., & Wu, Z. (2019). Removing humic acid from aqueous solution using titanium dioxide: A review. *Polish Journal of Environmental Studies, 28*, 529–542. https://doi.org/10.15244/pjoes/85196

Vasilachi, I. C., Asiminicesei, D. M., Fertu, D. I., & Gavrilescu, M. (2021). Occurrence and fate of emerging pollutants in water environment and options for their removal. *Water, 13*, e181. https://doi.org/10.3390/w13020181

Vogler, S. & Zimmermann, N. (2016). Glossary of pharmaceutical terms. WHO Collaborating Centre for Pharmaceutical Pricing and Reimbursement Policies. Retrieved June 13, 2022. https://ppri.goeg.at/sites/ppri.goeg.at/files/inline-files/Glossary_Update2016_final.pdf

Wilkinson, J., Hooda, P. S., Barker, J., Barton, S., & Swinden, J. (2017). Occurrence, fate and transformation of emerging contaminants in water: An overarching review of the field. *Environmental Pollution, 231*, 954–970. https://doi.org/10.1016/j.envpol.2017.08.032

Yang, Q., Ma, Y., Chen, F., Yao, F., Sun, J., Wang, S., et al. (2019). Recent advances in photo-activated sulfate radical-advanced oxidation process (SR-AOP) for refractory organic pollutants removal in water. *Chemical Engineering Journal, 378*, e122149. https://doi.org/10.1016/j.cej.2019.122149

Yu, J. T., Bouwer, E. J., & Coelhan, M. (2006). Occurrence and biodegradability studies of selected pharmaceuticals and personal care products in sewage effluent. *Agricultural Water Management, 86*, 72–80. https://doi.org/10.1016/J.AGWAT.2006.06.015