


Pilot-scale study of UVC-based AOPs towards implementation at the outlet of domestic WWTPs

Anaëlle Gabet^{a,b}, Thomas Monot^a, Gilles Mailhot^b, Marcello Brigante^b, Christine de Brauer^a and H  l  ne M  tivier ^{a,*}

^a Univ Lyon, INSA Lyon, DEEP, EA7429, Villeurbanne 69621, France

^b Universit   Clermont Auvergne, CNRS, Clermont Auvergne INP, Institut de Chimie de Clermont-Ferrand, Clermont-Ferrand F-63000, France

*Corresponding author. E-mail: helene.metivier@insa-lyon.fr

 HM, 0000-0002-4664-8975

ABSTRACT

The degradation of a mixture of ibuprofen, naproxen, and diclofenac in various effluents by UVC/H₂O₂ or UVC/S₂O₈²⁻ was studied to assess the impact of the matrix composition and of the oxidant precursor on process efficiency. Experiments were carried out in a 20-L laboratory pilot (a scaled-down version of a full-scale pilot). In effluents collected during dry weather, the rural constructed wetland effluent allowed faster degradation than the urban conventional WWTP effluent, regardless of the nature of the targets or of the oxidant precursor. This was mainly attributed to a three-times higher chemical oxygen demand in the urban effluent, likely to quench the oxidative species. UV fluences to reach 90% degradation of the three compounds were 3,800 and 5,500 mJ cm⁻² in the rural effluent, whereas they were 6,600 and 6,100 mJ cm⁻² in the urban effluent with H₂O₂ and S₂O₈²⁻, respectively. After a rainfall event, the rural effluent composition was not significantly affected compared to that of the urban effluent that underwent the dilution effect. Therefore, the stability of the rural effluent composition allowed comparable degradation efficiency, whereas the dilution effect led to a significant increase in the degradation rate constants in the urban effluent (up to four times higher).

Key words: AOPs, hydroxyl radical, micropollutants, pilot-scale, sulphate radical, UV fluence

HIGHLIGHTS

- UVC-based process efficiency varies with weather and effluent composition.
- Downstream effluent composition seems more consistent in a rural constructed wetland than in an urban WWTP.
- UVC-based AOPs are more appropriate to treat effluents with low and consistent organic matter concentration.
- S₂O₈²⁻ allows for faster degradation of NAP and H₂O₂ for faster degradation of IBU.

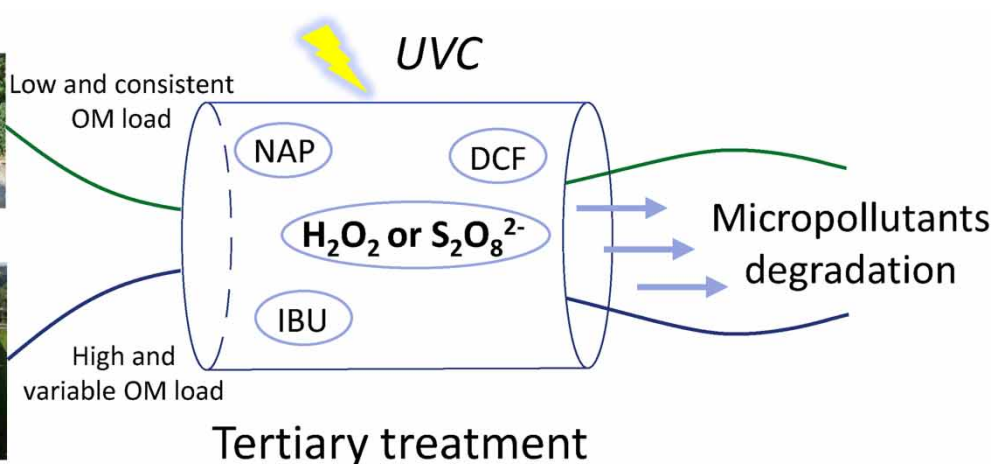
This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY-NC-ND 4.0), which permits copying and redistribution for non-commercial purposes with no derivatives, provided the original work is properly cited (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

GRAPHICAL ABSTRACT

Rural WWTP



Urban WWTP



ABBREVIATIONS

AOP	advanced oxidation process
COD	chemical oxygen demand
DCF	diclofenac
IBU	ibuprofen
NAP	naproxen
SHE	standard hydrogen electrode
UHPLC	ultra high-performance liquid chromatography
WWTP	wastewater treatment plant

1. INTRODUCTION

Pharmaceuticals and their metabolites are ubiquitous in surface and groundwater around the world (Luo *et al.* 2014). Although their concentrations are mostly under $\mu\text{g/L}$, adverse effects on aquatic plants and wildlife have been reported, such as alterations in the reproduction or in the development of organisms and changes in behaviour (Patel *et al.* 2019). The ecotoxicity of pharmaceuticals is generally assessed for isolated substances, for which environmental concentrations are mostly under no observed effect concentrations (Zhou *et al.* 2019). However, a high number of substances are present in water resources and many studies have shown that the toxicity of pharmaceutical cocktails is very complex, including additive and synergistic effects (Vasquez *et al.* 2014). While there is still a need to develop knowledge about mixture effects, ways to prevent the spread of pharmaceuticals into aquatic ecosystems must also be explored.

Wastewater treatment plants (WWTPs) are one of the major sources of pharmaceuticals in the environment because they are not designed to treat micropollutants. Although the average removal rate of micropollutants is between 50 and 60%, it varies widely depending on the nature and the concentration of the molecule, the type of treatment and on the environmental conditions (weather, season), especially in nature-based technologies (Li *et al.* 2014). Various removal efficiencies are depicted in the literature for diclofenac (0–70%), ibuprofen (60–96%) and naproxen (>70%) (Coquery *et al.* 2010; Dagot 2018). The French project AMPERES concluded that 90% of incoming pharmaceuticals were found at the outlet of 21 WWTPs at concentrations above $100 \text{ ng}\cdot\text{L}^{-1}$ (Coquery *et al.* 2010). As a result, rivers downstream from WWTPs face higher contamination levels than other surface waters (Comber *et al.* 2018). It is therefore necessary to increase WWTP performance.

As the goal of our research programme is to provide solutions to improve the quality of the effluents in small- and medium-sized WWTPs (hereafter referred to as rural WWTPs) that require low maintenance and cheap treatments, UVC-based advanced oxidation processes (AOPs) are chosen. AOPs are based on the generation of highly oxidative species. They are promising techniques due to their effectiveness against refractory micropollutants and pathogens, their low cost and low

maintenance requirements and the easy integration at the outlet of existing WWTPs (Starling *et al.* 2019). Processes that do not require pH adjustments such as UVC/H₂O₂ and UVC/S₂O₈²⁻ are particularly attractive. UV photolysis of H₂O₂ and S₂O₈²⁻ leads to the generation of oxidizing radicals: HO• and SO₄^{•-}, respectively ($E_{\text{HO}^\bullet/\text{HO}^-}^0 = 2.80 \text{ V/SHE}$ and $E_{\text{SO}_4^{\bullet-}/\text{SO}_4^{2-}}^0 = 2.60 \text{ V/SHE}$ at neutral pH). As the radicals are not selective, degradation rates of micropollutants can be affected by the presence of organic matter or inorganic ions in wastewaters.

The present study investigates the degradation of model micropollutants by UVC photolysis, UVC/H₂O₂ and UVC/S₂O₈²⁻ on a laboratory pilot which represents a scaled-down and simplified version of a test pilot installed at the outlet of a rural constructed wetland WWTP. The main goals are to assess the impact of photolysis, to compare both oxidant precursors, to study the influence of various WWTP effluents on process efficiency and to gain knowledge towards real scale implementation in WWTP, especially the fluence required.

Three pharmaceuticals are chosen as model micropollutants: ibuprofen (IBU), naproxen (NAP), and diclofenac (DCF). According to Garcia-Rodríguez *et al.* (2014), IBU is biodegradable, DCF is photolabile and NAP is both. Nonetheless, they are among the most detected pharmaceuticals in domestic wastewaters and have been widely detected in surface waters at concentrations higher than tens of ng L⁻¹ (Patrolecco *et al.* 2015; Lindholm-Lehto *et al.* 2016; Madikizela & Chimuka 2017). Their degradation by UVC-based AOPs has already been investigated in the literature at concentrations from 0.1 to 10 µM (Kwon *et al.* 2015; Gao *et al.* 2017; Fu *et al.* 2019) at a laboratory scale on small volumes (around 50 mL) and degradation pathways were suggested (Fu *et al.* 2019). However, to the best of our knowledge, no comparative study of UVC/H₂O₂ and UVC/S₂O₈²⁻ was carried out on a mixture of these three pharmaceuticals at a pilot scale on real effluents.

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

Ibuprofen sodium salt (98.5%), diclofenac sodium salt (98.5%) and naproxen (98.5%) were purchased from Sigma–Aldrich, as well as sodium persulphate (Na₂S₂O₈) (>98%). Acetonitrile and methanol were supplied by VWR Chemicals (HPLC grade). Ultrapure water was obtained from a milli-Q® system. Formic acid was purchased from Chimie-plus Laboratories. Hydrogen peroxide (H₂O₂) (30% in water) was supplied by ITW reagents.

Persulphate solutions (1 M) as well as IBU and DCF stock solutions (10 mM) were prepared in milli-Q® water. NAP stock solution (5 mM) was prepared in acetonitrile.

2.2. Irradiation experiments

2.2.1. UV pilot unit

Experimental apparatus is shown in Figure 1. The system is composed of a cylindrical UVC reactor (COMAP WT, 1.12 L, 81.5 cm) connected to a 50-L thermoregulated and mechanically stirred glass tank. The flow rate is measured by a flow meter and monitored. The reactor contains a 54 W (operating power = 17.5 W) monochromatic ($\lambda = 254 \text{ nm}$) low-pressure lamp (Philips) placed in a quartz sleeve. The effluent runs through a 1-cm layer around the sleeve. Its recirculation allows to increase the contact time with the UV lamp and therefore to increase the UV fluence.

The UV fluence was calculated with the UVCalc®2A software which considers the geometry of the reactor, the effluent transmittance and the lamp characteristics (Bolton Photosciences Inc., Canada).

2.2.2. Aqueous matrices composition

Local drinking water was used as a simple matrix to perform first irradiation experiments. It was collected directly from the tap (city of Villeurbanne, France). Then, experiments were performed on spiked WWTP effluents collected in two WWTPs based on different processes with different treatment capacities. The effluents referred to as ‘urban wastewaters’ were collected in the morning at the outlet of a large-scale conventional WWTP (activated sludge process) (300,000 population equivalent, Villeurbanne, France). The effluents referred as ‘rural wastewaters’ were collected at the outlet of a small-scale WWTP equipped by a vertical flow constructed wetland preceded by a trickling filter (1,100 population equivalent, Vercia, France). Samples were collected during dry and wet weathers in 30-L plastic containers and used within 24 h after collection. The rural wet weather effluent was collected after 28 mm of rainfall over 24 h, whereas the urban one was collected after 24 h of severe rain leading to 106 mm of rainfall. The main physico-chemical parameters of the matrices are depicted in Table 1.

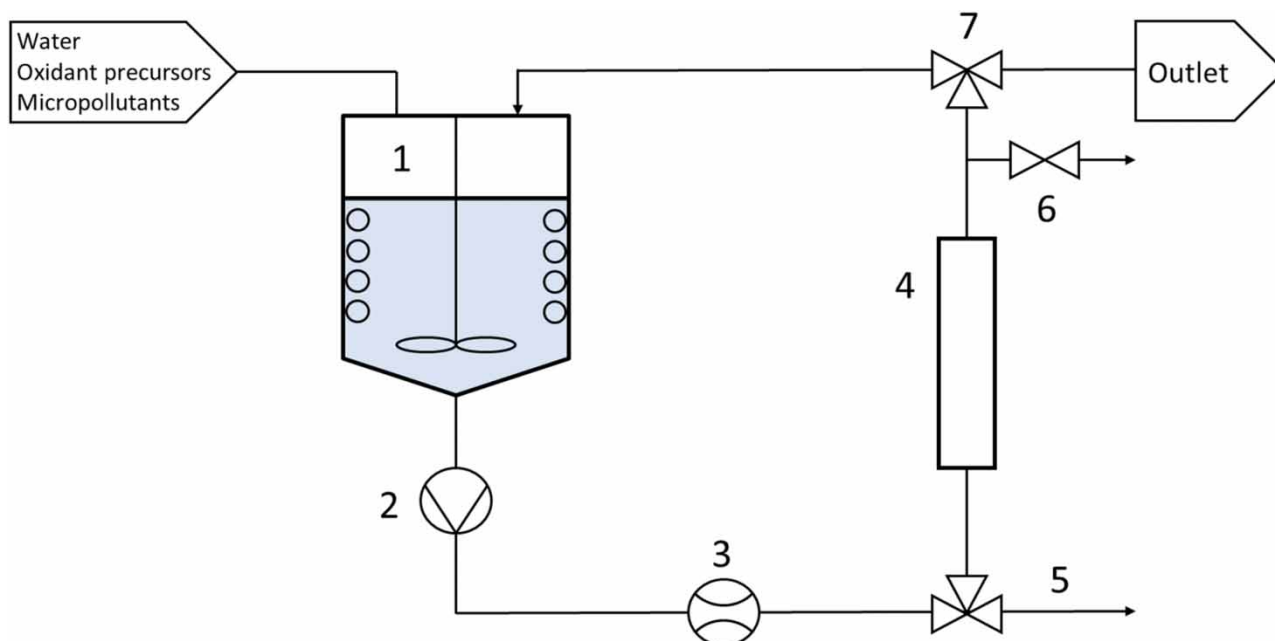


Figure 1 | The apparatus used during experiments. (1) Thermoregulated and mechanically stirred glass tank; (2) pump; (3) flow meter; (4) UVC reactor and UV intensity measurement; (5) and (6) sampling points; and (7) recirculation valve.

Table 1 | Main physico-chemical parameters of the local drinking water and the WWTP effluents used in the study

	Local drinking water	Urban - dry weather	Urban - wet weather	Rural - dry weather	Rural - wet weather
pH	7.7	7.9	7.4	7.1	7.2
UV _{254nm} transmittance	98%	55%	64%	65%	60%
Conductivity ($\mu\text{S cm}^{-1}$)	395	964	250	994	911
COD ($\text{mgO}_2 \text{ L}^{-1}$)	<5	46.4	31.8	14.5	14.6
HCO ₃ ⁻ (mg L^{-1})	220	231	63	203	189
Cl ⁻ (mg L^{-1})	10	66	50	183	151
NO ₃ ⁻ (mg L^{-1})	5.1	22.6	7.1	19.0	25.2
NO ₂ ⁻ (mg L^{-1})	-	1.33	0.30	0.06	0.07

2.2.3. Experimental procedure

The total volume introduced into the system was $20.0 \pm 0.5 \text{ L}$ and the recirculation flow was fixed at $20.0 \pm 0.5 \text{ L min}^{-1}$. In these conditions, the hydraulic retention time in the reactor per cycle was 3.5 s. Experiments were carried out at $22 \pm 2^\circ\text{C}$. The UVC lamp was preheated for 10 min and turned off during solution preparation.

Matrices were first spiked with IBU, NAP, and DCF at $5 \mu\text{M}$ each. This concentration is higher than environmental concentrations, but it was chosen because it does not require pre-concentration before ultra high-performance liquid chromatography (UHPLC) analysis. Then, an appropriate volume of oxidant precursor was added to reach 0.5 mM and the light was turned on at the start of the experiment. Oxidant precursor concentration was set according to preliminary experiments (Cédât *et al.* 2016).

Five millilitres of the solutions were withdrawn at fixed time intervals for UHPLC quantification of the pharmaceuticals. Volume variations in the system were under 0.1% during irradiation experiments.

A Shimadzu 2450 UV-visible spectrophotometer was used to measure the aqueous matrix transmittances at 254 nm, the UV-visible spectra of pharmaceuticals and oxidant precursors (Supplementary material, Figures S1 and S2, respectively).

2.2.4. Determination of the photolysis constants of H₂O₂ and S₂O₈²⁻

Experiments were performed in the experimental apparatus in the same conditions as described above. The only changes are related to the concentrations of H₂O₂ or S₂O₈²⁻ which became 5 mM and with the addition of 0.5% of MeOH (100 mL) before the experiment in order to quench HO[•] and SO₄^{•-} and avoid their reactions with the oxidant precursors. Five millilitres of solutions were withdrawn at fixed time intervals for the quantification of H₂O₂ and S₂O₈²⁻ by UV-visible spectrophotometry (Shimadzu, 2450) at 240 and 215 nm, respectively.

2.3. Micropollutants analysis

Samples were filtered through 0.45 µm PVDF filters (Millex HV) before analysis. IBU, NAP and DCF analyses were performed in duplicate using an UHPLC ultimate 3000+ (Thermo Fischer) system equipped with a X-Bridge BEH column (75 × 4.6 mm × 2.5 µm) and coupled to a diode array detector (detection wavelengths: λ_{IBU} = λ_{NAP} = 226 nm, λ_{DCF} = 281 nm).

The mobile phase was a mixture of acetonitrile and milli-Q water (60/40) both acidified with 0.1% formic acid and the flow rate was 1.5 mL min⁻¹. The column temperature was fixed at 40 °C and the injection volume was 40 µL. Limits of detection were 0.12, 0.10 and 0.09 µM for IBU, NAP and DCF, respectively, and limits of quantification were calculated as 3.3 × LOD.

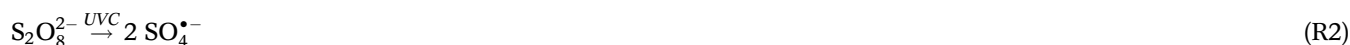
2.4. Data processing

In this study, UV fluence (mJ cm⁻²) was used as a reference unit for degradation rate constants. According to Bolton & Stefan (2002), UV fluence is defined as the total radiant power incident from all directions onto an infinitesimally small sphere of cross-sectional area *dA*, divided by *dA*. It depends on the configuration of the system and on the absorbance of the matrix which causes a decrease in the number of photons available for photolysing the targets.

Under UVC photolysis, IBU, NAP and DCF degradation kinetics followed first order rates. They were fitted by the following equation: $\ln C/C_0 = -k'_p F$, where *C*₀ and *C* are, respectively, the initial concentration and the concentration at UV fluence *F* of the compound of interest and *k*'_{*p*} is its first order degradation rate constant (cm² mJ⁻¹).

k'_{*p*} depends on two main physical properties of the compound of interest: the molar absorption coefficient (ε, L mol⁻¹ cm⁻¹) and the photolysis quantum yield (Φ) at the studied wavelength. ε determines the ability of the compound to absorb photons and therefore quantifies the photons available for photolysis. Φ is the number of photolysed molecules divided by the number of absorbed photons (Hokanson *et al.* 2016).

H₂O₂ and S₂O₈²⁻ photolysis generate hydroxyl and sulphate radicals by homolytic cleavage, respectively (reactions R1 and R2). Both radicals are very reactive species able to degrade the targets:



Therefore, in the presence of H₂O₂ or S₂O₈²⁻, the pollutant degradation kinetics include both their photolysis and their oxidation by HO[•] or SO₄^{•-}. According to Sharpless & Linden (2003), these degradation kinetics are governed by the following pseudo-first order equation: $\ln C/C_0 = -(k'_p + k'_{ox})F = -k'F$, where *C*₀ and *C* are, respectively, the initial concentration and the concentration at UV fluence *F* of the compound of interest, *k*'_{*p*} is its photolysis first order rate constant and *k*'_{*ox*} is the pseudo-first order rate constant for radical-based oxidation. This constant depends on the steady-state concentration of the radical and on the second order reaction rate between the radical and the compound of interest (Shu *et al.* 2016). *k*' is the overall pseudo-first order rate constant.

The error bars associated with the degradation constants equal to 3σ, derived from the scattering of the experimental data around the fit curves (intra-series variability).

3. RESULTS AND DISCUSSION

3.1. IBU, NAP, and DCF degradation in drinking water

3.1.1. UVC photolysis

IBU, NAP, and DCF photolysis follow first order rate under UV_{254nm} radiation. Table 2 depicts their photolysis rate constants (*k*'_{*p*}) in drinking water (5 µM each). *k*'_{*p*} DCF is around 17 times higher than *k*'_{*p*} NAP and 50 times higher than *k*'_{*p*} IBU. This is

Table 2 | First-order degradation rate constants in drinking water, quantum yields, and molar absorption coefficients at 254 nm

	IBU	NAP	DCF
k'_p (cm ² mJ ⁻¹)	$(1.15 \pm 0.15) \times 10^{-4}$	$(3.34 \pm 0.09) \times 10^{-4}$	$(5.65 \pm 0.31) \times 10^{-3}$
$\Phi_{254\text{nm}}$ (mol Einstein ⁻¹)	0.086–0.192 ^a	0.036 ^b	0.094 ^b
$\epsilon_{254\text{nm}}$ (L mol ⁻¹ cm ⁻¹)	320	4,400	5,520

$\epsilon_{254\text{nm}}$ was determined in this work. ^aLuo *et al.* (2018); ^bPacker *et al.* (2003).

attributed to the photosensitivity of the compounds which is mainly based on their molar absorption coefficient (ϵ) and their quantum yield (Φ). As seen in Table 2, ϵ_{NAP} and ϵ_{DCF} are of the same order of magnitude and are much higher than ϵ_{IBU} . As a consequence, their photolysis is faster than that of IBU. However, Φ_{NAP} is around three times lower than Φ_{DCF} which could explain the slower degradation of NAP compared to DCF.

In order to reach more than 90% degradation, DCF and NAP require around 400 and 8,000 mJ cm⁻², respectively. However, IBU is only degraded by 64% at 9,600 mJ cm⁻². Based on these results, the use of UVC radiation seems appropriate for the degradation of DCF which is photosensitive. On the other hand, it would be irrelevant and energy inefficient for the removal of NAP and IBU. In the literature, Kim *et al.* (2009) had drawn similar conclusions and reported that UVC radiation only allowed complete removal of DCF traces in secondary WWTP effluent under 923 mJ cm⁻², whereas NAP required 2,768 mJ cm⁻² to reach 90% degradation. Zupanc *et al.* (2013) have also shown that it is not appropriate for the degradation of IBU.

3.1.2. Influence of oxidant precursors

In the presence of H₂O₂ or S₂O₈²⁻, IBU, NAP and DCF degradation kinetics follow pseudo-first order rates. Figure 2 represents their degradation rate constants without oxidant precursor and with H₂O₂ or S₂O₈²⁻ (0.5 mM) in drinking water. All experiments were carried out in duplicate with acceptable relative standard deviations (between 2 and 17%). The generation of HO[•] or SO₄^{•-} in the presence of H₂O₂ or S₂O₈²⁻, respectively, enhances the degradation rate of the compounds of interest compared to UVC photolysis only. Indeed, as seen in Section 2.4, $k' = k'_p + k'_{ox}$. The results also show that S₂O₈²⁻ is more efficient than H₂O₂, which is attributed to its photolysis constant in the pilot ($k'_{\text{S}_2\text{O}_8^{2-}} = 5.21 \times 10^{-4}$ cm² mJ⁻¹) almost 3.4 times higher than that of H₂O₂ ($k'_{\text{H}_2\text{O}_2} = 1.54 \times 10^{-4}$ cm² mJ⁻¹). However, the presence of oxidant precursors has a different impact on each pollutant.

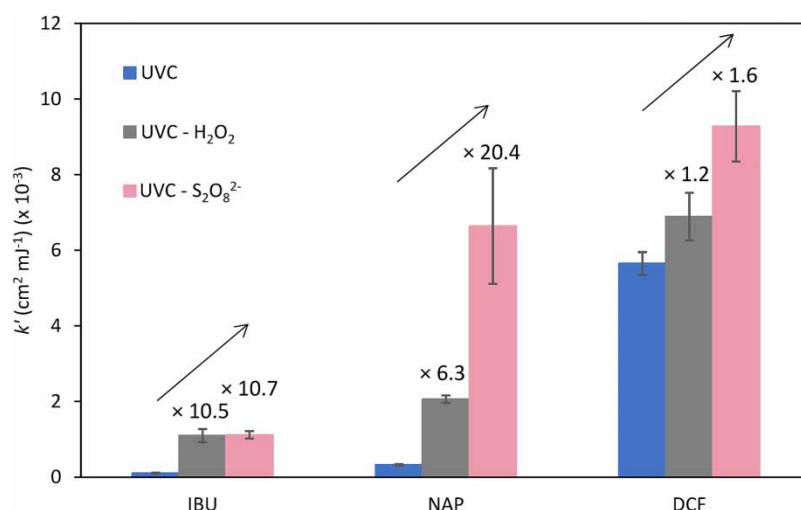


Figure 2 | IBU, NAP, and DCF (5 μM each) first-order degradation rate constants (k') in drinking water under UVC radiation. H₂O₂ and S₂O₈²⁻ = 0.5 mM.

Regarding DCF, a very photosensitive molecule, the addition of oxidant precursors has a moderated impact on its removal: degradation rate constants are multiplied by 1.2 and 1.6 with H_2O_2 and $\text{S}_2\text{O}_8^{2-}$, respectively, which means that UV fluences can be divided by 1.2 and 1.6 to reach complete degradation in the same conditions, compared to photolysis only. Indeed, $k'_{p\text{ DCF}}$ ($5.65 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$) is 4.6 and 1.6 times higher than $k'_{ox\text{ DCF}}$ with HO^\bullet ($1.24 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$) and $\text{SO}_4^{\bullet-}$ ($3.63 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$), respectively, indicating that photolysis is prevailing. This was also observed by Packer *et al.* (2003) in a UVC/ H_2O_2 system.

Regarding IBU and NAP, which are less photosensitive than DCF, the use of oxidant precursors significantly increases their degradation rates. They allow the multiplication of k'_{IBU} by almost 11 compared to photolysis only, regardless of the nature of the oxidant precursor. k'_{NAP} is multiplied by approximately 6 in the presence of H_2O_2 , whereas it is multiplied by 20 in the presence of $\text{S}_2\text{O}_8^{2-}$. As a consequence, coupling oxidant precursors to UVC radiation can significantly reduce the energy consumption of the process. For example, the complete degradation of IBU (implying the complete removal of DCF and NAP) requires around 4,000 and 2,500 mJ cm^{-2} in the presence of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$, respectively, whereas it is degraded by less than 35% at 4,000 mJ cm^{-2} under UVC only.

3.2. Influence of aqueous matrix on the degradation rates of IBU, NAP, and DCF

The same UVC/ H_2O_2 and UVC/ $\text{S}_2\text{O}_8^{2-}$ experiments were then carried out in effluents from a rural constructed wetland (rural effluent) and an urban conventional WWTP (urban effluent) spiked with the mixture of pharmaceuticals. Effluent compositions are reported in Table 1.

3.2.1. Comparison between drinking water and WWTP effluents

Figure 3 compares the pseudo-first order degradation rate constants of the three pharmaceuticals by UVC/ H_2O_2 and UVC/ $\text{S}_2\text{O}_8^{2-}$ in drinking water to those observed in the urban and the rural effluents collected in summer during dry weather (standard conditions). Regardless of the nature of the oxidant precursors, micropollutants have lower degradation rate constants when experiments are performed in the WWTP effluent than in drinking water. With H_2O_2 , k' decreased by 11–56% in the rural effluent and by 19–68% in the urban effluent. In the presence of $\text{S}_2\text{O}_8^{2-}$, they decreased by 17–63% in the rural effluent and by 31–66% in the urban one.

It was previously reported in the literature that the decrease in advanced oxidation performances in secondary effluents is attributed to the quenching of HO^\bullet and $\text{SO}_4^{\bullet-}$ by various species, causing a reduction in the number of available radicals. Indeed, it was observed in the present study that DCF is mainly photolysed, whereas IBU and NAP are mainly oxidized and, from drinking water to secondary effluents, k'_{DCF} only decreased by 11–31%, whereas k'_{IBU} and k'_{NAP} were more impacted. As a consequence, it can also be concluded that the quenching of the radicals played a significant role in the decrease in performance.

The quenching depends on the nature and concentration of the quenching species, of the targeted micropollutants and of the oxidants. In the present study, both WWTP effluents have higher chemical oxygen demands (COD) and Cl^- concentrations than drinking water, whereas HCO_3^- concentrations are comparable (Table 1). The urban effluent induces a stronger decline in the degradation rates than the rural effluent and its COD is three times higher (46.4 mg L^{-1}) than that of the rural effluent (14.5 mg L^{-1}), whereas its Cl^- concentration is almost three times higher in the rural effluent and HCO_3^- concentrations are similar. Therefore, the organic matter seems to be the main quencher of HO^\bullet and $\text{SO}_4^{\bullet-}$.

In the literature, Gabet *et al.* (2021) and Olmez-Hanci *et al.* (2015) concluded that the organic matter is the main quencher for HO^\bullet and $\text{SO}_4^{\bullet-}$ in WWTP effluents. Other authors also observed the influence of inorganic anions such as Cl^- (Sharma *et al.* 2015) or HCO_3^- (Fu *et al.* 2019). However, they seem to have a minor impact on process efficiency at the concentrations of secondary effluents.

Regarding UV fluences to reach 90% degradation of IBU (implying complete degradation of NAP and DCF), it increased from 2,100 mJ cm^{-2} in drinking water to 6,600 and 3,800 mJ cm^{-2} in the urban and the rural effluents, respectively, in the presence of H_2O_2 and from 2,100 mJ cm^{-2} to 6,100 and 5,500 mJ cm^{-2} in the urban and the rural effluents, respectively, with $\text{S}_2\text{O}_8^{2-}$.

3.2.2. Impact of the weather on process performances

Previous experiments on WWTP effluents collected during dry weather were repeated on effluents collected during wet weather in order to gain knowledge about the potential variations in the effluent composition and their impact on treatment performances.

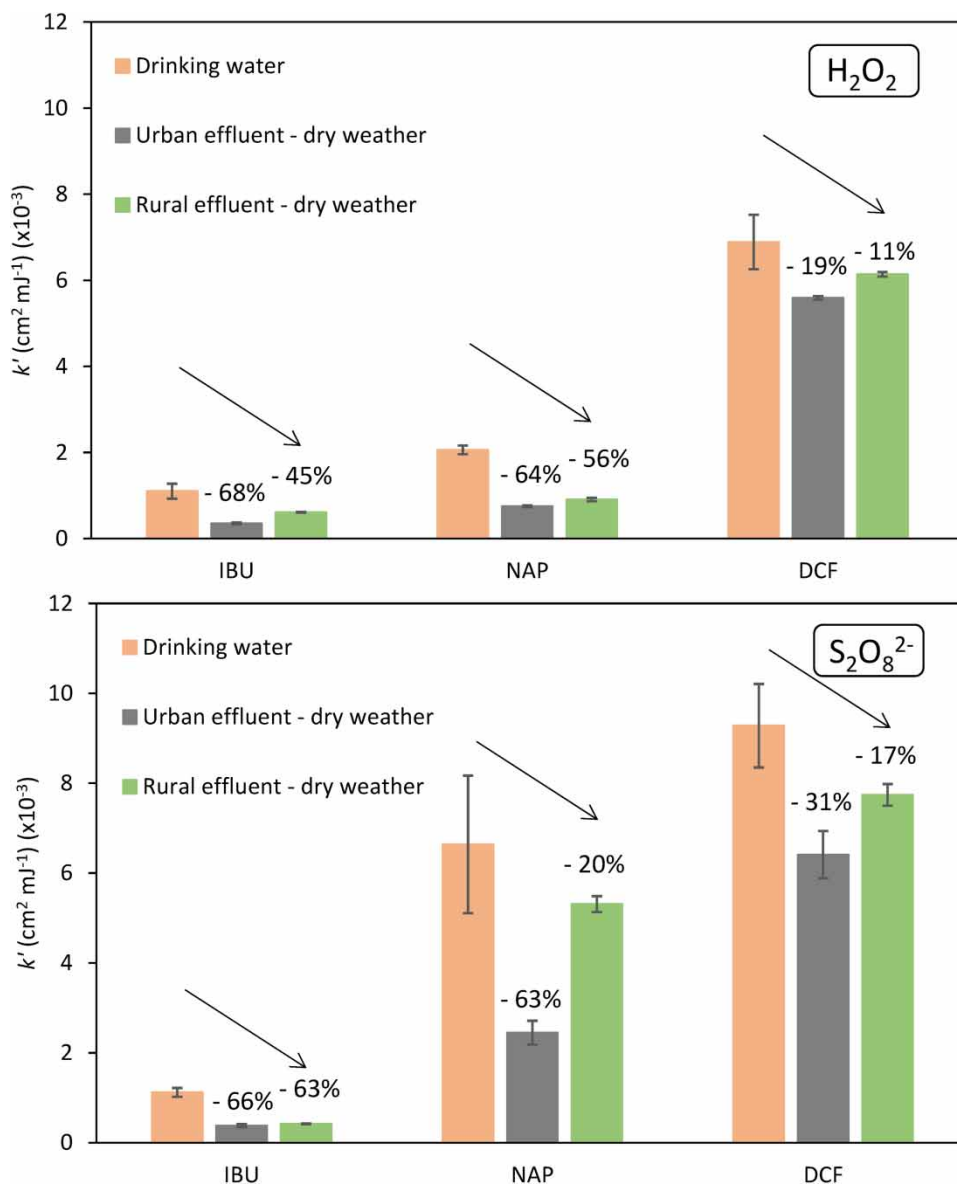


Figure 3 | Degradation rate constants of IBU, NAP, and DCF ($5 \mu\text{M}$ each) in various matrices under UVC radiation in the presence of H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ (0.5 mM). Indicated values represent the inhibition percentage from drinking water to WWTP effluents.

As seen in Table 1, the concentrations in COD and anions of the urban effluent decreased from dry to wet weather. This is attributed to the dilution of domestic effluents by stormwater leaks received, particularly after a strong rainfall (106 mm in 24 h), and leads to an increase in the $\text{UV}_{254\text{nm}}$ transmittance by 9%. On the contrary, the composition of the rural effluent showed minor variations (Table 1) from dry to wet weather. Only a 5% transmittance decrease was noticed, which is the average of the fluctuations observed during this work and in previous work (Cédât 2016) on the effluent of this rural WWTP. Therefore, there seems to be good stability of the effluent composition over time and good resilience of the rural system.

Pseudo-first order degradation rate constants (k') of the micropollutants in dry and wet weather effluents are depicted in Figure 4. In the urban WWTP, k' are significantly enhanced in the effluent collected during wet weather: k'_{IBU} and k'_{NAP} follow a similar trend and are both multiplied by 3.6 ± 0.1 and 2.6 with H_2O_2 and $\text{S}_2\text{O}_8^{2-}$, respectively, whereas k'_{DCF} is only multiplied by 1.3 and 1.5 with H_2O_2 and $\text{S}_2\text{O}_8^{2-}$, respectively. This is attributed to the variations in effluent composition: during wet weather the COD decreased by more than 30% while the concentration of HCO_3^- was divided by more than 3 and Cl^- decreased by 25%. In the rural effluent on the other hand, k' are similar between both weathers for the three

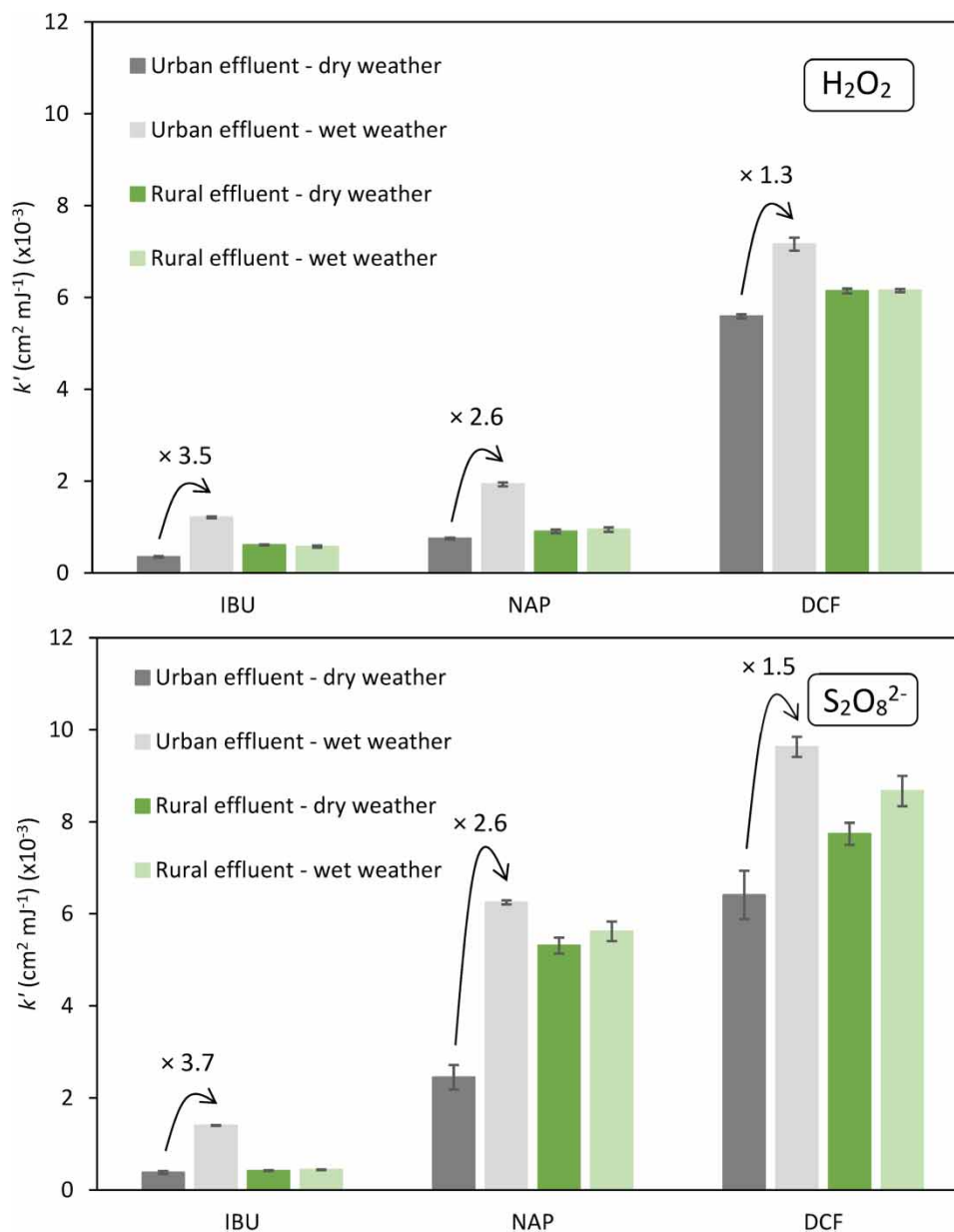


Figure 4 | Degradation rate constants of IBU, NAP, and DCF ($5 \mu\text{M}$ each) in effluents collected during dry and wet weather in an urban and a rural WWTP with H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ (0.5 mM).

pharmaceuticals with H_2O_2 and for IBU and NAP with $\text{S}_2\text{O}_8^{2-}$. Only k'_{DCF} is slightly higher (+12%) with $\text{S}_2\text{O}_8^{2-}$ during wet weather. Although rainfall increased the water flow to be treated by the rural WWTP (from 3.8 to $7.8 \text{ m}^3 \text{ h}^{-1}$), it did not significantly impact the matrix composition: both effluents have similar concentrations in organic and inorganic carbon. Only NO_3^- concentration is higher (+33%) and Cl^- concentration is slightly lower (−17%) in the wet weather effluent.

This difference in behaviour between the effluents of the two WWTPs could be attributed to the difference in the treatment process, influent composition and WWTP capacity. As a consequence, the effluent composition stability of the rural WWTP seems to enable consistent and efficient removal of the micropollutants by both processes regardless of weather conditions, whereas fluctuating results were obtained with the urban effluent. However, the rural wet weather effluent was collected after a normal rain event, unlike the urban effluent that was collected after heavy rain, likely to result in greater impacts on the effluent composition.

3.3. Elements of choice for an oxidant precursor

3.3.1. Efficiency

In the present study, the efficiency of the UVC/H₂O₂ and UVC/S₂O₈²⁻ processes was determined on a mixture of IBU, NAP, and DCF at 5 μM each. In these conditions, S₂O₈²⁻ allowed 3–6 times faster degradation of NAP than H₂O₂. Then, both oxidant precursors allowed degradation rates of the same order of magnitude for DCF and for IBU. DCF was degraded faster in the presence of S₂O₈²⁻ than in the presence of H₂O₂, however, k'_{DCF} was only 1.1–1.4 times higher. Regarding IBU, H₂O₂ allowed a faster degradation of IBU in the rural effluent ($\times 1.4 \pm 0.1$), whereas it was faster in the presence of S₂O₈²⁻ in the urban effluent ($\times 1.1$). As a consequence, the faster photolysis of S₂O₈²⁻ under UVC radiation does not seem favourable for the degradation of all the micropollutants, which also mainly depends on the reactivity between the species. In order to determine the most efficient oxidant precursors for implementation at the outlet of a WWTP, a wider range of compounds would have to be studied. However, oxidant precursor choice also has to involve other criteria such as process cost and implementation.

3.3.2. Process cost

Compared to H₂O₂, the use of S₂O₈²⁻ for compounds such as NAP and DCF that are more easily degraded by sulphate radicals would allow a decrease in the electrical cost of the process. The economic gain corresponds to the ratio between the UV fluence required with S₂O₈²⁻ to that required with H₂O₂. For example, the significant difference regarding NAP would allow to divide the electrical cost by 3–6 times in the presence of S₂O₈²⁻ compared to H₂O₂. However, this benefit is only slightly applicable to DCF and not applicable to IBU. As a consequence, the use of S₂O₈²⁻ does not necessarily imply electricity savings compared to the use of H₂O₂.

Moreover, raw materials and labour costs also have to be considered in process cost comparison. For instance, the solid form of S₂O₈²⁻ requires higher labour, inducing higher cost.

The initial oxidant precursor concentration will also have a significant impact on the cost of the process. In the present study, experiments were performed with a constant initial concentration (0.5 mM), in order to compare both oxidant precursors. It was previously reported in the literature that an increase in the initial concentration of oxidant precursor increases the degradation rate constants to a certain extent and that an excess of radical precursor is required for process efficiency, regardless of the initial concentration (Cédât 2016). However, too much of an increase could also lead to an unnecessary increase in process cost and waste of reagent. Therefore, it seems necessary to perform on-site studies in order to assess the required initial concentration for cost/performance ratio optimization.

3.4. Implementation in a WWTP

The economic and technical interests of the implementation of a UVC-based process at the outlet of rural WWTPs were previously shown by Cédât (2016) in a preliminary study on a 1,100 population equivalent constructed wetland. However, experiments were only carried out on a one-off basis and did not include effluent composition or condition variations. The present study allowed to conclude that the effluent composition stability and the lower organic matter load during dry weather of the rural secondary effluent make UVC-based AOPs more appropriate for the removal of micropollutants at the outlet of rural WWTPs compared to urban ones. Moreover, Besnault *et al.* (2014) compared several processes for the removal of micropollutants and observed that the WWTP size has an impact on treatment cost. They reported that UVC-based processes are economically and technically competitive with other processes such as ozone-based ones in medium-sized WWTPs (>60,000 population equivalent), whereas they are less economically and technically interesting in large WWTPs (>200,000 population equivalent) because of the high number of UVC lamps required, leading to a large footprint and elevated investment costs. As a consequence, it can be concluded that UVC-based processes seem to be more adapted for micropollutant removal to rural and small-sized WWTPs, from an economic and technical perspective.

4. CONCLUSION

This work is aimed at assessing and comparing the abilities of UVC/H₂O₂ and UVC/S₂O₈²⁻ for the removal of micropollutants in various effluents towards an implementation in domestic WWTPs. It was carried out in a 20-L pilot and IBU, NAP and DCF were used as model micropollutants. Preliminary experiments carried out in a simple matrix indicated that DCF is photolabile enough to be degraded in a UVC process. However, IBU and NAP were seen to require the addition of H₂O₂ or S₂O₈²⁻ that strongly enhanced their degradation rates.

Then, the use of WWTP effluents collected during dry weather inhibited degradation rates. This inhibition was stronger in the urban effluent: the required UV fluences to reach more than 90% degradation of all the compounds were 74 and 10% higher in the urban effluent than in the rural one, in the presence of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$, respectively. This was mainly attributed to the three times higher COD in the urban effluent that was likely to increase HO^\bullet and $\text{SO}_4^{\bullet-}$ quenching. During wet weather, the stable composition and transmittance of the rural effluent allowed similar degradation rates than the effluent collected during dry weather, whereas strong dilution of the urban effluent, collected after unusual heavy rain, allowed to multiply the degradation rates by 1.3–3.7 compared to the dry weather effluent. As a consequence, this study showed that the effluents of rural WWTP, that are often small and medium-sized WWTPs, seem to allow for higher and more consistent performances of UVC-based AOPs than urban WWTPs. This adds to conclusions previously made in the literature regarding the economic and technical attractiveness of these processes for the removal of micropollutants in small- and medium-sized WWTPs.

Finally, despite the faster photolysis of $\text{S}_2\text{O}_8^{2-}$, both H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ were seen to be efficient in degrading the targets and presented various performances depending on the compound. NAP underwent faster degradation in the presence of $\text{S}_2\text{O}_8^{2-}$, which was also the case of DCF but to a lesser extent. However, IBU was degraded faster in the presence of H_2O_2 in the rural effluents.

Despite the faster photolysis of $\text{S}_2\text{O}_8^{2-}$ allowing faster degradation of DCF and NAP, IBU underwent faster degradation in the presence of H_2O_2 in the rural effluents. Moreover, although faster degradation induces lower electrical cost to reach similar degradation, treatment cost also includes reagent and labour cost. With the aim of choosing the oxidant precursor that provides the best efficiency/cost ratio, further experiments on a wider cocktail of compounds at real concentrations would be required. Finally, the consideration of the disinfection capacities of both processes would also allow complete comparison towards a full-scale implementation.

DECLARATION OF COMPETING INTEREST

All authors declare no conflict of interest.

ACKNOWLEDGEMENTS

The authors wish to acknowledge ‘Région Auvergne-Rhône-Alpes’ for their financial support through the ‘Pack Ambition Recherche’. This work was performed within the framework of the EUR H2O’Lyon (ANR-17-EURE-0018) of Université de Lyon (UdL), within the programme ‘Investissements d’Avenir’ operated by the French National Research Agency (ANR). This work was also supported by the ‘Federation des Recherches en Environnement’ through the CPER ‘Environnement’ founded by the ‘Région Auvergne,’ the French government and FEDER from European community. The authors thank Marie-Joëlle N’Tcho Kokrobie who performed preliminary experiments for this study during her internship in the DEEP laboratory.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

- Besnault, S., Martin, S., Baig, S., Budzinski, H., Ménach, K. L., Esperanza, M., Noyon, N., Gogot, C., Miege, C., Dherret, L., Galle, A. R. & Coquery, M. 2014 *Réduction des micropolluants par les traitements complémentaires: procédés d’oxydation avancée, adsorption sur charbon actif (Micropollutant Removal by Complementary Treatments: Advanced Oxidation Processes and Activated Carbon Adsorption)*.
- Bolton, J. R. & Stefan, M. I. 2002 [Fundamental photochemical approach to the concepts of fluence \(UV dose\) and electrical energy efficiency in photochemical degradation reactions](#). *Research on Chemical Intermediates* **28** (7–9), 857–870.
- Cédât, B. 2016 *Evaluation du procédé UV/H₂O₂ pour la désinfection et l’élimination des micropolluants en vue d’une réutilisation des eaux usées traitées en petites stations d’épuration (UV/H₂O₂ Assessment for Disinfection and Micropollutant Removal Towards Treated Wastewater Reuse in Small-Sized WWTPs)*.

- Cédât, B., de Brauer, C., Métivier, H., Dumont, N. & Tutundjan, R. 2016 Are UV photolysis and UV/H₂O₂ process efficient to treat estrogens in waters? Chemical and biological assessment at pilot scale. *Water Research* **100**, 357–366.
- Comber, S., Gardner, M., Sörme, P., Leverett, D. & Ellor, B. 2018 Active pharmaceutical ingredients entering the aquatic environment from wastewater treatment works: A cause for concern? *Science of The Total Environment* **613–614**, 538–547.
- Coquery, M., Choubert, J. M., Ruel, S. M., Esperanza, M., Miege, C., Gourlay-Francé, C. & Budzinski, H. 2010 *Projet AMPERES – Analyse de micropolluants prioritaires et émergents dans les rejets et les eaux superficielles (AMPERES Project – Analysis of Priority and Emerging Micropollutants in Effluents and Surface Waters)*.
- Dagot, C. 2018 Traitement des résidus de médicaments dans les ouvrages d'épuration des eaux (Treatment of drug residues in WWTPs). *Environnement, Risque et Santé* **17**, 13.
- Fu, Y., Gao, X., Geng, J., Li, S., Wu, G. & Ren, H. 2019 Degradation of three nonsteroidal anti-inflammatory drugs by UV/persulfate: Degradation mechanisms, efficiency in effluents disposal. *Chemical Engineering Journal* **356**, 1032–1041.
- Gabet, A., Métivier, H., de Brauer, C., Mailhot, G. & Brigante, M. 2021 Hydrogen peroxide and persulfate activation using UVA-UVB radiation: Degradation of estrogenic compounds and application in sewage treatment plant waters. *Journal of Hazardous Materials* **405**, 124693.
- Gao, Y., Gao, N., Yin, D. & Chen, J. 2017 Comparative study of naproxen degradation in water by UV/persulfate and UV/H₂O₂ processes. *Desalination and Water Treatment* **80**, 317–325.
- Garcia-Rodríguez, A., Matamoros, V., Fontàs, C. & Salvadó, V. 2014 The ability of biologically based wastewater treatment systems to remove emerging organic contaminants – a review. *Environmental Science and Pollution Research* **21** (20), 11708–11728.
- Hokanson, D. R., Li, K. & Trussell, R. R. 2016 A photolysis coefficient for characterizing the response of aqueous constituents to photolysis. *Frontiers of Environmental Science & Engineering* **10** (3), 428–437.
- Kim, I., Yamashita, N. & Tanaka, H. 2009 Performance of UV and UV/H₂O₂ processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. *Journal of Hazardous Materials* **166**, 1134–1140.
- Kwon, M., Kim, S., Yoon, Y., Jung, Y., Hwang, T.-M., Lee, J. & Kang, J.-W. 2015 Comparative evaluation of ibuprofen removal by UV/H₂O₂ and UV/S₂O₈²⁻ processes for wastewater treatment. *Chemical Engineering Journal* **269**, 379–390.
- Li, Y., Zhu, G., Ng, W. J. & Tan, S. K. 2014 A review on removing pharmaceutical contaminants from wastewater by constructed wetlands: design, performance and mechanism. *Science of The Total Environment* **468–469**, 908–932.
- Lindholm-Lehto, P. C., Ahkola, H. S. J., Knuutinen, J. S. & Herve, S. H. 2016 Widespread occurrence and seasonal variation of pharmaceuticals in surface waters and municipal wastewater treatment plants in central Finland. *Environmental Science and Pollution Research* **23** (8), 7985–7997.
- Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., Liang, S. & Wang, X. C. 2014 A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of The Total Environment* **473–474**, 619–641.
- Luo, S., Gao, L., Wei, Z., Spinney, R., Dionysiou, D. D., Hu, W.-P., Chai, L. & Xiao, R. 2018 Kinetic and mechanistic aspects of hydroxyl radical-mediated degradation of naproxen and reaction intermediates. *Water Research* **137**, 233–241.
- Madikizela, L. M. & Chimuka, L. 2017 Occurrence of naproxen, ibuprofen, and diclofenac residues in wastewater and river water of KwaZulu-Natal Province in South Africa. *Environmental Monitoring and Assessment* **189** (7), 348.
- Olmez-Hanci, T., Dursun, D., Aydin, E., Arslan-Alaton, I., Girit, B., Mita, L., Diano, N., Mita, D. G. & Guida, M. 2015 S₂O₈²⁻/UV-C and H₂O₂/UV-C treatment of Bisphenol A: Assessment of toxicity, estrogenic activity, degradation products and results in real water. *Chemosphere* **119**, S115–S123.
- Packer, J. L., Werner, J. J., Latch, D. E., McNeill, K. & Arnold, W. A. 2003 Photochemical fate of pharmaceuticals in the environment: Naproxen, diclofenac, clofibrac acid, and ibuprofen. *Aquatic Sciences – Research Across Boundaries* **65** (4), 342–351.
- Patel, M., Kumar, R., Kishor, K., Mlsna, T., Pittman, C. U. & Mohan, D. 2019 Pharmaceuticals of emerging concern in aquatic systems: Chemistry, occurrence, effects, and removal methods. *Chemical Reviews* **119** (6), 3510–3673.
- Patrolecco, L., Capri, S. & Ademollo, N. 2015 Occurrence of selected pharmaceuticals in the principal sewage treatment plants in Rome (Italy) and in the receiving surface waters. *Environmental Science and Pollution Research* **22** (8), 5864–5876.
- Sharma, J., Mishra, I. M. & Kumar, V. 2015 Degradation and mineralization of Bisphenol A (BPA) in aqueous solution using advanced oxidation processes: UV/H₂O₂ and UV/S₂O₈²⁻ oxidation systems. *Journal of Environmental Management* **156**, 266–275.
- Sharpless, C. M. & Linden, K. G. 2003 Experimental and model comparisons of low- and medium-pressure Hg lamps for the direct and H₂O₂ assisted UV photodegradation of N-Nitrosodimethylamine in simulated drinking water. *Environmental Science & Technology* **37** (9), 1933–1940.
- Shu, Z., Singh, A., Klammerth, N., McPhedran, K., Bolton, J. R., Belosevic, M. & Gamal El-Din, M. 2016 Pilot-scale UV/H₂O₂ advanced oxidation process for municipal reuse water: Assessing micropollutant degradation and estrogenic impacts on goldfish (*Carassius auratus* L.). *Water Research* **101**, 157–166.
- Starling, M. C. V. M., Souza, P. P., Le Person, A., Amorim, C. C. & Criquet, J. 2019 Intensification of UV-C treatment to remove emerging contaminants by UV-C/H₂O₂ and UV-C/S₂O₈²⁻: Susceptibility to photolysis and investigation of acute toxicity. *Chemical Engineering Journal* **376**, 120856.
- Vasquez, M. I., Lambrianides, A., Schneider, M., Kümmerer, K. & Fatta-Kassinos, D. 2014 Environmental side effects of pharmaceutical cocktails: What we know and what we should know. *Journal of Hazardous Materials* **279**, 169–189.

- Zhou, S., Di Paolo, C., Wu, X., Shao, Y., Seiler, T.-B. & Hollert, H. 2019 Optimization of screening-level risk assessment and priority selection of emerging pollutants – The case of pharmaceuticals in European surface waters. *Environment International* **128**, 1–10.
- Zupanc, M., Kosjek, T., Petkovšek, M., Dular, M., Kompare, B., Širok, B., Blazeka, Z. & Heath, E. 2013 Removal of pharmaceuticals from wastewater by biological processes, hydrodynamic cavitation and UV treatment. *Ultrasonics Sonochemistry* **20**, 1104–1112.

First received 27 April 2023; accepted in revised form 18 July 2023. Available online 8 September 2023