ABSTRACT

In this work, the degradation of cefalexin, norfloxacin, and ofloxacin was examined via various advanced oxidation processes (AOPs). Direct photolysis by ultraviolet (UV) and vacuum ultra violet (VUV) was less effective for the degradation of fluoroquinolone antibiotics such as norfloxacin and ofloxacin than that of cefalexin. Both hydrogen peroxide (H_2O_2) and potassium persulfate ($K_2S_2O_8$) assisted UV/VUV process remarkably enhanced fluoroquinolone degradation. The addition of $K_2S_2O_8$ was superior to H_2O_2 under VUV irradiation, with the best removal efficiency of norfloxacin and ofloxacin being almost 100% within 3 min in the presence of VUV/$K_2S_2O_8$. The ofloxacin degradation rate was accelerated as concentrations of H_2O_2 and $K_2S_2O_8$ was increased to 3 mM, but the degradation rate was slightly decreased with excess H_2O_2 (> 3 mM). The performance of modified VUV processes (*i.e.*, VUV/H_2O_2 and VUV/$K_2S_2O_8$) was inhibited at highly alkaline condition (pH 11). The co-existence of halides (Cl^- and Br^-) enhanced antibiotics degradation via the modified VUV processes, but the reaction was almost unaffected in the presence of single halides. This study demonstrated that modified VUV processes (especially VUV/$K_2S_2O_8$) are efficient for eliminating fluoroquinolone antibiotics from water, which can be considered as a clean and green method for the treatment of antibiotics-containing industrial wastewater.

Keywords: fluoroquinolone antibiotics; persulfate radicals; chlorides/bromides; vacuum-ultraviolet light; catalytic degradation; sustainable remediation.

1. Introduction

Discharge of pollutants from a variety of industries to soil, water, and air has increased the importance of using proper treatment for pollutants with different characteristics (Hou et al., 2017; Song et al., 2018; Zhang et al., 2018). In particular, pharmaceutical and personal care products (PPCPs) have been an emerging concern due to their harmful effects on aquatic organisms and human health (Jin et al., 2018). Water contamination associated with PPCPs has become a serious problem due to increasing population and rapid industrialization in many countries. Among the broad span of PPCPs, antibiotics that easily enter into water matrices have gained considerable attention because of their extensive use in field and persistent nature (Sun et al., 2017; Copete-Pertuz et al., 2018; Guo et al., 2018). Long-term exposure to antibiotics in the environment may increase the number of antibiotic-resistant bacteria (Zhu et al., 2015). The occurrence and risk assessment of sixteen antibiotics had been surveyed in several sewage treatment plants (STPs) in Hong Kong, where the major antibiotics were found to be cefalexin (CEX) and ofloxacin (OFX) (Leung et al., 2012). Norfloxacin (NOF) is a fluoroquinolone antibacterial agent ubiquitously detected in drinking water/wastewater and its bioaccumulation could pose a serious threat to the public health, aquatic organisms, and wildlife (Ahmed et al., 2014; Sun et al., 2017). Thus, one of the recent focuses of research is laid on the removal of antibiotics from water.

Non-biotic treatment methods that are able to eliminate antibiotics have been mainly considered since antibiotics are mostly designed to have strong resistance to hydrolysis, which is important for transformation of common organic pollutants in water (Ghauch et al., 2017). A variety of techniques including adsorption (Yan and Niu, 2018), electrochemical degradation (Lan et al., 2017), and oxidation processes (Lofrano et al., 2018) have been used to remove antibiotics from water. Among these techniques, oxidation processes including ultraviolet (UV) irradiation, hydrogen peroxide (H_2O_2), Fenton reaction (Fe(II)/H_2O_2), and ozone (O_3) have drawn great interest due to their high removal efficiencies for antibiotics (Mondal et al., 2018).

Advanced oxidation processes (AOPs) can degrade a variety of organic contaminants into less complex byproducts and finally mineralize them into carbon dioxide and water in both surface water and wastewater (Dhaka et al., 2018). Various UV-based processes can be significantly enhanced by the combination of technologies (MacDonald et al., 2018). UV process can overcome several problems in the other processes, such as long reaction time in biological processes, sludge production in coagulation process, regeneration of adsorbent in adsorption process, and acidic condition in Fenton oxidation (Rodríguez-Chueca et al., 2018). UV irradiation has been frequently used for drinking water purification due to its excellent removal efficiencies for aquatic pathogens and organic pollutants, which has the potential to be an economically feasible wastewater treatment process (Yuval et al., 2017).

To improve the degradation efficiency, the use of vacuum UV (VUV) irradiation at the wavelength of 185 nm as a promising alternative to UV irradiation (254 nm) has been investigated recently because it generates a large amount of reactive species via activation of water molecules (Xie et al., 2018). The VUV process generates both hydroxyl radical ($^{\bullet}OH$) and aqueous electrons (e^{-}) via homolysis/ionization of water molecules (*viz.* $H_2O + VUV_{185} \rightarrow {}^{\bullet}OH + H^{\bullet}$; $H_2O + VUV_{185} \rightarrow {}^{\bullet}OH + H^{+} + e^{-}$; $H^{\bullet} + H_2O \rightarrow H_3O^{+} + e^{-}$) (Kosma et al., 2015), and the oxidation rate of pollutants can be accelerated by these reactive species. The effectiveness of homogeneous VUV-based AOP in the degradation of antibiotics has been validated. For example, Pourakbar et al. (2016) observed efficient degradation and mineralization of amoxicillin by VUV irradiation under different solution pHs, initial amoxicillin concentrations, water ingredients, and hydraulic retention times (HRTs). The performance of VUV photolysis in the removal of acetaminophen in the presence of nitrate was evaluated using a continuous-flow photoreactor in which acetaminophen was completely oxidized with nitrate reduction to N_2 (~99%) at 80 min-HRT (Moussavi et al., 2016).

External chemical addition in UV-based process have also been tried to enhance the degradation efficiency. In particular, various types of UV-based AOPs supported by external chemical addition such as UV/H_2O_2 (Li

et al., 2015), UV/O_3 (Marquez et al., 2013), and UV/$S_2O_8^{2-}$ (Ghauch et al., 2017) were developed for better degradation of antibiotics. Recently, modified processes of VUV/UV and VUV/Fe^{2+} have been investigated for the feasibility of water treatment in bench- or pilot-scale tests (Li et al., 2017; Moussavi et al., 2018c). Nevertheless, the modified UV/VUV process required enormous chemical exhaustion at low pH condition with relatively moderate reaction rate. Meanwhile, the effect of inorganic anions commonly present in wastewaters showed various trends. Chloride (Cl^-) and carbonate (CO_3^{2-}) suppressed reaction rates of UV/$S_2O_8^{2-}$ and UV/H_2O_2 systems, whereas they elevated the degradation rates of UV/peroxymonosulfate (PMS) treatment (Dhaka et al., 2018).

Despite the increasing popularity of UV-based AOPs supported by external chemical addition, the feasibility of using chemical agents to improve the efficiency of VUV-based AOPs toward antibiotics removal remains uncertain. This substantiates the need for developing technology that can effectively remove these micro-contaminants under neutral pH condition with low chemical input and high efficiency in presence of effecting inorganic anions. In this study, the candidates of chemical agents that can be employed for the enhancement of VUV photolysis are H_2O_2 and $S_2O_8^{2-}$, because their oxidative ability has been proven for the decomposition of aqueous organics. Therefore, we aimed to examine the effects of H_2O_2 and $S_2O_8^{2-}$ addition on the degradation of various types of antibiotics (CEX, OFX, and NOF) in water under VUV irradiation in comparison with UV-based processes. In view of the significant effect of halides on oxidation processes (Wu et al., 2017), the single or binary presence of halides (Cl^- and Br^-) on the degradation of antibiotics was also examined. A three factorial Box-Behnken design was then employed to optimize the relevant parameters for the degradation of OFX under VUV irradiation.

2. Materials & Methods

2.1. Chemical reagents and materials

All chemicals were of analytical reagent grade and solvents were of HPLC grade. Cefalexin ($C_{16}H_{17}N_3O_4S$, CEX), norfloxacin ($C_{16}H_{18}FN_3O_3$, NOR), and ofloxacin ($C_{18}H_{20}FN_3O_3$, OFX) were purchased from Wako Pure Chemical Industries, Ltd., Japan. The physicochemical characteristics of antibiotics are summarized in Table S1. Sodium hydroxide (NaOH, 96%), sodium thiosulfate ($Na_2S_2O_3$), sodium chloride (NaCl, 99%), and potassium bromide (KBr) were obtained from Uni-Chem Co., Ltd., South Korea. Hydrogen peroxide (H_2O_2), potassium peroxydisulfate ($K_2S_2O_8$), acetonitrile (HPLC grade, C_2H_3N), and trimethylamine (HPLC grade, $C_6H_{15}N$) were purchased from VWR Chemicals (USA), Riedel-deHaën (Germany), DUKSAN (South Korea), and Alfa Aesar (USA), respectively.

2.2. Photo-oxidation experiments

A 300-mL (50 mm ID × 310 mm H) tailor-made reactor with a single-layered quartz sleeve inside was used as a photo-reactor coupled with a magnetic stirring apparatus. UV (254 nm) and VUV (185 nm) mercury containing lamps (39 W low pressure) were applied and the irradiance of 1.3×10^{-8} Einstein's L^{-1} s^{-1} was measured by iodide-iodate actinometry. The schematic of the photo-reactor is shown in Fig. 1. The photolytic experiments were performed at 23±2 °C, and the initial pH of solution was adjusted by orthophosphoric acid as needed. Appropriate amounts of stock solutions of CEX, NOF, and OFX in distilled de-ionized water (DDW) were spiked into the photo-reactor containing 300 mL DDW to obtain the initial concentration of antibiotics to 10 mg L^{-1}, which represented the concentrations of organic pollutants in antibiotics-containing industrial wastewaters (Shi et al., 2017). For the implementation of modified UV-C or VUV process, a certain amount of H_2O_2 or $K_2S_2O_8$ was added to the solutions and subjected to UV-C or VUV irradiation. The reactor was operated with rapid mixing by a magnetic stirring apparatus at the bottom of the reactor, and each photoreaction solution was stirred by intensive mixing. At each interval for sampling, a sample of 1.5 mL was withdrawn from the reactor and then further oxidation reactions were immediately stopped by adding excess

110 Na_2SO_3 that can quench radicals generated by H_2O_2 or $K_2S_2O_8$ (García-Galán et al., 2016). Then, the sample
111 was filtered through a 0.45-μm pore-size polyvinylidene fluroride syringe filter (Whatman, USA) and
112 analyzed for the antibiotics concentrations; 30% of the experiments were randomly replicated to ensure data
113 reproducibility and reliability. The pseudo-first order kinetics model (equation 1) was used to show the kinetic
114 data of degradation of antibiotics:

$$\ln\left(\frac{C_0}{C}\right) = k_{obs}t \quad (1)$$

115 where C_0 and C represent the antibiotics concentration before reaction and at the reaction time t, respectively;
116 and k_{obs} is the observed rate constant of degradation.
117
118 2.3. Analytical methods
119 The determination of antibiotics was performed by a high-performance liquid chromatograph (HPLC)
120 equipped with an Alltech Model 426 HPLC pump and a LINEAR UV/Visible 200 absorbance detector. A
121 Pinnacle DB C18 reversed phase column (250 mm × 4.6 mm with i.d. of 5 μm) was used for chromatographic
122 separations. For the quantification of antibiotics, the mobile phase consisted of acetonitrile, water, and
123 triethylamine (18:82:3, v/v), and the solution pH value was adjusted to 3. The mobile phase was filtered
124 through a 0.2-μm pore-size polytetrafluoroethylene membrane filter (Whatman, USA) and degassed for 30
125 min. The mobile phase was pumped at a flow rate of 1 mL min^{-1} and then 20-μL sample was injected into the
126 HPLC system. The UV/Visible detector was set at a wavelength of 261 nm, 270 nm, and 294 nm for CEX,
127 NOF, and OFX, respectively. The solution pH was measured by a PHS-3C digital pH meter.
128
129 2.4. Box-Behnken Experimental Design
130 Responsible surface method (RSM) is a statistical approach to determine the significance and effects of

131 independent variables (input variables) as well as to optimize the responses (output variables) in experimental
132 process. The RSM was applied to investigate the effects of three variables that have been identified as main
133 parameters from previous studies for organic removal by UV/VUV-based AOPs: H_2O_2 concentration (0-1
134 mM), $K_2S_2O_8$ concentration (0-1 mM), and solution pH (5-9) on the degradation kinetics of OFX in this work.
135 For the investigation on the effects of three variables, 17 experiments designed by Box-Behnken were
136 conducted, and the pseudo-first-order rate constant (k_{obs}) of OFX degradation by VUV-based processes during
137 1.5 min was estimated as the response factor. The second-order quadratic polynomial equation was used to
138 determine the interaction effects between the variables, and the predicted response can be quantitatively
139 described as a quadratic function of three variables (Table S2). The equation can be expressed as follows:
140 $$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (2)$$
141 where solution pH is X_1, initial concentration of H_2O_2 is X_2, and initial concentration of $K_2S_2O_8$ is X_3. Y is the
142 estimated response (k_{obs} value of OFX degradation); X_1, X_2, and X_3 are independent variables; β_0 is the
143 intercept; $\beta_1, \beta_2,$ and β_3 are liner coefficients; $\beta_{12}, \beta_{13},$ and β_{23} are squared coefficients;
144 $\beta_{11}, \beta_{22},$ and β_{23} are quadratic coefficients. The accuracy of the proposed polynomial model was
145 examined by analysis of variance (ANOVA). The three real levels and coded levels are presented in Table S3.
146
147 **3. Results & Discussion**
148 3.1. Degradation of OFX, NOF, and CEX by UV- and VUV based processes
149 The photolytic degradation experiments of antibiotics (OFX, NOF, and CEX) by UV- or VUV-based
150 processes were conducted, and the degradation kinetics data and k_{obs} values are presented in Fig. 2. Without
151 excitation of light source, only 14-43% of OFX was degraded during 30-min reaction when either H_2O_2 or
152 $K_2S_2O_8$ was added only (Fig. S1), despite the oxidative capacities of H_2O_2 ($E°$= 1.8 V) (Fuku et al., 2016) and

153 $S_2O_8^{2-}$ (E° = 2.01 V) (Matzek and Carter, 2016). The values of k_{obs} for CEX degradation rate under
154 homogeneous UV and VUV processes reached approximately 1.0 min^{-1}, while those of NOF and OFX were
155 slow at the same conditions with the values of k_{obs} lower than 0.25 min^{-1}. Direct photolysis might be the main
156 degradation mechanism for effective CEX degradation. However, the degradation rate of OFX was
157 comparatively low in the homogeneous UV and VUV processes, with 40% and 97% removal of OFX for 30
158 min, respectively. This observation suggests that fluoroquinolone antibiotics (FQs) are more resistant to the
159 photolysis compared to sulfur-containing antibiotics (e.g., CEX). As a result, an individual process by either
160 chemical agents or irradiation alone was not sufficient to remove the FQs from water.
161 The addition of chemical agents (H_2O_2 or $K_2S_2O_8$) remarkably increased the degradation rates of the three
162 antibiotics, and the effects were more pronounced for FQs degradation under VUV irradiation in the presence
163 of H_2O_2 or $K_2S_2O_8$ individually. As illustrated in Fig. 2a&b, the degradation efficiencies of OFX and NOF
164 dramatically increased in the following order: UV < VUV < UV/H_2O_2 < UV/$K_2S_2O_8$ < VUV/H_2O_2 <
165 VUV/$K_2S_2O_8$ (0.04 to 2.05 min^{-1}), indicating that UV or VUV irradiation is more compatible with $K_2S_2O_8$
166 addition than H_2O_2 addition. On the contrary, the degradation of CEX showed the opposite tendency. The
167 addition of H_2O_2 resulted in slightly faster degradation of CEX under UV or VUV irradiation than $K_2S_2O_8$
168 addition (Fig. 2c).
169 The higher CEX degradation efficiency via UV/VUV with H_2O_2 addition compared to that with $K_2S_2O_8$
170 could be justified by the relatively slow reaction of β-lactams rings in CEX with $SO_4^{\bullet-}$ than $^{\bullet}OH$ (He et al.,
171 2016). The accelerated degradation rate after H_2O_2 addition in the presence of UV light might result from a
172 larger amount of generated $^{\bullet}OH$ during photolysis (*viz.* $H_2O_2+UV_{254} \rightarrow 2^{\bullet}OH$) (Mondal et al., 2018), which
173 apparently could facilitate the faster degradation of CEX. By contrast, more degradation of FQs in the
174 presence of $K_2S_2O_8$ under UV or VUV irradiation compared to the case in the presence of H_2O_2 could be
175 explained by the cleavage of C-F bonds of the FQs via defluorination, hydroxylation of the FQs through self-

sensitized photo-process, and piperazine ring cleavage by the attack of $^{\bullet}OH/SO_4^{\bullet-}$ radicals (Ao et al., 2018). Meanwhile, Jin et al. (2018a) proposed that free radicals of $SO_4^{\bullet-}$ and $^{\bullet}OH$ could attack active sites of antibiotics (*e.g.*, aromatic rings and olefinic double bonds) *via* one electron transfer producing carbon-centered radical cations, which further transformed into the OH adducts after hydrolysis. Moreover, hydrogen abstraction induced hydroxyl-organic radical that was eventually mineralized into smaller organic molecules, CO_2, and H_2O (Jin et al., 2018b; Wang et al., 2018). The simultaneous, multi-pathway mediated FQs degradation in UV/$K_2S_2O_8$ could contribute to the enhancement of the reaction rate.

One interesting observation is the synergistic effect arising from the combination of chemical addition and VUV irradiation, which accounted for the fastest degradation rate of FQs. The k_{obs} values of VUV/H_2O_2 and VUV/$K_2S_2O_8$ for OFX and NOF were comparable to the k_{obs} of CEX at the same condition (> 2.0 min^{-1}), which can be attributed to the generation of abundant reactive radical species of $^{\bullet}OH/SO_4^{\bullet-}$ in the modified VUV processes (Moussavi et al., 2018a). The VUV/H_2O_2 process was reported to allow better degradation of clofibric acid (over 99% removal efficiency) compared to that by either UV/H_2O_2 or VUV alone (Li et al., 2011). Recently, Moussavi et al. (2018a) revealed the enhancement of degradation of cyanide in industrial wastewater when employing VUV/$K_2S_2O_8$ process, possibly due to the simultaneous production of reactive radical species in a short period of time.

Considering less degradation of OFX and NOF by $^{\bullet}OH$ generated from water photolysis in the presence of modified UV processes (Fig. 2a&b), the effectiveness of chemical addition might be further amplified under VUV irradiation. Moreover, $S_2O_8^{2-}$ activation can be largely affected by the wavelength of light irradiation. The relatively fast activation by 185 nm light irradiation compared to that by 254 nm light irradiation has been validated with the corresponding loss rate of $S_2O_8^{2-}$ at different wavelengths (185 nm and 254 nm) (An et al., 2015).

3.2. Comparison of OFX degradation in VUV/H_2O_2 and VUV/$K_2S_2O_8$

To get more insights into the effects of chemical agents on the degradation of antibiotic under VUV irradiation, the degradation kinetics of OFX at different concentrations of H_2O_2 and $K_2S_2O_8$ (0.25-5 mM) were investigated and the results are shown in Fig. 3a and Fig. 3b. The degradation rate of OFX increased gradually with the increasing concentration of H_2O_2 from 0.25 to 1 mM under VUV irradiation, with the highest k_{obs} of 2.8 min^{-1} at 1 mM H_2O_2 (Fig. 3a). This observation suggests that H_2O_2 activated by VUV irradiation could generate more reactive species thus leading to promoted degradation of OFX. However, further addition of H_2O_2 over 1 mM slightly retarded the degradation rate, possibly due to the scavenged $^{\bullet}OH$ through a chain termination reaction (equations 3 and 4) at a high dosage of H_2O_2 (Gu et al., 2012), thereby decreasing the overall degradation capacity.

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (3)$$

$$^{\bullet}OH + HO_2^{\bullet} \rightarrow O_2 + H_2O \quad (4)$$

The degradation of OFX in VUV/$K_2S_2O_8$ process was more effective than that in VUV/H_2O_2 process at the same concentration, which can be explained by the wider gap of redox potential between OFX and $^{\bullet}OH$ (E° = 1.8-2.7 V) than $SO_4^{\bullet-}$ (E° = 2.5-3.1 V) (O'Connor et al., 2018). Increasing the concentration of $K_2S_2O_8$ remarkably boosted the degradation rate of OFX (Fig. 3b), i.e., the k_{obs} value increased from 1.70 to 9.05 min^{-1} with increasing $K_2S_2O_8$ concentration from 0.25 to 5 mM. This observation implies the simultaneous production of $^{\bullet}OH/SO_4^{\bullet-}$ via a variety of reaction pathways (*viz.* $H_2O + VUV_{185\,nm} \rightarrow {}^{\bullet}OH + H^{\bullet}$; $H_2O + VUV_{185\,nm} \rightarrow {}^{\bullet}OH + H^+ + e_{aq}^-$; $S_2O_8^{2-} + VUV_{185\,nm} \rightarrow 2SO_4^{\bullet-}$; $S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^{2-} + SO_4^{\bullet-}$) without the critical scavenging reaction that eliminates the reactive radicals (Moussavi et al., 2018a). Moreover, this rate enhancement was probably associated with the continuous activation of $S_2O_8^{2-}$ by $^{\bullet}OH$ and e_{aq}^- generated from VUV photolysis so that a large amount of $SO_4^{\bullet-}$ with a high redox potential could be produced. However, further addition of $K_2S_2O_8$ over 3 mM did not increase the degradation rate, because the restrained reaction

of $SO_4^{\bullet-}$ by either H_2O or $S_2O_8^{2-}$ (*viz.* $SO_4^{\bullet-} + H_2O \rightarrow HSO_4^- + {}^{\bullet}OH$ or $SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-}$) produced less reactive radicals due to the excessive concentration of $SO_4^{\bullet-}$ (Yu et al., 2004). Therefore, the results indicate that, under VUV irradiation, $K_2S_2O_8$ was more effective than H_2O_2 for enhancing the degradation rate of FQs, especially when a high dose of chemical agent was applied.

The degradation efficiency of OFX observed in the VUV/$K_2S_2O_8$ process was compared with the processes reported in the literature although the experimental conditions were different from each other, and the result are summarized in Table 2. For example, modified mesoporous iron oxide catalyzed H_2O_2 oxidation process needed 50-min reaction time to completely degrade 12 mg L^{-1} OFX at pH 6.4 (Tian et al., 2017), which implies the slow degradation kinetics rate of OFX without irradiation. The process of polyvinylidene fluoride membrane soaked with 42 mM $Na_2S_2O_8$ solution only exhibited 54% removal of 5 mg L^{-1} OFX in 30 min under UV irradiation at 395 nm (Wang et al., 2017). The UV/H_2O_2 process applied to wastewater containing 9 mM H_2O_2 rapidly degraded 0.5 mg L^{-1} OFX in 8.5 min (Urbano et al., 2017), but the complete degradation of 10 mg L^{-1} OFX needed longer reaction time of 30 min in the presence of 7.94 mM H_2O_2 under UV irradiation at 254 nm (Lin et al., 2016). Compared to the above processes, VUV/$K_2S_2O_8$ in this study showed relatively fast degradation of OFX in a very short period of time, i.e., almost 100% removal within 2 min.

The effect of solution pH on the degradation rate of OFX by VUV/H_2O_2 and VUV/$K_2S_2O_8$ was investigated and the results are shown in Fig. 3c and Fig. 3d. The overall degradation rates of OFX were highly dependent on the solution pH in both VUV/H_2O_2 and VUV/$K_2S_2O_8$ systems. Basically, an increase of solution pH resulted in the decline of the degradation rate. This was because the formation of negatively charged OFX molecules under alkaline condition (pK_{a1} = 6.05 and pK_{a2} = 8.11) reduced the degradation rate in both processes where ${}^{\bullet}OH$ was more reactive to non-ionic molecules (Liao et al., 2016). The decreasing redox potential of ${}^{\bullet}OH$ with increasing pH might be another reason for the lower degradation rate of OFX

(Moussavi et al., 2018b). Considering that the predominant reactive species were •OH in VUV/H_2O_2 system, the OFX degradation associated with •OH could render the VUV/H_2O_2 irradiation sensitive to the increase of solution pH. The pronounced decline of the degradation rate was apparent at pH 11 (Fig. 3c), which was ascribable to the active self-decomposition of H_2O_2 (*viz.* $2H_2O_2 \rightarrow H_2O + O_2$). The elevation of solution pH gradually decreased the degradation rate of OFX (Fig. 3d) in VUV/$K_2S_2O_8$ system, which could be attributed to the consumption of $SO_4^{\bullet-}$ by •OH (*viz.* $SO_4^{\bullet-} + OH^- \rightarrow {}^{\bullet}OH + SO_4^{2-}$) forming less reactive radical (Guan et al., 2011). The accelerated degradation rate was observed at low pH in VUV/$K_2S_2O_8$ process with the k_{obs} value of 1.93 min^{-1} at pH 3 (Fig. 3d). This observation suggests that the decomposition of $S_2O_8^{2-}$ can be catalytically accelerated by the protonation reaction of $S_2O_8^{2-}$ (*viz.* $S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^-$; $HS_2O_8^- \rightarrow 2SO_4^{\bullet-} + H^+$) (House, 1962). Interestingly, the highest OFX removal rate was achieved in both VUV/H_2O_2 and VUV/$K_2S_2O_8$ processes when the solution pH was not adjusted (7.5-8.0). This phenomenon could be associated with the greater resistance of cationic form of OFX at low pH (< 6.05) to the electrophilic attack of radicals (Li et al., 2017).

3.3. Effects of halide ions on degradation of antibiotics

To examine how the single or binary existence of halides (*i.e.*, chloride and bromide) influences the degradation of antibiotics by VUV photolysis, the removal of NOF and CEX in presence of halide ions under VUV irradiation was investigated and the results are shown in Fig. 4. Following the similar level of halide ions selected in relevant studies (Li et al., 2015), the concentration of Cl ions ranged from 0.03 to 0.2 M while the low concentration range of 0.05-0.25 mM was chosen for Br ions. The degradation rates of CEX and NOF by VUV photolysis were 0.967 and 0.266 min^{-1} in the absence of Cl^- and Br^-, respectively. Meanwhile, the addition of 0.03 M Cl^- contributed to a slight enhancement in the degradation rate, probably because the chlorine radical ($Cl^{\bullet}$) and e_{aq}^- were generated under these conditions (*viz.* $Cl^- + VUV_{185\ nm} \rightarrow Cl^{\bullet} + e_{aq}^-$)

facilitating the degradation of CEX (Furatian and Mohsenr, 2018). However, further increasing Cl^- concentration from 0.03 to 0.2 M lowered the k_{obs} values of CEX and NOF from 1.02 and 0.42 min^{-1} to 0.85 and 0.32 min^{-1}, respectively. This observation could be attributed to the scavenging of $^{\bullet}OH$ caused by the reaction between Cl^- and $^{\bullet}OH$ at high levels of Cl^- (*i.e.*, saline water) (Grebel et al., 2010), thereby decreasing the overall degradation rate. The impeded degradation of CEX in the presence of Br^- is because of the $^{\bullet}OH$ consumption by Br^- in VUV photolysis forming another reactive radical (*viz.* $Br^- + {}^{\bullet}OH \rightarrow BrOH^{\bullet-}$) (Cheng et al., 2018).

Contrasting to the inhibition of CEX degradation by the Br^- addition, the k_{obs} value for NOF degradation gradually increased to 0.395 min^{-1} with Br^- concentration increasing from 0.05 to 0.25 mM. The unexpected enhancement of NOF degradation by Br^- addition was attributable to the electron-rich moieties of FQs with higher susceptibility toward reactive halogen species (RHS) radicals (Cheng et al., 2018). Thus, the participation of RHS radicals in the FQs degradation could offset the efficiency loss caused by $^{\bullet}OH$ scavenging (Grebel et al., 2010). Compared with the presence of single halide ions, the co-existence of chloride and bromide slightly increased the k_{obs} values under VUV irradiation, which was likely due to the conversion of non-selective $^{\bullet}OH$ to selective RHS radicals (primarily $ClBr^{\bullet-}$) (Heeb et al., 2014). As a result, owing to the more unsaturated bonds readily to be attacked by $^{\bullet}OH$, the degradation of FQs was much more susceptible to the presence of halides in VUV photolysis than CEX.

The effect of halides on the degradation of OFX in VUV/H_2O_2 and VUV/$K_2S_2O_8$ processes was examined and the results are shown in Fig. 5. As illustrated in Fig. 5a, the presence of Cl^- showed no obvious impact on OFX degradation in VUV/H_2O_2 and VUV/$K_2S_2O_8$ processes. This observation could result from the dynamic equilibrium between the formation and the dissociation of $ClOH^{\bullet-}$ (*viz.* $Cl^- + {}^{\bullet}OH \leftrightarrow ClOH^{\bullet-}$) ($k = 4.3 \times 10^9$ M^{-1} s^{-1}) such that the level of $^{\bullet}OH$ could be stabilized (Yin et al., 2018). For VUV/$K_2S_2O_8$ process, the addition of Br^- at low level (0.05 mM) promoted the degradation rate of OFX, even though the

halide ions have been well-known as primary scavengers of $^{\bullet}OH$ and $SO_4^{\bullet-}$ (equations 5-9) (Yang et al., 2014).

$$^{\bullet}OH + Br^- \leftrightarrow BrOH^{\bullet-} \quad (5)$$

$$BrOH^{\bullet-} + H^+ \leftrightarrow Br^{\bullet} + H_2O \quad (6)$$

$$Br^{\bullet} + Br^- \leftrightarrow Br_2^{\bullet-} \quad (7)$$

$$BrOH^{\bullet-} + Br^- \leftrightarrow Br_2^{\bullet-} + OH^- \quad (8)$$

$$SO_4^{\bullet-} + Br^- \leftrightarrow Br^{\bullet} + SO_4^{2-} \quad (9)$$

Interestingly, the co-existence of Cl^- and Br^- facilitated the highest degradation of OFX in both VUV/H_2O_2 and VUV/$K_2S_2O_8$ processes (Fig. 5b). As reported by Li et al. (2015), $ClBr^{\bullet-}$ possibly dominated the OFX degradation via the following reactions (equations 10-14),

$$Cl_2^{\bullet-} + Br^- \rightarrow ClBr^{\bullet-} + Cl^- \quad (10)$$

$$ClOH^{\bullet-} + Br^- \rightarrow ClBr^{\bullet-} + OH^- \quad (11)$$

$$Cl^{\bullet} + Br^- \rightarrow ClBr^{\bullet-} \quad (12)$$

$$BrOH^{\bullet-} + Cl^- \rightarrow ClBr^{\bullet-} + OH^- \quad (13)$$

$$Br^{\bullet-} + Cl^- \rightarrow ClBr^{\bullet-} \quad (14)$$

As a result, a variety of radical species including Br-containing radicals (especially $Br^{\bullet}$, $Br_2^{\bullet-}$, and $ClBr^{\bullet-}$), non-radicals (HOX, X_2, and X_3^-), and RHS radicals were formed in the presence of halides and possibly rendered the faster degradation of the antibiotics.

3.4. Optimization of chemical addition in VUV system based on RSM

The Box-Behnken experimental design consisted of 17 experiments with three independent variables: (1) solution pH, (2) initial concentration of H_2O_2, and (3) initial concentration of $K_2S_2O_8$. The k_{obs} values of OFX degradation within 1.5-min reaction from the 17 experiments are shown in Table 2. Multiple regression

analysis was employed to identify the relationship between the response and three variables. The results indicate that the model-predicted responses were in good agreement with the experimental data. The polynomial second order analysis (equation 15) illustrated the relationship between the response and the three variables,

$$Y = 2.37 - 0.071X_1 + 0.59X_2 + 0.69X_3 + 0.0084X_1X_2 - 0.055X_1X_3 - 0.18X_2X_3 - 0.25X_1^2 - 0.33X_2^2 \quad (15)$$

where Y is the predicted k_{obs} value of OFX degradation within 1.5-min reaction, and the X_1, X_2, and X_3 are the solution pH and initial concentrations of H_2O_2 and $K_2S_2O_8$, respectively.

The ANOVA analysis of the above model is provided in Table S4, and the F-value of 23.2 implied the model was accurate. The probability value (P) was employed to identify the significance of terms, which are considered as significant to the predicted response when $P < 0.05$. X_2, X_3, X_{12}, X_{22}, and X_{32} were significant ($P < 0.05$) for predicted response, while X_1, X_1X_2, X_1X_3, and X_2X_3 were insignificant ($P > 0.1$) model terms. The "Lack of Fit F-value" of 3.12 suggested the lack of fit was not significant relative to the pure error, which had a 15.0% chance of noise interruption and was fitted well by the model.

The determination coefficient (R^2) was used to confirm the suitability of the quadratic model. The value of adjusted R^2 was calculated as 0.926 (Fig. S1a). The standard error design of model H_2O_2 dose versus solution pH at fixed $K_2S_2O_8$ dose at central level (Fig. S1b) indicated that the design space could be directed by the proposed model. The data of Studentized residuals were distributed at either side of line homogeneously, indicating a satisfactory suitability of the proposed quadratic model in this work ($R^2 = 0.968$) (Fig S1c). To obtain the optimal conditions for the removal of OFX (Y), the 3D response surface plots were generated (Fig. 6) and used to investigate the influence of any two independent variables on the measured responses with one variable fixed at the central level.

Although solution pH was not an influencing parameter on the OFX removal in water, better removal efficiency was achieved in acidic solution. Alkaline condition was unfavorable for the antibiotic degradation

with $K_2S_2O_8$ addition. The Y increased with the increasing H_2O_2 and $K_2S_2O_8$ concentrations until Y reached the highest value. According to the optimization analysis (Table 2), the optimal value of each concentration for Y was both 1 mM when a single chemical agent was applied. As demonstrated in Section 3.2, however, increasing the single amount of H_2O_2 and $K_2S_2O_8$ has a limit in enhancing the degradation rate. As UV/H_2O_2 process could be enhanced at a low H_2O_2 concentration by the addition of $S_2O_8^{2-}$ due to more generation of $SO_4^{\bullet-}$ (Chu et al., 2006), it is worth simulating if the co-use of H_2O_2 and $K_2S_2O_8$ would be effective for the degradation of OFX under VUV irradiation before experimental validation. As a result, the optimal values of H_2O_2 and $K_2S_2O_8$ concentrations were found to be 0.82 and 0.97 mM under the co-existence condition. Given the simulation results, combinations of H_2O and $K_2S_2O_8$ in VUV process should be examined in an empirical way in order to maximize and accelerate the degradation of antibiotics in further study.

4. Implications for industrial applications

In a previous study, a pilot-scale UV/H_2O_2 system has been successfully run for over two months to remove 15 trace organic chemicals from the effluent of municipal wastewater treatment plant (Miklos et al., 2018). Nevertheless, when considering the known disadvantages of H_2O_2 (*e.g.*, corrosiveness of process water and self-disintegration loss during its transport), the use of $K_2S_2O_8$ is preferable for practical application. Moreover, for industrial application, it is very difficult to maintain the solution pH at 2-3 and after treatment the wastewater has to be neutralized before effluent discharge. The current study shows that the removal of antibiotics from waters can be achieved at neutral pH condition. Besides, previous research indicated that the VUV/$S_2O_8^{2-}$ system was a more proficient and economical ($6.26 /$m^3$ water) process for the removal of organics than other AOP (*e.g.*, heat-activated $S_2O_8^{2-}$, Fenton, photo-Fenton, UV/H_2O_2, and UV/PMS) methods (Dhaka et al., 2018). Based on the overall results, VUV/$K_2S_2O_8$ process appears to be a promising method for the degradation of CEX, OFX, and NOF in saline antibiotics-containing wastewaters.

5. Conclusions

The degradation rates of CEX, NOF, and OFX via various UV- and VUV-based processes were evaluated and compared. The degradation rates of OFX and NOF (fluoroquinolones) by the sole application of UV or VUV were inferior to that of CEX. The $K_2S_2O_8/H_2O_2$ assisted photolysis improved the antibiotics degradation, while $K_2S_2O_8$ was more effective than H_2O_2 with the observed rate constant (k_{obs}) (2.05-0.04 min^{-1}) decreasing in the following order: $VUV/K_2S_2O_8 > VUV/H_2O_2 > UV/K_2S_2O_8 > UV/H_2O_2 > VUV > UV$. The adverse effect (*i.e.*, $^{\bullet}OH$ loss by scavenging reaction) due to the excess use of H_2O_2 was not observed in $VUV/K_2S_2O_8$ process. The single presence of halide ions (Cl^- and Br^-) exhibited a negative impact on the NOF degradation by VUV photolysis, which was mitigated by co-existence of Cl^- and Br^-. However, the co-existence of halides accelerated the OFX degradation rate in VUV/H_2O_2 and $VUV/K_2S_2O_8$ processes due to the generation of abundant reactive radicals. The concentrations of H_2O_2 and $K_2S_2O_8$ were evaluated as critical variables and optimized for maximizing the OFX removal via RSM. This proposed AOP has advantages of less chemical input, fast kinetics, no sludge production, and high degree of mineralization, which can be considered as a cleaner treatment option for the elimination of recalcitrant pollutants in future work.

Acknowledgement

The authors appreciate the financial support from the Hong Kong Research Grants Council (PolyU 15217818 and E-PolyU503/17) for this study.

References

Ahmed, M.J. and Theydan, S.K., 2014. Fluoroquinolones antibiotics adsorption onto microporous activated carbon from lignocellulosic biomass by microwave pyrolysis. J. Taiwan Inst. Chem. E. 45, 219-226.

382 An, D., Westerhoff, P., Zheng, M., Wu, M., Yang, Y., Chiu, C.A., 2015. UV-activated persulfate oxidation and
383 regeneration of NOM-saturated granular activated carbon. Water Res. 73, 304-310.
384 Ao, X., Liu, W., Sun, W., Cai, M., Ye, Z., Yang, C., Lu, Z.D., Li, C., 2018. Medium pressure UV-activated
385 peroxymonosulfate for ciprofloxacin degradation: Kinetics, mechanism, and genotoxicity. Chem. Eng.
386 J. 345, 87-97.
387 Cheng, S.S., Zhang, X., Yang, X., Shang, C., Song, W., Fang, J., Pan, Y., 2018. The multiple role of bromide
388 ion in PPCPs degradation under UV/chlorine treatment. Environ. Sci. Technol. 52, 1806-1816.
389 Chu, W., Lau, T.K., Fung, S.C., 2006. Effects of combined and sequential addition of dual oxidants
390 ($H_2O_2/S_2O_8^{2-}$) on the aqueous carbofuran photodegradation. J. Agr. Food Chem. 54, 10047-10052.
391 Copete-Pertuz, L.S., Plácido, J., Serna-Galvis, E.A., Torres-Palma, R.A., Mora, A., 2018. Elimination of
392 Isoxazolyl-Penicillins antibiotics in waters by the ligninolytic native Colombian strain Leptosphaerulina
393 sp considerations on biodegradation process and antimicrobial activity removal. Sci. Total Environ. 630,
394 1195-1204.
395 Dhaka, S., Kumar, R., Lee, S.H., Kurade, M.B., Jeon, B.H., 2018. Degradation of ethyl paraben in aqueous
396 medium using advanced oxidation processes: Efficiency evaluation of UV-C supported oxidants. J.
397 Clean. Prod. 180, 505-513.
398 Fuku, K., Miyase, Y., Miseki, Y., Gunji, T., Sayama, K., 2016. Enhanced oxidative hydrogen peroxide
399 production on conducting glass anodes modified with metal oxides. Chemistryselect 1, 5721-5726.
400 Furatian, L. and Mohsenr, M., 2018. Influence of major anions on the 185 nm advanced oxidation process -
401 Sulphate, bicarbonate, and chloride. Chemosphere 201, 503-510.
402 García-Galán, M.J., Anfruns, A., Gonzalez-Olmos, R., Rodríguez-Mozaz, S., Comas, J., 2016. UV/H_2O_2
403 degradation of the antidepressants venlafaxine and O-desmethylvenlafaxine: Elucidation of their
404 transformation pathway and environmental fate. J. Hazard. Mater. 311, 70-80.

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. Chem. Eng. J. 317, 1012-1025.

Grebel, J.E., Pignatello, J.J., Mitch, W.A., 2010. Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters. Environ. Sci. Technol. 44, 6822-6828.

Guan, Y.H., Ma, J., Li, X.C., Fang, J.Y., Chen, L.W., 2011. Influence of pH on the formation of sulfate and hydroxyl radicals in the UV/peroxymonosulfate system. Environ. Sci. Technol. 45, 9308-9314.

Guo, Y., Tsang, D.C.W, Zhang, X., Yang, X., 2018. Cu(II)-catalyzed degradation of ampicillin: effect of pH and dissolved oxygen. Environ. Sci. Pollut. Res. 25, 4279-4288.

Gu, X., Lu, S., Qiu, Z., Sui, Q., Miao, Z., Lin, K., Liu, Y., Luo, Q., 2012. Comparison of photodegradation performance of 1, 1, 1-trichloroethane in aqueous solution with the addition of H_2O_2 or $S_2O_8^{2-}$ oxidants. Ind. Eng. Chem. Res. 51, 7196-7204.

Heeb, M.B., Criquet, J., Zimmermann-Steffens, S.G., Von Gunten, U., 2014. Oxidative treatment of bromide-containing waters: Formation of bromine and its reactions with inorganic and organic compounds - A critical review. Water Res. 48, 15-42.

He, X., Mezyk, S.P., Michael, I., Fatta-Kassinos, D., Dionysiou, D.D., 2014. Degradation kinetics and mechanism of beta-lactam antibiotics by the activation of H_2O_2 and $Na_2S_2O_8$ under UV-254 nm irradiation. J. Hazard. Mater. 279, 375-383.

Hou, D.Y, Qi, S., Zhao, B., Rigby, M., O'Connor, D., 2017. Incorporating life cycle assessment with health risk assessment to select the 'greenest' cleanup level for Pb contaminated soil. J. Clean. Prod. 162, 1157-1168.

House, D.A., 1962. Kinetics and mechanism of oxidations by peroxydisulfate. Chem. Rev. 62, 185-203.

Jin, J., Feng, T., Gao, R., Ma, Y., Wang, W., Zhou, Q., Li, A., 2018. Ultrahigh selective adsorption of zwitterionic PPCPs both in the absence and presence of humic acid: Performance and mechanism. J. Hazard. Mater. 348, 117-124.

Jin, Q., Wang, H., Hu, C., Chen, Z., Wang, X., 2018a. Effects of NOM on the degradation of chloramphenicol by UV/H_2O_2 and the characteristics of degradation products. Sep. Purif. Technol. 191, 108-115.

Jin, Q., Zhang, S., Wen, T., Wang, J., Gu, P., Zhao, G., Wang, X., Chen, Z., Hayat, T., Wang, X., 2018b. Simultaneous adsorption and oxidative degradation of Bisphenol A by zero-valent iron/iron carbide nanoparticles encapsulated in N-doped carbon matrix. Environ. Pollut. 243, 218-227.

Kosma, C.I., Lambropoulou, D.A., Albanis, T.A., 2015. Comprehensive study of the antidiabetic drug metformin and its transformation product guanylurea in Greek wastewaters. Water Res. 70, 436-448.

Lan, Y., Coetsier, C., Causserand, C., Serrano, K.G., 2017. On the role of salts for the treatment of wastewaters containing pharmaceuticals by electrochemical oxidation using a boron doped diamond anode. Electrochim. Acta. 231, 309-318.

Leung, H.W., Minh, T.B., Murphy, M.B., Lam, J.C.W., So, M.K., Martin, M., Lam, P.K.S., Richardson, B.J., 2012. Distribution, fate and risk assessment of antibiotics in sewage treatment plants in Hong Kong, South China. Environ. Int. 42, 1-9.

Liao, Q.N., Ji, F., Li, J. C., Zhan, X., Hu, Z.H., 2016. Decomposition and mineralization of sulfaquinoxaline sodium during UV/H_2O_2 oxidation processes. Chem. Eng. J. 284, 494-502.

Li, M., Wang, C., Yau, M., Bolton, J.R., Qiang, Z., 2017. Sulfamethazine degradation in water by the VUV/UV process: Kinetics, mechanism and antibacterial activity determination based on a mini-fluidic VUV/UV photoreaction system. Water Res. 108, 348-355.

Lin, C.C., Lin, H.Y., Hsu, L.J., 2016. Degradation of ofloxacin using UV/H_2O_2 process in a large photoreactor. Sep. Purif. Technol. 168, 57-61.

Li, W., Lu, S., Qiu, Z., Lin, K., 2011. UV and VUV photolysis vs. UV/H_2O_2 and VUV/H_2O_2 treatment for removal of clofibric acid from aqueous solution. Environ. Technol. 32, 1063-1071.

Li, Y., Song, W., Fu, W., Tsang, D.C.W., Yang, X., 2015. The roles of halides in the acetaminophen degradation by UV/H_2O_2 treatment: Kinetics, mechanisms, and products analysis. Chem. Eng. J. 271, 214-222.

Lofrano, G., Libralato, G., Casaburi, A., Siciliano, A., Iannece, P., Guida, M., Pucci, L., Dentice, E.F., Carotenuto, M., 2018. Municipal wastewater spiramycin removal by conventional treatments and heterogeneous photocatalysis. Sci. Total Environ. 624, 461-469.

MacDonald, M.J., Cho, D.W., Iris, K.M., Tsang, D.C.W., Yip, A.C., 2018. Photo-Fenton abatement of aqueous organics using metal-organic frameworks: An advancement from benchmark zeolite. Sci. Total Environ. 644, 389-397.

Márquez, G., Rodríguez, E.M., Beltrán, F.J., Álvarez, P.M., 2013. Determination of rate constants for ozonation of ofloxacin in aqueous solution. Ozone-Sci. Eng. 35, 186-195.

Matzek, L.W. and Carter, K.E., 2016. Activated persulfate for organic chemical degradation: A review. Chemosphere. 151, 178-188.

Miklos, D.B., Hartl, R., Michel, P., Linden, K.G., Drewes, J.E., Hübner, U., 2018. UV/H_2O_2 process stability and pilot-scale validation for trace organic chemical removal from wastewater treatment plant effluents. Water Res. 136, 169-179.

Mondal, S.K., Saha, A.K., Sinha, A., 2018. Removal of ciprofloxacin using modified advanced oxidation processes: Kinetics, pathways and process optimization. J. Clean. Prod. 171, 1203-1214.

Moussavi, G. and Shekoohiyan, S., 2016. Simultaneous nitrate reduction and acetaminophen oxidation using the continuous-flow chemical-less VUV process as an integrated advanced oxidation and reduction process. J. Hazard. Mater. 318, 329-338.

474 Moussavi, G., Pourakbar, M., Aghayani, E., Mahdavianpour, M., 2018a. Investigating the aerated VUV/PS
475 process simultaneously generating hydroxyl and sulfate radicals for the oxidation of cyanide in aqueous
476 solution and industrial wastewater. Chem. Eng. J. 350, 673-680.
477 Moussavi, G., Pourakbar, M., Shekoohiyan, S., Satari, M., 2018b. The photochemical decomposition and
478 detoxification of bisphenol A in the VUV/H_2O_2 process: Degradation, mineralization, and cytotoxicity.
479 Chem. Eng. J. 331, 755-764.
480 Moussavi, G., Rezaei, M., Pourakbar, M., 2018c. Comparing VUV and VUV/Fe^{2+} processes for
481 decomposition of cloxacillin antibiotic: Degradation rate and pathways, mineralization and by-product
482 analysis. Chem. Eng. J. 332, 140-149.
483 O'Connor, D., Hou, D., Ok, Y.S., Song, Y., Sarmah, A., Li, X., Tack, F.M., 2018. Sustainable in situ
484 remediation of recalcitrant organic pollutants in groundwater with controlled release materials: A review.
485 J. Control. Release. 283, 200-213.
486 Pourakbar, M., Moussavi, G., Shekoohiyan, S., 2016. Homogenous VUV advanced oxidation process for
487 enhanced degradation and mineralization of antibiotics in contaminated water. Ecotox. Environ. Safe.
488 125, 72-77.
489 Rodríguez-Chueca, J., Laski, E., García-Cañibano, C., de Vidales, M.M., Encinas, Á., Kuch, B., Marugán, J.,
490 2018. Micropollutants removal by full-scale UV-C/sulfate radical based Advanced Oxidation Processes.
491 Sci. Total Environ. 630, 1216-1225.
492 Shi, X., Leong, K.Y., Ng, H.Y., 2017. Anaerobic treatment of pharmaceutical wastewater: a critical review.
493 Bioresource Technol. 245, 1238-1244.
494 Song, Y.N., Hou, D.Y., Zhang, J.L., O'Connor, D., Li, G.H., Cu, Q.B., Li, S.P., Liu, P., 2018. Environmental
495 and socio-economic sustainability appraisal of contaminated land remediation strategies: A case study at
496 a mega-site in China. Sci. Total Environ. 610, 391-401.

497 Sun, J.T., Zeng, Q., Tsang, D.C.W., Zhu, L.Z., Li, X.D., 2017. Antibiotics in the agricultural soils from the
498 Yangtze River Delta, China. Chemosphere 189, 301-308.
499 Tian, X., Jin, H., Nie, Y., Zhou, Z., Yang, C., Li, Y., Wang, Y., 2017. Heterogeneous Fenton-like degradation
500 of ofloxacin over a wide pH range of 3.6-10.0 over modified mesoporous iron oxide. Chem. Eng. J. 328,
501 397-405.
502 Xie, P., Yue, S., Ding, J., Wan, Y., Li, X., Ma, J., Wang, Z., 2018. Degradation of organic pollutants by
503 Vacuum-Ultraviolet (VUV): Kinetic model and efficiency. Water Res. 133, 69-78.
504 Urbano, V.R., Peres, M.S., Maniero, M.G., Guimarães, J.R., 2017. Abatement and toxicity reduction of
505 antimicrobials by UV/H_2O_2 process. J. Environ. Manage. 193, 439-447.
506 Wang, H., Zhang, L., Hu, C., Wang, X., Lyu, L., Sheng, G., 2018. Enhanced degradation of organic pollutants
507 over Cu-doped $LaAlO_3$ perovskite through heterogeneous Fenton-like reactions. Chem. Eng. J. 332,
508 572-581.
509 Wang, G., Wang, D., Dong, X., Zhang, X., Ma, H., 2017. Sodium persulfate based PVDF membrane for
510 concurrent advanced oxidation and ultrafiltration of ofloxacin in water. Chem. Eng. J. 315, 509-515.
511 Wu, Z., Guo, K., Fang, J., Yang, X., Xiao, H., Hou, S.D, Kong, X.J., Shang, C., Yang, X., Meng, F.A., Chen,
512 L.W., 2017. Factors affecting the roles of reactive species in the degradation of micropollutants by the
513 UV/chlorine process. Water Res. 126, 351-360.
514 Yan, B. and Niu, C.H., 2018. Adsorption behavior of norfloxacin and site energy distribution based on the
515 Dubinin-Astakhov isotherm. Sci. Total Environ. 631-632, 1525-1533.
516 Yang, Y., Pignatello, J.J., Ma, J., Mitch, W.A., 2014. Comparison of halide impacts on the efficiency of
517 contaminant degradation by sulfate and hydroxyl radical-based advanced oxidation processes (AOPs),
518 Environ. Sci. Technol. 48, 2344-2351.
519 Yin, K., Deng, L., Luo, J., Crittenden, J., Liu, C., Wei, Y., Wang, L., 2018. Destruction of phenicol antibiotics

using the UV/H_2O_2 process: Kinetics, byproducts, toxicity evaluation and trichloromethane formation potential. Chem. Eng. J. 351, 867-877.

Yuval, A., Eran, F., Janin, W., Oliver, O., Yael, D., 2017. Photodegradation of micropollutants using V-UV/UV-C processes; Triclosan as a model compound. Sci. Total Environ. 601, 397-404.

Yu, X.Y., Bao, Z.C., Barker, J.R., 2004. Free radical reactions involving $Cl^{\bullet}$, $Cl_2^{-\bullet}$, and $SO_4^{-\bullet}$ in the 248 nm photolysis of aqueous solutions containing $S_2O_8^{2-}$ and Cl. J. Phys. Chem. A 108, 295-308.

Zhang, P., Hou, D.Y., O'Connor, D., Li, X., Pehkonen, S.O., Varma, R.S., Wang, X., 2018. Green and size-specific synthesis of stable Fe-Cu oxides as earth abundant adsorbents for malachite green removal. ACS Sustain. Chem. Eng. 6, 9229-9236.

Zhu, X., Tsang, D.C.W., Chen, F., Li, S., Yang, X., 2015. Ciprofloxacin adsorption on graphene and granular activated carbon: kinetics, isotherms, and effects of solution chemistry. Environ. Technol. 36, 3094-3102.