1 **Enhanced removal of antibiotics in hospital wastewater by Fe-ZnO activated**
2 **persulfate oxidation**

3
4 Gnougon Nina COULIBALY^{1,2}, Sungjun BAE², Joohyun KIM², Aymen Amin ASSADI¹,
5 Khalil HANNA^{1*}

6
7
8 ¹Univ. Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR-UMR 6226, F-
9 35000 Rennes, France

10 ²Department of Civil and Environmental Engineering, Konkuk University, 120 Neungdong-ro,
11 Gwangjin-gu, Seoul 05029, Republic of Korea

12
13 *Corresponding author: khalil.hanna@ensc-rennes.fr

Graphical Abstract

A recirculation reactor system using Fe-doped zinc oxide supported membrane and UVA irradiation was designed to remove fluoroquinolones in hospital wastewaters.

50Abstract

51Removal of two widely used antibiotics, flumequine (FLU) and ciprofloxacin (CIP), in
52synthetic and real hospital wastewaters was investigated using Fe-doped zinc oxide (Fe-ZnO)
53and UVA irradiation. The Fe-ZnO was supported on cellulose acetate membrane and integrated
54in a recirculation reactor system, designed for continuous oxidative treatment of contaminated
55wastewaters. Addition of low concentration of persulfate (e.g. 0.5 mM) improved considerably
56the degradation extent, where sulfate radicals were found to be the most involved oxidizing
57species. Oxidation rate constants decreased in mixture systems with respect to those of
58individual compounds, because of competition effects with radical species. Wastewater
59constituents like those found in hospital effluents affected the removal of both CIP and FLU,
60but CIP degradation is less impacted probably because of its higher reactivity with sulfate
61radicals. Inorganic anions altered slightly the oxidation rate, while the organic compounds
62commonly found in wastewaters considerably reduced the degradation efficiency. ZnO doped
63with Fe exhibited photoactivity higher than bare zinc oxide and a commercial TiO_2 , especially
64in hospital wastewater. The Fe-ZnO supported membrane can also be re-used for several
65oxidation runs, making this system quite suitable for larger applications in wastewater
66treatment processes.

67

68**Keywords:** antibiotics; supported catalysts; oxidation; hospital wastewater, recirculation
69reactor.

70

71

72

73

74

5

6

75

Water impact statement

76

77A recirculation reactor system was designed to remove fluoroquinolones (FQs) in hospital
78wastewaters. FQs containing cyclopropane/piperazine rings have shown greater reactivity with
79radical species, and is less impacted in multi-component wastewater systems, though natural
80organic matter affect considerably the degradation efficiency. This new system exhibited higher
81photoactivity than classical TiO_2 in wastewater and can be re-used for several oxidation cycles.

82

85Antibiotics, disinfectants, cytostatics, contrast agents, metals and other medicinal residues are
86present at significant concentrations in hospital wastewater.¹ Fluoroquinolones (FQs) represent
87the third largest group of antibiotic with an increased use in hospitals, households and
88veterinary.^{2,3} Among FQs, flumequine (FLU) and ciprofloxacin (CIP) can be found at relatively
89high concentrations in environmental settings. For instance, FLU can be detected at $6.9 \mu\text{g g}^{-1}$
90in soil and from 2.5 to 50 ng L^{-1} in aquatic environments.^{4,5} CIP concentration in treated
91hospital wastewater was found higher ($\sim 16 \mu\text{g L}^{-1}$) than in environmental systems
92($0.6 \mu\text{g L}^{-1}$).⁶⁻⁸ Although these compounds often co-exist with other inorganic and organic
93compounds, most of previous works have mainly focused on removal processes in mono-
94component systems, and in pure water or synthetic contaminated waters.⁹

95In order to remove antibiotics from wastewaters, advanced oxidation processes has attracted
96great attention through generation of reactive oxygen species (ROS).⁹⁻¹¹ Among these
97processes, photocatalysis has been widely used in order to remove organic compounds in
98contaminated waters. This process involves irradiation of semiconductor such as TiO_2 or ZnO ,
99and when energy photons are greater than the width of semiconductor gap band, electronic gaps
100(commonly called holes and noted h^+ and electron overload noted e^-) are created.¹¹⁻¹⁸ These
101charges migrate to the surface, act as electron donors or electron acceptors and initiate the
102redox reactions, generating radical species.¹² ZnO is considered as an environmentally friendly
103catalyst due to its non-toxic nature coupled with low cost.¹⁹ For TiO_2 or ZnO , the photocatalytic
104activity is, however, still suffering from lower quantum efficiency because of very fast
105recombination of photogenerated electron/hole pairs. To address this issue, incorporation of
106metallic (e.g. Fe)^{20,21} and non-metallic species²² have been proposed in order to enhance the
107photocatalytic activity. Although some studies were dedicated to the use of Fe-ZnO in
108decontamination reactions,^{20,21} much remains to be learned on the ability of this material to

effectively remove contaminant mixture and in real wastewaters. Indeed, very few investigations have been conducted to develop cost-effective methods for the elimination of antibiotics in multi-component systems, and much less in real wastewaters where target contaminants are found with many other colloidal or dissolved substances. Furthermore, supporting these reactive phases on materials such as membrane filters may offer great advantages for high-scale applications, especially in continuous wastewater treatment pilot.^{23–25}

In this study, the ability of iron doped-zinc oxide (Fe-ZnO) supported on cellulose acetate (CA) membrane to effectively remove two FQs, FLU and CIP, separately and in mixture was investigated under UV-A irradiation. Different water matrices [i.e., ultra-pure water (UPW), synthetic wastewater (SWW) and real hospital wastewater (RHW)] were used in order to test the impact of wastewater constituents on the removal performance. The CA membrane filter was selected as a support material because it is flexible, cheap and chemically stable in water. Fe-ZnO catalysts were characterized using high resolution-field emission scanning electron microscopy with energy dispersive X-ray (HR-FESEM-EDX), and X-ray diffraction (XRD). The effect of addition of oxidants such as hydrogen peroxide (H_2O_2), persulfate ion ($S_2O_8^{2-}$) on the removal kinetics of FLU and CIP was also investigated. Quenching experiments were conducted to identify the main reactive species in the investigated system. The reusability of iron doped-zinc oxide (Fe-ZnO) has been evaluated in successive oxidation cycles, and compared with a commercial TiO_2 under the same operational conditions.

128

1292. Material and methods

1302.1. Chemicals

Flumequine ($C_{14}H_{12}FNO_3$, purity > 98%), Ciprofloxacin ($C_{17}H_{18}FN_3O_3$, purity > 98%), zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, purity > 99%), iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, purity > 99.95 %), absolute ethanol (C_2H_5OH , 100%), iso-propanol (i-PrOH,

134C₃H₈O), *tert*-butanol (t-BuOH, C₄H₁₀O), potassium iodide (KI), sodium persulfate (Na₂S₂O₈),
135sodium chloride (NaCl), disodium phosphate (Na₂HPO₄), citric acid (C₆H₈O₇), ascorbic acid
136(C₆H₈O₆) and sucrose (C₁₂H₂₂O₁₁) were purchased from the Sigma–Aldrich chemical company.
137The standard Leonardite Humic acid (LHA) was provided by International Humic Substances
138Society (IHSS), hydrogen peroxide (35%, v/v), NaOH and HCl (37% extra pure) were provided
139from Acros Organics. Standard solutions were prepared with high-purity water obtained from a
140Millipore Milli-Q system with 18.2 MΩ cm resistivity. A cellulose support impregnated with
141TiO₂ (5 to 10 nm) made Ahlstrom company was used.

142

1432.2. Preparation and characterization of Fe-ZnO supported on CA membrane

144Solvothermal method was used to synthesize Fe-ZnO nanoparticles following a modified
145procedure of Jia et al. (2009).²⁶ Briefly, 0.86 g of zinc acetate dihydrate and different amount
146(0–1.4 % wt) of iron (III) nitrate nonahydrate was added to ethanol (60 mL) under vigorous
147stirring for 2 h at room temperature. At the same time, 2.4 g of NaOH was dissolved into 100
148mL ethanol, and then the prepared Fe-Zn solution was added into NaOH-ethanol solution by
149dropwise under constant stirring for 1 h. The mixed solution was transferred to Teflon-lined
150autoclave and thermo-treated for 20 h at 150 °C. The dried sample was collected by
151centrifugation and washed several times with water and ethanol. Finally, washed particles were
152dried for 15 h at 60°C and only Fe-ZnO nanoparticles were calcined for 2 h at 500 °C.

153In order to support Fe-ZnO nanoparticles on CA membrane filter, we followed the method
154previously reported in Zhao et al. (2016).²⁷ Different amounts of Fe-ZnO nanoparticles were
155dispersed in 100 mL ultra-pure water under ultra-sonication. Then, the suspension was filtered
156on a piece of CA membrane (64 mm in diameter and 0.45 μm in pore size). Lastly, the
157membrane was pressed under nitrogen gas of 0.3 MPa for 1 h and the Fe-ZnO/CA membrane
158was dried for 24 h at room temperature.

159The morphology and particle size of synthesized Fe-ZnO were identified by HR-FESEM
160(SU8010, Hitachi High Technologies Corporation) equipped with EDX. The mineral phases in
161Fe-ZnO were analyzed with XRD (JP/MAX-3C, Rigaku) in the range of 2-theta 10–90° at a
162scan speed of 2°/min.

1632.3. Recirculation reactor and degradation experiments

164The degradation of FQs using ZnO and Fe-ZnO was investigated using a recirculation glass
165reactor described in Fig. S1†. A peristaltic pump (Easy-Load Masterflex Head XX80 ELO 05)
166was used to circulate the contaminated solutions or wastewaters into the photoreactor
167continuously at a constant flow rate (222 mL min⁻¹). A UV-A lamp (PL-S 9W/10/2P; Philips, 9
168W) was used as a light source at intensity of 3.4 mW cm⁻² measured by Radiometer (VLX- 3W
169equipped with a sensor CX 365, ALYS Technologies, Switzerland). All photocatalytic
170experiments were performed under similar conditions at ambient temperature and initial pH 7.0
171± 0.2. The pH value determined at the end of the reactions showed a pH around 6.9±0.3. Total
1721 L of a 5 µM FLU and/or CIP solutions reacted with CA supported photocatalyst for 12 h in
173the dark condition to achieve the adsorption–desorption equilibrium prior to the photoreaction,
174then they were later exposed to UV irradiation for decontamination. At each time interval, 1.5
175mL of treated solution was collected to determine the concentration of each compound by high
176performance liquid chromatography (HPLC). In order to investigate the effect of water
177matrices for photo-oxidation of FLU and CIP, we prepared a synthetic wastewater as
178previously described.²⁸ A real hospital wastewater sample was provided by the University
179Hospital Center of Rennes (Rennes city, France).

180FLU and CIP concentrations were measured using an Alliance UV controller HPLC system
181equipped with an auto-sampler (Waters 717 plus), a C18 column (250 mm×4.6 mm i.d., 5 µm)
182and a UV detector (246 nm for FLU or 275 nm for CIP, Alliance UV 2489). The mobile phase

183 was a mixture of water/acetonitrile (55:45 v/v and 15:85 v/v for FLU and CIP respectively)
184 containing 0.1% of formic acid. The flow rate of the mobile phase was set at 1 mL min⁻¹ in an
185 isocratic mode. Total organic carbon (TOC) was determined using a TOC-meter (Shimadzu
186 TOC-VCSH). All experiments of kinetic reactions were conducted in triplicates and showed a
187 good reproducibility within 5% of relative standard deviation.

1883. Results and discussion

1893.1. Characterization of Fe-ZnO supported materials and UV-assisted oxidation 190 tests

191 XRD patterns showed that the crystallographic structure of Fe-ZnO (0.7 wt % Fe) correspond
192 to that of ZnO with no apparent iron oxides detected, probably due to the low detection limit of
193 XRD measurement (needed > 2 wt. %) (Fig. 1). However, SEM images showed the effect of Fe
194 on particle size and morphology of ZnO. Indeed, pure ZnO was nanowire in shape with 30-40
195 nm in diameter (Fig. 2a), while the presence of Fe caused a decrease of particle length but also
196 a modification of morphology, *i.e.* rectangular shape nanoparticles (Fig. 2b). Incorporation of
197 Fe³⁺ ions into ZnO lattice may suppress crystal growth leading to a decrease in particle size.²⁹
198 We also observed a successful deposition of Fe-ZnO nanoparticles on CA membrane (Fig. 2b).
199 Furthermore, the EDX analysis clearly showed the presence of Zn, Fe, O and their
200 homogeneous distribution on CA membrane (Fig. S2† and Table S1†).

201 The ability of different samples of Fe-ZnO (0, 0.07, 0.14, 0.28 and 0.7 wt % Fe) to remove
202 FLU was then tested under UV-A irradiation. Generally, the degradation kinetics of organic
203 compounds by reactive species is typically described by a second-order reaction:

204

$$\frac{d[Flu]}{dt} = -k[FLU][ROS] \quad (1)$$

where [ROS] is steady-state concentration of active species, [FLU] is concentration of FLU in water, k is the second-order rate constant, and t is the reaction time. By assuming that concentration of active species was constant, the degradation kinetics of FLU can be described by the pseudo-first-order equation:

$$[FLU](t) = [FLU]_0 \exp^{-k_{app} \cdot t} \quad (2)$$

Where k_{app} is obtained by linear regression of $\ln(C_t/C_0)$ versus time t .

The kinetic rate constant as well as the degradation efficiency increased with Fe content increased (Fig. 3a). It is worth noting that the initial rate constant calculated over the first stage of reaction (i.e., 5 h) is very close to the rate constant calculated over the entire reaction time, thereby supporting that the ROS concentration can be assumed constant for the entire duration of experiment (i.e. confirming the validity of eq. 2).

65% of FLU removal ($k_{app} = 0.042 \text{ h}^{-1}$) extent was observed in the absence of Fe (i.e., ZnO alone) indicating an activation of the semiconductor by UV-A light. Additional tests showed that removal of FLU by adsorption to supported solids is negligible. The direct photolysis of FLU under UV-A was less than 8% in 24 h ($k_{app} = 0.004 \text{ h}^{-1}$, Fig. S3†). Increase in Fe content to 0.7 wt % enhanced the FLU removal up to 80% ($k_{app} = 0.063 \text{ h}^{-1}$) after 24 h of reaction time. However, increasing the catalyst density from 7.77 to 15.54 g m⁻²/CA membrane with a constant Fe content (0.7 wt %), has no significant effect on the kinetic behavior (Fig S4†). Since the membrane surface is likely fully covered at 7.77 g m⁻², further increase in catalyst loading would form a multilayer-like aggregation on CA membrane, and therefore the amount of surface that is subject for irradiation remains unchanged in the recirculation reactor system.

The increase in Fe-ZnO activity under irradiation could be explained by the redox chemistry of

229iron and the high production of reactive oxygen species. Indeed, Fe acts as a trap for the
 230photogenerated charges, thereby preventing the electrons/holes recombination^{20,30} through one
 231or combination of two mechanisms : (i) Fe^{3+} ion can react with the photogenerated electrons
 232and be reduced to Fe^{2+} which subsequently reacts with the oxygen adsorbed on the
 233semiconductor surface to generate superoxide anion radical ($\text{O}_2^{\cdot-}$); (ii) Fe^{3+} ion could also react
 234with hole, resulting in formation of high valence iron (e.g. Fe^{4+}), which attacks directly the
 235target compounds or combines with the surface hydroxyl groups to produce the $\cdot\text{OH}$ radicals.
 236The involvement of hole and hydroxyl radicals in the FLU removal was confirmed here using
 237quenching experiments as previously described.^{16,19,21}

238Higher Fe content (i.e. > 0.7 wt %) inhibited the degradation process (data not shown), which
 239can be attributed to an increase in electron/hole recombination because of modification of
 240crystallinity and surface properties of catalysts.^{20,31}

241

2423.2. Impact of oxidant addition in single and binary systems

243The addition of oxidant [hydrogen peroxide (H_2O_2) or persulfate (PS)] to the reactor system
 244allowed faster removal kinetics (Fig.3b). Kinetic rate constants first increased with increasing
 245 H_2O_2 concentration and then decreased at higher oxidant dose. This typical behavior can be
 246explained by the scavenging effect of reactive species by an excess amount of H_2O_2 ($k_{\text{H}_2\text{O}_2, \cdot\text{OH}} =$
 247 $2.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$,³²). PS showed higher degradation rate constants, which continuously increased
 248with increasing PS concentration ($k_{app} = 0.184 \text{ h}^{-1}$ at 0.5 mM PS). This great removal efficiency
 249is probably due to the chemical activation of PS and generation of sulfate radicals. Formation
 250of the latter species ($\text{SO}_4^{\cdot-}$) was confirmed here using iso-propanol ($k_{i-\text{PrOH}, \cdot\text{OH}} = 1.9 \times 10^9 \text{ M}^{-1}$
 251 s^{-1} and $k_{i-\text{PrOH}, \text{SO}_4^{\cdot-}} = 4.742 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$)^{32,33} and t-butanol ($k_{t-\text{BuOH}, \cdot\text{OH}} = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$,
 252 $k_{t-\text{BuOH}, \text{SO}_4^{\cdot-}} = 4.84 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$),^{32,34} as specific scavengers in quenching experiments.³⁵⁻³⁷

Furthermore, the most involved radical species seem to form at the surface of solid, since addition of KI (known to react with surface bound radicals)^{38,39} completely inhibited the FLU removal in the Fe-ZnO/PS/UVA system (data not shown). Photochemical activation of oxidants without Fe-ZnO (i.e., 0.5 mM PS and 0.2 mM H₂O₂) showed lower kinetic rate constants (0.074 h⁻¹ and 0.005 h⁻¹) (Fig. S3‡).

Higher kinetic rate constants were observed for CIP than FLU (Fig. 4a), probably due to its strong reactivity with sulfate radicals ($k_{CIP,SO_4^{\cdot-}} = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ⁴⁰). Compounds containing cyclopropane and piperazine rings (e.g. CIP) have shown greater reactivity with radical species because the cleavage of the cyclopropane moiety via loss of one or two CH₂ units and the presence of piperazine ring containing two amine-N in which the lone pair electrons is conducive to a strong reaction with SO₄^{•-}.^{41,42} Compared to the single system, 1.5- and 1.8-fold decreases in degradation rate constant were observed for CIP and FLU in the mixture system (Fig. 4b), respectively, due probably to the competition effects of compounds towards reactive species.

267

3.3. Effect of water matrices

Removal kinetics of FLU or CIP in different water matrices (UPW, SWW, RHW) (See Table S2‡ for composition) were investigated under the optimal experimental condition (i.e., 0.5 mM PS, [Fe-ZnO] = 7.77 g m⁻² membrane). Significant inhibition of FLU degradation in SWW and RHW was observed, while degradation of CIP was reduced only in RHW (Fig. S5‡). Indeed, less than 7-fold decrease in k_{app} value was observed for FLU (0.184 h⁻¹ (UPW) to 0.025 h⁻¹ and 0.027 h⁻¹ in SWW and RHW, respectively), while less than 2-fold decrease was observed for CIP (UPW (0.943 h⁻¹), SWW (0.979 h⁻¹) and RHW (0.456 h⁻¹) (Fig. 5a). Similar degradation behavior was observed for FLU and CIP in the binary system (Fig. S6‡) where k_{app} values decreased in RHW (Fig. 5b), probably due to competition and/or scavenging effects of

278wastewater components. To address this issue, the competitive effects of organic and inorganic
 279compounds commonly found in wastewater were tested in the Fe-ZnO/PS/UVA system. A
 280significant inhibitive effect of organic compounds (i.e., sucrose, acetic acid, citric acid and
 281LHA) was observed, while inorganic species showed lesser impact on the FLU degradation
 282(Fig. 6). Indeed, the inorganic compounds (i.e., phosphate, nitrate, sulfate, and chloride) have
 283lower kinetic rate constants with sulfate and hydroxyl radicals at neutral pH ($k_{SO_4^{\cdot-}, HPO_4^{2-}} = 1.2 \times$
 284 $10^6 \text{ M}^{-1} \text{ s}^{-1}$,³³ $k_{OH^{\cdot}, HPO_4^{2-}} = 1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$,³² $k_{SO_4^{\cdot-}, NO_3^-} = 2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$,⁴³ $k_{SO_4^{\cdot-}, Cl^-} = 3.0 \times 10^8 \text{ M}^{-1}$
 285 s^{-1} ,⁴⁴ $k_{OH^{\cdot}, Cl^-} = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$,⁴⁵) in comparison with organic anions at the same pH ($k_{OH^{\cdot}, AH^-}$
 286 $= 1.2 \pm 0.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$,³² $k_{OH^{\cdot}, Sucrose} = 2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$,³²), AH^- represents ascorbate anion.
 287Therefore, inhibition of FLU degradation observed in RHW may be likely ascribed to the
 288presence of organic compounds (measured as 50 mg of TOC per L of RHW).

2893.4. Reusability tests in hospital wastewater

290Reusability of supported catalysts were investigated and compared with that of a conventional
 291photocatalyst (i.e. TiO_2) under similar experimental conditions in hospital wastewater (Fig. 7).
 292The same mass of Fe-ZnO and TiO_2 was used, though TiO_2 has much higher surface area than
 293Fe-ZnO (300 vs 15 $\text{m}^2 \text{ g}^{-1}$). In contrast to Fe-ZnO, activity of TiO_2 decreased significantly from
 294the second cycle test. This strong inhibition in TiO_2 photoactivity could be probably due to the
 295presence of organic and inorganic compounds in hospital wastewater which can affect the
 296(photo) chemical mechanisms on TiO_2 surfaces.

297As an attempt to assess the impact of these ligands, two experimental series were performed in
 298pure water containing the most common wastewater components. First, adsorption experiments
 299of inorganic ligands ($[Phosphate]_0 = 150 \text{ mg L}^{-1}$, $[Nitrate]_0 = 10 \text{ mg L}^{-1}$, $[Sulfate]_0 = 120 \text{ mg L}^{-1}$
 300and $[Chloride]_0 = 250 \text{ mg L}^{-1}$) were performed in the same reactor under dark and no-oxidative
 301conditions. The results revealed higher adsorbed amounts (expressed in mg of ligand per g of

302solid) of inorganic anions onto TiO_2 than Fe-ZnO (Fig. S7†). In the same way, the adsorbed
303amount of organic matter on TiO_2 (153 mgC of LHA per g of solid) was ~ 6 times higher than
304on Fe-ZnO (26 mgC/g). When normalized to surface area of solids, the opposite trend can be,
305however, observed. At neutral pH, TiO_2 surface is positively charged (point of zero charge pH
306= 6.20),⁴⁶ and thus able to sorb effectively anionic ligands species.⁹ In case of FLU ($pK_a = 6.5$),
307more FLU adsorption to TiO_2 results in better photocatalytic activity ($k_{app} = 0.264 \text{ h}^{-1}$) compared
308to Fe-ZnO (Fig. 8).

309In a second experimental series, removal rate constants of FLU were determined in presence of
310inorganic species and LHA separately at a concentration corresponding to that measured in
311hospital wastewater (Fig. 8). For both catalysts, the pseudo-first order rate constant decreased
312in presence of organic or inorganic compounds, but this fall is more pronounced in case of
313 TiO_2 , and particularly in presence of LHA. Indeed, kinetic rate constant decreases from $k_{app} =$
3140.264 h^{-1} to $k_{app} = 0.015 \text{ h}^{-1}$ in presence of LHA (40 mgC L^{-1}). LHA possesses a high oxidation
315state and high aromaticity, and contains oxygenated polycyclic aromatics and carboxylic
316compounds which have greater affinity to metal oxides.^{47–49} The binding of LHA compounds to
317metal-oxides may poison the catalyst surface and/or scavenge radical species.^{9,50}

318The dissolved iron concentration measured in solution at the end of oxidation run showed a
319very low release of Fe from Fe-ZnO (i.e. $< 0.1 \mu\text{M}$). In addition, XRD diffractogram recorded
320at the end of oxidation reaction was found to be quite similar with that recorded before reaction
321(Fig. 1). The stability of the catalytic activity of Fe-ZnO confirmed through reusability tests in
322successive oxidation cycles, could be partially attributed to the very low iron leaching during
323oxidation cycles and to the structural stability of the solid.

324

3254. Conclusion

326 We have notably demonstrated that the PS/Fe-ZnO/UV-A system can be effectively used for
327 the removal of fluoroquinolones antibiotics in hospital wastewater, and in a new recirculation
328 reactor system. Based on the probe and scavenging experiments, sulfate radicals were mainly
329 involved in the heterogeneous oxidation reaction. The higher degradation rate constant of CIP
330 relative to those of FLU could be explained by the high reactivity of $\text{SO}_4^{\cdot-}$ radical with
331 cyclopropane ring. Kinetic rate constants were found lower in binary systems with respect to
332 those of individual compounds. The most common inorganic anions found in wastewaters can
333 reduce the degradation efficiency, but they have much less impact compared to the organic
334 compounds. The organic ligands and natural organic matter exhibited strong inhibition effects
335 on TiO_2 activity compared to Fe-ZnO. The Fe-ZnO system exhibited better efficiency than
336 TiO_2 and especially in hospital wastewater, and can be re-used for several oxidation cycles.
337 Without ligands or organic matter, TiO_2 worked much better than Fe-ZnO, but when these
338 compounds were present, they exhibited strong inhibition effects on TiO_2 activity compared to
339 Fe-ZnO. The Fe-ZnO system exhibited better efficiency than TiO_2 in hospital wastewater and
340 can be re-used for several oxidation cycles. Therefore, we expect that the developed system
341 could be efficiently applied to remove antibiotics from contaminated waters, as a suitable
342 alternative to TiO_2 in wastewater treatment technologies.

343 Conflicts of interest

344 There are no conflicts to declare.

345

346 Acknowledgements

347 We thank the Ministère de l'Enseignement Supérieur et de la Recherche Scientifique of Ivory
348 Coast for a Ph.D. grant. This work was supported by Campus France (PHC-STAR program)
349 and the framework of International Cooperation Program managed by National Research
350 Foundation of Korea (NRF-2017K1A3A1A21013653).

351

352**Footnote**

353‡ Electronic supplementary information (ESI) associated with this article can be found, in the
354online version.

355

356References

- 3571 O. Frédéric and P. Yves, Pharmaceuticals in hospital wastewater: Their ecotoxicity and
358 contribution to the environmental hazard of the effluent, *Chemosphere*, 2014, **115**, 31–39.
- 3592 A. J. Watkinson, E. J. Murby, D. W. Kolpin and S. D. Costanzo, The occurrence of
360 antibiotics in an urban watershed: From wastewater to drinking water, *Sci. Total Environ.*,
361 2009, **407**, 2711–2723.
- 3623 S. Rodriguez-Mozaz, S. Chamorro, E. Marti, B. Huerta, M. Gros, A. Sánchez-Melsió, C. M.
363 Borrego, D. Barceló and J. L. Balcázar, Occurrence of antibiotics and antibiotic resistance
364 genes in hospital and urban wastewaters and their impact on the receiving river, *Water Res.*,
365 2015, **69**, 234–242.
- 3664 F. Tamtam, F. van Oort, B. Le Bot, T. Dinh, S. Mompelat, M. Chevreuil, I. Lamy and M.
367 Thiry, Assessing the fate of antibiotic contaminants in metal contaminated soils four years
368 after cessation of long-term waste water irrigation, *Sci. Total Environ.*, 2011, **409**, 540–547.
- 3695 F. Tamtam, F. Mercier, B. Le Bot, J. Eurin, Q. Tuc Dinh, M. Clément and M. Chevreuil,
370 Occurrence and fate of antibiotics in the Seine River in various hydrological conditions, *Sci.*
371 *Total Environ.*, 2008, **393**, 84–95.
- 3726 S. Castiglioni, F. Pomati, K. Miller, B. P. Burns, E. Zuccato, D. Calamari and B. A. Neilan,
373 Novel homologs of the multiple resistance regulator marA in antibiotic-contaminated
374 environments, *Water Res.*, 2008, **42**, 4271–4280.
- 3757 L. Kovalova, H. Siegrist, H. Singer, A. Wittmer and C. S. McArdell, Hospital Wastewater
376 Treatment by Membrane Bioreactor: Performance and Efficiency for Organic
377 Micropollutant Elimination, *Environ. Sci. Technol.*, 2012, **46**, 1536–1545.
- 3788 I. Michael, L. Rizzo, C. S. McArdell, C. M. Manaia, C. Merlin, T. Schwartz, C. Dagot and
379 D. Fatta-Kassinos, Urban wastewater treatment plants as hotspots for the release of
380 antibiotics in the environment: A review, *Water Res.*, 2013, **47**, 957–995.
- 3819 A. R. Lado Ribeiro, N. F. F. Moreira, G. Li Puma and A. M. T. Silva, Impact of water
382 matrix on the removal of micropollutants by advanced oxidation technologies, *Chem. Eng.*
383 *J.*, 2019, **363**, 155–173.
- 38410 G. Boczkaj and A. Fernandes, Wastewater treatment by means of advanced oxidation
385 processes at basic pH conditions: A review, *Chem. Eng. J.*, 2017, **320**, 608–633.

38611 D. B. Miklos, C. Remy, M. Jekel, K. G. Linden, J. E. Drewes and U. Hübner, Evaluation of
 387 advanced oxidation processes for water and wastewater treatment – A critical review, *Water*
 388 *Res.*, 2018, **139**, 118–131.

38912 S. Waclawek, V. V.T. Padil, M. Černík, Major Advances and Challenges in Heterogeneous
 390 Catalysis for Environmental Applications: A Review. *Ecol. Chem. Eng. S.* 2018, **25**, 9-34.

39113 M. Pelaez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G. Kontos, P. S. M. Dunlop,
 392 J. W. J. Hamilton, J. A. Byrne, K. O'Shea, M. H. Entezari and D. D. Dionysiou, A review on
 393 the visible light active titanium dioxide photocatalysts for environmental applications, *Appl.*
 394 *Catal. B Environ.*, 2012, **125**, 331–349.

39514 M. N. Chong, B. Jin, C. W. K. Chow and C. Saint, Recent developments in photocatalytic
 396 water treatment technology: A review, *Water Res.*, 2010, **44**, 2997–3027.

39715 K. M. Lee, C. W. Lai, K. S. Ngai and J. C. Juan, Recent developments of zinc oxide based
 398 photocatalyst in water treatment technology: A review, *Water Res.*, 2016, **88**, 428–448.

39916 N. Daneshvar, D. Salari and A. . Khataee, Photocatalytic degradation of azo dye acid red 14
 400 in water on ZnO as an alternative catalyst to TiO₂, *J. Photochem. Photobiol. Chem.*, 2004,
 401 **162**, 317–322.

40217 S. Sakthivel, B. Neppolian, M. V. Shankar, B. Arabindoo, M. Palanichamy and V.
 403 Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic
 404 efficiency of ZnO and TiO₂, *Sol. Energy Mater. Sol. Cells*, 2003, **77**, 65–82.

40518 C. Gomez-Solis, J. C. Ballesteros, L. M. Torres-Martínez, I. Juárez-Ramírez, L. A. Díaz
 406 Torres, M. Elvira Zarazua-Morin and S. W. Lee, Rapid synthesis of ZnO nano-corn-cobs
 407 from Nitral solution and its application in the photodegradation of methyl orange, *J.*
 408 *Photochem. Photobiol. Chem.*, 2015, **298**, 49–54.

40919 F. Sordello, I. Berruti, C. Gionco, M. C. Paganini, P. Calza and C. Minero, Photocatalytic
 410 performances of rare earth element-doped zinc oxide toward pollutant abatement in water
 411 and wastewater, *Appl. Catal. B Environ.*, 2019, **245**, 159–166.

41220 M. C. Paganini, A. Giorgini, N. P. F. Gonçalves, C. Gionco, A. Bianco Prevot and P. Calza,
 413 New insight into zinc oxide doped with iron and its exploitation to pollutants abatement,
 414 *Catal. Today*, 2019, **328**, 230–234.

41521 R. Saleh and N. F. Djaja, UV light photocatalytic degradation of organic dyes with Fe-doped
 416 ZnO nanoparticles, *Superlattices Microstruct.*, 2014, **74**, 217–233.

41722 L. Pan, T. Muhammad, L. Ma, Z.-F. Huang, S. Wang, L. Wang, J.-J. Zou and X. Zhang,
 418 MOF-derived C-doped ZnO prepared via a two-step calcination for efficient photocatalysis,
 419 *Appl. Catal. B Environ.*, 2016, **189**, 181–191.

42023 A. Rajeswari, S. Vismaiya and A. Pius, Preparation, characterization of nano ZnO-blended
 421 cellulose acetate-polyurethane membrane for photocatalytic degradation of dyes from water,
 422 *Chem. Eng. J.*, 2017, **313**, 928–937.

42324 P. S. Chauhan, R. Kant, A. Rai, A. Gupta and S. Bhattacharya, Facile synthesis of ZnO/GO
 424 nanoflowers over Si substrate for improved photocatalytic decolorization of MB dye and
 425 industrial wastewater under solar irradiation, *Mater. Sci. Semicond. Process.*, 2019, **89**, 6–
 426 17.

42725 L. Valenzuela, A. Iglesias, M. Faraldos, A. Bahamonde and R. Rosal, Antimicrobial surfaces
 428 with self-cleaning properties functionalized by photocatalytic ZnO electrosprayed coatings,
 429 *J. Hazard. Mater.*, 2019, **369**, 665–673.

43026 T. Jia, W. Wang, F. Long, Z. Fu, H. Wang and Q. Zhang, Fabrication, characterization and
 431 photocatalytic activity of La-doped ZnO nanowires, *J. Alloys Compd.*, 2009, **484**, 410–415.

43227 H. Zhao, S. Chen, X. Quan, H. Yu and H. Zhao, Integration of microfiltration and visible-
 433 light-driven photocatalysis on g-C₃N₄ nanosheet/reduced graphene oxide membrane for
 434 enhanced water treatment, *Appl. Catal. B Environ.*, 2016, **194**, 134–140.

43528 S. Babić, M. Periša and I. Škorić, Photolytic degradation of norfloxacin, enrofloxacin and
 436 ciprofloxacin in various aqueous media, *Chemosphere*, 2013, **91**, 1635–1642.

43729 S. Sriwichai, H. Ranwongsa, K. Wetchakun, S. Phanichphant and N. Wetchakun, Effect of
 438 iron loading on the photocatalytic performance of Bi₂WO₆ photocatalyst, *Superlattices*
 439 *Microstruct.*, 2014, **76**, 362–375.

44030 M. M. Ba-Abbad, A. A. H. Kadhum, A. B. Mohamad, M. S. Takriff and K. Sopian, Visible
 441 light photocatalytic activity of Fe³⁺-doped ZnO nanoparticle prepared via sol–gel technique,
 442 *Chemosphere*, 2013, **91**, 1604–1611.

44331 Priyanka and V. C. Srivastava, Photocatalytic Oxidation of Dye Bearing Wastewater by Iron
 444 Doped Zinc Oxide, *Ind. Eng. Chem. Res.*, 2013, **52**, 17790–17799.

44532 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, Critical Review of rate
 446 constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}$
 447 $^-$ in Aqueous Solution, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513–886.

44833 P. Neta, R. E. Huie and A. B. Ross, Rate Constants for Reactions of Inorganic Radicals in
449 Aqueous Solution, *J. Phys. Chem. Ref. Data*, 1988, **17**, 1027–1284.

45034 M. Anbar and P. Neta, A compilation of specific bimolecular rate constants for the reactions
451 of hydrated electrons, hydrogen atoms and hydroxyl radicals with inorganic and organic
452 compounds in aqueous solution, *Int. J. Appl. Radiat. Isot.*, 1967, **18**, 493–523.

45335 Y. Wu, A. Bianco, M. Brigante, W. Dong, P. de Sainte-Claire, K. Hanna and G. Mailhot,
454 Sulfate Radical Photogeneration Using Fe-EDDS: Influence of Critical Parameters and
455 Naturally Occurring Scavengers, *Environ. Sci. Technol.*, 2015, **49**, 14343–14349.

45636 E. M. Rodríguez, G. Márquez, M. Tena, P. M. Álvarez and F. J. Beltrán, Determination of
457 main species involved in the first steps of TiO₂ photocatalytic degradation of organics with
458 the use of scavengers: The case of ofloxacin, *Appl. Catal. B Environ.*, 2015, **178**, 44–53.

45937 M. Kamagate, A. Amin Assadi, T. Kone, L. Coulibaly and K. Hanna, Activation of
460 persulfate by irradiated laterite for removal of fluoroquinolones in multi-component systems,
461 *J. Hazard. Mater.*, 2018, **346**, 159–166.

46238 S. T. Martin, A. T. Lee and M. R. Hoffmann, Chemical mechanism of inorganic oxidants in
463 the TiO₂/UV process: increased rates of degradation of chlorinated hydrocarbons, *Environ.*
464 *Sci. Technol.*, 1995, **29**, 2567–2573.

46539 L. Xu and J. Wang, Magnetic Nanoscaled Fe₃O₄/CeO₂ Composite as an Efficient Fenton-
466 Like Heterogeneous Catalyst for Degradation of 4-Chlorophenol, *Environ. Sci. Technol.*,
467 2012, **46**, 10145–10153.

46840 M. Mahdi-Ahmed and S. Chiron, Ciprofloxacin oxidation by UV-C activated
469 peroxymonosulfate in wastewater, *J. Hazard. Mater.*, 2014, **265**, 41–46.

47041 C. Jiang, Y. Ji, Y. Shi, J. Chen and T. Cai, Sulfate radical-based oxidation of
471 fluoroquinolone antibiotics: Kinetics, mechanisms and effects of natural water matrices,
472 *Water Res.*, 2016, **106**, 507–517.

47342 H. Guo, T. Ke, N. Gao, Y. Liu and X. Cheng, Enhanced degradation of aqueous norfloxacin
474 and enrofloxacin by UV-activated persulfate: Kinetics, pathways and deactivation, *Chem.*
475 *Eng. J.*, 2017, **316**, 471–480.

47643 H. Gao, J. Chen, Y. Zhang and X. Zhou, Sulfate radicals induced degradation of Triclosan in
477 thermally activated persulfate system, *Chem. Eng. J.*, 2016, **306**, 522–530.

47844 Y. Yang, J. J. Pignatello, J. Ma and W. A. Mitch, Comparison of Halide Impacts on the
479 Efficiency of Contaminant Degradation by Sulfate and Hydroxyl Radical-Based Advanced
480 Oxidation Processes (AOPs), *Environ. Sci. Technol.*, 2014, **48**, 2344–2351.

48145 S. Khan, X. He, J. A. Khan, H. M. Khan, D. L. Boccelli and D. D. Dionysiou, Kinetics and
482 mechanism of sulfate radical- and hydroxyl radical-induced degradation of highly
483 chlorinated pesticide lindane in UV/peroxymonosulfate system, *Chem. Eng. J.*, 2017, **318**,
484 135–142.

48546 A. A. Dougna, B. Gombert, T. Kodom, G. Djaneye-Boundjou, S. O. B. Boukari, N. K. V.
486 Leitner and L. M. Bawa, Photocatalytic removal of phenol using titanium dioxide deposited
487 on different substrates: Effect of inorganic oxidants, *J. Photochem. Photobiol. Chem.*, 2015,
488 **305**, 67–77.

48947 K. Yang, D. Lin and B. Xing, Interactions of Humic Acid with Nanosized Inorganic Oxides,
490 *Langmuir*, 2009, **25**, 3571–3576.

49148 H. Kerndorff and M. Schnitzer, Sorption of metals on humic acid, *Geochim. Cosmochim.*
492 *Acta*, 1980, **44**, 1701–1708.

49349 S. Jayalath, H. Wu, S. C. Larsen and V. H. Grassian, Surface Adsorption of Suwannee River
494 Humic Acid on TiO₂ Nanoparticles: A Study of pH and Particle Size, *Langmuir*, 2018, **34**,
495 3136–3145.

49650 M. Drosos, M. Ren and F. H. Frimmel, The effect of NOM to TiO₂: interactions and
497 photocatalytic behavior, *Appl. Catal. B Environ.*, 2015, **165**, 328–334.

498

499

500

501

502**Fig. 1.** X-Ray Diffractograms of ZnO and 0.7 wt % Fe-ZnO before and after five consecutive
503oxidation runs in hospital wastewater.

504

505

506

507

508

509

510

511

512

513

514

Fig. 2. HR-FESEM images of (a): ZnO/CA membrane and (b): Fe-ZnO (0.7 wt % Fe)/CA membrane. Abbreviations: high resolution-field emission scanning electron microscopy with energy dispersive X-ray (HR-FESEM-EDX).

530

531**Fig. 3.** Kinetic rate constants, k_{app} of FLU removal as a function of (a) Fe loading on ZnO
 532supported catalyst and (b) oxidant concentration using 0.7 wt % Fe-ZnO catalyst. Experimental
 533conditions: [FLU]₀ = 5 μM, [catalyst] = 7.77 g m⁻² on CA membrane, UV-A reaction time = 24
 534h, pH₀ = 7.0 ± 0.2, V = 1 L, recirculation flow rate = 222 mL min⁻¹ (the correlation coefficients
 535were more than 0.99 for all experiments). Abbreviations: FLU = flumequine, PS = Persulfate,
 536H₂O₂ = hydrogen peroxide.

537

538

539

540

541

542

543

544

545

546**Fig. 4.** Degradation kinetics of FLU and CIP in single (a) and binary (b) systems under UV-A
 547irradiation. Experimental conditions: $[FLU]_0 = 5 \mu M$, $[0.7 \text{ wt } \% \text{ Fe-ZnO}] = 7.77 \text{ g m}^{-2} \text{ CA}$
 548membrane, UV-A reaction time = 24 h, $pH_0 = 7.0 \pm 0.2$, $V = 1 \text{ L}$, recirculation flow rate = 222
 549 ml min^{-1} . The correlation coefficients for kinetic model are more than 0.98 for all experiments.
 550Abbreviations: FLU = flumequine, CIP = ciprofloxacin, PS = persulfate.

551

552

553

554

555

556

557

558

559 **Fig. 5.** Kinetic rate constants of FLU and CIP degradation obtained in different water matrices
 560 in (a) single and (b) binary systems. Experimental conditions: $[FLU]_0 = [CIP]_0 = 5 \mu M$, $[Fe-$
 561 $ZnO] = 7.77 \text{ g m}^{-2}$ CA membrane, $[PS]_0 = 0.5 \text{ mM}$, UV-A reaction time = 24 h for CIP and
 562 FLU in UPW and 72 h for FLU in SWW and RHW, $pH_0 = 7.0 \pm 0.2$, $V = 1 \text{ L}$, recirculation
 563 flow rate = 222 mL min^{-1} (the correlation coefficients were more than 0.99 for all experiments).
 564 Abbreviations: FLU = flumequine and CIP = ciprofloxacin, PS = persulfate, UPW = Ultra-pure
 565 water, SWW = Synthetic wastewater, RHW = Real hospital wastewater.

566

567

568

569

570

571

572

573

574

575

576**Fig. 6:** Effect of inorganic ions and LHA (a) and organic ligands (b) on FLU removal using 0.7
 577wt % Fe-ZnO. Experimental conditions: $[FLU]_0 = 5\mu M$, $[PS]_0 = 0.5mM$, $pH_0 = 7.0 \pm 0.2$, $[Fe-$
 578 $ZnO] = 7.77 g m^{-2}$ CA membrane, $[Phosphate]_0 = 150 mg L^{-1}$, $[Nitrate]_0 = 10 mg L^{-1}$, $[Sulfate]_0$
 579 $= 120 mg L^{-1}$, $[Chloride]_0 = 250 mg L^{-1}$, $[LHA]_0 = 40 mgC L^{-1}$, $[Ascorbic acid]_0 = 30 mg L^{-1}$,
 580 $[Citric acid]_0 = 50 mg L^{-1}$, $[Sucrose]_0 = 100 mg L^{-1}$, reaction time = 24 h, $V = 1 L$, mass of
 581catalyst = 0.025 g, recirculation flow rate = $222 mL min^{-1}$. The correlation coefficients were
 582more than 0.98 for all experiments. Abbreviation: FLU = flumequine, PS = persulfate, LHA =
 583Leonardite Humic Acid.

584

585

586

587**Fig. 7.** Reusability cycles of Fe-ZnO in hospital wastewater. (a): 0.7 wt % Fe-ZnO and (b):
 588TiO₂. Experimental conditions: [FLU] ₀ = 5 μM, [PS] ₀ = 0.5 mM, mass of catalyst = 0.025 g,
 589UV-A reaction time = 72 h, pH ₀ = 7.0 ± 0.2, V = 1 L, recirculation flow rate = 222 mL min⁻¹.
 590The correlation coefficients were more than 0.98 for all experiments. Abbreviations: FLU =
 591flumequine, PS = Persulfate

592

593

594

595

596

597

598

599

600

601**Fig. 8:** Effect of humic acids and inorganic ligands on removal kinetics using 0.7 wt % Fe-ZnO
 602or TiO₂ under UVA irradiation. Experimental conditions: [FLU]₀ = 5 μM, [PS]₀ = 0.5 mM, pH₀
 603= 7.0 ± 0.2, [Phosphate]₀ = 150 mg L⁻¹, [Nitrate]₀ = 10 mg L⁻¹, [Sulfate]₀ = 120 mg L⁻¹,
 604[Chloride]₀ = 250 mg L⁻¹, [LHA]₀ = 40 mg C L⁻¹, reaction time = 24 h, V = 1 L, catalyst mass =
 6050.025 g, recirculation flow rate = 222 mL min⁻¹. Abbreviations: FLU = flumequine, PS =
 606persulfate, LHA = Leonardite Humic Acid.

607

608

609

610

611

612

613