Enhancement of iron-mediated activation of persulfate using catechin: From generation of reactive species to atenolol degradation in water

Yanlin Wu, Olivier Monfort, Wenbo Dong, Marcello Brigante, Gilles Mailhot

Enhancement of iron-mediated activation of persulfate using catechin: from generation of reactive species to atenolol degradation in water

Yanlin Wu[a,b,c], Olivier Monfort[b], Wenbo Dong[a,c], Marcello Brigante[b*], Gilles Mailhot[b]

[a]Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China

[b]Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France

[c]Shanghai institute of pollution control and ecological security, Shanghai 200092, China

[*]marcello.brigante@uca.fr ; 24 avenue Blaise Pascal,63178 Aubière Cedex, France

Abstract

Persulfate (PS) activation reaction, which forms sulfate radical ($SO_4^{\bullet-}$), can be used to degrade organic pollutants in water. However, a drawback of this reaction is that the regeneration of ferrous ions requires a high concentration of hydrogen peroxide (Fenton-like reaction) or use of UV radiation. Catechin (CAT), a non-toxic antioxidant of natural origin from tea, is used in this work to improve the sulfate radical-mediated degradation of atenolol (ATL, a model pollutant) in water using relatively low concentrations of reactive chemical species (less than 100 µM).

To the best of the author's knowledge, the direct effect of CAT on the oxidation state of iron, which is promoted by the reduction of ferric into ferrous ions with the enhancement of $SO_4^{\bullet-}$ formation in the presence of PS, is demonstrated for the first time. The enhancement versus inhibition effect of CAT and the chemical mechanism of the iron-based activation process are explained. Results show that UVA radiation, which is representative of solar light, accelerates the

initial degradation of ATL by more than 30% through ferric iron photolysis. Finally, a reaction mechanism leading to the formation of hydroxyl radicals ($HO^{\bullet}$) and $SO_4^{\bullet-}$ is proposed considering the implication of different activation/reaction chemical steps.

Keywords: Pollutant degradation, sulfate radical, hydroxyl radical, iron reduction

Highlights

- Catechin efficiently reduced ferric to ferrous ions in water
- The positive versus negative effect of CAT on the persulfate activation was assessed
- The degradation of atenolol was strongly improved in the presence of CAT
- A reaction mechanism considering the involvement of radical species was proposed

1. Introduction

The Fenton process based on the Fe(II/III) redox cycle in the presence of hydrogen peroxide was described for the first time in 1894 (Fenton, 1894) and has been used for the degradation of a wide range of organic contaminants. In the last decades, many works focusing on the modified Fenton-like process have been proposed to stabilize and generate additional Fe(II) species and improve the removal efficiency of organic contaminants in water (Kaur et al., 2019; Li et al., 2016; Romero et al., 2016; Tian et al., 2017). These modified reactions, such as ferric ion (Fe(III)) photoreduction or complexation with organic ligands, have also been used for persulfate (PS) activation to generate additional Fe(II) and sulfate radical ($SO_4^{\bullet-}$) (Bi et al., 2016; Jiang et al., 2017; Wu et al., 2015). Furthermore, the reaction mechanism was becoming increasingly clear, and the concentration of ferrous iron in water was found to be the most critical parameter.

Therefore, researchers investigated different technologies, such as reaction in acidic media (Velo Gala et al., 2014), use of irradiation (Giannakis et al., 2018; Hinojosa Guerra et al., 2019), presence of organic ligands (De Luca et al., 2015; Huang et al., 2013; Wang et al., 2019), and reduction conditions (Nazari et al., 2018; Wu et al., 2016), to enhance the Fe(II) formation/regeneration.

Antioxidant agents, such as polyphenolic compounds, are known for their anti-aging, anti-carcinogenetic, and anti-atherosclerotic properties (Brown et al., 2011). Green tea is rich in polyphenolic compounds, especially (+)-catechin (CAT) (Yang et al., 2018). CAT has catecholate groups that easily chelate Fe^{3+}, which makes it susceptible to undergo light-induced ligand oxidation and Fe^{3+} reduction (Barbeau, 2006; Barbeau et al., 2001). Dong et al. already used another polyphenolic compound (gallic acid), which played an important role on Fe(II) formation/regeneration and promoted the efficiency of H_2O_2/Fe(III) system in the degradation of methyl orange (Dong et al., 2016). However, we believe that studies assessing the mechanism of radical generation and reactivity through iron reduction have not been reported.

Atenolol (ATL), a widely used pharmaceutical which exhibits toxicity on freshwater species and inhibition on human embryonic cell growth, was selected as the target pollutant (de Jesus Gaffney et al., 2015). ATL is also considered a recalcitrant pollutant due to its slow biodegradation and high persistence under sunlight in water (Yamamoto et al., 2009). Under chlorination or UV treatment, ATL leads to the fast formation of products with high toxicity in water (DellaGreca et al., 2009; Diniz et al., 2015).

In the present work, the mechanism of $SO_4^{\bullet-}$ generation in the Fe(III)/PS system, as well as the formation of Fe(II) and ATL degradation, was investigated for the first time using CAT.

Interestingly, as a non-toxic extract from green tea, CAT shows high stability and solubility in water, which makes it a good candidate for contaminant removal application. The effect of CAT, Fe(III), and PS concentrations on the degradation efficiency of ATL was also studied, and the role of oxidative radicals as well as the second-order reaction rate constants with generated radicals ($HO^{\bullet}/SO_4^{\bullet-}$) was elucidated. An activation and reactivity system, in which CAT plays a key role, was proposed to assess the enhancement versus inhibition role of antioxidant agents as reduction species for iron but also as radical scavengers in water. Finally, the effect of solar spectrum UVA radiation on the CAT-mediated persulfate activation system was evaluated.

2. Materials and methods

2.1 Chemicals

Sodium persulfate ($Na_2S_2O_8$, PS), Atenolol (ATL), (+)-catechin (CAT), Ferrozine, isopropanol (2-Pr), and tert-Butanol (t-BuOH) were obtained from Sigma-Aldrich. Ferric perchlorate ($Fe(ClO_4)_3$) was obtained from Fluka. Perchloric acid ($HClO_4$) and sodium hydroxide were used to adjust the pH of the solutions. All chemicals were utilized without further purification. All solutions were prepared in milli-Q water (18.2 MΩ cm). Unless otherwise stated, all experiments were performed at pH 3.3 to maintain soluble iron in water (homogeneous reactivity).

2.2 Experimental Procedure

All experiments in the absence of light (dark) were conducted in a brown bottle at ambient temperature (298 ± 2 K). A total of 50 mL mixture was magnetically stirred during the reaction, and samples were withdrawn at fixed intervals. The samples were then analyzed using UV-vis

93 spectroscopy and high-performance liquid chromatography (HPLC-UV) (section 2.3). A total of
94 10 μM of ATL was used in all the experiments. The effect of different concentrations of CAT, PS,
95 and iron was investigated at pH approximately 3.3. Irradiation experiments were conducted in a
96 homemade photoreactor equipped with four UVA lamps (TLD 15W/05, Philips, Netherlands)
97 located on the top of the solution. The emission spectrum of the lamp is shown in Fig. S1.
98
99 *2.3 Quantitative analysis of ATL and iron*
100 The ATL concentration in the samples was determined using ultra-performance liquid
101 chromatography (UPLC) (Waters, USA) with C18 column (BEH, 100 mm × 2.1 mm × 1.7 μm),
102 and the mobile phase was an ammonium acetate (0.01 M)/methanol solution with 70:30 (v/v). The
103 flow rate was 0.25 $mLmin^{-1}$, and the detection wavelength was 224 nm. The CAT concentration
104 was determined by HPLC (Waters, USA) with C18 column (Agilent, 250 mm × 4.6 mm × 5 μm),
105 and the mobile phase was an acetonitrile/formic acid (0.5%) solution with 25:75 (v/v). The flow
106 rate was 0.6 mL min^{-1}, and the detection wavelength was 279 nm. Fe(II) was quantified using a
107 colorimetric method based on ferrozine complexation (Stookey, 1970).
108
109 *2.4 Second-order kinetic constants determination*
110 Two different methods were used to determine the second-order rate constant of ATL and CAT
111 with sulfate and hydroxyl radicals ($SO_4^{\bullet-}$ and $HO^{\bullet}$), respectively. For $HO^{\bullet}$, the transient absorption
112 spectroscopy was adopted to investigate the reactivity with CAT and ATL. In this approach, a laser
113 flash photolysis (LFP) system using an excitation wavelength of 266 nm coupled with UV-vis
114 detection could follow the radical absorption signal decay or its formation in the presence of

different CAT and ATL concentrations. Similar experimental procedures and conditions were already detailed in previous works, and only a brief description is provided in the SM section (Huang et al., 2018; Wu et al., 2015).

For the reactivity between $SO_4^{\bullet-}$ and ATL, the formation of a new transient species absorbed around 450 nm close to the signal of $SO_4^{\bullet-}$ interfered with the kinetic decay (Fig. S2). Hence, a different method using a competition kinetic approach under steady-state irradiation (UVA) in the presence of Bisphenol A (BPA) was used to determine the reactivity constant between $SO_4^{\bullet-}$ and ATL. Meanwhile, the reactivity constant between $SO_4^{\bullet-}$ and CAT of the transient-state absorption of $SO_4^{\bullet-}$ could be directly investigated.

3. Results and discussion

3.1 Reactivity of hydroxyl and sulfate radicals with ATL and CAT

The reactivity between ATL and CAT with generated radicals ($SO_4^{\bullet-}$/$HO^{\bullet}$) was determined to assess the effect of different reaction pathways during the Fenton-like reaction. For the reactivity between $SO_4^{\bullet-}$ and CAT, a solution containing 10 mM of PS was used to generate $SO_4^{\bullet-}$ under UVA irradiation (R1). BPA was used as a reference compound, and no direct photolysis under UVA irradiation was observed (Huang et al., 2018). A competition kinetic approach considering the decays of ATL and BPA concentrations during times (R2 and R3) was used to determine the second-order rate constant (R2 and R3) following Eq. 1.

$$S_2O_8^{2-} \xrightarrow{UVA} 2SO_4^{\bullet-} \quad \text{(R1)}$$

$$SO_4^{\bullet-} + ATL \rightarrow products_1 \qquad k_{SO_4^{\bullet-},ATL} \quad \text{(R2)}$$

$$SO_4^{\bullet-} + BPA \rightarrow products_2 \qquad k_{SO_4^{\bullet-},BPA} = 4.7 \times 10^9\ M^{-1}\ s^{-1}\ \text{(Huang et al., 2018)} \quad \text{(R3)}$$

The competition kinetic reaction gives:

$$\ln\frac{[ATL]_0}{[ATL]_t} = \frac{k_{SO_4^{\bullet-},ATL}}{k_{BPA,ATL}} \ln\frac{[BPA]_0}{[BPA]_t}, \qquad \text{(Eq1)}$$

where $[ATL]_0$ and $[BPA]_0$ were the initial concentrations (25 µM), and $[ATL]_t$ and $[BPA]_t$ were the remaining concentrations at time *t*. The slope of the linear fit of $\ln[ATL]_0/[ATL]_t$ versus $\ln[BPA]_0/[BPA]_t$ provided the second-order rate constant $k_{SO_4^{\bullet-},ATL}$ = (1.65 ± 0.25) × 10^9 M^{-1} s^{-1}. Other constants with $HO^{\bullet}$ were determined using chemical competition reactivity in the presence of thiocyanate anion (SCN^-), which led to the formation of di-thiocyanate radical anion ($SCN_2^{\bullet-}$) followed at 470 nm using LFP experiments (see SM for experimental procedure and Fig. S3).

CAT was found to be approximately twice more reactive with $SO_4^{\bullet-}$ and $HO^{\bullet}$ than ATL (Table 1). The high reactivity of CAT toward electron transfer reaction (main reactive pathway of $SO_4^{\bullet-}$) is attributed to the presence of two lone electron pairs on the phenolic groups. This high affinity with radical species also suggests a possible scavenging effect of CAT (*i.e.*, negative contribution) during the ATL degradation experiments.

3.2 Reactivity between Fe^{3+} and CAT

UV-vis spectroscopy was used to investigate the possible reactivity between CAT and ferric ions (Fe^{3+}) in the solution. A total of 100 µM CAT solution was found to be stable in dark condition at least five days. The spectroscopic analysis of solutions at different pH is presented in Fig. S4. From pH 2.5 to 6.0, no significant differences in the UV-vis spectra of CAT were observed, and the same absorption maximum at 279 nm was found (ε_{279} = (3610 ± 70) M^{-1} cm^{-1}). A bathochromic shift (from 279 nm to 290 nm) was observed when the pH increased from 7.8 to 11.3, and a shoulder appeared at 320 nm at a high pH. This redshift corresponded to the

159 deprotonation of phenolic groups on CAT occurrence at high pH values (pKa approximately 9.0).
160 In the presence of 100 µM of CAT at pH 3.3, the UV-vis spectrum of 100 µM solution of ferric
161 ions was strongly modified (Fig. 1); no additional absorption was observed at wavelengths higher
162 than 300 nm. The UV-vis spectrum of the solution indicated the absence of CAT in the solution,
163 whereas no spectroscopic contribution of Fe^{3+} was observed. Moreover, the UV-vis spectrum of
164 solution demonstrated a slight bathochromic shift compared with that of pure CAT. This effect was
165 due to the possible electron transfer from the phenolic groups of CAT to Fe^{3+}, leading to the
166 formation of quinone groups as previously observed during selective oxidation of CAT (Tanaka
167 and Kouno, 2003). No significant differences between the spectra of Fe^{3+} and Fe^{2+} in the presence
168 of CAT were observed (Fig. 1 insert).
169 The concentration of Fe^{2+} in the solution was monitored during the mixture of 100 µM of Fe^{3+}
170 with different CAT concentrations to clarify the interaction mechanism between CAT and Fe^{3+}. As
171 reported in Figure 2A, the formation of a significant amount of Fe^{2+} from Fe^{3+} solution (100 µM)
172 was strongly correlated to the initial CAT concentration. The plot of ratios between [Fe^{2+}] and
173 [Fe_{tot}] as function of initial CAT/Fe^{3+} concentrations ([CAT]/[Fe^{3+}]) reported in Figure 2B
174 indicated the significant formation of Fe^{2+}. Fe^{2+} immediately reached a plateau in all experiments.
175 This finding suggests that Fe^{3+} was quantitatively converted into Fe^{2+} following a reaction with a
176 stoichiometry (R4) of 1 mole of CAT with 2 moles of Fe^{3+}. To explain the ferrous ions generation,
177 we can consider that semiquinone and quinone (CAT_{ox}) might stepwise be formed with each step
178 being a single electron transfer from the two phenolic groups.
179
180 $2Fe^{3+} + CAT \rightarrow 2Fe^{2+} + CAT_{ox}$ (R4)

181

182 *3.3 Effect of CAT on the modified PS activation process*

183 *3.3.1 ATL degradation*

184 The reactivity of CAT (5 μM) in the solution containing 50 and 100 μM of Fe^{3+} and PS,
185 respectively, was investigated by monitoring the degradation of ATL and the formation of Fe^{2+}
186 during the reaction (Fig. 3). No ATL degradation was observed after 60 min in blank experiments,
187 that is, using ATL + PS, ATL + Fe^{3+}, ATL + CAT, ATL + PS + CAT, and ATL + Fe^{3+} + CAT;
188 meanwhile, only 10% degradation could be determined in the system Fe^{3+} + PS (Fig. 3). However,
189 in Fe^{2+} + PS system, a fast ATL initial degradation rate (R_{ATL}^{d}) was be observed during the first 10
190 min ($2.51\pm0.50 \times 10^{-7}$ M min^{-1}) and followed by a plateau. ATL (30%) was degraded in Fe^{2+} + PS
191 system after 60 min of reaction. This reactivity could be explained by considering the formation of
192 $SO_4^{\bullet-}$ through the well-known PS activation reaction (R5). The plateau was due to the fast
193 reactivity of Fe^{2+} in the system, while no additional Fe^{3+} could be converted back to Fe^{2+} without a
194 reducing agent. When 50 μM of Fe^{3+} was previously mixed with 5 and 100 μM of CAT and PS,
195 respectively, a similar trend was observed for the first 10 min ($R_{ATL}^{d} = 2.12 \pm 0.44 \times 10^{-7}$ M min^{-1}),
196 whereas ATL concentration continued to decrease by up to 52% of the initial concentration after
197 60 min (Fig. 3).

198 The enhancing effect observed in the presence of CAT could be explained by observing the Fe^{2+}
199 formation during the reaction (insert Fig. 3). As expected, approximately 10 μM of Fe^{2+} was
200 observed when 50 μM of Fe^{3+} was mixed with 5 μM of CAT (R4), and Fe^{2+}concentration
201 remained stable during its time in the ATL + Fe^{3+} + CAT system. However, when 100 μM of PS
202 was present in the solution (ATL + Fe^{3+} + CAT + PS), Fe^{2+} could activate PS for $SO_4^{\bullet-}$ formation

(R5), thereby leading to enhance ATL degradation (R6).

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet-} \quad \text{(R5)}$$

$$SO_4^{\bullet-} + ATL \rightarrow SO_4^{2-} + products \quad \text{(R6)}$$

The higher efficiency in the presence of CAT/Fe^{3+}/PS than that of Fe^{2+}/PS highlighted the role of CAT for the regeneration of Fe^{2+} during the process and its capability to activate the cycle between Fe^{2+} and Fe^{3+}.

3.3.2 Antagonist role of CAT and oxidant species occurrence

Although CAT could enhance $SO_4^{\bullet-}$ formation via Fe^{2+} generation, it could also scavenge generated radicals (Table 1), thus partially inhibiting the ATL degradation. The stability of CAT in the presence of Fe^{3+}, ATL, and PS is reported in Figure 4A. No direct reaction between CAT and ATL was observed. Meanwhile, slight CAT oxidation occurred in the presence of PS (approximately 25% after 1 h). However, approximately 75% of CAT was degraded in the presence of Fe^{3+} after 60 min (with a pseudo-first-order decay k`= 8.4 ± 1.3 × $10^{-2}$ $min^{-1}$) due to the oxidation corresponding to the formation of $Fe^{2+}$ through electron transfer reaction (R4). Complete degradation of CAT was achieved in the $Fe^{3+}$+PS system after 10 min (k`= 2.7 ± 0.5 × 10^{-1} min^{-1}) due to the reaction of generated $SO_4^{\bullet-}$ with CAT. When ATL was observed in the Fe^{3+} + PS system, CAT degradation slightly decreased (k`= 2.3 ± 0.1 × 10^{-1} min^{-1}) due to the competitive reaction of $SO_4^{\bullet-}$ with ATL. Therefore, finding the optimal concentration of CAT for efficient wastewater treatment and assessment of positive versus negative effect on modified

activation of PS is crucial.

ATL degradation was monitored using different CAT concentrations (from 0 to 25 μM) in the presence of 50 μM of Fe^{3+} and 100 μM of PS (Fig. 4B). When the CAT concentration was raised up to 5 μM, the pseudo-first-order decay of ATL ($k`_{ATL}$) increased by approximately two orders of magnitude (from 2.3×10^{-3} to 1.6×10^{-1} min^{-1}) (R5) through the formation of Fe^{2+} (R4) due to PS activation. The ATL degradation rate at 60 min was enhanced from 10% to 52% with CAT concentration up to 5 μM. When the CAT concentration was raised to 25 μM, the $k`_{ATL}$ decreased to 8.6×10^{-3} min^{-1}, and ATL degradation rate decreased to 32%. This negative effect observed at high CAT concentrations was attributed to the reactivity between CAT (or its oxidation products) and $SO_4^{\bullet-}$, which competed with ATL degradation. Given the second-order rate constants reported in Table 1, the initial ATL and CAT concentrations, and the similar reactivity of CAT oxidation products (reasonably quinone derivatives), the $SO_4^{\bullet-}$ selectivity on each reactive species in solution ($S_X^{SO_4^{\bullet-}}$ (%)) can be estimated as follows:

$$S_X^{SO_4^{\bullet-}}(\%) = \frac{k''_{SO_4^{\bullet-},X} \times [\mathrm{X}]}{\sum_i k''_{SO_4^{\bullet-},S_i} \times [S_i]} \times 100,$$

where [X] was the initial concentration of reference compounds, and $k''_{SO_4^{\bullet-},X}$ is the second-order rate constant with $SO_4^{\bullet-}$. $\sum_i k''_{SO_4^{\bullet-},S_i} \times [S_i]$ was calculated from the sum of the contribution of the initial concentration of all reactive species in the solution (i.e., CAT, PS, and ATL) with the second-order rate constant of $SO_4^{\bullet-}$.

Under adopted experimental conditions reported in Figure 4B, when CAT concentration was 5 μM, approximately 57% of $SO_4^{\bullet-}$ reacted with ATL while 43% reacted with CAT. However, in the presence of 25 μM of CAT, only 21% of $SO_4^{\bullet-}$ reacted with ATL and up to 79% reacted with CAT. In all experiments, less than 0.5% of $SO_4^{\bullet-}$ was scavenged by PS due to the low reactivity constant

($k''_{SO_4^{\bullet-},PS}$ = 1.2 × 10^6 M^{-1} s^{-1}) (Neta et al., 1988).

3.4 UVA effect on modified PS activation system

The effect of UVA irradiation on ATL degradation is reported in Figure 5 using different systems. No ATL degradation was observed under UVA with or without CAT (blank experiments not reported in Figure 5). However, approximately 10% and 35% of ATL degradation could be achieved after 60 min using either 100 µM of PS or 50 µM of Fe^{3+}, respectively. This process could be attributed to the UVA-mediated formation of $SO_4^{\bullet-}$ (PS photolysis) (R7) and $HO^{\bullet}$ (iron–aqua complex photolysis) (R8) in the solution. A redox cycle including $HO^{\bullet}$ and $SO_4^{\bullet-}$ enhanced the ATL degradation with the presence of PS and Fe^{3+} in the solution. The ATL degradation extent was increased from 52% to 80% in the presence of UVA in the system containing 10 µM of ATL mixed with 5 µM of CAT, 50 µM of Fe^{3+}, and 100 µM of PS.

$$S_2O_8^{2-} \xrightarrow{UVA} SO_4^{\bullet-} + SO_4^{\bullet-} \quad \text{(R7)}$$

$$Fe^{3+} + H_2O \xrightarrow{UVA} Fe^{2+} + H^+ + HO^{\bullet} \quad \text{(R8)}$$

Thus, high efficiency was observed in the presence of light. This finding indicates the presence of an important complementarity between the formation of Fe^{2+} through Fe^{3+} reduction by UVA radiation and CAT.

3.5 Radical species involvement

Scavenging experiments were performed by using isopropanol (2-Pr) and tert-butanol (t-BuOH) to assess the involvement of different radical species during ATL degradation in the presence of Fe^{3+}

and PS. Meanwhile, 2-Pr was used as a quencher of $HO^{\bullet}$ and $SO_4^{\bullet-}$ ($k_{2\text{-Pr},HO^{\bullet}}$ = 1.9 × 10^9 M^{-1} s^{-1}, $k_{2\text{-Pr},SO_4^{\bullet-}}$ = 6.9 × 10^7 M^{-1} s^{-1}), and t-BuOH selectively reacted with $HO^{\bullet}$ rather than with $SO_4^{\bullet-}$ due to differences between reactivity constants of the two radicals ($k_{BuOH,HO^{\bullet}}$ = 6.0 × 10^8 M^{-1} $s^{-1}$and $k_{BuOH,SO_4^{\bullet-}}$ = 8.4 × 10^5 M^{-1} s^{-1}) (Buxton et al., 1988; Neta et al., 1988). A concentration of 10 mM of each scavenger was adopted to trap specific radical species (in the case of (t-BuOH) efficiently also considering the possible competition effect of CAT in the solution.

The effect of 2-Pr and t-BuOH was compared when 10 µM of ATL was used in the presence of 5 µM of CAT, 50 µM of Fe^{3+}, and 100 µM of PS at pH = 3.3. No significant difference in ATL degradation was observed with t-BuOH (for both system k` approximately 1.2 ± 0.1 × $10^{-2}$ $min^{—1}$) (Figure 6A). By contrast, the ATL degradation was completely inhibited using 2-Pr, indicating that only $SO_4^{\bullet-}$ was generated under dark conditions. Under UVA irradiation (Fig. 6B), the ATL degradation was partially inhibited with t-BuOH (k` without scavengers = 3.2 ± 0.3 × 10^{-2} min^{-1} and k` with t-BuOH = 1.8 ± 0.2 × 10^{-2} min^{-1}). However, almost no degradation could be observed in the presence of 2-Pr. Considering the reactivity constants of radical with ATL and scavengers, approximately 77% and 23% of ATL degradation under UVA were attributed to $SO_4^{\bullet-}$ and $HO^{\bullet}$, respectively. The generation of the two radicals was considered an asset for the degradation of water containing different kind of pollutants.

4. Conclusions

Ferrous iron was the key parameter in PS activation processes, and many efforts have been made in the direction of formation/regeneration of reactive species under different conditions. For the first time, the present work investigated the use of CAT, a non-toxic and natural antioxidant, on the

reduction capability of Fe^{3+} into Fe^{2+} in a modified PS activation process (Fe^{3+}/CAT/PS). An optimal concentration of CAT (5 µM) was utilized for systems containing 50 µM of Fe^{3+} and 100 µM of PS to limit the competitive reaction with generated radicals and target pollutant (ATL). Under such low concentration conditions, the high degradation extent of 10 µM ATL could be achieved in the dark after 60 min (approximately 50%). CAT was complementary to PS in the reduction/oxidation cycle of Fe(III)/Fe(II). Under UVA irradiation, the modified PS activation process was enhanced and reached almost 80% of ATL degradation. Moreover, the only reactive species involved in the dark conditions was the $SO_4^{\bullet-}$. Meanwhile, $HO^{\bullet}$ also contributed up to approximately 25% of the total radical generation under UVA. Moreover, products from waste green tea leaves were proven useful in Fe(III) reduction to produce Fe(II). This work strengthened the possible use of waste (tea leaves) for water application treatments.

ACKNOWLEDGMENTS

Authors acknowledge financial support from National Natural Science Foundation of China (NSFC 21607116), the Region Council of Auvergne Rhône Alpes, and the "Fédérationdes Recherchesen Environnement" through the CPER "Environment" founded by the Region AURA, the French government, the FEDER from the European Community and PRC program CNRS/NSFC n°270437, and the CAP 20-25 I-site project.

References

Barbeau K., 2006. Photochemistry of organic iron(III) complexing ligands in oceanic systems. Photochem. Photobiol. 82, 1505-1516.

Barbeau K., Rue E.L., Bruland K.W., Butler A., 2001. Photochemical cycling of iron in the surface ocean mediated by microbial iron(III)-binding ligands. Nature 413, 409-413.

Bi W., Wu Y., Wang X., Zhai P., Dong W., 2016. Degradation of oxytetracycline with SO_4^- under simulated solar light. Chem. Eng. J. 302, 811-818.

Brown A.L., Lane J., Holyoak C., Nicol B., Mayes A.E., Dadd T., 2011. Health effects of green tea catechins in overweight and obese men: a randomised controlled cross-over trial. Br. J. Nutr. 106, 1880-9.

Buxton G.V., Greenstock C.L., Helman W.P., Ross A.B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (°OH/O°-) in aqueous solution. J. Phys. Chem. Ref. Data 17, 513-886.

de Jesus Gaffney V., Almeida C.M.M., Rodrigues A., Ferreira E., Benoliel M.J., Cardoso V.V., 2015. Occurrence of pharmaceuticals in a water supply system and related human health risk assessment. Water Res. 72, 199-208.

De Luca A., Dantas R.F., Esplugas S., 2015. Study of Fe(III)-NTA chelates stability for applicability in photo-Fenton at neutral pH. Appl. Catal., B 179, 372-379.

DellaGreca M., Iesce M.R., Pistillo P., Previtera L., Temussi F., 2009. Unusual products of the aqueous chlorination of atenolol. Chemosphere 74, 730-734.

Diniz M.S., Salgado R., Pereira V.J., Carvalho G., Oehmen A., Reis M.A.M., et al., 2015. Ecotoxicity of ketoprofen, diclofenac, atenolol and their photolysis byproducts in zebrafish (Danio rerio). Sci. Total Environ. 505, 282-289.

Dong H., Sans C., Li W., Qiang Z., 2016. Promoted discoloration of methyl orange in H_2O_2/Fe(III) Fenton system: Effects of gallic acid on iron cycling. Sep. Purif. Technol. 171, 144-150.

Fenton H.J.H., 1894. LXXIII.—Oxidation of tartaric acid in presence of iron. J. Chem. Soc. Trans. 65, 899-910.

Giannakis S., Le T.-T.M., Entenza J.M., Pulgarin C., 2018. Solar photo-Fenton disinfection of 11 antibiotic-resistant bacteria (ARB) and elimination of representative AR genes. Evidence that antibiotic resistance does not imply resistance to oxidative treatment. Water Res. 143, 334-345.

Hinojosa Guerra M.M., Oller Alberola I., Malato Rodriguez S., Agüera López A., Acevedo Merino A., Lopera A.E.-C., et al., 2019. Oxidation mechanisms of amoxicillin and paracetamol in the photo-Fenton solar process. Water Res. 156, 232-240.

Huang W., Bianco A., Brigante M., Mailhot G., 2018. UVA-UVB activation of hydrogen peroxide and persulfate for advanced oxidation processes: Efficiency, mechanism and effect of various water constituents. J. Hazard. Mater. 347, 279-287.

Huang W., Brigante M., Wu F., Mousty C., Hanna K., Mailhot G., 2013. Assessment of the Fe(III)–EDDS complex in Fenton-like processes: From the radical formation to the degradation of Bisphenol A. Environ. Sci. Technol. 47, 1952-1959.

Jiang M., Lu J., Ji Y., Kong D., 2017. Bicarbonate-activated persulfate oxidation of acetaminophen. Water Res. 116, 324-331.

Kaur B., Kuntus L., Tikker P., Kattel E., Trapido M., Dulova N., 2019. Photo-induced oxidation of ceftriaxone by persulfate in the presence of iron oxides. Sci. Total Environ. 676, 165-175.

Li R., Zhao C., Yao B., Li D., Yan S., O'Shea K.E., et al., 2016. Photochemical transformation of aminoglycoside antibiotics in simulated natural waters. Environ. Sci. Technol. 50, 2921-2930.

Nazari R., Rajic L., Xue Y., Zhou W., Alshawabkeh A.N., 2018. Degradation of 4-chlorophenol in aqueous solution by

356 sono-electro-Fenton process. Int. J. Electrochem. Sci. 13, 9214-9230.

357 Neta P., Hule R.E., Ross A.B., 1988. Rate constant for reactions of inorganic radicals in aqueous solution. J. Phys. Chem.

358 Ref. Data 17, 1027-1284.

359 Romero V., Acevedo S., Marco P., Giménez J., Esplugas S., 2016. Enhancement of Fenton and photo-Fenton processes

360 at initial circumneutral pH for the degradation of the β-blocker metoprolol. Water Res. 88, 449-457.

361 Stookey L.L., 1970. Ferrozine - a new spectrophotometric reagent for iron. Anal. Chem. 42, 779-781.

362 Tanaka T., Kouno I., 2003. Oxidation of tea catechins: Chemical structures and reaction mechanism. Food Sci. Technol.

363 Res. 9, 128-133.

364 Tian X., Jin H., Nie Y., Zhou Z., Yang C., Li Y., et al., 2017. Heterogeneous Fenton-like degradation of ofloxacin over a

365 wide pH range of 3.6–10.0 over modified mesoporous iron oxide. Chem. Eng. J. 328, 397-405.

366 Velo Gala I., López‐Peñalver J., Sánchez-Polo M., Rivera-Utrilla J., 2014. Comparative study of oxidative degradation

367 of sodium diatrizoate in aqueous solution by H_2O_2/Fe^{2+}, H_2O_2/Fe^{3+}, Fe (VI) and UV, H_2O_2/UV, $K_2S_2O_8$/UV.

368 Chem. Eng. J. 241, 504-512.

369 Wang X., Dong W., Brigante M., Mailhot G., 2019. Hydroxyl and sulfate radicals activated by Fe(III)-EDDS/UV:

370 Comparison of their degradation efficiencies and influence of critical parameters. Appl. Catal., B 245,

371 271-278.

372 Wu T., Wu C., Xiang Y., Huang J., Luan L., Chen S., et al., 2016. Kinetics and mechanism of degradation of chitosan by

373 combining sonolysis with H_2O_2/ascorbic acid. RSC Adv. 6, 76280-76287.

374 Wu Y., Bianco A., Brigante M., Dong W., de Sainte-Claire P., Hanna K., et al., 2015. Sulfate radical photogeneration

375 using Fe-EDDS: Influence of critical parameters and naturally occurring scavengers. Environ. Sci. Technol. 49,

376 14343-14349.

377 Yamamoto H., Nakamura Y., Moriguchi S., Nakamura Y., Honda Y., Tamura I., et al., 2009. Persistence and partitioning

of eight selected pharmaceuticals in the aquatic environment: Laboratory photolysis, biodegradation, and sorption experiments. Water Res. 43, 351-362.

Yang H., Xue X., Li H., Apandi S.N., Tay-Chan S.C., Ong S.P., et al., 2018. The relative antioxidant activity and steric structure of green tea catechins - A kinetic approach. Food Chem. 257, 399-405.

Figure captions

Figure 1: UV-vis spectra of CAT 100 µM, Fe^{3+} 100µM and CAT + Fe^{3+} (both at 100µM) in water solution at pH 3.3.

Figure 2: (A) Formation of Fe^{2+} from 100 µM of Fe^{3+} using different CAT concentrations for 1 hour. (B)Correlation between ratios $[Fe^{2+}]/[Fe_{tot}]$ and$[CAT]/[Fe^{3+}]$. Values are determined after 2 min in order to ensure that reduction of Fe^{3+} due to the reactivity of CAT is achieved.

Figure 3: Degradation of ATL (10 µM)using different solution in which 5 µM of CAT are mixed with 50 µM of Fe^{2+} or $Fe^{3+}$and/or 100 µM of PS at pH = 3.3. Insert:Formation of $Fe^{2+}$when $Fe^{3+}$and CAT are mixed in the presence and in the absence PS.

Figure 4: CAT stability (A) by monitoring its degradation under different conditions (10µM ATL, 50µM Fe^{3+} and 100µM PS) and (B) by analyzing the pseudo-first order decay of 10µM ATL using various CAT concentration (from 0 to 25µM). Insert: corresponding degradation curves of ATL as a function of CAT concentration.

Figure 5 : Effect of UVA radiation on the ATL (10 µM) degradation in different solutions containing 5 µM of CAT, 50 µM of Fe^{3+} and 100 µM of PS at pH 3.3.

Figure 6: Scavenging experiments using 10 mM of 2-Pr ort-BuOH under dark (**A**) and UVA (**B**) experiments.10 µM of ATL are mixed with 5 µM of CAT, 50 µM of Fe^{3+} and 100 µM of PS at pH

407 3.3.

408