Mineralization of pentachlorophenol by ferrioxalate-assisted solar photo-Fenton process at mild pH

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Abstract

This work reports the use of ferrioxalate complexes to assist solar photo-Fenton treatment of pentachlorophenol (PCP) in aqueous medium at mild pH, which inhibits the precipitation of iron hydroxides and allows working at a low iron dosage. The experimental parameters were optimized by assessing the effect of initial concentrations of H_2O_2 (0-2.5 mM) and Fe(II) (2-10 mg/L), pH (3.0-9.0) and iron/oxalic acid molar ratios (1:0-1:13.5) on total organic carbon (TOC) removal. Ferrioxalate-assisted solar photo-Fenton achieved 97.5% mineralization in 120 min, clearly outperforming conventional Fenton and solar photo-Fenton. The presence of photosensitive ferrioxalate complexes accounted for the enhancement, as a result of Fe(II) regeneration that accelerated the hydroxyl radical ($^{\bullet}OH$) production. The time course of H_2O_2 and Fe(II) concentrations was evaluated under different iron/oxalic acid ratios. The five carboxylic acids determined by ion-exclusion HPLC and the eight aromatic by-products identified by GC-MS allowed the proposal of a degradation pathway that included hydroxylation, dechlorination and dimerization steps. Complete chloride ion release was achieved after 90 min of treatment.

Keywords: Ferrioxalate complexes; Mild pH; Mineralization; Pentachlorophenol; Solar photo-Fenton

1. Introduction

Chlorophenols, listed as priority pollutants by most water directives worldwide due to their high toxicity, are still massively employed in industrial and agricultural activities (Hechmi et al., 2016; Khuzwayo and Chirwa, 2017). Pentachlorophenol (PCP, C_6HCl_5O), the highest chlorinated phenol, is widely used as herbicide, fungicide, insecticide and disinfectant, showing main applications in agriculture, wood preservation and industry (Amendola et al., 2017; Tsoufis et al., 2017). Although large-scale manufacture and application of PCP have been banned in Taiwan and mainland China since 1984 and 1997, respectively, its presence in water and soil has been regularly reported in the last three decades (Shih et al., 2016). Due to its long-term persistence, high toxicity and carcinogenicity, wastewater contaminated with PCP must be conveniently treated before being discharged or reused (Cui et al., 2017).

The solubility of PCP, with $pK_a = 4.75$ (He et al., 2015; Guemiza et al., 2017), is highly dependent on pH, being low at pH < 5.0 (≤ 14 mg/L) but very high at pH > 6.0 (> 100 mg/L) since its anionic form is predominant. As a result, it has been detected in industrial wastewater of pH 9.0 at a concentration of 490 mg/L (Rahmani et al., 2018). Various technologies have been developed for the treatment of PCP in water, including biodegradation (Khan et al., 2017), adsorption (Zhou et al., 2014), chemical oxidation and reduction (Shih et al., 2016), electrochemical oxidation (Niu et al., 2013) and photocatalysis (Khuzwayo and Chirwa, 2017). Unfortunately, most of these methods exhibit several weaknesses like long treatment times required, high energy

consumption, insufficient ability to ensure total removal and inefficient mineralization that causes the accumulation of toxic intermediates.

Nowadays, advanced oxidation processes (AOPs), including those based on Fenton's reaction, ozone and light irradiation, have been proven excellent to degrade highly recalcitrant organic compounds because of the action of hydroxyl radical ($^{\bullet}$OH), which is the second strongest oxidant after fluorine with a high standard redox potential (E = 2.80 V|SHE) (Martínez-Huitle et al., 2015). Among AOPs, Fenton's reaction is recognized as a very simple way to generate $^{\bullet}$OH. However, inefficient Fe(II) regeneration usually results in the need of large amounts of such catalyst, which must be carefully managed upon treatment completion (Brillas et al., 2009). The addition of UV irradiation gives rise to photo-Fenton process, which can readily regenerate Fe(II) and produce additional $^{\bullet}$OH amounts (Eq. (1)), as well as photodecarboxylate the Fe(III) complexes generated during the oxidation of most organics (Eq. (2)) (Ye et al., 2016).

$$[\mathrm{Fe(OH)}]^{2+} + h\nu \rightarrow \mathrm{Fe}^{2+} + {}^{\bullet}\mathrm{OH} \quad (1)$$

$$[\mathrm{Fe(OOCR)}]^{2+} + h\nu \rightarrow \mathrm{Fe}^{2+} + \mathrm{CO_2} + \mathrm{R}^{\bullet} \quad (2)$$

Nonetheless, conventional Fenton process with simple soluble salts presents two critical limitations: (i) it demands acidic conditions (pH 2.5-3.5) to maintain a high performance, which restricts the application of photo-Fenton process for wastewater treatment at large scale; and (ii) reaction (1) exhibits a quite low quantum yield for Fe(III) photoreduction (Φ(Fe(II)) = 0.14 ± 0.04 at 313 nm), and might also be

inhibited by the reduced light penetration when treating colored solutions (Pignatello et al., 2006).

To overcome these disadvantages, some chelating agents such as oxalate, citrate, ethylenediamine-N,N'-disuccinic acid (EDDS), ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) have been investigated to upgrade the conventional photo-Fenton process (Klamerth et al., 2012; Manenti et al., 2015; Clarizia et al., 2017). Such compounds are able to form stable complexes with ferric ions, thereby maintaining the iron soluble at less acidic pH and acting as photoactive species that greatly enhance the performance of photo-Fenton process. Among these agents, oxalate has been shown to be preferred (Kwan and Chu, 2007). The advantages of ferrioxalate-assisted photo-Fenton as compared to other systems include (Luca et al., 2014; Souza et al., 2014; Clarizia et al., 2017): (i) the soluble ferrioxalate complex allows working at neutral pH values; (ii) this complex has a higher quantum yield for Fe(II) regeneration (Eqs. (3,4)); (iii) it exhibits more intense light absorption, with a range up to 580 nm; and (iv) additional H_2O_2 production can occur from participation of dissolved oxygen (Eqs. (5-8)). The reaction network was summarized as follows (Souza et al., 2014; Clarizia et al., 2017):

$$[Fe(C_2O_4)_n]^{3-2n} + h\nu \rightarrow Fe^{2+} + (n-1)C_2O_4^{2-} + C_2O_4^{\bullet-} \quad (3)$$

$$C_2O_4^{\bullet-} + [Fe(C_2O_4)_n]^{3-2n} \rightarrow Fe^{2+} + nC_2O_4^{2-} + 2CO_2 \quad (4)$$

$$C_2O_4^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + 2CO_2 \quad (5)$$

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\bullet-} \quad (6)$$

$$O_2^{\bullet-} + H^+ \leftrightarrow HO_2^{\bullet} \qquad pK_a = 4.8 \quad (7)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (8)$$

Considering the high energy consumption using artificial UV light sources, sunlight can be alternatively employed to operate the ferrioxalate-assisted solar photo-Fenton process, which has been proven to be an efficient wastewater treatment technology (Monteagudo et al., 2010; Souza et al., 2014; Expósito et al., 2018). The present work investigates the mineralization and dechlorination of PCP by ferrioxalate-assisted solar photo-Fenton process at mild pH with a low iron concentration. The effect of main experiment parameters, such as initial concentrations of H_2O_2 and Fe(II), pH and iron/oxalic acid molar ratios on total organic carbon (TOC) abatement has been assessed, and the accumulation of H_2O_2, Fe(II) and dissolved O_2 has also been determined. In addition, a schematic reaction mechanism involving the iron cycle, radical reactions and PCP mineralization has been proposed. A possible pathway for the degradation of PCP is presented according to the identified intermediates.

2. Experimental

2.1 Chemicals

PCP was purchased from Sigma Aldrich (97% purity) and used without further purification. Hydrogen peroxide, ferrous sulfate heptahydrate and oxalic acid dihydrate were obtained from Union Chemical, Merck and Sigma Aldrich, respectively. The solution pH was adjusted with diluted NaOH or H_2SO_4. Other chemicals used herein were of analytical grade. Laboratory-grade deionized water

from a reverse osmosis system (resistivity > 18.2 MΩ cm) was used to prepare all aqueous solutions.

2.2 Experimental procedures

The experiments were carried out in an undivided glass cell filled with 1 L of PCP solution, under constant magnetic stirring and pH monitoring (see setup in Fig. S1). All the trials were performed with the initial PCP concentration fixed at 50 mg/L, which is almost the solubility limit of PCP at circumneutral pH. In the dark, oxalic acid was mixed with the pollutant solution and then, the Fe(II) salt was added as catalyst source. The mixture was homogenized for 5 min before pH adjustment. Finally, as the cell was exposed to sunlight, a small H_2O_2 volume was added to initiate the photo-Fenton treatment. Samples were withdrawn at different time intervals, being immediately mixed with NaOH to quench the reaction and then analyzed after filtration on a 0.22 μm syringe filter. The pH was controlled along the experiments to keep an almost constant value. The average UVA irradiance upon exposure to sunlight was measured on a UV radiometer (SENTRY®, ST-513), placed next to the cell, which measured within the wavelength range from 290 to 370 nm. All the trials were performed between 11 am and 2 pm on sunny days from May to June 2017 at Tainan (Taiwan). As can be observed in Fig. S2, during this period the average UVA irradiance was around 40 W/m^2. Note that, UVA irradiance showed approximately 7.6 W/m^2 difference at 11 AM between May and June. Fortunately, it is believed that such difference has insignificant influence on the performance of ferrioxalate-assisted solar photo-Fenton process (Souza et al., 2014).

142 *2.3 Analytical methods*

143 The mineralization of PCP solutions was assessed from the time course of TOC,
144 measured on a TOC analyzer (Sievers 900, GE). The residual amount of H_2O_2 during
145 the treatment was analyzed using the titanium sulfate method (Eisenberg, 1943). The
146 Fe(II) concentration was measured using the 1,10-phenanthroline method (Tamura et
147 al., 1974). Released Cl^- ions were quantified by inductively coupled plasma optical
148 emission spectrometry (Ultima 2000 ICP-OES spectrometer from Horiba Scientific).
149 Dissolved oxygen (DO) was measured on an Oxi 3210 instrument from WTW. The
150 carboxylic acids were determined at λ = 210 nm by ion-exclusion HPLC using a
151 Waters 600 LC fitted with a Bio-Rad Aminex HPX 87H, 300 mm × 7.8 mm, column
152 at 35 ºC. The elution was carried out by using 4 mM H_2SO_4 as mobile phase at 0.6
153 mL/min. The aromatic by-products were analyzed by gas chromatography coupled to
154 mass spectrometry (GC-MS) using an Agilent Technologies system composed of a
155 6890N gas chromatograph and a 5975C mass spectrometer operating in EI mode at 70
156 eV. Around 150 mL of aqueous sample was withdrawn from the cell to extract the
157 organic components with CH_2Cl_2 in three times (25 mL each). The resulting organic
158 solution was dried over anhydrous Na_2SO_4, filtered and concentrated to less than 1
159 mL under reduced pressure to be further analyzed. The mass spectra were identified
160 with support from NIST05 MS library.

161 **3. Results and discussion**

162 *3.1. Comparative study of PCP mineralization*

First, a comparative study on the mineralization of PCP from an aqueous solution containing 50 mg/L (i.e., 14 mg/L TOC) at pH 5.0 by different processes was conducted. As shown in Fig. 1, direct solar photolysis had no effect on TOC abatement for 120 min. This agrees with the low photodegradation rate constants at PCP concentrations of 0.4-2.1 mg/L, within the range of 4.9×10^{-2}-7.1×10^{-2} h^{-1}, which informs about the great persistence of this pollutant in the environment (Agbo et al., 2011). The PCP mineralization by conventional Fenton process with 2 mM H_2O_2 was also very inefficient due to the low Fe(II) dosage (i.e., 5 mg/L) and the expected Fe(III) precipitation at pH 5.0. When the same trial was carried out in the presence of 1.2 mM oxalic acid, a negligible enhancement of mineralization was achieved. Under such conditions, in spite of the solubilization of Fe(III) upon chelation with oxalate, the regeneration of Fe(II) to promote Fenton's reaction was quite poor. A much better performance was shown by processes with sunlight irradiation. Solar photo-Fenton process with 5 mg/L Fe(II) and 2 mM H_2O_2 yielded 21% TOC decay after 120 min. Such an upgrade as compared to trials in the dark can be mainly explained by the photoreduction of Fe(III)-hydroxy complexes to generate Fe(II) and $^{\bullet}OH$ (Eq. (1)), along with the photodecarboxylation of Fe(III) complexes of by-products formed during the degradation of PCP (Eq. (2)). TOC abatement increased up to 50% in ferrioxalate-assisted solar photolysis process with 1.2 mM $H_2C_2O_4$. According to Eqs. (3)-(8), $O_2^{\bullet-}$ and $^{\bullet}OH$ can be generated via several chain reactions in the presence of O_2 and hence, these two radical species may play key roles for the degradation of the parent molecule and its by-products. However, the limited dissolved oxygen

concentration in the solution significantly restricted the importance of Eqs. (5) and (6), which allows explaining the slower PCP removal from 30 min. The most effective process to degrade PCP was ferrioxalate-assisted solar photo-Fenton, yielding 97.5% TOC removal at 120 min, accompanied by the precipitation of iron hydroxide. Note that, although the addition of 1.2 mM $H_2C_2O_4$ accounted for 28.8 mg/L TOC, almost total abatement organic carbon from PCP and oxalic acid was attained in the ferrioxalate-assisted solar photo-Fenton process. This positive result is attributed to the high yield of $^{\bullet}OH$ formed in the presence of sufficient H_2O_2 and efficiently regenerated Fe(II) by Eqs. (3) and (4).

3.2. Effect of H_2O_2 and Fe(II) dosage

The amount of added H_2O_2 plays a relevant role in ferrioxalate-assisted solar photo-Fenton process, as it is the source of $^{\bullet}OH$ upon catalyzed decomposition with Fe(II). Several trials were carried out with solutions of 50 mg/L PCP with 5 mg/L Fe(II) and 1.2 mM $H_2C_2O_4$ at pH 5.0, employing different H_2O_2 concentrations. As shown in Fig. 2a, the decay of TOC after 120 min of irradiation increased from 50% to 97% when the H_2O_2 content was increased from 0 to 1.5 mM. Further increase of H_2O_2 dosage up to 2.5 mM resulted in a quicker mineralization during the first 60 min, whereupon close profiles were observed until reaching the same TOC removals at the end of the treatments. The significant acceleration using up to 1.5 mM H_2O_2 was then due to the faster production of $^{\bullet}OH$ from Fenton's reaction (Soares et al., 2015). However, an excess of H_2O_2 was detrimental because: (i) it acts as a radical scavenger, greatly reducing the amount of $^{\bullet}OH$ according to Eqs. (9) and (10), and (ii)

it accelerates its self-decomposition from Eq. (11) (Vedrenne et al., 2012; Pouran et al., 2015).

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (9)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (10)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (11)$$

In order to elucidate the effect of Fe(II) dosage on the mineralization ability of the ferrioxalate-assisted solar photo-Fenton treatment of solutions of 50 mg/L PCP, Fe(II) catalysts amounts within the range of 2-10 mg/L were added in the presence of 2.0 mM H_2O_2 and 1.2 mM $H_2C_2O_4$ at pH 5.0. The results depicted in Fig. 2b illustrate a significant enhancement of TOC abatement upon increase of Fe(II) dosage within the early stage (~ 20 min). Hence, a higher catalyst concentration greatly accelerated the decomposition of H_2O_2, which resulted in a larger accumulation of $^{\bullet}OH$ responsible for the mineralization. However, the final TOC removal at 120 min decreased from 97.5% to 91.4% when the dosage was increased from 5 mg/L to 10 mg/L. On the one hand, an excessive addition of Fe(II) promotes partial radical scavenging according to Eq. (12) (Monteagudo et al., 2010).

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-} \quad (12)$$

Furthermore, rapid accumulation of $^{\bullet}OH$ during the initial stage is associated to a quicker decomposition of oxalate ligand and iron/oxalate complex (Eq. (13)). As the treatment proceeds, an increasing amount of Fe(III) cannot be complexed and maintained soluble and stable, which stimulates the formation of $[Fe(OH)]^{2+}$ (Eq. (14)) and its further hydrolysis and precipitation as $Fe(OH)_3$ (Eq. (15)) (Pliego et al., 2014).

$$[Fe(C_2O_4)_n]^{3-2n} + {}^{\bullet}OH \rightarrow Fe^{3+} + \text{Oxidized products} \quad (13)$$

$$Fe^{3+} + H_2O \rightleftharpoons [Fe(OH)]^{2+} + H^+ \quad (14)$$

$$[Fe(OH)]^{2+} + 2H_2O \leftrightarrow Fe(OH)_3 \downarrow + 2H^+ \quad (15)$$

In addition, a larger quantity of Fe(III) hydroxyde sludge may reduce the transparency of the solution, thus reducing the photocatalysis efficiency.

3.3. Effect of pH and iron/oxalic acid ratio

Since PCP is quite insoluble at low pH, supersaturated PCP solutions (i.e., 50 mg/L) were prepared to start the experiments at pH 5.0. After 15 min of ferrioxalate-assisted solar photo-Fenton treatment, the pH was adjusted to a given value to investigate its effect on TOC decay. As can be seen in Fig. 2c, similar trends reaching more than 95% TOC removal at 120 min were obtained at pH ≤ 6.0 in the presence of 5 mg/L Fe(II), 2 mM H_2O_2 and 1.2 mM $H_2C_2O_4$, which demonstrates the feasibility of working at mild pH thanks to the use of ferrioxalate complexes. In contrast, at pH ≥ 7, TOC remained almost constant, probably as a result of massive iron precipitation. Indeed, pH plays a crucial role regarding the speciation of iron, oxalic acid and ferrioxalate complexes (Panias et al., 1996). Different species including $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$ may coexist in aqueous medium, since oxalic acid exhibits two ionization equilibria (pK_1 = 1.25 and pK_2 = 4.27). $C_2O_4^{2-}$, the predominant species at pH > 4.27, is considered as the main source to form different ferrioxalate complexes in the presence of iron, being the complex formed by $HC_2O_4^-$ negligible at pH > 2.0 (Souza et al., 2014). The performance of ferrioxalate-assisted solar photo-Fenton process highly depends on the photoactivity and stability of iron

complexes, whose species distribution depends on both, solution pH and iron/oxalic acid ratio. Fig. S3 reveals the Fe(III) speciation diagrams as a function of pH in the presence of 5 mg/L Fe(II) with different iron/oxalic acid molar ratios, as determined using MATLAB. The corresponding equilibrium reactions and constants are listed in Table S1. As can be seen in Fig S3 (e), which shows the speciation corresponding to the case in which the same Fe(II) and oxalic acid concentrations of trials of Fig. 2c are used, the predominant species are $Fe(C_2O_4)_3^{3-}$ and $Fe(C_2O_4)_2^-$ at 3.0 < pH < 7.0. The former ferrioxalate complex is considered as the most stable and photoactive iron complex (Faust and Zepp, 1993), being efficiently photoreduced to Fe(II) that reacts with H_2O_2 to generate $^{\bullet}OH$. This is highly consistent with the profiles presented in Fig. 2c, evidencing an outstanding performance and negligible difference of TOC decays when pH varied from 3.0 to 6.0. Conversely, only 3.7% mineralization was achieved once the pH of the PCP solution was adjusted to 7.0, which can be accounted for by: (i) the preferential precipitation of Fe(III) over ferrioxalate formation (Fig. S3e), (ii) the gradual photodecarboxylation of ferrioxalate complexes, which accelerates the formation of $Fe(OH)_{3(s)}$, and (iii) the enhanced transformation of $^{\bullet}OH$ into $O_2^{\bullet-}$ at high pH.

Several experiments were performed at pH 5.0 to evaluate the effect of the iron/oxalic acid ratio. As shown in Fig. 2d, almost complete TOC removal was obtained at molar ratios of 1:6, 1:10 and 1:13.5, whereas only 21.4% mineralization was achieved without the addition of oxalic acid. In the absence of oxalate anion, the predominant Fe(III) species at pH 5.0 is $[Fe(OH)_2]^+$ (Fig. S3a), which is much less

photoactive than $[Fe(OH)]^{2+}$ that is typically formed in conventional Fenton process at pH ~ 3.0 (Eq. (1)). Using the 1:3 iron/oxalic acid ratio, $Fe(C_2O_4)_3^{3-}$ (56.0%) and $Fe(C_2O_4)_2^{-}$ (43.1%) account for the largest proportion of Fe(III) species at pH 5.0 (Fig. S3b). The higher photoactivity of these complexes enhances the regeneration of Fe(II), yielding a greater mineralization as compared to the trial with 1:0 ratio (Fig. 2d). Increasing the iron/oxalic acid ratio to 1:6 (Fig. S3c), the molar fraction of the very photoactive $Fe(C_2O_4)_3^{3-}$ complex increases to 89.9% , with $Fe(C_2O_4)_2^{-}$ decreasing to 10.1% at pH 5.0, which justifies the faster and almost complete TOC decay. The abatement was slightly decelerated at ratios of 1:10 and 1:13.5 (Fig. 2d), despite the fact that the $Fe(C_2O_4)_3^{3-}$ species accounted for more than 95% of Fe(III), because of the significant increase of initial TOC in solution from oxalic acid that competed with PCP to react with $^{\bullet}OH$.

It can then be concluded that the optimum performance of the ferrioxalate-assisted solar photo-Fenton process takes place at pH 5.0, with an iron/oxalic acid molar ratio of 1:6.

3.4. Evolution of H_2O_2, Fe(II) and dissolved O_2

The evolution of H_2O_2 and Fe(II) along the ferrioxalate-assisted solar photo-Fenton treatments collected in Fig. 2d is depicted in Fig. 3a and b, respectively. As shown in Fig. 3a, 40% consumption of H_2O_2 was achieved after 120 min in the absence of oxalic acid, whereas it reached more than 93% in only 60 min at all iron/oxalic acid ratios, thus confirming the efficient Fe(II) regeneration upon photoreduction of the ferrioxalate complexes. More in detail, rising the molar ratio

295 from 1:3 to 1:6 accelerated the decomposition of H_2O_2, but further increase of oxalic
296 acid content slowed down the H_2O_2 disappearance. In fact, the H_2O_2 concentration
297 measured at 2 and 5 min using a molar ratio of 1:13.5 was even higher than that at
298 time zero, which can be attributed to the additional generation of H_2O_2 from the
299 reaction sequence given by Eqs. (3)-(8). As can be observed, DO plays a major role in
300 the formation of H_2O_2 and hence, its evolution with treatment time was evaluated in
301 different cases. As depicted in Fig.4, the concentration of oxygen dissolved in the
302 PCP solution decreased considerably in ferrioxalate-assisted solar photo-Fenton and
303 solar photolysis processes, whereas it remained stable in conventional Fenton and
304 solar photo-Fenton, which verifies the key role of DO in the aforementioned reactions
305 to form H_2O_2. This means that this additional amount of H_2O_2 is able to react with
306 Fe(II) to generate $^{\bullet}OH$, which combined with other radical species ($C_2O_4^{\bullet-}$, $CO_2^{\bullet-}$ and
307 $O_2^{\bullet-}$) is responsible for the greater TOC abatement in ferrioxalate-assisted solar
308 processes (Fig. 1). Note that the DO concentration in both ferrioxalate systems tended
309 to increased again from 30 min, which can be explained by the quick chemical and
310 photochemical decomposition of ferrioxalate complexes, especially in solar
311 photo-Fenton process (Fig. 1).

312 On the other hand, Fig. 3b reveals the evolution of Fe(II) at different iron/oxalic
313 acid ratios. The catalyst concentration decreased to less than 1 mg/L in only 2 min in
314 the absence of oxalate because of the quick consumption by H_2O_2. The resulting
315 Fe(III) ion was pre-eminently in a poorly photoactive form at pH 5.0 ($[Fe(OH)_2]^+$, see
316 Fig. S3a), thus being difficult to regenerate Fe(II). The decrease in Fe(II)

concentration was greatly decelerated upon increase of oxalic acid content, which confirms the very efficient photoreduction of ferrioxalate complexes. Nevertheless, owing to oxalic acid decomposition, the generated Fe(III) tended to precipitate at pH 5.0, eventually causing the decrease of Fe(II) concentration. Theoretically, all iron should be complexed at iron/oxalic acid molar ratios higher than 1:3 (Souza et al., 2014), but the continuous photodecarboxylation and decomposition of ferrioxalate complexes by $^{\bullet}OH$ could cause the partial precipitation of iron. However, the use of a large amount of oxalic acid ensures the ion stabilization by formation of ferrioxalate complexes, especially at pH higher than 3.1. As can be seen in Fig. 3b, the concentration of Fe(II) kept the highest value (i.e., 5 mg/L) for 20 min at an iron/oxalic acid molar ratio of 1:13.5, which is very positive to promote Fenton's reaction. Nonetheless, an excessively high amount of oxalic acid increases the operation costs, causes the competition with PCP to react with $^{\bullet}OH$ and results in a higher initial TOC and thus, the iron/oxalic acid ratio should be carefully considered for real applications.

3.5. Possible reaction mechanism of ferrioxalate-assisted solar photo-Fenton process

Based on all previous results, a reaction mechanism for the ferrioxalate-assisted solar photo-Fenton treatment of PCP is proposed in Fig. 5. Fe^{3+} can be complexed by oxalate, and the efficient photoreduction of the resulting Fe(III) complexes eventually yields Fe(II), either as free Fe^{2+} or complexed with oxalate, which readily reacts with H_2O_2 to generate $^{\bullet}OH$ and Fe(III) in a closed loop. However, owing to the progressive decomposition of ferrioxalate complexes, the excess of Fe(III) tends to precipitate as

339 $Fe(OH)_{3(s)}$ at pH higher than 3.1. In the presence of O_2, additional amounts of H_2O_2
340 and concomitant radical species ($C_2O_4^{\bullet-}$, $CO_2^{\bullet-}$, $HO_2^{\bullet}$ and $O_2^{\bullet-}$) can be generated
341 according to a series of radical reactions, although their oxidization ability is much
342 weaker than that of $^{\bullet}OH$. Therefore, the degradation and mineralization of PCP can be
343 pre-eminently explained in terms of reactions with $^{\bullet}OH$, as in the case if classical
344 Fenton's reaction.

345 *3.6. Identification of degradation by-products*

346 In surface water and sediments, the toxicity of PCP has been evidenced at
347 concentrations greater than 3 mg/L (Stepanova et al., 2000). Some intermediates
348 generated during the degradation of this target pollutant, like 3,4,5-trichlorophenol,
349 are known to be even more toxic, as the toxicity is related to the number of chlorine
350 atoms and their position (Lin et al., 2018). Therefore, the release of Cl^- and the
351 generation of PCP reaction by-products have been investigated. Fig. 6a reveals the
352 evolution of Cl^- ion with irradiation time during the ferrioxalate-assisted solar
353 photo-Fenton treatment of 50 mg/L PCP with 5 mg/L Fe(II), 2 mM H_2O_2 and 1.2 mM
354 $H_2C_2O_4$. As can be seen, the degradation of PCP was accompanied by a continuous
355 release of Cl^-, whose concentration increased with over time up to attain 33.5 mg/L
356 (i.e., 100% release) at 90 min, thus informing about the excellent dechlorination
357 performance and the total removal of organochlorine intermediates generated during
358 the degradation of PCP in this process. Fig. 6b reveals the evolution of five carboxylic
359 acids like oxalacetic, malonic, succinic, formic and acetic resulting from the cleavage
360 of the aromatic rings. The maximum concentration of succinic acid was 5.9 mg/L at

30 min, whereas lower contents of the other acids were accumulated, reaching maximum values of 2.1, 1.4, 0.9 and 0.7 mg/L for malonic, oxalacetic, formic and acetic acids at 20, 30, 45 and 45 min, respectively. The accumulation of these carboxylic acids entails the occurrence of competing Fe(III)-carboxylate complexes, which efficiently enhanced the Fe(II) regeneration via Eq. (2). Moreover, all the acids disappeared in 90-120 min, confirming the almost total mineralization achieved by ferrioxalate-assisted solar photo-Fenton process.

The main transformation products (TPs) identified by GC-MS analysis included four monobenzenic and four polycyclic molecules. As summarized in Table S2, these corresponded to tetrachlorophenol (TeCP), trichlorophenol (TriCP), trichlorohydroquinone (TrCHQ), tetrachlorohydroquinone (TeCHQ), hexachlorodibenzofuran (HCDF), pentachlorodibenzo-*p*-dioxin (PCDD), hexachlorodibenzo-*p*-dioxin (HCDD) and octachlorodibenzo-*p*-dioxin (OCDD). The cleavage of C-Cl bonds yielded lower chlorinated structures like TeCP and TriCP (Liu et al., 2004). The subsequent attack of $^{\bullet}OH$ onto their aromatic rings resulted in two hydroxylated TPs (TeCHQ and TrCHQ). Alternatively, the direct attack of $^{\bullet}OH$ on C-Cl bonds of PCP can give rise to TeCHQ, which may be further dechlorinated. On the other hand, several dimeric structures were identified. Since PCP mainly exists as anionic form (PCP^{-}) at pH > 4.7, hydroxylation of PCP^{-} leads to the generation of pentachlorophenoxy radical ($PCP^{\bullet}$). Then, the coupling reaction between two $PCP^{\bullet}$ species or $PCP^{\bullet}$ and PCP^{-} may yield OCDD and HCDF, respectively, with chloride release (Fukushima and Tatsumi, 2001). Further dechlorination of OCDD caused the

383 formation of lower chlorinated derivatives like HCDD and PCDD. The degradation
384 routes of PCP, which are depicted in Fig. 7, on the basis of the identified by-products,
385 involve three paths: dechlorination, hydroxylation and dimerization.

386 **4. Conclusions**

387 Promising results were obtained for the mineralization of PCP at near-neutral pH
388 using a low iron concentration by the ferrioxalate-assisted solar photo-Fenton process.
389 More than 95% TOC abatement were achieved in 120 min. The optimized operation
390 parameters were: 5 mg/L Fe(II), 1.5 mM H_2O_2, pH 5.0 and iron/oxalic acid molar
391 ratio of 1:6. The presence of oxalic acid greatly enhances the performance of solar
392 photo-Fenton process due to various reasons: (i) the ferrioxalate complex ensures the
393 iron solubility at mild pH; (ii) the Fe(III) complexes with oxalate are highly
394 photoactive, thus allowing the continuous Fe(II) regeneration; and (iii) additional
395 amounts of H_2O_2 and radical species are generated with the involvement of O_2. It was
396 shown that pH and iron/oxalic acid molar ratio play crucial roles on the Fe(III)
397 speciation in aqueous medium, greatly influencing the performance of the degradation
398 process. At pH 3.0-7.0 and iron/oxalic acid ratio higher than 1:3, all the iron is
399 complexed with oxalate, whereas the excess of oxalate ion remains in solution and
400 ensures the continuous formation of ferrioxalate complexes that impedes the iron
401 precipitation. The mineralization of PCP involves dechlorination, hydroxylation and

decarboxylation steps, as well as the formation of some dimers that can be gradually degraded by •OH and other radicals.

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